# Feasibility Study: Use of Hydrazine in BWRs for ECP Reduction during Startup

### 1016206

# Feasibility Study: Use of Hydrazine in BWRs for ECP Reduction during Startup

1016206

Technical Update, December 2007

EPRI Project Manager

S. Garcia

ELECTRIC POWER RESEARCH INSTITUTE
3420 Hillview Avenue, Palo Alto, California 94304-1338 ▪ PO Box 10412, Palo Alto, California 94303-0813 ▪ USA
800.313.3774 ▪ 650.855.2121 ▪ askepri@epri.com ▪ www.epri.com

# DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

THIS DOCUMENT WAS PREPARED BY THE ORGANIZATION(S) NAMED BELOW AS AN ACCOUNT OF WORK SPONSORED OR COSPONSORED BY THE ELECTRIC POWER RESEARCH INSTITUTE, INC. (EPRI). NEITHER EPRI, ANY MEMBER OF EPRI, ANY COSPONSOR, THE ORGANIZATION(S) BELOW, NOR ANY PERSON ACTING ON BEHALF OF ANY OF THEM:

(A) MAKES ANY WARRANTY OR REPRESENTATION WHATSOEVER, EXPRESS OR IMPLIED, (I) WITH RESPECT TO THE USE OF ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT, INCLUDING MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, OR (II) THAT SUCH USE DOES NOT INFRINGE ON OR INTERFERE WITH PRIVATELY OWNED RIGHTS, INCLUDING ANY PARTY'S INTELLECTUAL PROPERTY, OR (III) THAT THIS DOCUMENT IS SUITABLE TO ANY PARTICULAR USER'S CIRCUMSTANCE; OR

(B) ASSUMES RESPONSIBILITY FOR ANY DAMAGES OR OTHER LIABILITY WHATSOEVER (INCLUDING ANY CONSEQUENTIAL DAMAGES, EVEN IF EPRI OR ANY EPRI REPRESENTATIVE HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES) RESULTING FROM YOUR SELECTION OR USE OF THIS DOCUMENT OR ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT.

ORGANIZATION(S) THAT PREPARED THIS DOCUMENT

**Electric Power Research Institute (EPRI)**

**This is an EPRI Technical Update report. A Technical Update report is intended as an informal report of continuing research, a meeting, or a topical study. It is not a final EPRI technical report.**

## NOTE

For further information about EPRI, call the EPRI Customer Assistance Center at 800.313.3774 or e-mail askepri@epri.com.

Electric Power Research Institute, EPRI, and TOGETHER…SHAPING THE FUTURE OF ELECTRICITY are registered service marks of the Electric Power Research Institute, Inc.

Copyright © 2007 Electric Power Research Institute, Inc. All rights reserved.

# CITATIONS

This document was prepared by

Electric Power Research Institute
3420 Hillview Avenue
Palo Alto, CA 94304

Principal Investigator
S. Garcia

This document describes research sponsored by the Electric Power Research Institute (EPRI).

This publication is a corporate document that should be cited in the literature in the following manner:

*Feasibility Study: Use of Hydrazine in BWRs for ECP Reduction during Startup.* EPRI, Palo Alto, CA: 2007. 1016206.

# REPORT SUMMARY

Intergranular stress corrosion cracking (IGSCC) in BWRs is successfully mitigated during operation using hydrogen water chemistry (HWC) and noble metal chemical application (NMCA). However, these methods are only completely effective when the reactor is at power. This *Technical Update* describes the first phase of a collaborative program on the application of hydrazine and other chemical methods to reduce the electrochemical corrosion potential (ECP) during the start up phase before hydrogen starts to work, to minimize IGSCC throughout the entire BWR fuel cycle.

## Background

The oxidizing chemistry environment of BWR reactor water is the key factor promoting IGSCC (Intergranular Stress Corrosion Cracking) of stainless steel and nickel based alloys in the reactor coolant system piping and vessel internals. IGSCC in BWRs is mitigated during power operation with moderate hydrogen water chemistry (HWC-M) or noble metal chemical addition with hydrogen water chemistry (NMCA+HWC). However, hydrogen injection is not placed into service until the reactor is at operating temperature and at power greater than about 5% to 30%, depending on HWC system design. Consequently, the reactor water, which initially contains high dissolved oxygen levels from exposure to atmospheric air during cold shutdown, is oxidizing during heatup and low power operation. Laboratory data indicates that IGSCC rates are higher at intermediate temperatures during plant startup and shutdown processes than at operating temperatures. As a result, cracking can initiate and crack growth can occur when hydrogen injection is not in service. Hence, the initiation and propagation of IGSCC is probably greater during the start up phase than in the remainder of the cycle.

## Objectives

- To develop an Engineering Feasibility Study to eventually support the in-plant demonstration of hydrazine injection during a normal BWR plant startup.
- To identify key technical, operational or safety issues and define any further studies needed to proceed with a plant demonstration.

## Approach

The project team evaluated the current use of hydrazine in PWRs and carried out laboratory loop tests to determine the effectiveness of hydrazine in reducing ECP under BWR startup conditions after a refueling outage (up to 5-10% power). They prepared an engineering feasibility study on the use of hydrazine, including technical considerations and a preliminary study of plant application issues and safety issues. Additional work is already in progress, including a study of carbohydrazide and methanol, as alternatives to hydrazine. This work will be published in 2008. Further work will include a plant-specific evaluation of the application of one of these chemicals, and a detailed safety review of the proposed application.

## Results

Laboratory loop test results documented in this report support the feasibility of using hydrazine injection during the BWR heatup and early startup to substantially lower the ECP of surfaces on

which noble metals are deposited.  ECP reduction for prefilmed stainless steel (but not NMCA-treated) specimens was also achieved but was not as great as on the NMCA-treated specimens over the entire  temperature range studied.  This infers a greater catalytic effect of the NMCA treated surface on the oxygen/hydrazine reaction. The ECP decreases as the hydrazine to oxygen concentration ratio is increased, and hydrazine addition also decreases ECP with increasing temperature. The noble metals durability after exposure to hydrazine after laboratory simulated repeated BWR startup and shutdown evolutions is being tested.  Based on this preliminary evaluation, chemical injection during the reactor pressure leak test and in the heatup and low power parts of the startup process is concluded to be feasible.  Recommendations for future work are discussed in detail.

## EPRI Perspective

This document describes work from the first phase of a much larger project. Additional work is also in progress, including a study of carbohydrazide and methanol as alternatives to hydrazine, and will be published in 2008. This will complete the project funded by the EPRI Nuclear Power Sector New Project Startup Program.  Also, a plant-specific evaluation of the application of one of these chemicals is also in progress, funded by a US utility.  In 2008, a detailed safety review will be carried out under the BWRVIP Mitigation Program.  The ultimate objective is a plant demonstration at an operating BWR in 2009.

## Keywords

BWR chemistry
Hydrogen water chemistry
Noble metal chemical addition
Intergranular stress corrosion cracking
ECP

# ACKNOWLEDGEMENTS

This report was prepared by the EPRI BWRVIP Mitigation Committee’s Shutdown Guidelines Focus Group.

**Consultants**

Robert Cowan

Robert Law

**Finetech**

Joseph F. Giannelli

Alfred J. Jarvis

David J. Morgan

Jim Tangen

**NWT Corp.**

Steve Sawochka

**Electric Power Research Institute (EPRI)**

Susan Garcia

Christopher J. Wood

# CONTENTS

# LIST OF FIGURES

# LIST OF TABLES

# 1

# INTRODUCTION AND BACKGROUND

## 1.1 Introduction

Intergranular stress corrosion cracking (IGSCC) in BWRs is successfully mitigated during normal power operation using hydrogen water chemistry (HWC) or low HWC combined with noble metal chemical addition (NMCA). However, these methods are only effective when hydrogen is being injected, which currently occurs when the reactor is at power. As a result, the highest crack growth rates are indicated to occur during startup, particularly after refueling outages, before HWC can be initiated. Plant and laboratory data show that IGSCC rates can actually be higher at intermediate temperatures during heatup than at operating temperatures, so significant crack extension may occur during this period. Also, the electrochemical corrosion potential (ECP) is initially high in the oxygenated water environment established during the cold shutdown conditions of the outage. Hence, the initiation and rate of propagation of IGSCC can be greater during the startup phase than in the remainder of the cycle. While this is an important consideration for all plants, crack growth for NMCA plants during startup can expose surfaces without noble metal deposits which are not mitigated under low HWC, resulting in crack flanking.

This Technical Update describes the first phase of a collaborative program on the application of chemical methods to reduce the electrochemical corrosion potential during the startup phase before hydrogen injection can be initiated. This engineering feasibility study is limited to the use of hydrazine in the startup of a BWR after a refueling outage up to 5-10% power. Additional work is in progress, including a study of carbohydrazide and methanol injection as alternatives to hydrazine injection. Testing will also be performed with hydrogen injection for comparison. The results will be published later in 2008. Also, a plant-specific evaluation of the potential application/demonstration of one of these chemicals is in progress, funded by a U.S. utility. In 2008, a detailed safety review will be carried out under the BWRVIP Mitigation Program.

## 1.2 HWC for IGSCC Mitigation

The oxidizing chemistry environment of BWR reactor water is the key factor promoting IGSCC (Intergranular Stress Corrosion Cracking) of stainless steel and nickel based alloys used to construct reactor coolant system piping and vessel internals. Intergranular stress corrosion cracking (IGSCC) in BWRs is mitigated during power operation with moderate hydrogen water chemistry (HWC-M) or noble metal chemical addition with hydrogen water chemistry (NMCA+HWC). However, hydrogen injection is not placed into service during startup until the reactor is at operating temperature and at power greater than about 5% to >30%, depending on HWC system design. Consequently, the reactor water, which initially contains high dissolved oxygen levels from exposure to atmospheric air during cold shutdown, is oxidizing during heatup and low power operation. Laboratory data indicates that IGSCC rates may be higher at intermediate temperatures during plant startup and shutdown processes than at operating temperature. As a result, cracking can initiate and crack growth can occur, particularly during plant startup from refueling or mid-cycle outages, when hydrogen injection is not in service. For units with NMCA+HWC, crack growth during the startup and shutdown processes may result in crack flanking, in which existing cracks can continue to grow even after hydrogen injection is on. For units on HWC-M, mitigation of IGSCC during startup can provide additional margin to assure that mitigation goals are met.

As of August 2007, forty-four (44) plants of the 45 plants included in the EPRI BWR Chemistry Monitoring program were injecting hydrogen for IGSCC mitigation, and this number includes all U.S. BWRs. Twenty-nine (29) BWRs had implemented NMCA and fifteen (15) were on HWC-M. Only one (1) non-U.S. plant was not injecting hydrogen; this plant plans to implement NMCA+HWC in 2008.

This project investigates chemical methods to reduce the oxidant concentration during the heatup and low power operation in the startup process when there is no hydrogen injection. In this technical update, preliminary loop test results on the use of hydrazine to reduce the ECP (Electrochemical Corrosion Potential) at noble metal treated and untreated (pre-filmed) stainless steel surfaces under typical BWR startup and shutdown conditions are summarized. Injection of other chemicals, including carbohydrazide, methanol and hydrogen, during heatup and startup is included in the loop test program. The detailed test conditions and results will be published in a separate report in 2008.

This technical update provides preliminary engineering feasibility study input and considerations for qualification work leading up to an actual plant demonstration. Although the plant shutdown process also includes operation with no hydrogen injection (after hydrogen injection is turned off) at normal operating temperature through the cooldown to <200 $^{o}$F, emphasis is on suppression of IGSCC during the startup phase when the time at temperature greater than 200 $^{o}$F without hydrogen injection is longer and water quality is typically poorer than during the shutdown process.

A recent BWRVIP report [1] evaluated the initiation of hydrogen injection earlier in the startup process and also identified potential benefits from chemical injections prior to initiation of hydrogen injection. However, there is little or no full-scale BWR experience with this latter approach, particularly within the U.S. fleet of BWRs.

## 1.3 Normal Operation

During normal power operating conditions, hydrogen injection into the reactor water reduces the ECP of stainless steel and nickel based alloys, and thus mitigating IGSCC [2]. Hydrogen addition suppresses the radiolytic decomposition of water in the core region, which reduces the formation of oxidizing species such as oxygen and hydrogen peroxide. Hydrogen addition also provides an excess of dissolved hydrogen in the downcomer region, which promotes the radiolytic recombination of residual oxidants in the recirculating water. In regions where the concentration of oxidants in reactor water is reduced to <3 ppb (equivalent $O_2$) the ECP driving force for IGSCC is eliminated. Under NWC (normal water chemistry), the ECP of primary system materials is typically in the range of 0 to +250 mV (SHE). Laboratory and field testing has shown that when the ECP of sensitized stainless steel is lowered to <-230 mV (SHE) and the reactor coolant conductivity is <0.3 μS/cm at 25 $^{o}$C, IGSCC of BWR piping is mitigated.

HWC-M, under which 1.0 - 2.0 ppm hydrogen is added to the feedwater, is targeted at protecting reactor internals as well as piping. A drawback to HWC-M is that it causes main steam line radiation levels to increase by several times the level without hydrogen injection due to conversion of N-16 to volatile chemical forms that are transported with the steam.

Hydrogen injection with Noble Metal Chemical Addition (NMCA+HWC) provides a means of achieving the IGSCC protection of HWC-M without a large increase in main steam line radiation levels. NMCA involves the deposition of small amounts of noble metal (platinum, rhodium) on the wetted surfaces in contact with the reactor coolant. These catalyze recombination reactions of hydrogen with oxygen and hydrogen peroxide at those surfaces. The ECP response of the treated surfaces is similar to that of platinum. Mitigating ECPs are achieved when the molar ratio of hydrogen to total oxidant in reactor water reaches a value equal to or greater than two, which is reached at very low feedwater hydrogen concentrations (usually between 0.1 and 0.3 ppm), about an order of magnitude less than that required by HWC-M. A major advantage of NMCA is that there is little or no increase in main steam line radiation from N-16 activity at the low hydrogen addition levels. A disadvantage is that cracking, which may initiate or propagate during periods when hydrogen is not available, may not be mitigated when hydrogen is restored. When cracks grow beyond a critical length or depth, oxidants in the bulk water may raise the ECP within the crack, beyond where the catalyst penetrates, above -230 mV(SHE). This phenomenon is referred to as “crack flanking.”

HWC availability is defined as the percentage of time that the equivalent of ECP is suppressed to $\leq$-230 mV (SHE) when operating at >200 $^{o}$F when conductivity is $\leq$0.3 µS/cm (can be >0.3 µS/cm for up to 24 hours and can subtract contribution from soluble Fe and Zn) [3]. EPRI recommendations for hydrogen availability are >95% for HWC-M and >98% for NMCA+HWC [3]. Plants operating with NMCA+HWC strive for very high hydrogen availabilities and for limited hydrogen outages based on the concern for crack flanking.

## 1.4 Startup Considerations

Several plants have implemented methods to inject hydrogen during startup and low power (>5%) operation to minimize crack growth during these periods. However, in all cases hydrogen injection is not started until the reactor has reached normal operating temperature and pressure and some steam flow has been initiated, allowing the SJAE (Steam Jet Air Ejector) system to be placed in service. At some plants, the modifications required to allow low power hydrogen injection are prohibitive, causing a delay in the start of hydrogen injection until $\geq$30% power is attained. Hydrazine addition is being investigated as a means of achieving protective ECP during startup before hydrogen injection can be started.

In preparation for startup from a refueling outage, reactor coolant temperature increases above 200 $^{o}$F for the reactor hydrostatic pressure test, typically for a period of 12 – 24 hours. After the hydrostatic test, temperature is reduced to <200 $^{o}$F. During startup operations, the reactor coolant temperature is raised above 200 $^{o}$F and is gradually increased to normal operating temperatures of >500 $^{o}$F. For a typical startup, the total time at temperatures above 200 $^{o}$F to >500 $^{o}$F before hydrogen injection is started is about 60 – 75 hours. An order of magnitude estimate of crack growth can be made based on laboratory results (presented in Figure 1-4 below), using an average crack growth rate in the length direction of 1E-2 mm/h (~4E-4 inches/h) from >93 $^{o}$C to about 250 $^{o}$C (>200 $^{o}$F to 482 $^{o}$F) for 30 hours, and then the crack growth rate decreasing to 5E-4 mm/h (~2E-5 inches/h) for the an additional 30 hours without hydrogen injection as temperature increases above 250 °C (482 °F) to operating temperature. Assuming crack propagation in both length directions, the total crack growth would be 0.63 mm (about 25 mils). For an NMCA plant, startup crack growth may contribute to crack flanking, in which existing cracks can continue to grow even after hydrogen injection is on. Longer time durations at temperatures above 200 °F but below operating temperature without hydrogen injection can occur due to startup problems, as described in Section 3 for the Limerick 2 example.

Temperature effects on materials can be significant in light water reactors because of startup and shutdown cycles, with associated stresses from thermal gradients and water chemistry, and aggravated by higher oxidant and impurity concentrations [4]. These effects are shown in Figure 1-1, Figure 1-2 and Figure 1-3. Available published data from SSR (slow strain rate) and fracture mechanics tests show a peak in growth rate versus temperature predominantly in pure water at lower dissolved oxygen levels (lower corrosion potential, $E_{CORR}$). A monotonic increase in crack growth rate versus temperature was observed at higher dissolved oxygen and/or higher solution conductivity levels. The peak in crack growth rate versus temperature for low conductivity solutions at low dissolved oxygen concentration is attributed to two competing effects. The increase in the kinetics of mass transport with increasing temperature tends to increase the growth rate while $E_{CORR}$ (and thus the crack growth rate) tends to decrease with increasing temperature [4]. The data indicate a complex dependence on crack tip chemistry.

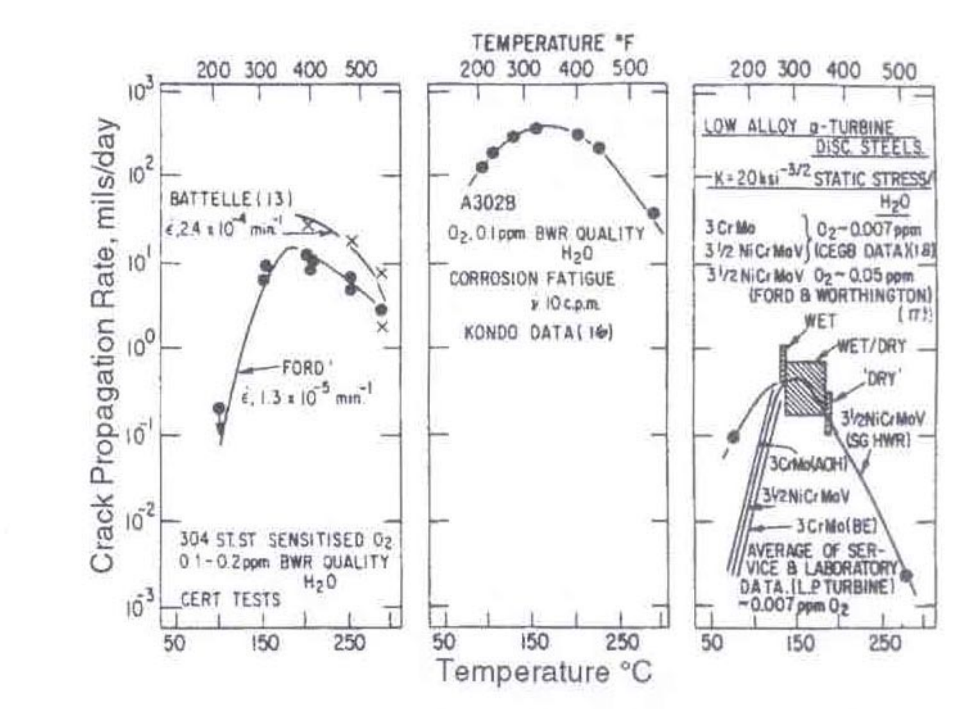

**Figure 1-1**
**Temperature dependence of crack growth rate for sensitized Type 304 stainless steel and turbine disc steel at moderate to low dissolved oxygen [4]**

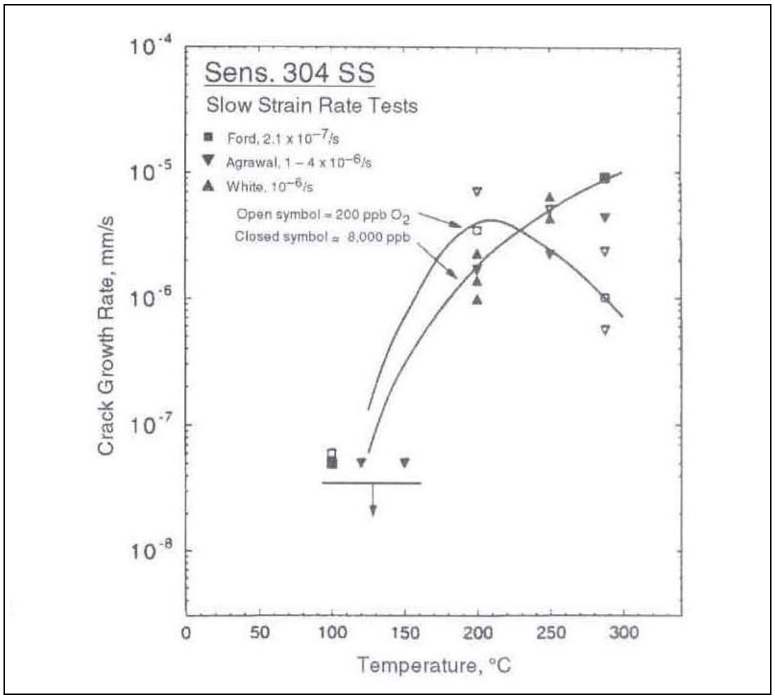

**Figure 1-2**
**Effect of temperature on average crack growth rate for sensitized Type 304 stainless steel at 200 ppb and 8000 ppb dissolved oxygen [4]**

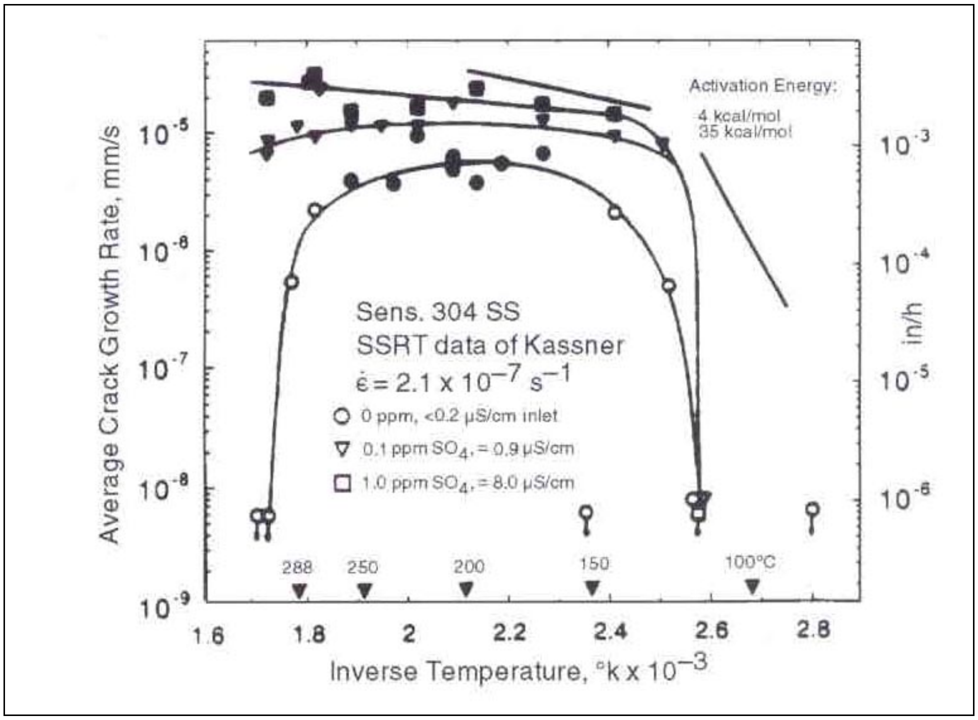

**Figure 1-3**
**Average crack growth rate vs. inverse temperature in CERT tests on sensitized Type 304 stainless steel at 200 ppb as a function of sulfuric acid concentration [4]**

Results of tests performed by General Electric on three different heats of sensitized type 304 stainless steel and one heat of sensitized alloy 600 showed a peak in crack growth rates in dilute solutions of sulfuric acid and hydrochloric acid, and in air saturated water, at approximately 200 $^{o}$C (392 $^{o}$F) [4]. This peak crack growth rate was approximately 30 – 100 times higher than at 288 $^{o}$C (550 $^{o}$F) or 25 $^{o}$C (77 $^{o}$F). Sulfate caused higher crack growth rates than chloride or carbonate (air saturated water) at temperatures below 250 $^{o}$C (482 $^{o}$F), while at 288 $^{o}$C the effects of sulfuric acid and hydrochloric acid were similar. A much less rapid fall off in crack growth rate at high temperature occurred at higher impurity levels. Crack growth rate responded rapidly to changes in temperature (particularly decreasing temperature), which is consistent with chemical equilibrium changes that apparently occurred rapidly as temperature was changed. A comprehensive summary of GE Global Research Center (GEGRC) and GE Nuclear Energy (GENE, now GE Hitachi Energy) laboratory crack growth data for three heats of Type 304 stainless steel and two heats of Alloy 600 versus temperature is presented in Figure 1-4 [2].

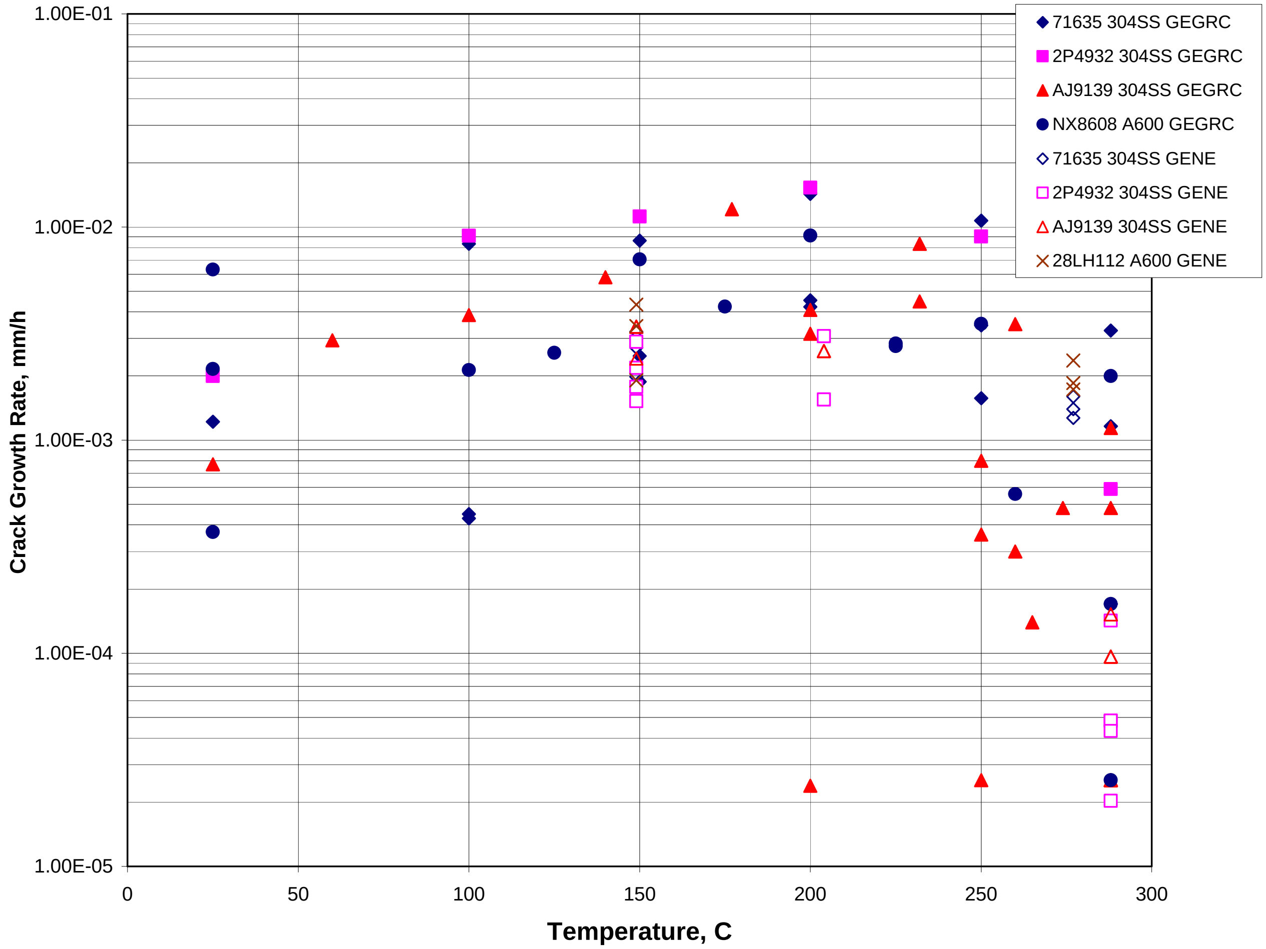

**Figure 1-4**
**Effect of Temperature on Sensitized Type 304 Stainless Steel and Sensitized Alloy 600 Crack Growth Rates in 200 ppb Oxygenated Water ($\leq$0.27 μS/cm) (Provided by GE Nuclear Energy) [2]**

Studies by Studsvik implied that the crack growth rate in furnace sensitized Type 304 stainless steel peaks at approximately 150°C with 100 ppb sulfate (0.89 μS/cm) [2]. The GE crack growth rate versus temperature studies indicated a peak in crack growth rate at approximately 200°C (392°F) in water with a conductivity of ≤ 0.27 µS/cm. This may indicate that the peak occurs at lower temperature with higher conductivity. Other Studsvik work indicated a monotonic increase in crack growth rate with increasing temperature in very pure water environment (<0.08 µS/cm). Based on the available data, it appears that in relatively high purity/non-transient/below Action Level 1 BWR environments the crack growth rate of BWR structural materials such as Type 304 stainless steel and Alloy 600 reach a maximum crack growth rate at approximately 150 to 200°C (302 to 392°F) [5]. It is expected that in lower purity/transient type environments (e.g., >1 µS/cm), the crack growth rates would increase with increasing temperature.

## 1.5 Use of Amines During BWR Heatup/Startup

The addition of amines, such as hydrazine or carbohydrazide, is being considered for lowering the ECP of reactor internals and recirculation piping during the early startup process. In particular, the ECP reduction on noble metal treated stainless steel surfaces under typical BWR startup conditions during the initial heatup to >93 °C (>200 °F), through the temperature range of 150 to 200 °C (302 to 392 °F) where laboratory data indicate peak crack growth rates can occur, to the normal operating temperature of approximately 550 °F (288 °C) and up to ≤10% power is considered. This range of plant conditions is defined as Startup/Hot Standby in BWRVIP-130 [2]. Injection of other chemicals, such as methanol which is briefly discussed later in this section, may be considered later. Techniques such as co-injection of hydrogen and hydrazine or other chemicals to reduce ECP during normal power operating conditions [6, 7] are beyond the scope of this initial study.

### *1.5.1 Use of Hydrazine*

The molecular structure of hydrazine is depicted in Figure 1-5.

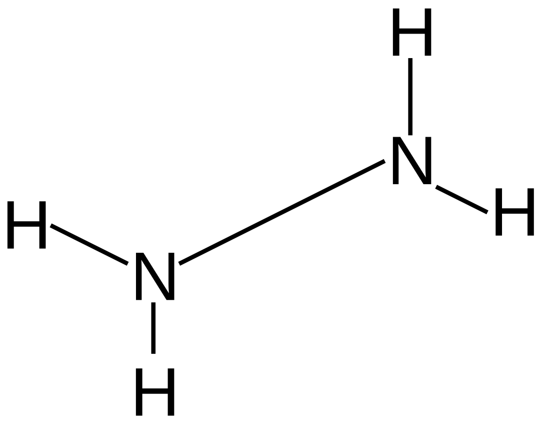

**Figure 1-5**
**Hydrazine Molecular Structure**

Hydrazine reacts with oxygen as follows:

$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$

The reaction products, nitrogen and water, do not pose a corrosion concern in the BWR. Since the molecular weights of hydrazine and oxygen are the same, and that they react on a mole per mole ratio, the stoichiometric molar and weight ratios are equal.

Hydrazine also decomposes to form ammonia, nitrogen and hydrogen, as shown in the equation below. Unfortunately, since the decomposition rate is known to be surface catalyzed, it can only be stated that the decomposition rate markedly increases with temperature and the actual stoichiometry is unclear.

$N_2H_4 \rightarrow aNH_3 + bN_2 + c2H_2$

Several issues exist relative to the effects of adding $N_2H_4$ to the BWR during startups. First, the effect of $N_2H_4$ on the ECP of oxidized stainless steel and oxidized stainless steel treated with noble metals as a function of temperature and oxygen concentration had not been measured at the BWR conditions of interest. Second, it is unknown if $N_2H_4$ could poison or solubilize the noble metal coating thereby eliminating its beneficial effect on ECP. Third, the ammonia formed by decomposition of the hydrazine will exhaust a portion of the reactor water cleanup system cation resin capacity and increase the solution pH. This could decrease anion resin capacity and demineralizer impurity removal efficiency. Similar effects can occur on the condensate demineralizer system resins if ammonia is carried over with steam or added to the condenser by letdown from the reactor coolant system. Also, the effects of ammonia in plants with copper and copper-alloy materials must be considered.

Reasonable data on the kinetics of the hydrazine/oxygen reaction in water solutions as a function of temperature in the absence of radiation are available as are data on the effect of hydrazine addition to PWR feedwater on the ECP of stainless steels and Alloys 600 and 690 [8]. However, the ECP data were at relatively low oxygen and hydrazine concentrations and at elevated pH (controlled by ammonia or amine additions). In addition, the extent of catalysis of the hydrazine/oxygen reaction occurring on NMCA treated stainless steel surfaces and the resulting decrease in ECP was not known.

Results of a laboratory test program to evaluate the effect of hydrazine on the ECP of NMCA treated and untreated oxidized stainless steel specimens at BWR startup conditions in the absence of gamma radiation are summarized in Section 2. Although it is known based on both theoretical and experimental results that the oxygen/hydrazine reaction will be catalyzed by core flux [9, 10], the test program did not consider radiation effects on this reaction and thus are considered conservative relative to the magnitude of the ECP reduction that can be achieved by hydrazine addition during a BWR startup. Note that a significant gamma flux is present in-core even at the end of a refueling outage. The hydrazine radical $\bullet N_2H_3$ formed from hydrazine under irradiation is indicated to react quickly with oxygen [6].

Hydrazine is a potential carcinogen, which requires special procedures for handling. Procedures for safe handling can be readily imported from the PWRs, where hydrazine is used widely on the secondary side. However, inadvertent releases of hydrazine to the environment have occurred and been documented in NRC Event Notification Reports. NRC Event Notification Report Number 41301 “Hydrazine Release To Settling Pond Exceeded Allowed Release Rate” and Number 38056 “Offsite Notification Of Hydrazine Spill” are two documented occurrences.

### *1.5.2 Carbohydrazide as an Alternative to Hydrazine*

Carbohydrazide is a hydrazine alternative that is not a carcinogenic concern. The molecular structure of carbohydrazide is depicted in Figure 1-6.

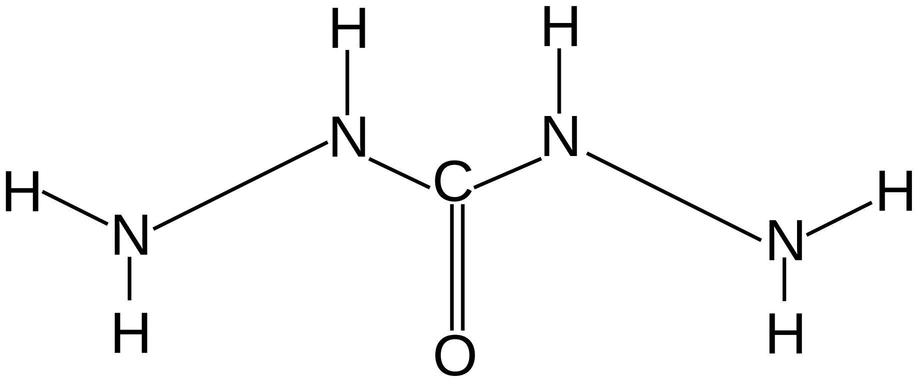

**Figure 1-6**
**Carbohydrazide Molecular Structure**

Handling requirements for carbohydrazide are standard for any bulk chemical, such as adequate ventilation and the use of gloves and goggles. Tank materials recommended for bulk storage are polyethylene, polypropylene or stainless steel.

Carbohydrazide reacts directly with oxygen to produce nitrogen, carbon dioxide and water, as depicted below:

$$2O_2 + (N_2H_3)_2CO \rightarrow 2N_2 + 3H_2O + CO_2$$

The carbohydrazide/oxygen molar ratio of this reaction is 0.5. The weight ratio to yield a stoichiometric reaction is approximately1.4.

As with hydrazine, the rate of reaction of carbohydrazide with oxygen is reported to increase as temperature increases and at higher pH [11]. As temperature increases, carbohydrazide decomposition to hydrazine and carbon dioxide becomes significant, so the reaction with oxygen can take place either directly (as shown above) or indirectly with the hydrazine produced [12]:

$$H_2O + (N_2H_3)_2CO \rightarrow 2N_2H_4 + CO_2$$

$$2O_2 + 2N_2H_4 \rightarrow 2N_2 + 4H_2O$$

Carbohydrazide is reported to decompose to hydrazine when temperatures exceed 250 $^{o}$F and is almost completely decomposed to hydrazine at 350 $^{o}$F [11]. The hydrazine decomposes to ammonia, nitrogen and hydrogen, although the stoichiometry is not quantifiable as discussed previously. Concerns with the impact of ammonia production on ion exchange processes are therefore essentially the same with hydrazine or carbohydrazide. Also, the effects of ammonia in plants with copper and copper-alloy materials must be considered. The formation of $CO_2$ as a reaction product must also be considered, as carbonic acid in water will ionize to bicarbonate and carbonate ions, with the carbonate fraction increasing as pH increases.

## 1.6 Hydrazine and Carbohydrazide Use in PWRs

The initial chemical additives to be investigated for reducing the ECP of BWR reactor internals and recirculation piping during the early startup process are hydrazine and carbohydrazide. These chemicals are commonly used to reduce dissolved oxygen on the PWR secondary side during layup and power operating conditions.

### *1.6.1 Hydrazine Use During PWR Primary System Heatup*

Hydrazine treatment of PWR reactor coolant is normally used for startup deoxygenation [13, 14, 15]. There are no U.S. PWRs known to be injecting carbohydrazide into the primary system. Hydrazine treatment is most effective when dissolved oxygen has been reduced to a few ppm by mechanical methods. Hydrazine can be added early in the heatup process as temperature reaches about 150 $^{o}$F to allow time for the reaction to proceed at the reduced rate at lower temperature, but deoxygenation proceeds more rapidly at higher temperatures. The thermal reaction kinetics improve substantially as the temperature is increased from 120 $^{o}$F to 350 $^{o}$F, and the hydrazine reaction with oxygen also proceeds radiolytically in the presence of $\gamma$-radiation. The thermal reaction of hydrazine with oxygen occurs in solution and at surfaces, with the reaction catalyzed by metal ions, such as copper. The reaction rates will be less under acidic conditions in the reactor coolant, but this may be counteracted by surface and metal ion catalyzed reactions.

If the hydrazine addition can be limited to about 2 liters of 35% hydrazine, the amount of ammonia generated is not expected to impact the CVCS (Chemical Volume Control System) demineralizer operation [13, 14, 15]. The scavenging procedure may be judged to be complete when the reactor coolant dissolved oxygen is reduced to <100 ppb.

There have been no reported adverse impacts of hydrazine on fuel after many years of use in treating PWR primary coolant.

### *1.6.2 PWR Secondary Side Use of Hydrazine and Carbohydrazide*

Hydrazine is the most commonly used oxygen scavenger in PWR secondary applications [16]. Oxygen scavengers other than hydrazine, such as carbohydrazide, may be used as long as their use has been evaluated for the applications involved, and their concentrations provide similar reducing environments as the recommended concentrations of hydrazine. Efforts are made to minimize oxidant development and ingress at all stages of steam generator shutdown, layup and startup.

Exposure of steam generators to oxidizing conditions during startup is minimized. Before introducing feedwater into the steam generators, oxygen levels in the condensate – feedwater system should be reduced to <100 ppb, and preferably lower, using condenser vacuum and high levels of hydrazine or carbohydrazide, and heating the feedwater as much as possible [16]. High hydrazine levels, e.g., 2 ppm, are maintained during startup and until low power operation (approximately 1 to 3% power) is reached. The intent is to reduce any oxides that may have developed in or been transported to steam generator crevice areas. At some plants, hydrazine decomposition may limit acceptable concentrations to lower levels.

During shutdown periods, steam generators are often put into a controlled wet layup to protect the internal parts from corrosion damage during the shutdown period, to promote the return of impurities from deposits and crevices, and to minimize oxidation of materials and deposits in the steam generator that could aggravate corrosion during subsequent power operation. The *PWR Secondary Water Chemistry Guidelines* require that wet layup use hydrazine at a minimum concentration of 75 ppm and have a minimum pH of 9.8 [17].

Hydrazine is a suspected carcinogen and is controlled in plant discharges [17]. Environmental discharge limits on hydrazine and ammonia (produced by decomposition of hydrazine) and ammonia attack of copper alloys are concerns with the use of high hydrazine concentrations. Copper can be partially dissolved under the high pH/high hydrazine chemistry of layup and, if removal is not accomplished by draining, it will likely redeposit during heatup. The resulting widely distributed layer of redeposited copper could increase risks of oxidation and elevation of ECP during subsequent operation. Situations involving the possible exposure of workers to elevated atmospheric concentrations of hydrazine and ammonia, or to oxygen deficient environments, may require special precautions and the interruption of normal conditions. Because of the hazardous nature of hydrazine, there is interest in using alternative oxygen scavengers such as carbohydrazide that are considered less hazardous. Some plants have started to use carbohydrazide and have found that, because of carbon dioxide released by its decomposition, a minimum pH of 9.8 may not be achieved.

## 1.7 Use of Methanol

Other reducing chemicals, such as methanol, are being considered for future work in assessing the feasibility of chemical injection to suppress ECP during BWR startups. Test data reported in the literature suggest that alcohol injection into a BWR feedwater, as an alternate source of hydrogen, decreases the ECP on structural materials in high temperature water [18]. The oxidation reaction produced by injecting an alcohol, such as methanol, into the feedwater is shown as follows:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$

The net reactions with oxygen and hydrogen peroxide, assuming the reactions go to completion, produce carbon dioxide and water:

$$3O_2 + 2CH_3OH \rightarrow 2CO_2 + 4H_2O$$

$$3H_2O_2 + CH_3OH \rightarrow CO_2 + 5H_2O$$

Limited laboratory autoclave test data have been reported in the literature on the effectiveness of methanol injection in reducing ECP of test specimens in 288 $^{o}$C (550 $^{o}$F) water [18]. The autoclave results suggest that dissolved oxygen reduction and significant ECP reduction are achievable at operating temperature, particularly on surfaces containing or composed of platinum, at normal BWR operating temperatures. However, data are not available at lower temperatures during heatup and early startup. Loop tests planned using methanol as part of the EPRI BWR startup ECP reduction project cover the 200 $^{o}$F – 400 $^{o}$F temperature range in the absence of radiation. The effectiveness of an alcohol is expected to be enhanced in the presence of a radiation field.

## 1.7 References

1. BWRVIP-156: BWR Vessel and Internals Project, Generic Guidelines for Improvement in HWC System Availability. EPRI, Palo Alto, CA: 2006. 1013397.
2. BWRVIP-130: BWR Vessel and Internals Project, BWR Water Chemistry Guidelines – 2004 Revision, EPRI, Palo Alto, CA: 2004. 1008192.
3. BWRVIP-159: BWR Vessel and Internals Project, HWC/NMCA Experience Report and NMCA Applications Guidelines. EPRI, Palo Alto, CA: 2006. 1011706.
4. Andresen, P.L., “Effects of Temperature on Crack Growth Rate in Sensitized Type 304 Stainless Steel and Alloy 600,” Corrosion 49, No. 9 (September 1993), p. 714.
5. Effect of Water Chemistry and Temperature Transients on the IGSCC Extension in BWR Components, EPRI, Palo Alto, 2007. DRAFT.
6. Kazushige Ishida, Yoichi Wada, Masahiko Tachibana, Motohiro Aizawa, Motomasa Fuse, Eiichi Kadoi, “Hydrazine And Hydrogen Co-injection to Mitigate Stress Corrosion Cracking of Structural Materials in Boiling Water Reactors, (I) Temperature Dependence of Hydrazine Reactions,” Journal of Nuclear Science and Technology, Vol. 43, No. 1, p. 65-76 (2006).
7. Hidetoshi Karasawa, Kazushige Ishida, Yoichi Wada, Masao Endou, Yoshitaka Nishino, Motohiro Aizawa, Motomasa Fuse, Eiichi Kadoi and Hideki Takiguchi, “Hydrazine And Hydrogen Co-injection to Mitigate Stress Corrosion Cracking of Structural Materials in Boiling Water Reactors, (III) Effects of Adding Hydrazine on Zircaloy-2 Corrosion,” Journal of Nuclear Science and Technology, Vol. 43, No. 10, p. 1218-1223 (2006).
8. Kassen, W.R., “Electrochemical Potential Monitoring in the PWR Secondary Cycle of St. Lucie 2,” Electric Power Research Institute, March 1995 (TR-104951).
9. Kazushige Ishida et. al., “Reaction of Hydrazine with Oxygen with or without Gamma Irradiation in High-Temperature Water”, Jeju, 2007.
10. M. C. Kent and H. E. Sims, "The Radiation Chemistry of Hydrazine with Relevance to Reactor Coolants", Proc. Water Chemistry of Nuclear Reactor Systems 6, Bournemouth UK, Oct. 12-15, 1992, Vol. 2, 322.
11. Fugiwara, K., Kawamura, H., and Hirano, H., “Evaluation of Thermal Decomposition Rate of Carbohydrazide and its Reducing Effect on Carbon Steel Corrosion,” NACE Corrosion 97.
12. Zupanovich, John D., “Oxidation and Degradation Products of Common Oxygen Scavengers, Analyst, Fall, 2002.
13. PWR Primary Water Chemistry Guidelines: Volume 1, Revision 4, EPRI, Palo Alto, CA: 1999. TR-105714-V1R4.
14. PWR Primary Water Chemistry Guidelines: Volume 2, Revision 4, EPRI, Palo Alto, CA: 1999. TR-105714-V2R4.
15. 2005 Interim Review of the PWR Primary Water Chemistry Guidelines – Revision 5, EPRI, Palo Alto, CA: 2005. 1009933.
16. Source Book on Limiting Exposure to Startup Oxidants, EPRI, Palo Alto, CA: 1999. TR-112967
17. Pressurized Water Reactor Secondary Water Chemistry Guidelines – Revision 6, EPRI, Palo Alto, CA: 2004. 1008224.

18. Kim, Y.J., "Evaluation of Alternate Reductants for Application in Light Water Reactors," Corrosion, Vol. 62, No. 9, September 2006.

# 2

# OBJECTIVES AND TEST PROGRAMS RESULTS

## 2.1 Objectives

This work investigates the injection of alternate reducing agents to react with oxidants on noble metal treated surfaces and untreated (prefilmed) stainless steel surfaces under BWR startup/shutdown and operating conditions when feedwater hydrogen injection is not available. The objective is to demonstrate that these alternatives are capable of reducing the oxidant concentration on the surface, and therefore the ECP (Electrochemical Corrosion Potential), to levels at which IGSCC is mitigated. The initial investigation is focused on evaluating the effectiveness of injecting hydrazine for mitigating IGSCC during the startup phase when there is significant time at temperature greater than 200 $^{o}$F without hydrogen injection and the risk of crack initiation and growth, particularly of noble metal treated surfaces, is of concern. The test program will also include carbohydrazide injection, hydrogen injection (at a hydrogen to oxygen molar ratio above 2) and methanol injection at temperatures of 200 $^{o}$F to 400 $^{o}$F. Available results with hydrazine are summarized below.

## 2.2 Hydrazine Effectiveness

To support this feasibility study, a laboratory test program was performed to quantify the effect of hydrazine on the ECP on NMCA treated and untreated oxidized stainless steel specimens at BWR startup conditions in the absence of gamma radiation. The complete program details and results are to be documented in a separate report [1]. The test program evaluated the effect of hydrazine on the ECP on oxidized stainless steel and oxidized stainless steel treated with noble metals as a function of temperature and oxygen concentration. Test program work is also being performed to evaluate if $N_2H_4$ could poison or solubilize the noble metal coating, thereby eliminating its beneficial effect on ECP. Hydrogen was added with the oxygen to form a molar ratio of 1 at the inlet of the test system.

### *2.2.1 Summary of Findings*

Loop test results show that hydrazine injection decreases the measured ECP on the surfaces of NMCA treated and untreated specimens. The ECP of an NMCA treated specimen was decreased to a significantly greater extent than that of an untreated filmed specimen over the temperature range of 200 $^{o}$F to 400 $^{o}$F. This indicates that the NMCA treatment enhances the catalytic effect of the oxygen/hydrazine reaction at the surface. The results also show that the ECP decreases as the hydrazine to oxygen concentration ratio (weight and molar ratio are the same for hydrazine and oxygen) is increased and as the temperature increases. With the NMCA treated specimen, significant ECP reduction is achieved with excess hydrazine over oxygen at 200 $^{o}$F and 300 $^{o}$F compared with the measured ECP at <2 ppb oxygen without hydrazine injection, while at 400 $^{o}$F the ECP with hydrazine injection over the range tested is similar to that with <2 ppb oxygen. The ECP reduction of the preoxidized untreated specimen with hydrazine injection at 200 $^{o}$F and 300 $^{o}$F compared with the ECP at <2 ppb oxygen is significantly smaller than that for the NMCA treated specimen, even at high hydrazine to oxygen ratios, while at 400 °F the ECP with hydrazine injection is similar to the measured value with <2 ppb oxygen in the test loop.

The loop tests were performed in the absence of radiation, which is expected to enhance the oxygen/hydrazine reaction. Therefore the loop test results are considered conservative relative to the magnitude of the ECP reduction that can be achieved by hydrazine addition during a BWR startup.

### 2.2.2 Summary of Hydrazine Loop Tests

Tubular NMCA treated and untreated preoxidized specimens (3/4-inch diameter by 0.083 wall thickness by 4-inch long) were provided by GENE for the tests. GENE reported that the NMCA treated specimens had average Pt and Rh loadings of 0.42 and 0.035 $\mu g/cm^2$, respectively. The untreated specimen was preoxidized for 500 hours but was not exposed to the NMCA process.

The specimen inlet oxygen and hydrogen concentrations were established by adjusting the system feed tank overpressure and gas composition. Hydrazine was injected into the process stream immediately upstream of the specimens at a flow rate of 2 to 4 grams/minute. The total flow rate through the specimens was 1 liter/minute.

In Phase 1 of the test program, the effect of hydrazine on the ECP of the treated and untreated specimens was determined at 200, 300 and 400°F. The feed tank gas concentration was controlled to give equilibrium oxygen and hydrogen concentrations of approximately 250 and 15 ppb, respectively (hydrogen:oxygen molar ratio approximately equal to 1), at a tank pressure of 18 psia. These concentrations should reasonably approximate those that will be achieved during a BWR startup at temperatures near 200 °F. Hydrazine concentrations were varied from approximately 400 ppb to 6000 ppb which yielded hydrazine to oxygen concentration ratios (weight or molar) of approximately 2 to 20.

A summary of test results for Phase I is given in Figure 2-1. Testing was initiated at 200°F. After obtaining baseline ECP values at this temperature at an oxygen concentration of approximately 260 ppb, hydrazine was increased to 400 and then 1200 ppb. Temperature was then increased to 300 °F with hydrazine at 1200 ppb. After increasing temperature to 400 °F, data were obtained with hydrazine at 400 and 1200 ppb following which the temperature was reduced to 200 °F. After several days of operation at 200 °F without hydrazine feed, additional data were obtained at 200 and 300 °F with the hydrazine concentration increased to 6 ppm.

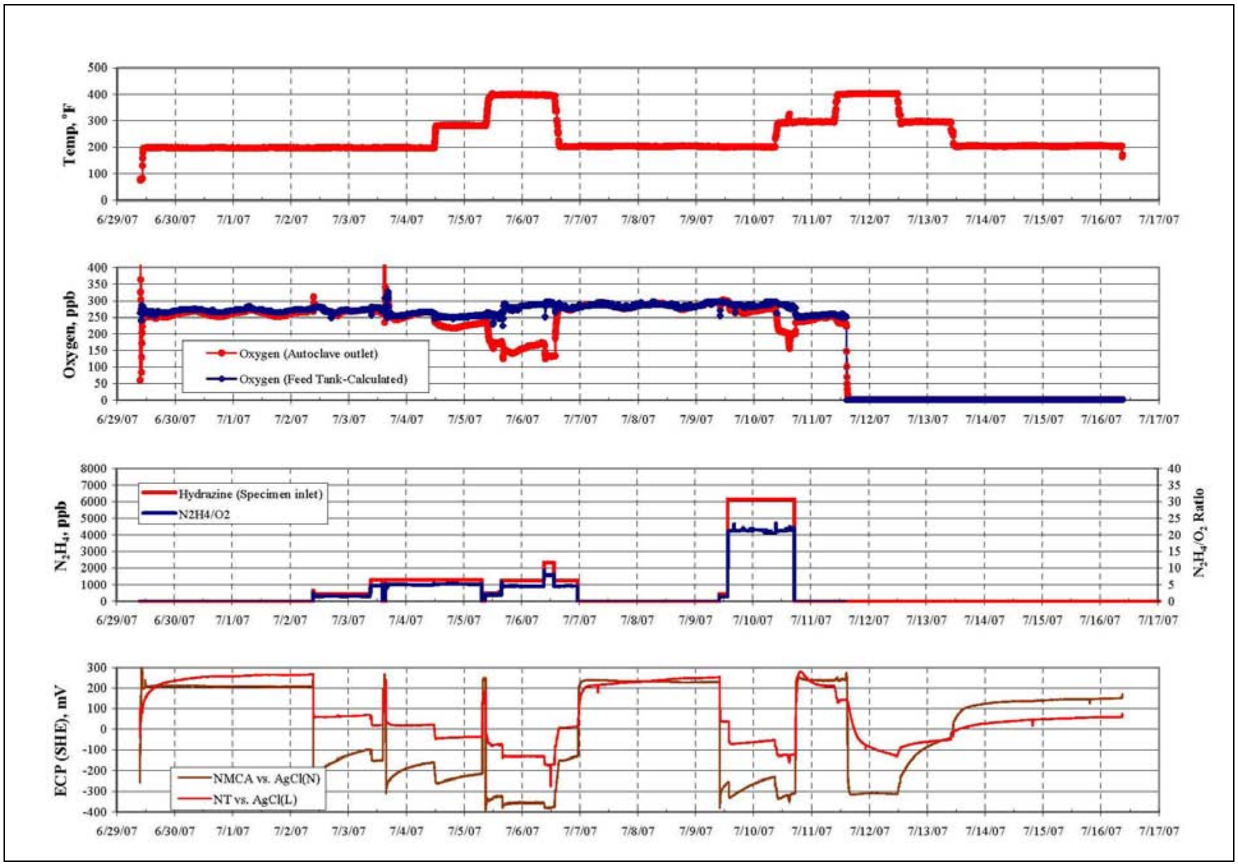

**Figure 2-1**
**Summary of the Effect of $N_2H_4/O_2$ Ratio on Untreated and NMCA Treated Tubular Specimens [1]**

ECP results for the NMCA treated specimens and prefilmed untreated specimens are summarized in Figure 2-2. In Figure 2-3, results have been corrected for the effect of $pH_T$ [1]. The pH corrected results should more accurately reflect the effect of hydrazine addition on the effective surface oxygen concentration. Conclusions that can be drawn from these results are as follows:

- The ECP decrease of the NMCA treated specimen is significantly greater than that of the untreated filmed specimen at all temperatures. This infers a greater catalytic effect of the NMCA treated surface on the oxygen/hydrazine reaction.
- The ECP decreases as the hydrazine to oxygen concentration ratio is increased.
- The ECP decreases with increasing temperature with hydrazine addition.

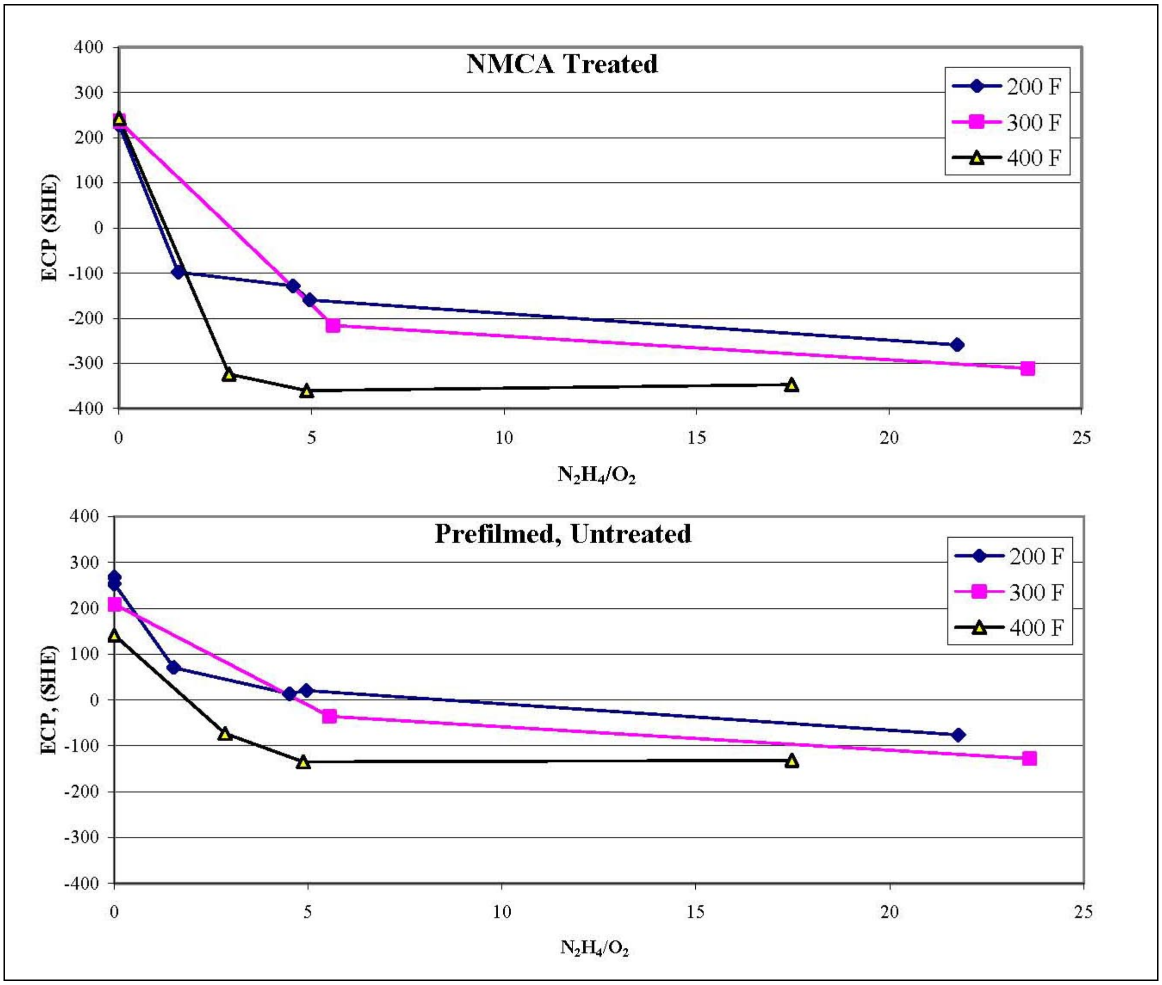

**Figure 2-2**
**Relationship of ECP to Hydrazine/Oxygen Ratio at 250 ppb Oxygen and 15 ppb Hydrogen [1]**

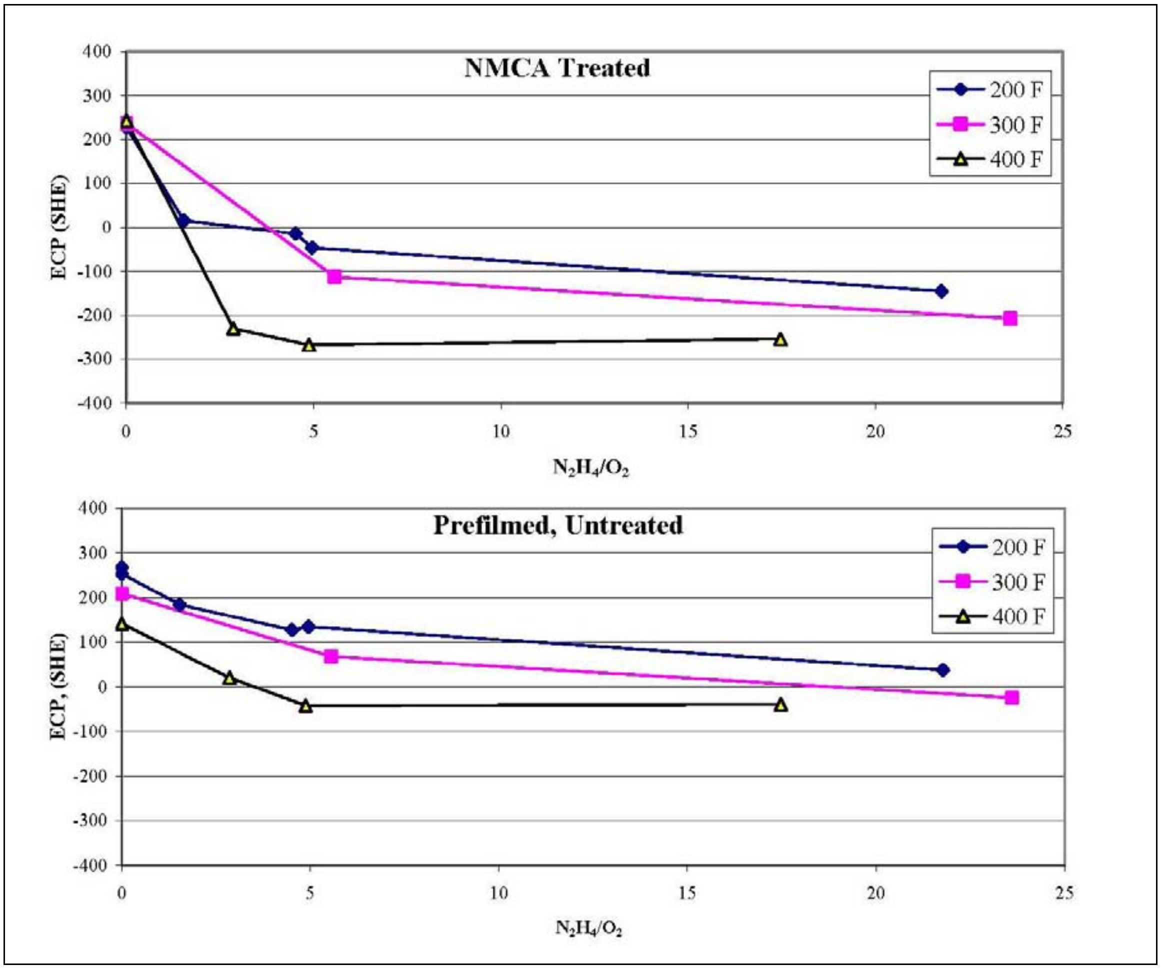

**Figure 2-3**
**Relationship of ECP to Hydrazine/Oxygen Ratio at 250 ppb Oxygen and 15 ppb Hydrogen (Corrected for $pH_T$ effect) [1]**

In addition to the results obtained at an oxygen concentration of 150 to 300 ppb, additional data were obtained with high purity nitrogen used for the feed tank cover gas which yielded an indicated oxygen concentration of 2 ppb at the specimen outlet. The actual concentration is believed to be <2 ppb based on the feed tank gas composition, pressure and temperature. Observed ECP results are summarized in Table 2-1 and Figure 2-4. Results corrected for $pH_T$ are given in Table 2-1 and Figure 2-5. Conclusions that can be drawn from these results are as follows:

1. At 200 $^oF$, the ECP of the NMCA treated specimen at hydrazine to oxygen ratios of 1.5 or greater is significantly less than that observed at an oxygen concentration of <2 ppb.
2. At 300 $^oF$, the ECP of the NMCA treated specimen at hydrazine to oxygen ratios of 5.6 or greater is less than that observed at an oxygen concentration of <2 ppb.
3. At 400 $^oF$, the ECP of the NMCA treated specimen at hydrazine to oxygen ratios of 2.9 to 18 is similar to that observed at an oxygen concentration of <2 ppb.

4. At 200 °F, the ECP of the prefilmed but untreated specimen at hydrazine to oxygen ratios of 1.5 to 4.5 is similar to that observed at <2 ppb oxygen. At a ratio of approximately 22, the ECP is approximately 100 mV less than that observed at <2 ppb oxygen.
5. At 300 °F, the ECP of the prefilmed but untreated specimen at a hydrazine to oxygen ratio of 5.6 is similar to that observed at <2 ppb oxygen. At a ratio of approximately 24, the ECP is approximately 50 mV less than that observed at <2 ppb oxygen.
6. At 400 °F, the ECP of the prefilmed but untreated specimen at hydrazine to oxygen ratios of 2.9 to 18 is similar to that observed at an oxygen concentration of <2 ppb.
7. Assuming that mitigation can be achieved at an ECP(SHE) that approaches that at low temperature at an oxygen concentration of ≤2 ppb, mitigation at test loop conditions can be achieved by hydrazine injection if a hydrazine to oxygen ratio of >5 to 10 can be achieved. Acceptable ECP values may also be achieved at lower ratios.

In Phase 2 of the evaluation, a BWR startup simulation test will be performed with hydrazine injection to achieve a hydrazine concentration that decreases the ECP to that observed at an oxygen concentration of <2 ppb. Specifically, the specimens will be exposed to the following chemistry and operating conditions:

1. Normal startup (gradual deoxygenation at a heatup rate of approximately 100°F per hour from air saturation to 150 ppb oxygen at operating temperature followed by approximately 2 days at operating temperatures at approximately 150 ppb oxygen and 40 ppb hydrogen)
2. Normal cooldown transient with gradual transition to air saturated conditions
3. Cold conditions with air saturation for 1 day
4. Normal startup transient (see (1) above)) with addition of hydrazine (at a concentration to be determined) followed by operating period as referenced in (1) above
5. Normal cooldown transient with gradual transition to air saturated conditions
6. Cold conditions with air saturation for 1 day

At the end of this evolution, the specimens will be removed from the test facility to measure the platinum and rhodium surface concentrations for comparison to the initial specimen loadings.

**Table 2-1**
**Summary of ECP Results [1]**

| Temp, °F | $O_2$, ppb | $N_2H_4$, ppb | $N_2H_4/O_2$ | NMCA, mV (SHE) | | Untreated, mV (SHE) | |
|---|---|---|---|---|---|---|---|
| | | | | Observed | pH corrected | Observed | pH corrected |
| 200 | 311 | 0 | 0.0 | 234 | 234 | 268 | 268 |
| 200 | 292 | 0 | 0.0 | 228 | 228 | 254 | 254 |
| 200 | 273 | 420 | 1.5 | -98 | 16 | 70 | 184 |
| 200 | 281 | 1268 | 4.5 | -129 | -15 | 14 | 127 |
| 200 | 261 | 1296 | 5.0 | -160 | -46 | 21 | 135 |
| 200 | 282 | 6143 | 21.8 | -259 | -145 | -76 | 38 |
| 200 | 2 | 0 | 0 | 150 | 150 | 59 | 59 |
| | | | | | | | |
| 300 | 254 | 0 | 0.0 | 237 | 237 | 209 | 209 |
| 300 | 233 | 1296 | 5.6 | -216 | -113 | -35 | 68 |
| 300 | 260 | 6143 | 23.6 | -311 | -208 | -128 | -24 |
| 300 | 2 | 0 | 0 | -41 | -41 | -50 | -50 |
| | | | | | | | |
| 400 | 230 | 0 | 0.0 | 243 | 243 | 142 | 142 |
| 400 | 169 | 483 | 2.9 | -324 | -231 | -73 | 20 |
| 400 | 260 | 1268 | 4.9 | -360 | -267 | -135 | -42 |
| 400 | 133 | 2331 | 17.5 | -347 | -254 | -132 | -39 |
| 400 | 2 | 0 | 0 | -314 | -314 | -131 | -131 |

**Note**:  A hydrogen concentration of 15 ppb was maintained for all tests to approximate the hydrogen concentration during a BWR startup at temperatures near 200°F.

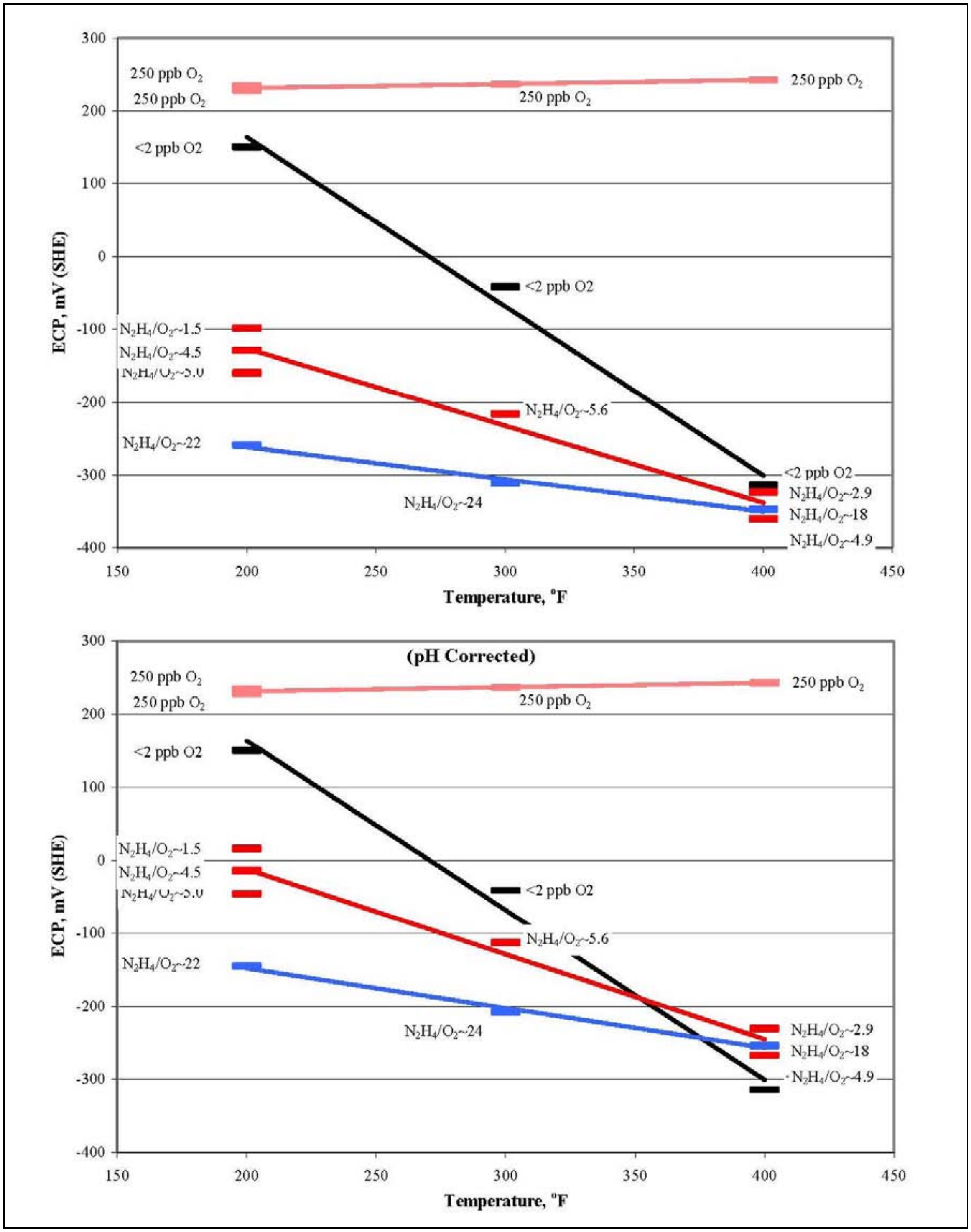

**Figure 2-4**
**Effect of Temperature, Oxygen and Hydrazine/Oxygen Ratio on ECP of NMCA Treated Stainless Steel [1]**

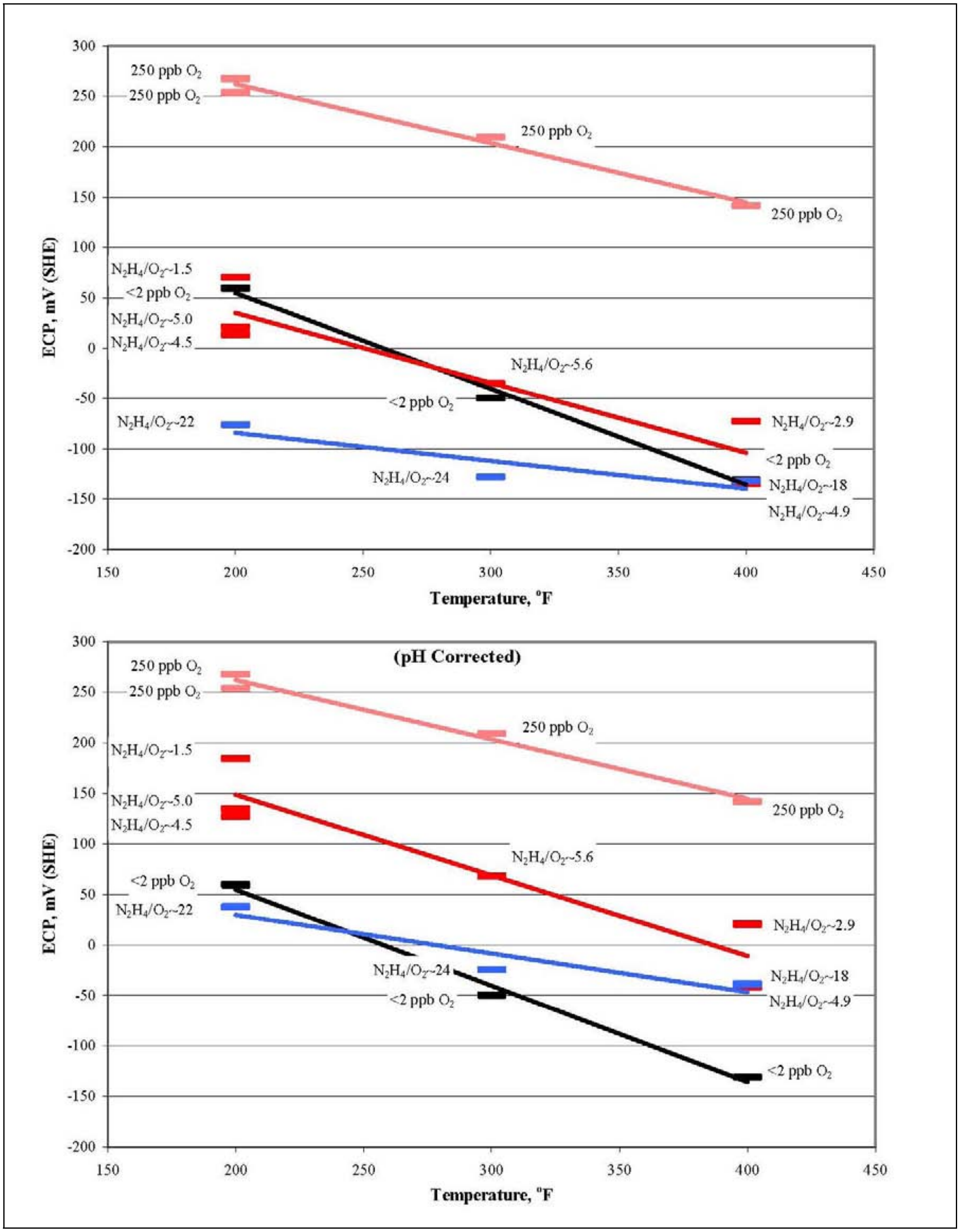

**Figure 2-5**
**Effect of Temperature, Oxygen and Hydrazine/Oxygen Ratio on ECP of Prefilmed Stainless Steel [1]**

## 2.3 Acceptance Criteria

For the hydrazine loop tests, ECP(SHE) at a measured oxygen concentration of <u><</u>2 ppb were used for comparison with the measured ECP(SHE) with hydrazine injection. The measured ECP values at an oxygen concentration of <u><</u>2 ppb from the loop tests discussed above for the NMCA treated and untreated prefilmed specimens at 200 °F, 300 °F and 400 °F are shown in Figure 2-6. Extrapolation of these results to 500 °F using the linear regression equations shown in Figure 2-6 results in ECP values of -231 mV (SHE) for the untreated specimen and -532 mV (SHE) for the NMCA specimen. While these are not considered quantitative criteria for mitigation, they provide an indication that mitigation can be achieved by hydrazine injection for the NMCA treated specimen and the untreated prefilmed specimen in the loop tests. A difficulty in interpreting these results is the uncertainty in the dissolved oxygen measurement in the 0 – 5 ppb range and the sensitivity of ECP to oxygen concentrations in this low range.

In addition, the ECP decrease with hydrogen injection in comparison with the results with 250 ppb oxygen and without hydrazine can be used as a measure of improvement. For example, with the 250 ppb $O_2$ data from Figure 2-4, the curve for the NMCA treated specimen can be used to establish the ECP suppression that is associated with IGSCC mitigation at the various temperatures.

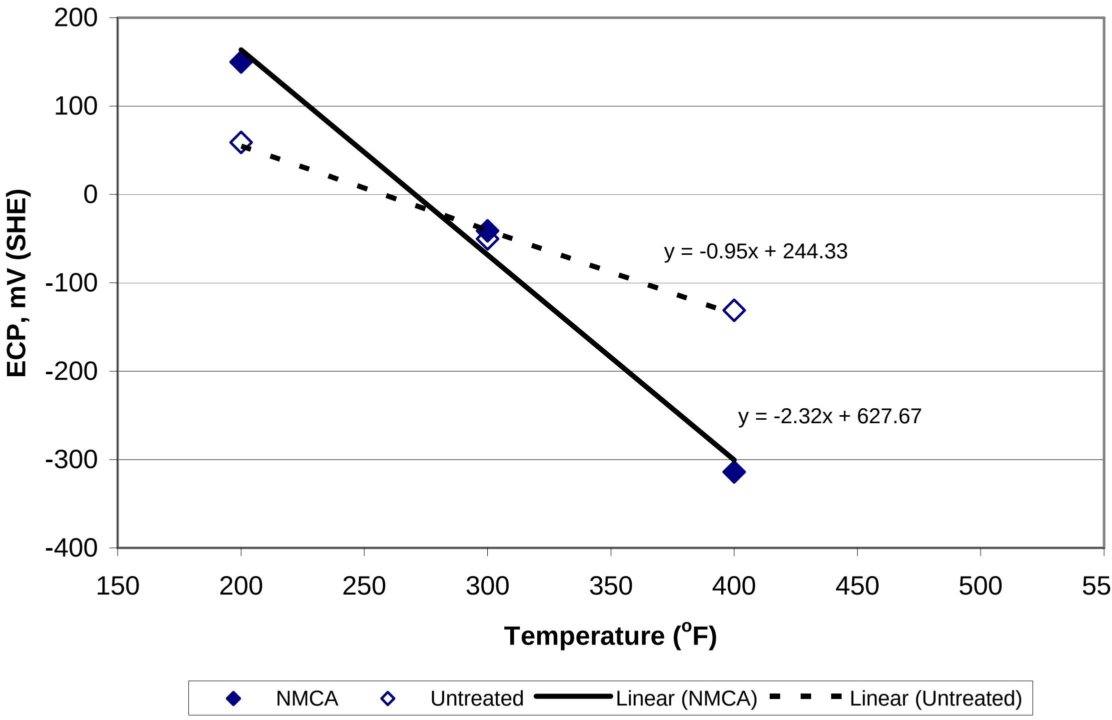

**Figure 2-6**
**Measured ECP at Oxygen <u><</u> 2 ppb for NMCA and Untreated Prefilmed Specimens [1]**

Mitigation acceptance criteria during startup, in the intermediate temperature range from 200 °F to lower than the normal power operation temperature, needs to be developed. An ECP of -230 mV(SHE) has been accepted for power operations. This value is associated with significant crack growth reduction. Under the conditions of hydrostatic testing and subsequent heatup/startup evolution, the relationship between crack growth rate and temperature has been measured under high oxidant conditions, where the growth rate peaks between 300 and 400 $^{o}$F.

ECP values at intermediate temperatures need to be defined to mitigate crack rates to acceptable limits. The goal of these limits would be to mitigate IGSCC during the startup period. Due to differences between autoclave and actual plant conditions, a plant demonstration will be necessary to measure the plant chemistry response.

## 2.4 References

1. EPRI Report on Laboratory Tests by NWT on "Effect of N2H4 on ECP of NMCA Treated Surfaces During a BWR Startup". To be published in 2008.

# 3
# BWR STARTUP EVOLUTIONS EXAMPLE

## 3.1 General

Plant evolutions to achieve cold shutdown conditions and evolutions during refuel outages related to water chemistry control are documented in BWRVIP-176: BWR Shutdown Chemistry Experience Report and Application Guidelines [1]. The last activities performed prior to startup are the reactor vessel reassembly and pressure leak testing. While reactor coolant temperatures are maintained <120 °F during refueling conditions, temperatures are increased to above 212 °F during the vessel pressure leak test (hydrostatic pressure test). Coolant temperatures are initially increased above normal shutdown temperatures to support setting and tensioning the reactor head. Once the head has been tensioned, a plant can prepare for the pressure leak test.

Plant procedures provide limits for heatup and cooldown rates during the pressure leak test. The time above 212 °F during the test is plant specific and may vary depending on the scope (boundaries) of the test. It could be range from as little as 4 to 8 hours, to as much as 12 to 24 hours. After the leak test is complete, the coolant temperature is lowered to less than 200 °F using shutdown cooling. The temperature is maintained typically between 130 °F and 150 °F as a station completes final reactor reassembly. One to two shifts (12 – 24 hours) after successful leak testing is typically required to complete the final reactor reassembly (setting the vessel head insulation package, setting the drywell dome, and installing the shield plugs).

Upon startup, shutdown cooling is secured and reactor recirculation pumps are started. The reactor is brought to critical condition and heatup above 200 °F commences. Initially, the reactor head vent may be opened until a few pounds pressure is established in the reactor vessel. The main steam line drains are opened as well to direct any condensed liquid to the main condenser. Condenser vacuum is initially established with mechanical vacuum pumps and later on with the steam jet air ejector system when reactor pressure increases to between 200 and 300 psig and sufficient steam flow is available. Main steam flow is routed to the main condenser through the turbine bypass valves. As condensate/feedwater flow increases, additional pumps are brought into service as required. The reactor is placed in the Run mode when reactor pressure increases to approximately 1000 psig, after which the main turbine is rolled and the generator is synchronized to the grid. Power ascension then continues at a rate within plant technical specification limits until 100% power is established.

Hydrogen injection is brought into service based on plant specific requirements. Individual plant information available from the EPRI BWR Chemistry Monitoring Database is shown in Table 3-1. As shown in the table, Oyster Creek and Dresden 2 and 3 are the only units currently reporting that hydrogen injection is started at less than 10% power. Several plants are investigating plant changes to place hydrogen injection in service earlier in the startup.

**Table 3-1**
**HWC Shutdown and Startup Power Levels [1]**

| Plant | Type | Power Level for Hydrogen Injection Shutdown | Power Level for Hydrogen Injection Startup | Comments |
|---|---|---|---|---|
| Brunswick | HWC-M | 40-45% | 65-70% | Design allows for starting at 17.3% power. In practice 2nd feed pump must be in service |
| Chinshan | HWC | 90% | 90% | |
| Columbia | NMCA+HWC | 25% | 25% | Planned modification to allow starting at 5-10% power |
| Cooper | NMCA+HWC | 25% (system trip) | 25% | Planned modification to allow starting below 15% power |
| Dresden 2 & 3 | NMCA+HWC | | 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 | 25% | 25% | Requires offgas recombiner in service |
| Hatch | NMCA+HWC | 100% | 30% | |
| Hope Creek | NMCA+HWC | 35% | 35% | Planned changes in progress to allow starting at ~ 5% power |
| Kuosheng | HWC | 90% | 90% | |
| LaSalle | NMCA+HWC | 30% | 50% | |
| Limerick | NMCA+HWC | | 30-40% | Requires 2nd feed pump in service for starting |
| Monticello | HWC-M | 75% | 50% | |
| Mühleberg | NMCA+HWC | 36-48 hrs prior | 40% | |
| Nine Mile Point 1 | NMCA+HWC (OLNC) | | 75% | |
| Nine Mile Point 2 | NMCA+HWC | | 70% | |
| Oyster Creek | NMCA + HWC | <5% | ~5% | Hydrogen injection operated until SJAE is secured; hydrogen started when SJAE is in service |
| Peach Bottom | NMCA+HWC (Unit 3 OLNC) | 15-20% | 15-20% | Revised to coordinate with turbine online and offline |

| Plant | Type | Power Level for Hydrogen Injection Shutdown | Power Level for Hydrogen Injection Startup | Comments |
|---|---|---|---|---|
| Perry | NMCA+HWC | 50% | 50% | Requires feed pump min flow valve closure |
| River Bend | HWC-M | 30% | ~70% | Third feed pump start for startup |
| Susquehanna | HWC-M | 30-60% | 30% | Usually start at 50% for dose reduction |

Plant specific startup data and procedures are presented and discussed below. Where startup chemistry and operational data were made available, startup milestones are noted. The initial focus is on Limerick Generating Station, since this plant is not able to start hydrogen injection until reactor power increases above 30%. Plant modifications to start hydrogen injection at lower power have been considered but were concluded to be prohibitive. Therefore, Limerick is a plant that could benefit from chemical injection to reduce ECP during startup, including heatup and low power operation.

## 3.2 Limerick 1 & 2

### *3.2.1 Limerick Design Data*

Key plant design data for Limerick 1 and 2 is summarized in Table 3-2. The electrical power output of each BWR-4 unit has been increased by 13.7% since commercial operation commenced. Each has Admiralty Brass condenser tubes that represent a significant source of copper in the condensate pump discharge stream. Both units were originally designed with condensate filter demineralizers, which resulted in high feedwater copper concentrations. A deep bed condensate demineralizer system was retrofitted to each unit downstream of the filter demineralizer system, which was converted to a non-precoat pre-filter employing pleated filter septa.

**Table 3-2**
**Limerick 1 and 2 Key Plant Design Parameters**

| Parameter | Limerick 1 | Limerick 2 |
|---|---|---|
| Commercial Operation Date | 2/86 | 1/90 |
| BWR Type | 4 | 4 |
| Capacity (MWth/MWe) | 3458/1200 | 3458/1200 |
| Condensate Polishing Type | Filter + Deep Bed | Filter + Deep Bed |
| Main Condenser Tube Material | Admiralty Brass | Admiralty Brass |
| Drains Path | Cascaded | Cascaded |
| RWCU Capacity (% of Feedwater Flow), Normal/Maximum | 1.1/1.1 | 1.1/1.1 |
| Chemistry Regime | HWC-NMCA; DZO (passive) | HWC-NMCA; DZO (passive) |

Major milestones for Limerick 1 and Limerick 2 are presented in Table 3-3 and Table 3-4, respectively. Both units have been on DZO since May 1997 after initially injecting NZO. Hydrogen injection was initiated at both units in 1998. The initial NMCA was performed at Limerick 1 in March 2000, and the initial coupon loading was 1.15 $\mu g/cm^2$. At Limerick 2, the initial application was performed in April 2001, and the initial coupon loading was 1.12 $\mu g/cm^2$. A classic reapplication was performed at Unit 2 in March 2007, providing a noble metal deposition of 0.56 $\mu g/cm^2$, which was about half of the initial application deposition.

During startup, hydrogen injection cannot commence at Limerick until the second reactor feed pump is in service. This typically occurs when reactor power is in the range of >30% to approximately 50%.

**Table 3-3**
**Limerick 1 Major Milestones**

| Milestone | Date | Comment |
|---|---|---|
| Pleated Filters | 10/94 | |
| Power Uprate | 1995 | Uprate (from 1055 $MW_e$) |
| | 2000 | Uprate (from 1160 $MW_e$) |
| RWCU Pipe Replacement | 4/00 | One of 3 50% pumps and nearby piping replaced with 100% pump |
| NZO | 9/92 | |
| Iron Injection | 2/97 | Iron Oxide |
| DZO | 5/97 | |
| HWC | 1998 | 5 – 10 scfm |
| NMCA | 3/00 | Application EOC 8 |

**Table 3-4**
**Limerick 2 Major Milestones**

| Milestone | Date | Comment |
|---|---|---|
| Pleated Filters | 4/95 | |
| Power Uprate | 1995 | from 1055 $MW_e$ |
| | 1999 | from 1160 $MW_e$ |
| RWCU Pipe Replacement | 4/01 | One of 3 50% pumps and nearby piping replaced with 100% pump |
| NZO | 1991 | |
| Iron Injection | 3/97 | Iron Oxide |
| DZO | 5/97 | |
| HWC | 1/98 | 5 – 10 scfm |
| NMCA | 4/01 | Application EOC 6 |
| | 3/07 | Classic reapplication EOC 9 |

The latest median values for feedwater iron, copper and zinc are shown in Table 3-5. Iron is removed from the condensate to less than detectable concentrations by the condensate pre-filter system, and is then added to the feedwater by injection of iron oxide (hematite) slurry. The condensate pump discharge stream median copper concentrations are 1.77 ppb for Limerick 1 and 2.10 for Limerick 2. However, copper concentrations in the final feedwater are very low at both units, as shown in Table 3-5, indicating effective removal by the condensate polishing system. Median feedwater zinc concentrations are less than the cycle average maximum of 0.4

ppb recommended in the EPRI Water Chemistry Guidelines – 2004 Revision for plants operating with NMCA+HWC.

**Table 3-5**
**Limerick 1 & 2 Latest Median Feedwater Metals**

| Parameter | Limerick 1 | Limerick 2 |
|---|---|---|
| FW Total Fe (ppb) | 0.516 | 0.443 |
| FW Total Cu (ppb) | 0.004 | 0.016 |
| FW Total Zn (ppb) | 0.222 | 0.261 |

Median concentrations of reactor water soluble Co-60 at Limerick 1 and Limerick 2 are 5.45E-05 µCi/ml and 1.91E-04 µCi/ml, respectively. The median Co-60(s)/Zn(s) ratio values are 4.43E-06 µCi/ml at Limerick 1 and 1.47E-05 µCi/ml at Limerick 2, both less than the 2E-5 µCi/ml value recommended for drywell shutdown dose rates at NMCA plants.

### *3.2.2 Reactor Pressure Vessel Leak Test (Hydrostatic Test) Summary*

The reactor pressure vessel leak test is of interest here because the temperature during the test is increased to >200 $^{o}$F and the time >200 $^{o}$F is counted as time when IGSCC is not mitigated. The leak test evolution is reviewed as an initial step in determining if injection of a chemical, such as hydrazine, to reduce ECP would be feasible.

Steps of the Limerick reactor pressure vessel leak test are summarized in Table 3-6. The RWCU F/Ds are removed from service during the test. The RWCU system is operating in decay heat removal mode (heat removed by Non-Regenerative Heat Exchanger), and CRD (Control Rod Drive) and RHR are aligned for operation. The letdown flow destination can be to the main condenser (hotwell), CST (Condensate Storage Tank) or radwaste Equipment Drain Collection Tank. Long path recirculation is secured, if in service, prior to the start of the hydrostatic test.

The RPV water level is maintained just below the RPV flange. Reactor head vents are closed to steam lines but open to radwaste. With RWCU blowdown secured, the RPV level is raised to 250 - 260" using condensate (preferred), CRD or condensate transfer water. RHR cooling is adjusted to maintain reactor coolant temperature as the water level is raised. When reactor water reaches the desired level, a blowdown flow rate of >30 gpm is established and, by imposing an equivalent input flow, the RPV level is stabilized.

The RHR/SDC heat exchanger is bypassed to raise the RPV metal temperature to 100 $^{o}$F (minimum), and the RPV level is slowly raised 300" (maximum). With RHR/SDC secured, a reactor recirculation pump is started (a second reactor recirculation pump may be started if required for heatup). Heatup is accomplished by raising the reactor recirculation pump speed to 28% and using RWCU for alternate decay heat removal. Plant Technical Specifications require a temperature of 212 $^{o}$F at the recirculation pump discharge or bottom head drain. The heat up rate must be <20 $^{o}$F per hour.

The RPV is then pressurized to 500 psig. The pressurization rate is limited to 100 psig/minute by controlling CRD flow $\geq$40 gpm and RWCU blowdown at 30 gpm (minimum). At 500 psig, inspections are performed for leakage into the drywell, outboard MSIV and subpile room.

The RPV pressure is raised toward 1045 psig using CRD input and letting down from RWCU. Heatup is continued by manipulating reactor recirculation pump speed. As pressure is increased to 950 psig, operators can consider performing scram time testing. At 1045 psig, the necessary inspections for leakage are performed.

When the pressure test is complete, RPV pressure is reduced by lowering reactor recirculation pump speed below 28% and raising RWCU letdown flow. The depressurization rate is not to exceed 20 psig/hr, with a maximum cooldown rate of 20 $^{o}$F/hr. RPV water level is lowered to the normal startup level using RWCU letdown flow (using reactor recirculation pumps). RPV draining may also be assisted by draining via Main Steam Line Drains, HPCI Steam Line Drains, RCIC Steam Line Drains, and RHR. When normal conditions are restored, the RWCU F/Ds may be returned to service.

**Table 3-6**
**Limerick Reactor Pressure Vessel Leak Test**

| **Limerick Reactor Pressure Vessel Leak Test** | |
|---|---|
| Plant | Limerick 1 & 2 |
| Procedure Number | GP-10 |
| Procedure Revision Number | 57 |
| | **Step** |
| **PREREQUISITES** | 2 |
| Notify Chemistry and HP prior to removal of RWCU F/D from service | 2.1.7 |
| Record Dump Flow destination as Condensate Hotwell, CST, Equipment Drain Collection Tank | 2.1.8 |
| Verify RWCU return path normal or alternate | 2.1.9 |
| Remove RWCU F/D from service | 2.1.10 |
| Verify RWCU in decay heat removal mode | 2.1.12 |
| Verify Control Rod Drive aligned | 2.1.14 |
| Verify RHR aligned | 2.1.15 |
| Verify Recirc Pump filled & vented | 2.1.16 |
| RPV level should be 205"-210", just below RPV flange | 2.3 (Note) |
| Verify head flange leak detection has been drained | 2.3.3 |
| Verify head vent to steam line C closed | 2.3.4 |
| Verify head vents to radwaste are open | 2.3.5 |
| Secure long path recirculation if in service | 2.3.6 |
| | |

| **Limerick Reactor Pressure Vessel Leak Test** | |
|---|---|
| RAISING LEVEL | 2.5 |
| Floodup to 250-260" using Condensate (preferred), CRD or Cond Transfer | 2.5.1.1 |
| Ensure RWCU Blowdown is secure | 2.5.1.2 |
| Adjust RHR cooling water temperature to maintain Rx temp as level is raised | 2.5.1.3 |
| When Rx water level reaches desired level, establish blowdown rate >30 gpm and stabilize level | 2.5.1.4 |
| | |
| RPV HEATUP | 2.6 |
| Bypass RHR/SDC HX to raise Rx metal temp to 100 F min | 2.6.1 |
| | |
| BYPASS REACTOR VESSEL HIGH PRESSURE SCRAM | 2.7 |
| | |
| RAISING LEVEL | 2.8 |
| Slowly raise level to 300" maximum | 2.8.1 |
| | |
| PROCEDURE | 3 |
| START REACTOR RECIRC PUMP & SECURE SHUTDOWN COOLIING | 3.1 |
| Secure RHR Shutdown Cooling | 3.1.4 |
| Start a Reactor Recirc Pump | 3.1.8 |
| Start a second Reactor Recirc Pump if required for Heat Up | 3.1.10 |
| | |
| Tech specs require temperature 212 F at recirc pump discharge or bottom head drain. Heatup rate < 20 deg F per hour | CAUTION before 3.2 |
| HEATUP | 3.2 |
| Heat up reactor by raising Recirc Pump speed to 28% and using RWCU for alternate decay heat removal | 3.2.2 |
| | |
| RPV PRESSURIZATION | 3.3 |
| Pressurization rate limited to 100 psig/minute, CRD flow > or = 40 gpm to maintain pressure control, minimum RWCU blowdown rate is 30 gpm. | NOTE before 3.3.8 |
| Pressurize RPV to 500 psig | 3.3.8 |
| At 500 psig, inspect for drywell leakage, outboard MSIV, subpile room | 3.5.1 |
| Pressurize to 1045 psig using CRD and RWCU dump control | 3.5.3 |
| Continue heatup by manipulating Recirc Pump speed | 3.5.4 |
| At 950 psig consider performing scram time testing | 3.5.6 |

| **Limerick Reactor Pressure Vessel Leak Test** | |
|---|---|
| At 1045 psig, perform the necessary inspections | 3.6.1 |
| When pressure test is complete, reduce pressure | 3.6.5 |
| Lower Recirc Pump speed below 28% | 3.8.1 |
| Raise RWCU dump flow for depressurization rate not to exceed 20 psig/hr (max. cooldown rate 20 deg F/hr) | 3.8.6 |
| Reduce RPV level to normal startup level by RWCU dump flow (RWCU system blowdown using Recirc Pumps) | 3.11.7 |
| Assist draining via Main Steam Line Drains, HPCI Steam Line Drains, RCIC Steam Line Drains, and RHR | 3.11.7.1 |
| RWCU RESTORATION | 3.12 |
| Restore RWCU Filter Demin to Service | 3.12.1.5 |

### *3.2.3 Startup Procedure Summary*

During the plant startup evolution from shutdown to full power, there is a significant time period when the reactor coolant temperature is >200 $^{o}$F and IGSCC is not mitigated. Hydrogen injection cannot be started at Limerick until power is between 30% and 50%. Chemical impurity inputs to the reactor during startups, particularly from cold shutdown conditions following refueling outages, are typically higher that at normal power operating conditions. The startup evolution is reviewed to provide the basis for determining the lineups and milestones at which injection of a chemical, such as hydrazine, to reduce ECP would be feasible.

Major milestones of the Limerick startup procedure are summarized in Table 3-6. In preparation for startup, the CRD, RWCU and Condensate systems are in service and the long path feedwater flush is completed. The reactor head vent is open. The condensate system is initially operating on short path recirculation with one or more demineralizers in service.

The first reactor recirculation pump is started followed by securing RHR shutdown cooling. At this point, reactor temperature is between 140 and 150 °F. The second reactor recirculation pump is started and then the mode switch is placed in Start-up/Hot Standby.

Heatup commences by initial control rod withdrawal to bring the reactor to critical. At temperatures less than 200 °F, the reactor head vent remains open. Main condenser vacuum is initially established with the mechanical vacuum pumps. The steam jet air ejector can be warmed with auxiliary boiler steam and the first stage can be operated with auxiliary steam. Main steam line drains are opened when the reactor coolant temperature is >200 $^{o}$F and condenser vacuum reaches 10.5 psia (8.5" Hg. vacuum). Control rod withdrawal continues until the coolant temperature is 212 °F, at which point the MSIVs can be opened under positive RPV pressure. Rod withdrawal continues while maintaining the heatup rate at <100 °F/hr. A chemistry hold point is included in the startup procedure prior to exceeding 50 psig (~ 296 °F) ensure that dissolved oxygen in the coolant meets requirements (less than 300 ppb is the suggested value in BWRVIP-130 [2]). The hold time is typically short if condenser vacuum has been established with the MSIVs and main steam line drains open.

At 100 psig reactor pressure, the SJAE and offgas preheater are switched to main steam. RWCU blowdown to the hotwell is secured when RPV level can no longer be maintained by CRD flow. The first turbine bypass valve is about 10-20% open at about 150 psig reactor pressure. Operability testing of the reactor core isolation cooling system (RCIC), if required, is performed before reactor pressure exceeds 150 psig. If RCIC test acceptance criteria are not met, reactor steam dome pressure must be reduced to <50 psig within 72 hours. Operability testing of the high pressure coolant injection system (HPCI), if required, is performed before reactor pressure exceeds 150 psig. If HPCI test acceptance criteria are not met, reactor steam dome pressure must be reduced to <200 psig within 72 hours.

The second condensate pump is started before reactor pressure exceeds 400 psig. At >400 psig reactor pressure, the first reactor feed pump is placed in service. The mode switch is placed into RUN when reactor pressure reaches approximately 960 psig. The main generator is synchronized to the grid between 10 and 15% power. The second reactor feed pump is placed in service prior to exceeding 33% power. The startup procedure states that hydrogen injection should be placed in service immediately after the second feed pump is in service. The third reactor feedwater pump is placed in service when reactor power is between 60 and 65% power.

The time of initial control rod withdrawal to the time reactor coolant temperature reaches 200 °F is normally about four hours. Hydrazine injection could commence shortly after shutdown cooling is secured and the second reactor recirculation pump is started to lower ECP when the temperature first reaches 200 °F. Hydrogen injection can not be started until the second reactor feedwater pump is in service, which occurs at about 33% power after the main generator is synchronized to the grid. The time between the coolant temperature reaching 200 °F and the second feed pump placement in service can vary significantly, depending upon problems encountered and the number of surveillance tests performed during the specific startup. Industry experience shows that performing RCIC and HPCI operability tests during startup can result in significant delays in power ascension, particularly if problems occur during the testing. During this testing, reactor pressure is maintained constant. The coolant temperature during this period is in an intermediate range where laboratory data indicate higher crack growth rates can occur.

The Limerick station has turbine driven reactor feedwater pumps. Plants with turbine driven reactor feedwater pumps have experienced pump operability issues, which can lead to further delays in power ascension. It is conceivable that reactor coolant temperature could exceed 200 $^{o}$F for 72 hours or more prior to starting the normal hydrogen injection system during a plant startup from a refueling outage.

## Table 3-7
## Limerick Normal Startup Procedure

| **LIMERICK STARTUP PROCEDURE** | |
|---|---|
| Plant | Limerick 1 & 2 |
| Procedure Number | GP-2 |
| Procedure Revision Number | 122 |
| | **Step** |
| **PREPARATION FOR STARTUP** | |
| Place CRD System in service | 3.1.13 |
| Prep for Condenser vacuum | 3.1.23 |
| RWCU System in service | 3.1.24 |
| Commence Feedwater Flush | 3.1.28 |
| Place Cond Demin beds in service | 3.1.29 |
| Reactor head venting at <200 F | 3.1.34 |
| Terminate FW flush; return to short path | 3.1.36 |
| **MODE SWITCH TO STARTUP** | |
| Start first Rx Recirc Pump | 3.2.11.5 |
| Secure RHR/SDC | 3.2.11.7 |
| Start second Rx Recirc Pump | 3.2.11.9 |
| Rx Mode Switch to Startup | 3.2.16 |
| Ready for Startup | 3.2.23 |
| Withdraw Ctrl Rods per Startup Plan | 3.2.25 |
| | |
| **HEATUP/PRESSURIZATION** | |
| Open Main Steam drain valves | 3.3.6 |
| Continue rod withdrawal to 212 F | 3.3.7 |
| Continue rod withdrawal per heat-up rate | 3.3.11 |
| Chem sampling for Cond (CRD) DO | 3.3.12 |
| At Rx pressure 75 psig, open RHR min bypass | 3.3.17 |
| At Rx pressure 75 psig, close RWCU orifice bypass | 3.3.17 |
| At Rx pressure 100 psig, transfer SJAE/Recombiner preheater supply to Main Steam | 3.3.18.2 |
| Secure RWCU blowdown | 3.3.18.8 |
| At Rx pressure 150 psig, establish FW flow bypass valve | 3.3.21.4 |
| Withdraw rods until one turbine bypass valve is open at 150 psig Rx pressure | 3.3.21.5 |
| Continue rod withdrawal to obtain two or three turbine bypass valves open | 3.3.21.7 |

| LIMERICK STARTUP PROCEDURE | |
|---|---|
| Raise Rx pressure to 200 psig by EHC pressure increase and rod withdrawal | 3.3.21.9 |
| Begin raising Rx pressure to 450 psig by EHC pressure increase and rod withdrawal | 3.3.23 |
| At Rx pressure 300 psig, ensure SJAEs on main steam | 3.3.26 |
| Before exceeding 400 psig, place second condensate pump in service | 3.3.27 |
| At >400 psig, place a Rx Feed Pump in service | 3.3.28 |
| At Rx pressure 450 psig, place FW oxygen addition in service per Chemistry | 3.3.29.1 |
| Raise Rx pressure by EHC pressure increase and rod withdrawal | 3.3.29.2 |
| Perform 500 psig drywell inspection | 3.3.29.2.b |
| Raise Rx pressure >756 psig by EHC pressure increase and rod withdrawal | 3.3.33 |
| | |
| **MODE SWITCH TO RUN** | |
| Plant Status: Two condensate pumps running, main turbine chest warmed, offgas recombiner in service | |
| Place Mode Switch to Run | 3.4.7 |
| At Rx pressure 960 psig and drywell inspections complete, inert primary containment | 3.4.11.5 |
| Roll turbine (4 turbine bypass valves open) | 3.4.23 |
| Synchronize generator to grid and raise load until all turbine BPVs are closed | 3.4.25 |
| Ensure sufficient CF/Ds in service (filters and demineralizers) | 3.4.38 |
| | |
| **POWER ASCENSION TO RATED POWER** | |
| Plant Status: Rx power 10%, gen sync to grid, recirc pumps speed 28%, 2 cond pumps | |
| Limit power ascension rate so 1st stage shell temp <126 F/hr and dT<60 F | 3.5.3 |
| At Rx Power 15%, monitor condenser back pressure | 3.5.5 |
| When Main Gen output >185 MWe, place FW heaters in service | 3.5.14 |
| At Rx Power 20%, full auto FW flow control and main condenser offgas H2 gas in service | 3.5.17 |
| At 25% Rx power, verify thermal limits | 3.5.19 |
| At nominal 30% Rx power, ensure chemistry primary sampling complete | 3.5.23.3 |
| Place HWC in service | 3.5.23.5 |
| At 50% Rx power, Chemistry initiate corrosion product sampling of FW | 3.5.29.1 |
| Place NMMS in service | 3.5.29.3 |

### *3.2.4 Limerick 2 Startup Review from RFO9 Startup*

Startup data from the Limerick 2 RFO9 refueling outage in 2007 is presented in Figures 3-1and 3-2. The unit was returned to a shutdown condition twice during startup in early April 2007. The second shutdown, which occurred toward the end of April, was the result of a full power reactor scram that occurred due to decreasing reactor vessel level. During the shutdown to RFO9, a classic noble metals reapplication was performed.

Reactor coolant temperature and dissolved oxygen trends are shown in Figure 3-1. The time scale is given in terms of hours after the reactor coolant temperature initially exceeded 200 °F during the startup. In the initial startup, the coolant temperature increased from 118 °F to > 200 °F in about 4.5 hours, and then increased to 327 °F about 1.5 hours after first exceeding 200 °F. Temperature increased to 500 °F about 12.5 hours after first exceeding 200 °F. Reactor power reached approximately 18% before the unit was forced to a cold shutdown (coolant temperature was lowered to about 117 °F) due to problems with the main generator. Temperature remained below 200 °F for a period of about 28 hours.

In the second startup, the reactor coolant temperature increased from 117 °F to >200 °F in about 4.5 hours, and then increased to >500 °F approximately 16 hours after first exceeding 200 °F. Hydrogen injection commenced at 69% power, about 55 hours after the coolant temperature first reached 200 °F during the second startup. The power ascension continued to 100% but remained at this level for only a short time, after which power was lowered to 75% in response to increased seal leakage from the #2 reactor water recirculation system pump. This eventually led to a forced shutdown. Hydrogen injection was secured at about 50% power during the shutdown evolution, and the unit continued to cold shutdown. From the time that hydrogen injection was secured to the time coolant temperature was lowered to less than 200 °F was about 13 hours.

The unit remained in cold shutdown for about 20 hours. During the third startup attempt, the coolant temperature was increased from 122 °F to 200 °F in approximately 5 hours. Hydrogen injection was again initiated approximately 36 hours after the coolant temperature first increased above 200 °F.

The total time above 200 $^{o}$F without hydrogen injection from the first startup attempt through achievement of normal power was approximately 154 hours (6.4 days). Although not typical, this example shows that the time period during a startup when reactor coolant temperature is above 200 $^{o}$F and IGSCC is not mitigated can be longer than expected.

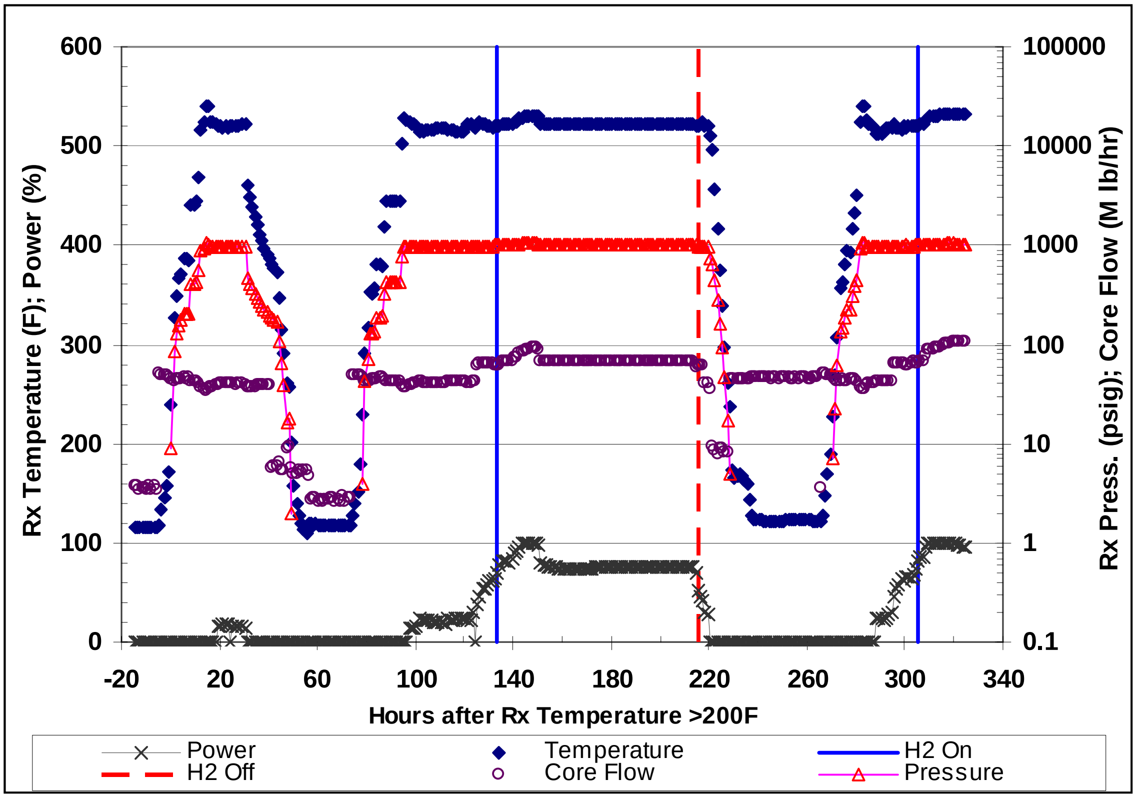

**Figure 3-1**
**Limerick 2 Cycle 10 Startup**

Reactor coolant chemistry data are plotted in Figure 3-2. The first few reported reactor water dissolved oxygen (DO) values during the initial startup were about 100 ppb. These values occurred at a coolant temperature of about 370 °F. The lowest value shown during the initial startup was about 10 ppb, which occurred as the unit was being shut down. The DO values for the second startup were similar, with levels near 100 ppb during the power ascension, prior to starting hydrogen injection. When hydrogen was started, DO values decreased to about 1 ppb. During the second shutdown, the reported DO value was 10 ppb. The DO value prior to starting hydrogen injection the second time was about 50 ppb. Dissolved oxygen decreased to about 1 ppb after hydrogen injection was returned to service.

Measured reactor water sulfate concentrations during the three startups and two shutdowns did not exceed the Action Level 1 limit of 5 ppb. The maximum reported reactor water sulfate value was approximately 3 ppb.

Reactor coolant conductivity declined during the initial startup from 0.7 µS/cm to less than 0.1 µS/cm. Most of the decline was likely due to the removal of dissolved carbon dioxide from the coolant as a result of the heatup and establishment of condenser vacuum. Reactor coolant dissolved carbon dioxide levels would be the highest during a refueling outage due to air saturation of the reactor cavity water. The increase in conductivity following the start of hydrogen injection is attributed to an increase in soluble metals, particularly iron, following the classic noble metal reapplication prior to going to cold shutdown conditions for the refueling outage.

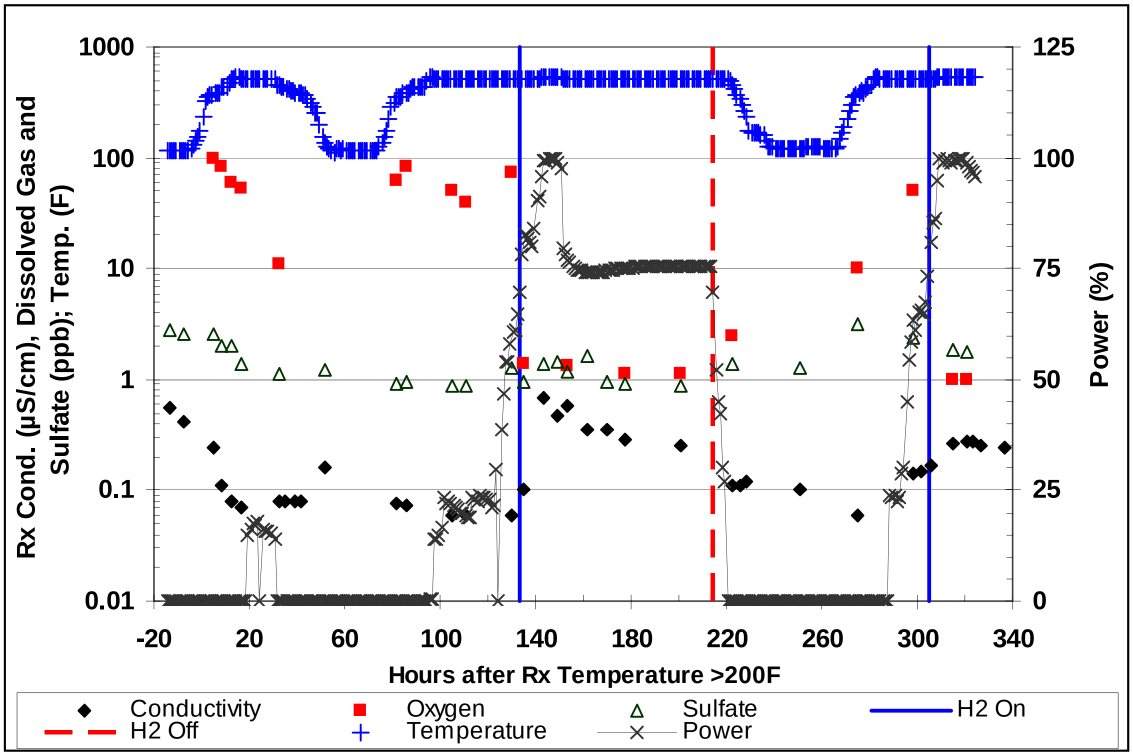

**Figure 3-2**
**Limerick 2 Cycle 10 Startup**

## 3.3 References

1. BWRVIP-176: BWR Vessel and Internals Project, BWR Shutdown Chemistry Experience Report and Application Guidelines. EPRI, Palo Alto, CA: 2007. 1014999.
2. BWRVIP-130: BWR Vessel and Internals Project, BWR Water Chemistry Guidelines – 2004 Revision, EPRI, Palo Alto, CA: 2004. 1008192.

# 4
# PROCESS DESCRIPTION

## 4.1 Approaches for Injection

Hydrazine injection was considered by General Electric along with options for hydrogen injection during the heatup and low power portions of plant startups as part of a study to improve HWC availability [1]. For a plant, such as Limerick, chemical injection for ECP reduction would be beneficial during the startup process to the point where hydrogen injection can be started, which may be at a power level exceeding 50%.

Three potential phases for chemical injection during the startup process are considered. These phases are encompassed by the Startup/Hot Standby condition as defined in BWRVIP-130 [2]. Startup Phase 1 encompasses the reactor hydrostatic pressure leak test and the initial heatup during startup when there is only minor venting from the reactor vessel. In Startup Phase 2, reactor power is very low (<1%) and there is only minor steam flow. In Startup Phase 3, power is increased up to 10%, and steam flow becomes significant.

The chemical injection process is initially focused on hydrazine based to its use in PWR applications. Carbohydrazide injection is also being considered based on the similarity with hydrazine, including its reactions with oxidants and decomposition products, while having industrial safety advantages over hydrazine. Injection of other chemicals, such as methanol, will also be considered, pending the outcome of loop tests.

### *4.1.1 Injection System*

Hydrazine or carbohydrazide would be injected as a liquid solution. It would be preferable if the same injection system could be used in all phases of startup where chemical injection will be performed. The design for BWR injection must consider the number of injection points, the range of injection rates that may be required, the pressure and temperature of the injection point and the need to assure positive isolation, particularly for high pressure/temperature injection. The need for plant process signals to the injection skid, such as for use as permissives to allow injection or to trip the injection pumps and isolate the skid, must be determined.

Hydrazine dilution and injection systems are commonly used in PWRs and are commercially available. The chemical injection configuration used for NobleChem$^{TM}$ is a demonstrated approach in BWRs which uses a chemical injection skid and a drive water skid [1]. The chemical injection skid includes solution tanks, metering pumps, valves, tubing, instrumentation and controls. Chemicals are metered from the chemical injection skid to the drive water skid. The drive water skid, which includes pumps, flow instrumentation and controls, and provides dilution water (approximately 1 gallon per minute) for chemical introduction. On-Line NMCA injection locations and equipment should also be evaluated since these locations are at operating pressure and require similar hardware.

### *4.1.2 Injection Locations*

Three potential injection locations considered are as follows:

- CRD (Control Rod Drive) System
- RWCU Effluent, downstream of the Regenerative Heat Exchanger
- Reactor Recirculation System

Identification of the exact injection point would be based on the results of a plant-specific design review and walkdown. A general discussion of the potential injection locations follows.

Identification of potential locations for chemical injection when the plant is in the reactor pressure vessel leak test lineup, the heatup phase or early startup must consider that there is little or no feedwater flow. Therefore, injection into the feedwater system upstream of the RWCU return connection is not viable. RHR/Shutdown Cooling is also not a viable injection point because this system is removed from service during the leak test and in preparation for startup.

In addition, to minimize complications it is preferred to limit the number of selected injection locations for a given plant. A single location at a specific plant would avoid the need to consider logistics of transporting the chemical to multiple locations in sufficient quantities and the possible need for more than one injection system. Moving chemicals from one location to another may increase risk of a spill, which could impact personnel access to the plant, HVAC, and drains. However, it may not be possible to avoid multiple injection locations to satisfy process requirements during leak testing, heatup and early startup. This is discussed in Section 4.3.

The potential for catalyst contamination on the surface of the selected injection line and its effects should also be considered.

#### 4.1.2.1 Injection into CRD System

The CRD system is in service from cold shutdown through power operation and therefore offers a convenient potential chemical injection location. During the plant heatup and startup period of interest, the CRD suction is normally fed from the condensate demineralizer effluent, so injection into the CRD suction would be at condensate demineralizer system effluent temperature and pressure. The injection point, if considered, would be most likely at a drain connection associated with the CRD pump piping. A major issue would be to verify that all the hydrazine would be uniformly mixed and there would be no gas phase possibilities from nitrogen and ammonia formation within the CRD hydraulic system that would compromise the rod insertion response. This may be difficult to validate. Also, the compatibility of the concentrated hydrazine solution with the materials of the control rod drive would need to be verified. Issues related to the safety classification and essential nature of this system would have to be considered and addressed prior to implementing a plant demonstration with injection into the CRD system [1].

#### 4.1.2.2 Injection into RWCU System

Flow is normally circulating through the RWCU system during reactor vessel pressure leak testing (with the cleanup demineralization vessels bypassed) and during the entire heatup and startup process. The RWCU system inlet is from a reactor recirculation loop and the vessel bottom drain, and most plants draw the normal reactor water sample that is routed to the reactor sample panel from this stream.  Most plants also provide sample flow to the NMMS (Noble Metal Monitoring System)/Durability Monitor from this point.  The RWCU return flow at most plants is to the feedwater system downstream of all feedwater heaters and just upstream of the reactor vessel connection.  The RWCU pump may be located in the “hot leg” just downstream of the takeoff from the recirculation system or in the “cold leg” after the regenerative and non-regenerative heat exchangers, either upstream or downstream of the cleanup filter demineralizers and/or deep bed demineralizers. The RWCU return flow path is through the shell side of the regenerative heat exchanger.  Potential injection tie-in locations may be upstream or downstream of the regenerative heat exchanger, although downstream would be preferred to minimize the contact surface area for hydrazine reactions prior to entry into the reactor vessel.  If RWCU materials of construction are largely carbon steel, the injection point should be as close as possible to the point where the RWCU return connects with the feedwater system to address flow accelerated corrosion issues.  Injection tie-ins to local drain lines with isolation valves are possible [1], and radiation dose rates would have to be considered in selecting the preferred location.  The preferred injection tie-in point is therefore plant specific.

An example of possible tie-in locations for chemical injection to the RWCU system at a BWR-4 design is shown in Figure 4-1.  Three possible connection points downstream of the last Regenerative Heat Exchanger unit are indicated.  This is a typical RWCU system configuration where piping is provided with a number of connection taps to ensure that the system can be filled and vented for startup and drained for maintenance.

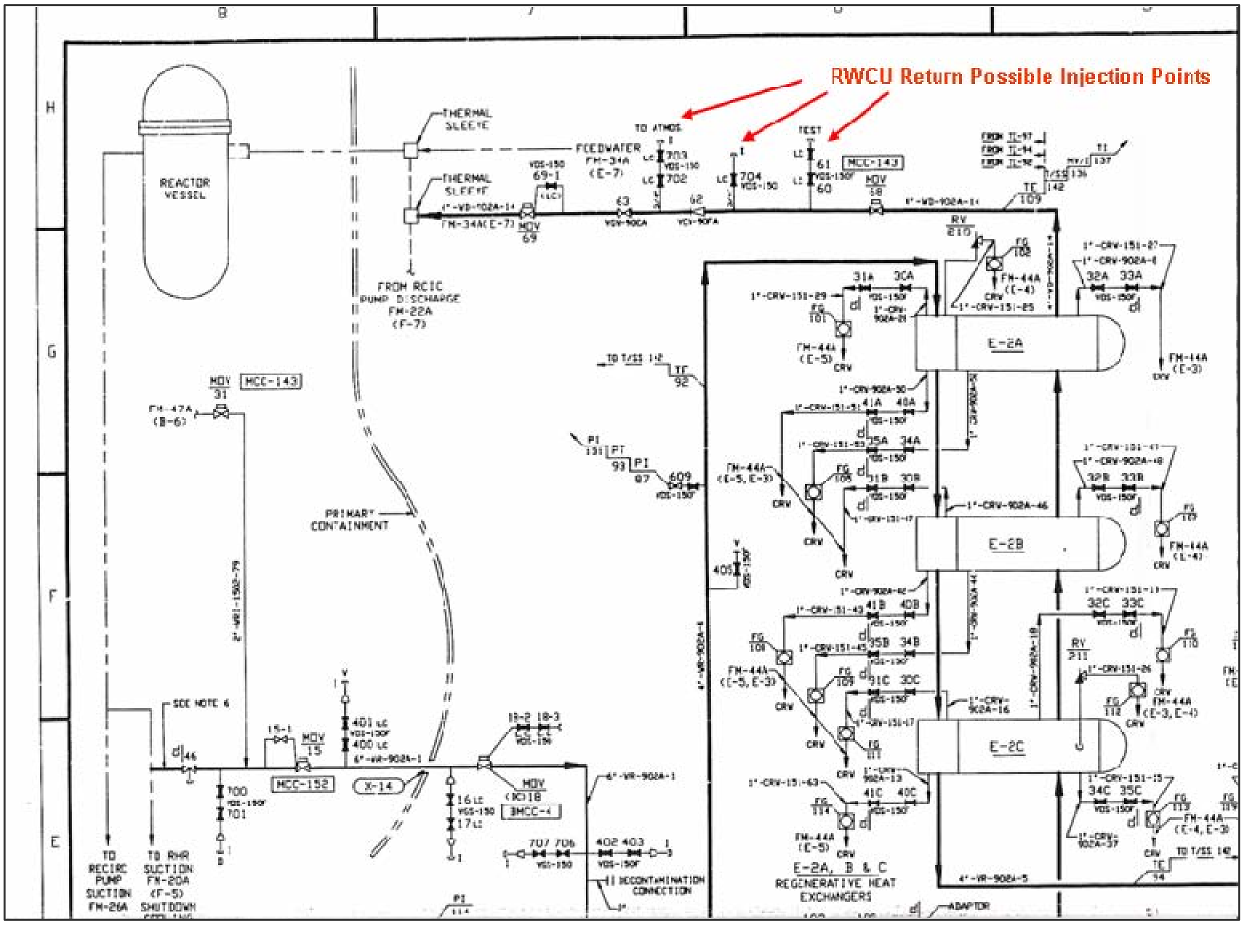

**Figure 4-1**
**Possible RWCU Injection Points for a BWR-4**

RWCU system piping is typically 6 to 8 inches in diameter. The feedwater piping at the tie-in point is typically 18 to 20 inches in diameter. During the vessel hydrostatic test and the initial heat-up for plant startup, there is essentially no feedwater flow. The feedwater piping at the tie-in point may or may not be full, depending upon the boundary for the hydrostatic test, which may be outage and plant specific. With only RWCU return flow, the velocity in the feedwater piping will be low, which increases residence time and contact time with the carbon steel feedwater pipe surface for hydrazine decomposition. The high volume to surface area ratio of the piping should limit the fraction of hydrazine injected that undergoes decomposition. In addition, at very low flow rates with only RWCU return, the flow will probably not be uniformly distributed around the top of the downcomer within the reactor vessel.

During the initial heat-up, as the reactor liquid inventory swells, and during the startup, there is a need to reject a portion of, or at times, possibly the full, RWCU flow to the hotwell to maintain RPV level. The reject tie-in point is upstream of the regenerative heat exchanger, so chemical injection downstream of this exchanger would not provide a flow path for chemicals to be injected directly to the condenser. However, during periods where all of the RWCU flow is rejected to the hotwell, chemicals could not be introduced to the reactor from this flow path.

Another consideration for chemical injection into the RWCU system is that some plants have difficulty with mechanical seals of the RWCU pumps, particularly when the pumps are located in the “hot leg.” Seal leakage problems can develop during startups due to the significant changes in pump operating temperature and pressure. The development of seal leakage may result in unplanned pump outages. While it is unlikely that a plant would commence or continue a startup with no cleanup flow, the loss of one RWCU pump in a plant designed to operate with two pumps would result in reduced flow. The lower flow rate would result in a longer residence time, and thus a greater extent of decomposition, if a chemical such as hydrazine were injected into the RWCU return line at reduced RWCU flow.

#### 4.1.2.3 Injection into Reactor Recirculation System

Hydrazine could be added directly to the reactor water recirculation system similar to injection approach used for the classic noble metal applications. The taps typically used for classic noble metal injection into the reactor water recirculation system are either the recirculation pump differential pressure instrument taps or the recirculation pump flow instrument taps. These taps, which can be accessed outside of primary containment, are small in diameter (3/4" to 1") and typically contain excess flow check valves to prevent gross leakage of reactor coolant outside of primary containment.

While these taps have been used during classic applications when the plant is in hot shutdown, there is no experience using these taps for injection during startup and early power operation. If these taps were used as injection points during startup, an evaluation of the potential impact of the injection flow on instrument indications would be required, including the consequences of potential signal transients.

Another possible injection location is into the root connection of the recirculation system sample point. A section of a P&ID from a BWR-4 is shown in Figure 4-2. At most BWRs, this sample point is from the discharge piping of one of the reactor water recirculation pumps (for the example shown in Figure 4-2, the sample point connection is in the “B” reactor recirculation pump discharge). The main sample line piping diameter inside containment is typically 3/4" or 1". The sample system usually contains inboard and outboard containment isolation valves. The piping typically contains drain connections that are used for performing local leak rate testing (LLRT) of the containment isolation valves during refueling outages. One set of LLRT drain connections is typically located outside containment, just upstream (based on sample flow direction) of the outboard isolation valve. Conceivably, the outboard containment isolation valve would be closed, the inboard valve open, and hydrazine could be injected into the LLRT drain connection between the containment isolation valves. Unlike injecting into the recirculation pump differential pressure or flow instrument line, hydraulic sensing instrumentation is not affected. At most plants, the primary (normally used) reactor coolant sample point is in the inlet to the RWCU system, and this sample would not be impacted by using the reactor recirculation system sample point. However, the reactor recirculation system sample point used for injection would not be available as an alternate or backup sample point when the chemical is being injected. The reactor recirculation system sample line would have to be adequately flushed prior to use after chemical injection.

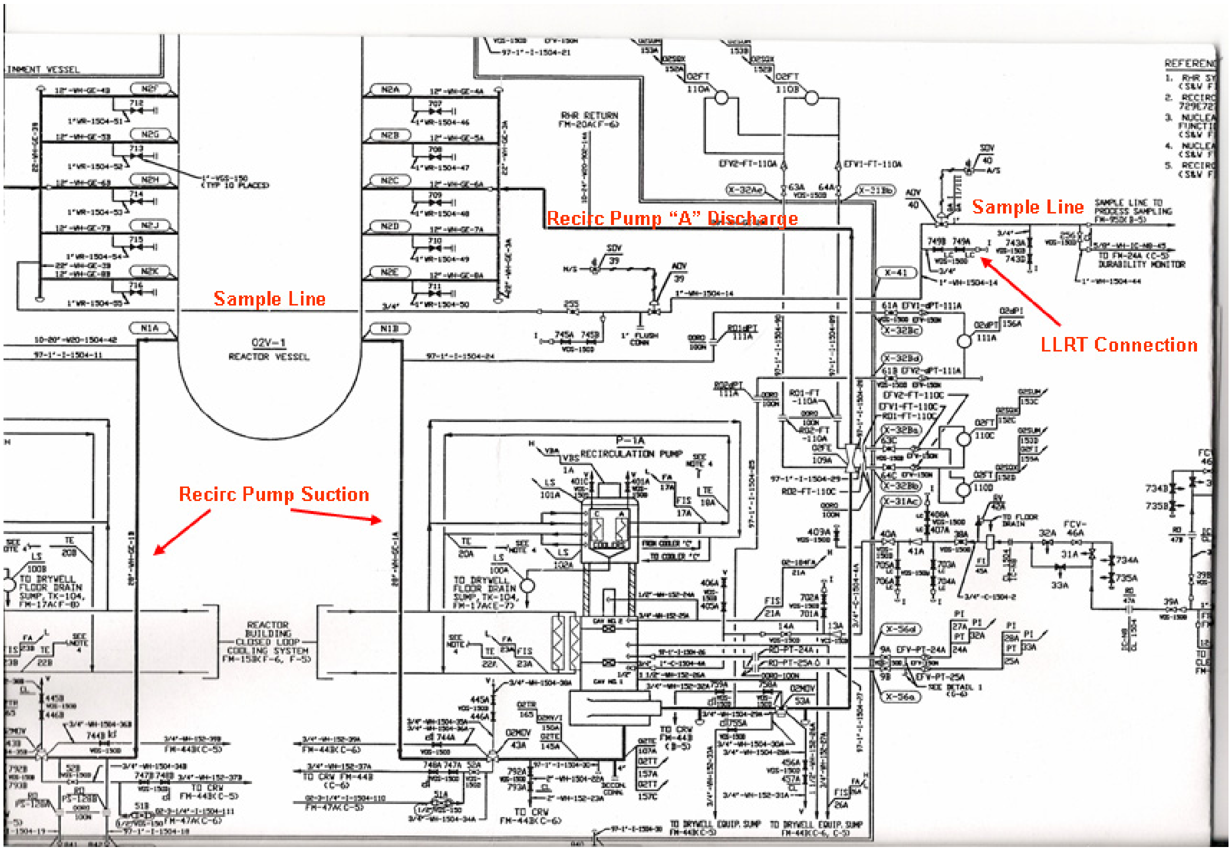

**Figure 4-2**
**Possible Hydrazine Injection Point into BWR-4 Reactor Recirculation System**

The sample line LLRT connections are not needed during RPV hydrostatic pressure leak test. At most plants, reactor coolant sample lines are not used during the hydrostatic pressure leak test because the sample line flow may affect the test results. Plants typically obtain required reactor coolant grab samples just before the start of the RPV hydrostatic pressure leak test and then isolate the sample lines until the next sample is taken after the test.

If a LLRT connection is not available outside of containment, upstream of the outboard isolation valve, it may be possible to connect the chemical injection line to the reactor recirculation sample line downstream of the outboard containment isolation valve. This could be either through another drain line connection or just prior to the sample line tie-in at the chemistry sample station. The recirculation system injection points offer the advantage over the RWCU system injection point that they are not dependent upon RWCU pump operability.

For the plant configuration shown in Figure 4-2, the "B" recirculation system sample tap also supplies flow to the Durability Monitor. This connection previously provided sample flow to a CAVS (Crack Arrest Verification System), which was removed and replaced by the Durability Monitor. For this plant, injecting chemical into the LLRT or sample line connection would not allow the NMMS/Durability Monitor to be available. However, at most plants the normal reactor coolant sample and NMMS/Durability Monitor flow is taken from the RWCU system inlet, so injecting into the recirculation system as discussed above would not affect the Durability Monitor availability.

As shown in Table 3-6, at Limerick the startup operating procedure places the NMMS in service when HWC is placed in service. The point at which the NMMS is normally placed in service is plant specific.

If chemical injection into both recirculation loops (two-loop plants) is required to assure effectiveness, an instrument tap would probably have to be used for one loop while the sample/LLRT connection could be used for the other loop. Considerations for the need to inject into both loops are discussed in Section 4.3 below. The actual selection of injection points would be site specific.

## 4.2 Injection Phases

### *4.2.1 Startup Phase 1 – Closed System (Minor Steam Venting)*

Startup Phase 1 applies to the conditions during the RPV hydrostatic pressure test and during the early startup period with only minor steam venting. The RPV hydrostatic pressure test represents the initial phase of preparation for startup where the reactor coolant temperature is heated up above 200 $^{o}$F. A simplified process schematic of key plant systems during the RPV hydrostatic pressure test is shown in Figure 4-3. The schematic shows the RWCU system operating with the RWCU water purification equipment bypassed. CRD supplies condensate water to the vessel and there is a letdown flow path from RWCU that is normally routed to the main condenser. Figure 4-3 shows the CRD suction lined up to the CST, but the CRD suction flow may be provided from the condensate demineralizer system effluent if a condensate pump is operating and the condensate demineralizer system is available. Temperature is raised to above 200 °F using reactor recirculation pump heat. The possible hydrazine injection points discussed previously are shown in Figure 4-3.

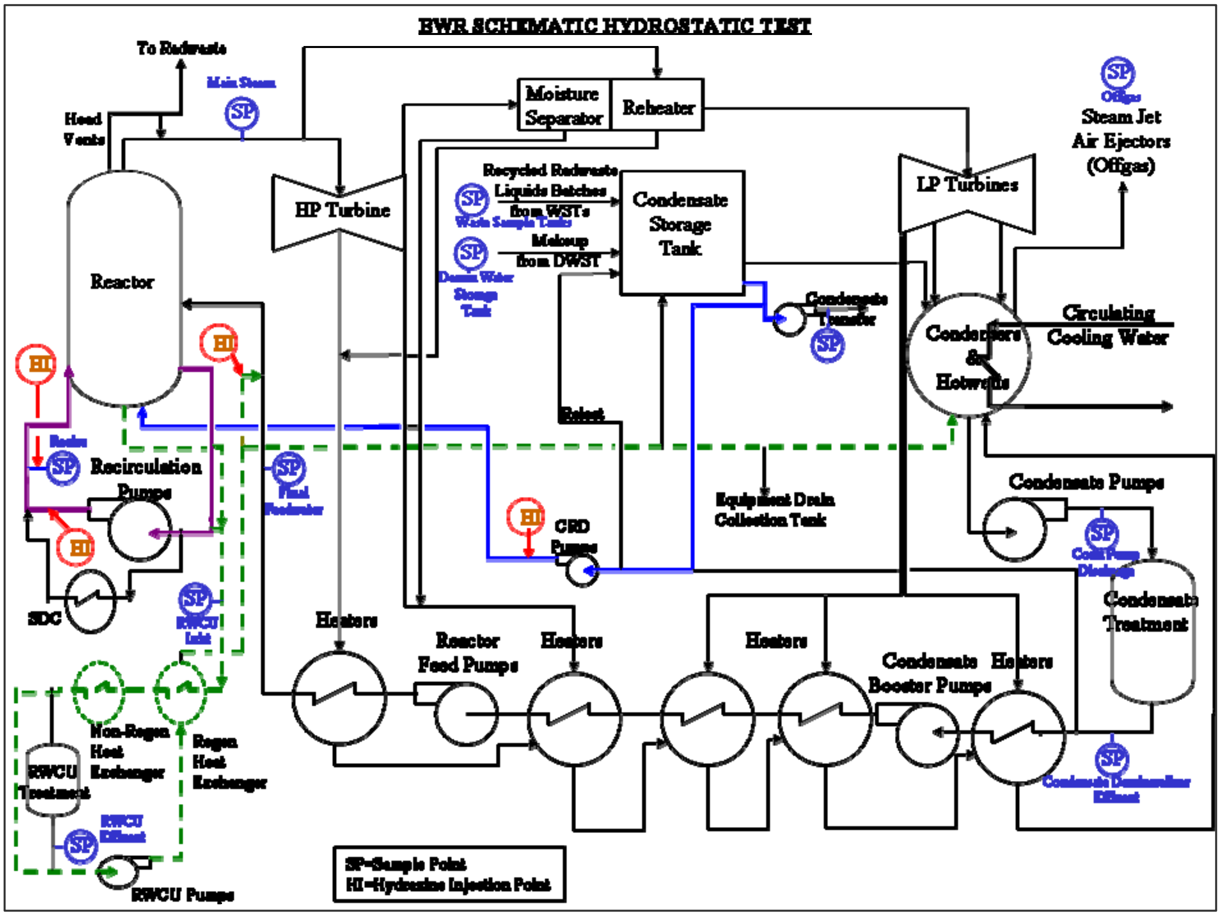

**Figure 4-3**
**Process Schematic during Startup Phase 1 - Hydrostatic Pressure Test and Early Startup**

Reactor coolant temperature data prior to, during, and following a RPV hydrostatic pressure test at a BWR-4 is presented in Figure 4-4. For this evolution, the reactor coolant temperature peaked at about 265 °F and was above 200 °F for a total period of about 18 hours. The time duration of 18 hours above 200 °F in this example is typical, but could be significantly longer if the test had to be repeated due to unacceptable leakage.

The coolant temperature was increased in steps, from an initial value of about 133 °F to approximately 153 °F, where the temperature remained constant for about five hours prior to the start of the heatup. It took approximately six hours to increase the temperature from 153 °F to >200 °F. Increasing reactor pressure was first indicated when temperature reached about 190 °F, and the peak pressure of about 1067 psig was reached in approximately 9 hours. The peak pressure was held for a period of about five hours. Pressure was then reduced to about 28 psig. After completion of the pressure test, the temperature decreased from the peak value of 265 °F to <200 °F in about 3 hours.

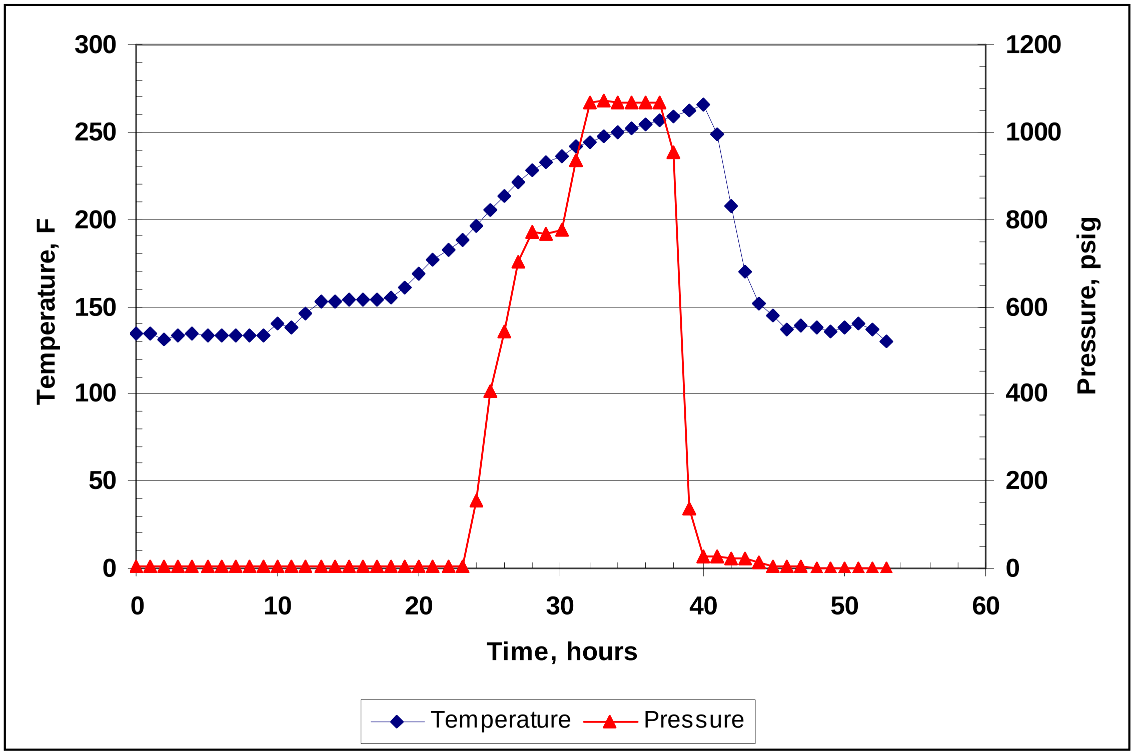

**Figure 4-4**
**RPV Hydrostatic Test Data from a BWR-4**

To ensure sufficient hydrazine is present at the time the coolant temperature is >200 °F, injection would need to start earlier. It may be possible to start hydrazine addition during the initial vessel fill prior to the start of the hydrostatic test. The time it takes to fill the vessel depends on plant-specific procedures. If the starting water level is at the normal operating level, a large mass of water would have to be added to reach the level needed for the hydrostatic pressure test. For example, at one 860 $MW_e$ BWR-4, the cold shutdown water inventory at normal RPV level, including the reactor recirculation system, is about 699,000 pounds. An additional 322,000 pounds (38,000 – 39,000 gallons) of water would be required to completely fill the RPV for the pressure test. Adding this volume via CRD would take on the order of 10 hours, while adding water from the condensate system via feedwater would take substantially less time. Some plants may also fill from the core spray system.

In addition, hydrazine could also be injected during the six hour period of coolant temperature increase from 150 °F to 200 °F. During this period, oxygen is transported into the reactor vessel with the CRD flow and production of hydrogen peroxide from the core gamma flux would continue. Letdown flow from RWCU also occurs at this time.

Additional hydrazine may have to be added after the temperature reaches >200 °F. Water added via CRD during the hydrostatic pressure test may approach air saturation levels as most plants do not have condenser vacuum established at that time. However, the sample line allowing flow to the NMMS ECP electrodes is likely unavailable during a hydrostatic pressure test because the test lineup typically requires isolation of the sample lines. Some plants may not have the capability to valve the NMMS ECP system in service until normal operating reactor coolant temperature and pressure are reached.

During the hydrostatic pressure test, injection through the recirculation system sample line or a recirculation pump differential pressure or flow tap would be preferred over injection into RWCU. Since there is no feedwater flow, the velocity in the large feedwater pipe from the RWCU flow would be very low. Injection into the recirculation system would provide better mixing within the piping and in the reactor vessel. However, coordination is required such that if only one reactor recirculation pump is operating during the reactor pressure test, the operating loop is the one that has been set up for hydrazine injection.

For a preliminary estimate hydrazine demand, the cold shutdown water inventory at normal RPV level the BWR-4 discussed above is estimated as 699,000 pounds, and an additional 322,000 pounds would be added for the fill for the pressure test. If the water is assumed to be air saturated at cold conditions, it could contain up to 8 ppm dissolved oxygen, and comparable concentrations of hydrogen peroxide. During the hydrostatic test, the oxygen source in the water is from air dissolution and not from radiolysis. The oxygen inventory alone would be about 3700 grams. At least an equivalent quantity of hydrazine would be required to consume the oxygen inventory assuming no other source terms. Since the rate of hydrazine reaction with oxygen is indicated to be slow at low temperature (~120°F) prior to heatup, it may be prudent to delay hydrazine injection until reactor water temperature is higher, approaching 200 $^{o}$F, where the reaction proceeds more rapidly. Residual hydrazine and its decomposition products would be removed with the letdown flow.

Oxygen should be removed from the reactor water by mechanical means, to the extent practical, to minimize the amount of hydrazine required. The available mechanical means would be to establish condenser vacuum with the mechanical vacuum pumps, and open main steam line drains to allow vacuum to be drawn on the reactor vessel (head vent would also have to be open). The ability to establish this condition prior to heat-up is plant specific.

Following the hydrostatic pressure test, the next opportunity for hydrazine injection is during the initial heatup and early startup. If hydrazine were added during the hydrostatic test, dissolved oxygen levels in the coolant would increase after the hydrostatic test is complete because of continuous input from CRD. Typically, startup commences within 24 hours after the hydrostatic test is completed. This time period could be longer due to emergent work or issues, which could further increase the dissolved oxygen content at startup.

In the early startup phase, oxygen input to the reactor coolant is from the condensate/feedwater, and small contribution from radiolysis in establishing reactor criticality. Initially, oxygen entering the reactor vessel from condensate/feedwater system is high due to oxygen dissolution from air, but the oxygen content declines following the establishment of condenser vacuum.

During heatup, when initial condenser vacuum is established using the mechanical vacuum pump, reactor coolant dissolved oxygen is typically approximately 250 ppb. Dissolved oxygen levels in the coolant will begin to decline as temperature increases due to decreased solubility. It usually requires operation of the steam jet air ejector system to lower the oxygen content of the condensate water to less than 100 ppb. Establishing condenser vacuum with open MSIVs and main steam line drains draws oxygen released from the heat-up from the reactor vessel.

The Limerick 2 startup data presented in Section 3 shows that it took about 4.5 hours during the initial heatup to increase the reactor coolant temperature to >200 °F. This heatup rate is somewhat more rapid than the initial heatup for the hydrostatic test. Prior to initial control rod movement, the plant startup procedure requires starting the reactor recirculation system and securing shutdown cooling. This would be the appropriate time to initiate hydrazine injection as the recirculation pump start will provide mixing in the reactor vessel. Starting hydrazine injection with shutdown cooling in service is not desirable since this would expose the hydrazine to substantial carbon steel surface area, which could accelerate hydrazine decomposition. For units that have copper alloy tubing in the RHR heat exchanger, corrosion due to hydrazine reactions on the tubing and exposure to ammonia from hydrazine decomposition should be considered.

### *4.2.4 Startup Phase 2 – Open System (Significant Steam Venting)*

A simplified schematic flow diagram during Startup Phase 2 of the startup, which encompasses the continuation of the heatup process, is shown in Figure 4-5. At this point, significant steam venting occurs. There is sufficient steam flow to open a turbine bypass valve, to perform operability test with the HPCI and RCIC turbine driven pumps (the design at most plants), and at some stations, to place the steam jet air ejectors in service.

As shown from the Limerick 2 data in Section 3, once heat-up begins it does not take long (between 6 to 10 hours) for the reactor temperature to reach about 350 °F. The corresponding reactor pressure at this temperature is about 134 psia. The dissolved oxygen level at this point in the Limerick 2 startup was approximately 100 ppb. Oxygen continued to decline as the temperature increased above 500 °F, indicating that the input from radiolysis was low. The lowest reported dissolved oxygen concentration prior to starting hydrogen injection following the Limerick 2 second startup attempt was 40 ppb at about 19% power at a reactor coolant temperature of about 520 °F. At that point in the power ascension the dissolved oxygen source is mainly from radiolysis.

Potential injection points previously discussed are also shown. Injection into the recirculation system during heatup should be viable. For the RWCU injection point, initially plants may be in the letdown lineup for reactor level control. As steam flow increases, letdown is secured. During the startup, Limerick secures letdown at approximately 100 psig reactor pressure (338 $^{o}$F saturation temperature), as noted in the startup procedure discussed in Section 3.

Hydrazine injection could begin upon starting the first reactor recirculation pump and securing shutdown cooling. Sufficient hydrazine could be added to build up an inventory so that mitigation can be achieved when the coolant temperature reaches 200 °F. If ECP is not available, it may be possible to assess effectiveness of hydrazine using reactor coolant sample dissolved gas (oxygen and hydrogen) and hydrazine measurements. These measurements could also be used as the basis for controlling the hydrazine injection rate.

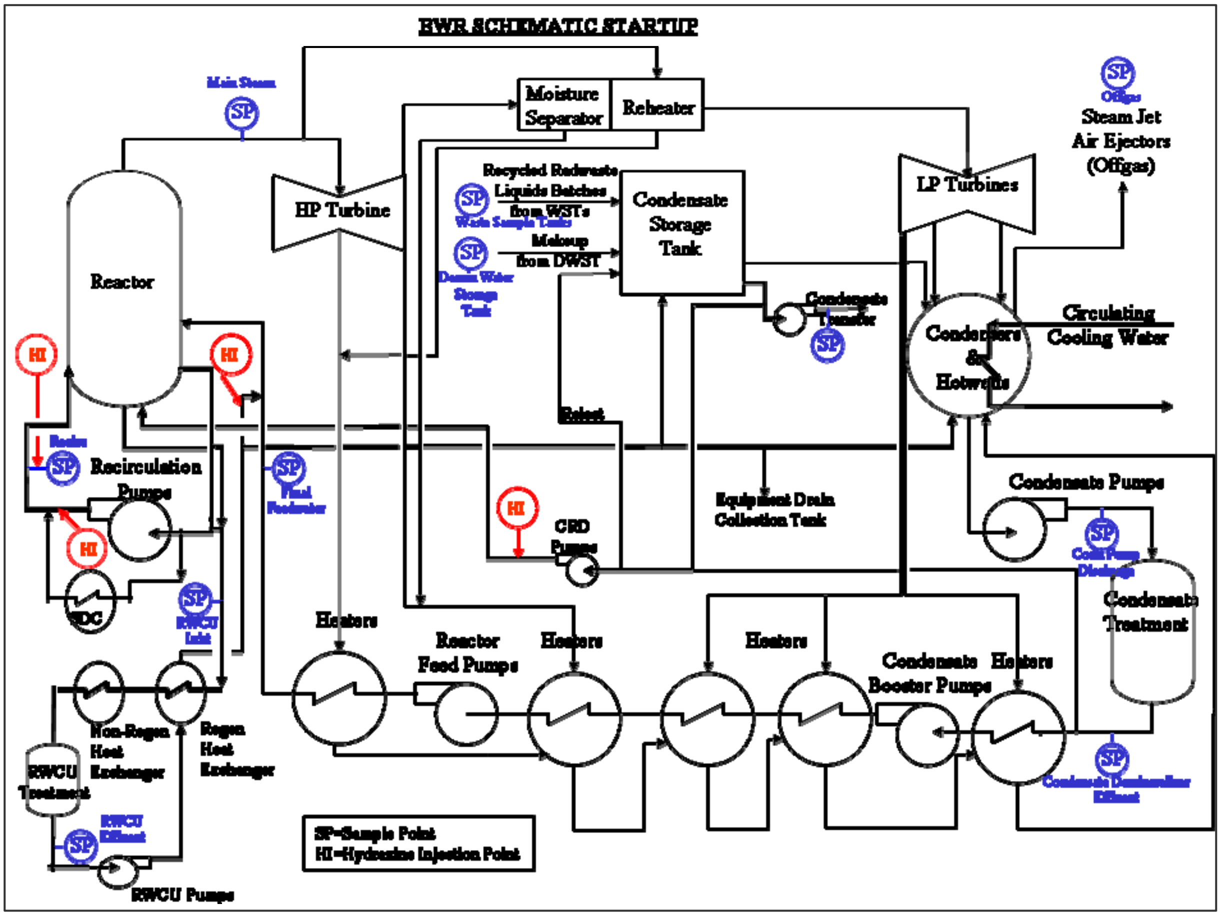

**Figure 4-5**
**Process Schematic During Startup Phase 2 – Initial Reactor Heatup**

### *4.2.3 Startup Phase 3 – Up to 5% Power*

When reactor coolant temperature increases to about 350 $^{o}$F, sufficient steam flow is available to require opening of the first turbine bypass valve and to perform operability testing of emergency system steam driven pumps. Plants with an auxiliary steam source may have the SJAE system in service at this temperature. If not, placing the SJAE system in service is typically one of the first activities performed as pressure is increased beyond 150 psig.

A process flow schematic during Startup Phase 3 is shown in Figure 4-6, which shows steam flow to the condenser from the turbine bypass. Initially, there is some flow through the condensate/feedwater system, but there is no steam flow to the feedwater heaters so feedwater temperature is cool compared to normal plant operating conditions.

If a plant is designed with condensate booster pumps, the first booster pump is typically placed in service when reactor pressure is between 150 and 200 psig. The first reactor feedwater pump is normally placed in service at when reactor pressure is between 400 and 500 psig. Once the first feedwater pump is placed in service, further control rod movement brings the reactor temperature to >500 °F and the reactor pressure to 950 - 1000 psig. The Limerick 2 startup data, discussed in Section 3, showed that the time to increase reactor temperature from 350 °F to about

520 °F was approximately 12 hours (average temperature increase rate approximately 14 °F per hour). This is comparable to the time for the same temperature increase for other BWR-4 startup data reviewed and therefore may be typical.

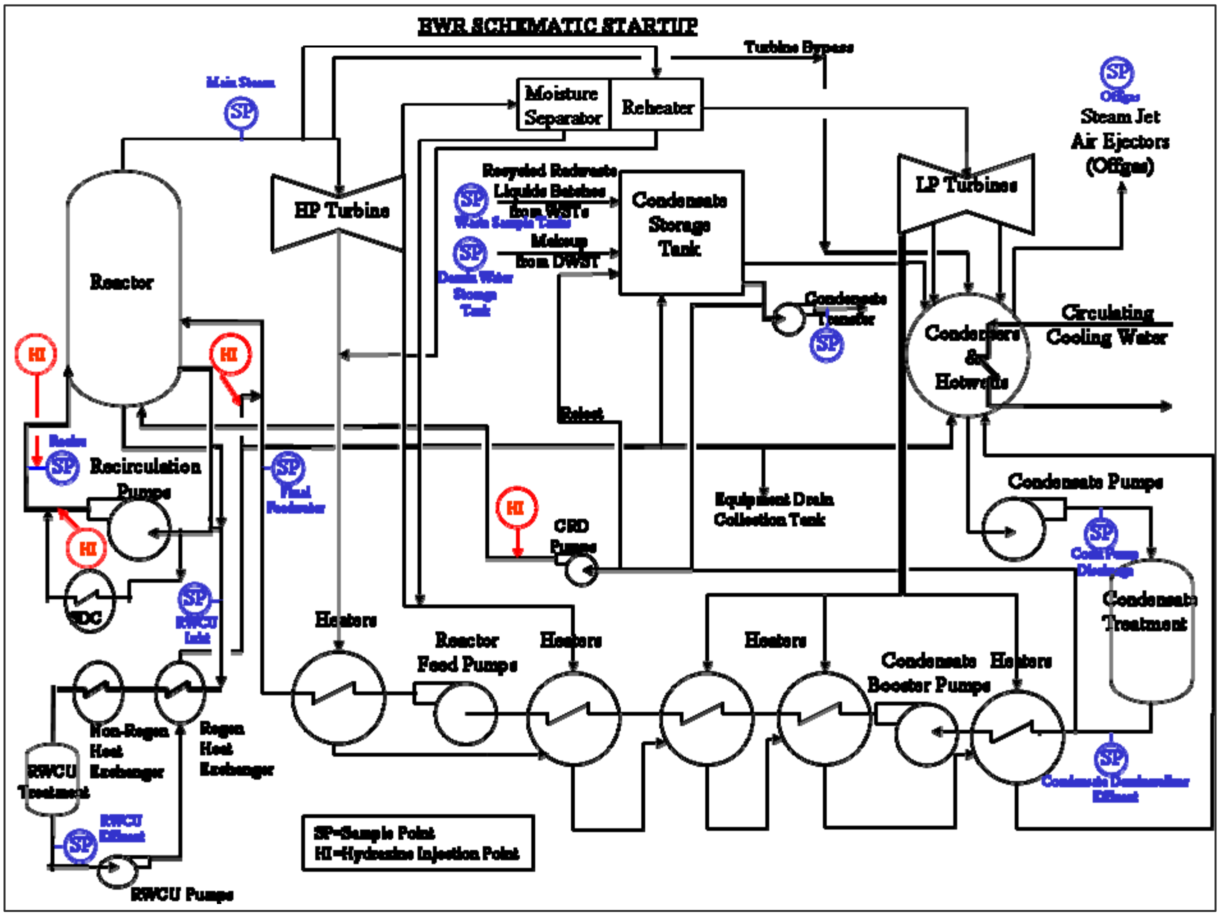

**Figure 4-6**
**Process Schematic for Startup Phase 3 – Final Heatup through Low Power (≤10%)**

Reactor coolant and condensate dissolved oxygen concentrations for a BWR-4 with NMCA during startup and power ascension, prior to the start of hydrogen injection, are plotted in Figure 4-7. Reactor coolant temperature and reactor power trends are also shown. The rapid decline in condensate oxygen from greater than 700 ppb to well below 100 ppb corresponds with starting SJAE operation. Generally, plants are required to secure the mechanical vacuum pumps prior to exceeding 5% power because of concerns related to explosive gas mixtures and radiological releases. Reactor coolant dissolved oxygen declined from about 400 ppb at a temperature of 223 °F to about 100 ppb at a temperature of about 363 °F. When condensate oxygen decreased to less than 100 ppb, coolant dissolved oxygen was at about 16 ppb.

The plant power data points in Figure 4-7 shows that when the coolant temperature first increased above 500 °F, power was between 8 and 9%. At most plants, the power readings reported are from APRMs (Average Power Range Monitors), which are typically not on scale until about 8% power. Other power indicators (Intermediate Range Power Monitors and Source Range Monitors) are used at lower power.

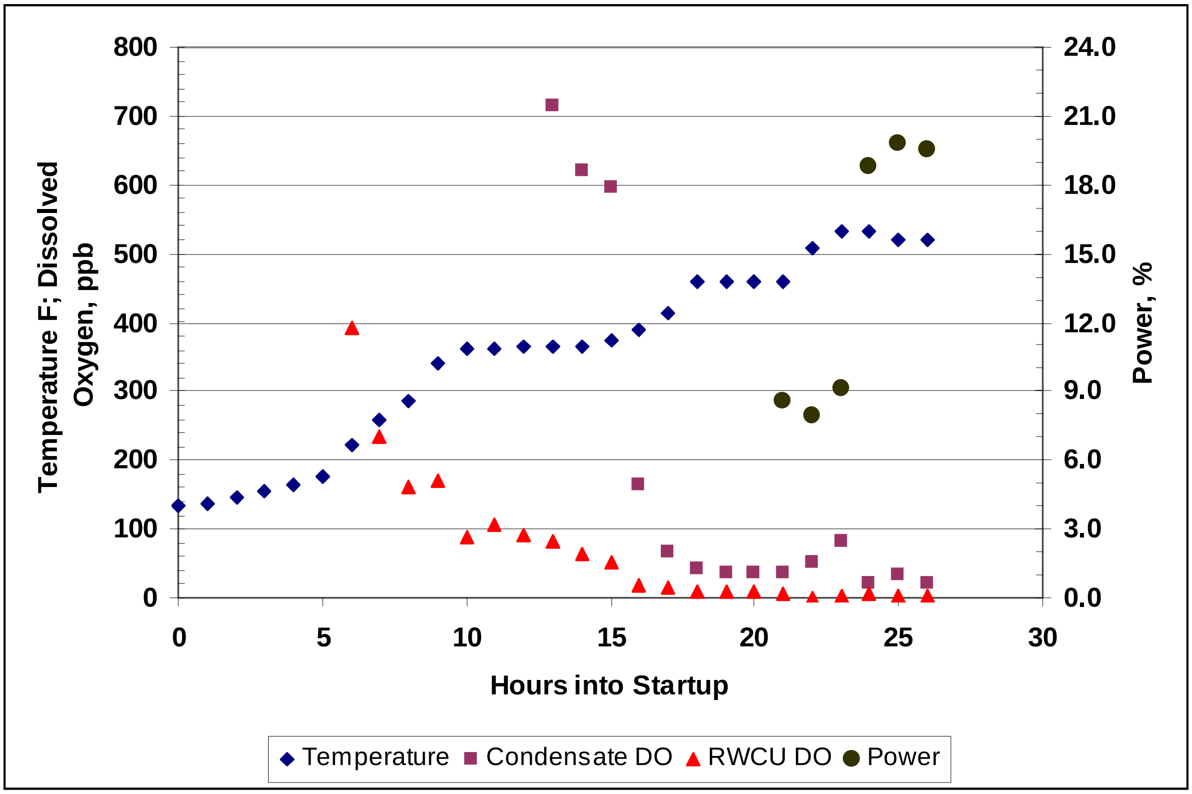

**Figure 4-7**
**Reactor Coolant Temperature and Dissolved Oxygen during Startup (BWR-4, Prior to the start of hydrogen injection)**

Hydrazine demand to lower ECP from the point of significant steam flow (reactor pressure at approximately 150 psig) through 5% power may be relatively low, based on the dissolved oxygen trend shown in Figure 4-7, which is prior to the start of hydrogen injection. There should be no operating issue with injecting into RWCU during this period since letdown from RWCU is secured and the residence time in the feedwater piping would be lower due to increasing feedwater flow. Injection into the recirculation system sample line should also be acceptable. Monitoring for effectiveness could be achieved using RWCU dissolved gas and chemical (hydrazine) measurements and ECP, if available.

After reaching 5% power, a plant will focus on increasing reactor pressure and temperature to provide enough steam to begin warming the main turbine in preparation for roll and synchronization to the grid. Plants typically synchronize to the grid at about 20% power. Reactor coolant dissolved oxygen levels will increase due to oxidants from radiolysis reactions and possibly from increases in oxygen input from the condensate/feedwater system due to increases in air inleakage as subsystems and components in direct communication with the condenser are first placed in service. While it is conceivable that hydrazine injection could continue beyond 10% power, results from a demonstration plant at low power (up to 10%)

should be evaluated first in deciding whether >10% power is feasible. A number of plants are evaluating plant changes to allow hydrogen injection to start at <5% to 10% power.

## 4.3 Reaction Considerations

Hydrazine will be consumed by reaction with oxidants, by decomposition and by reaction with dissolved carbon dioxide. These reactions are temperature-dependent, and the first two are surface catalyzed. In particular, the presence of copper in steam generator crud deposits has been observed to accelerate the rate of hydrazine decomposition relative to crud deposits from all-ferrous systems. During heatup and startup, hydrazine-bearing water will pass through the core, which has a large surface area coated (except for fresh fuel) with corrosion products and catalyst. Radiation from decay of second and third cycle fuel in the core, and later from fission following initial criticality, will accelerate reaction rates. The consumption of hydrazine by reaction with oxidants and decomposition as water passes through the core region is expected to be significant, although the decomposition reaction stoichiometry is not well understood. Therefore, sufficient hydrazine must be injected to assure that a favorable ratio of hydrazine to oxidants exists in all regions of the reactor vessel and reactor coolant system where IGSCC mitigation is desired.

When a jet pump plant is shutdown with the recirculation system in service, coolant is pumped from the discharge of the recirculation pumps through the jet pumps to the lower vessel head. From there, the coolant flows up through the core region, the upper plenum and the steam separators, returning to the upper downcomer. Coolant flows down the downcomer, splitting at the jet pump nozzles, where a portion of the flow is drawn into the jet pump and the remainder flows to the suction of the recirculation pump(s). If only one loop is in operation, the other loop sees little if any flow. Also, flow rates on the side of the vessel with the operating loop are likely to be higher than on the side with the shutdown loop, possibly resulting in stagnant flow areas in the downcomer region. Therefore, if mitigation of IGSCC is desired in the recirculation loop and in the downcomer, both loops should be in operation with hydrazine injected to both loops.

Injection of hydrazine into both loops of the reactor recirculation system is expected to provide sufficient mixing of the injected hydrazine into the bulk flow through the jet pumps to the lower vessel head and up into the core region. Based on the large diameter stainless steel piping (low surface area to volume ratio) and high velocity, hydrazine decomposition in the piping during heatup may not occur to a great extent. However, chemical reaction and decomposition reactions are likely to be more significant in higher surface area regions such as the jet pumps, lower plenum region and particularly the core region. Depending on the relative rates of reaction with oxidants to decomposition, the water exiting the core may be deficient in hydrazine for mitigating IGSCC in the upper plenum, mixing plenum and downcomer. The extent of decomposition is expected to increase as the temperature increases. Sufficient hydrazine must be injected into the reactor recirculation pump discharges to assure that the desired ratio of hydrazine to oxygen is maintained in the reactor recirculation pump suctions to reduce oxidants at the NMCA treated surfaces. Monitoring water chemistry parameters and ECP (when NMMS is available) at the RWCU Inlet, which is taken from a recirculation pump suction and bottom head drain, may be considered. For units with carbon steel RWCU systems, significant losses of hydrazine and oxidants may occur as a result of reactions with carbon steel surfaces. In this case, alternate sample points (such as the reactor recirculation sample line after adequate flushing) may be needed to monitor effectiveness.

Nitrogen will be produced by the reaction of hydrazine with oxidants. However, since the molar ratio of nitrogen generated to oxygen consumed is 1:1, there will be no increase in dissolved gases from this reaction, and only a small change in the partial pressure of dissolved gases due to the difference in solubility. Decomposition of hydrazine will produce nitrogen and hydrogen gas, although the actual extent of this reaction is unclear. Except for hydrazine lost to reactor letdown or to the RWCU system, the hydrazine added will either react or decompose. The maximum volume of gas generated can be bounded from the total quantity of hydrazine injected. These gases are expected to partition to the steam dome during heatup and will be released to the condenser when the reactor is vented.

The maximum concentration of ammonia from hydrazine decomposition can also be bounded from the total quantity of hydrazine injected. Ammonia will either be removed by the RWCU system or will be vented off to the condenser, where it will be removed by the condensate demineralizer system. The impact of ammonia in condensate on the operation of the one or two condensate demineralizers that may be in service is likely to be trivial for deep beds, but perhaps may affect a filter-demineralizer run time. Hydrazine injection may require additional backwashes of RWCU filter-demineralizers during heatup and startup, until the steam flow is sufficient to transport ammonia to the condenser. The effect of ammonia on the operation of a RWCU with a deep bed demineralizer should be evaluated, but is likely to be insignificant.

Hydrazine injection to the feedwater through the RWCU return lines has the advantage of avoiding the core flow region and delivering hydrazine to the top of the downcomer, which is beneficial to assuring that the hydrazine to oxidant ratio is high enough to mitigate IGSCC of the shroud O.D. and downcomer components such as the jet pump beams and recirculation riser welds. This injection point may be considered during floodup for the hydrotest, particularly if condensate is used for flooding. However, during RWCU operation without condensate flow, the flow rate through the feedwater lines will be low (~1% of full power with a 1% RWCU system) and the volume may be large, depending on plant geometry. There may be significant losses of hydrazine by surface catalyzed reactions with the carbon steel piping and the distribution of hydrazine around the internal circumference of the vessel is likely to be non-uniform. As above, with this injection mode both recirculation loops should be in operation to provide uniform distribution of hydrazine throughout the vessel and recirculation system.

For plants that flood up for the hydrotest from core spray, it may be possible to inject a chemical into the core spray system if an accessible connection is available. The low pressure core spray system typically includes test connections at the pump suction which could be used for injection.

## 4.4 References

1. BWRVIP-156: BWR Vessel and Internals Project, Generic Guidelines for Improvement In HWC System Availability. EPRI, Palo Alto, CA. 1011706
2. BWRVIP-130: BWR Vessel and Internals Project, BWR Water Chemistry Guidelines – 2004 Revision, EPRI, Palo Alto, CA: 2004. 1008192.

# 5
# TECHNICAL CONSIDERATIONS

A preliminary review of technical considerations for hydrazine injection is summarized in this section. These considerations are also used as input to recommendations for future work.

## 5.1 Oxide Restructuring

Hydrazine can react with iron and copper oxides, both on plant surfaces and particulates suspended in reactor water, reducing their oxidation states. Although the extent of such reactions is not expected to be large, some hematite may be converted to magnetite or gamma-hematite, and cupric oxide to cuprous oxide and potentially metallic copper, although it is uncertain if the reduction would progress that far. These are considered to be passivating reactions in terms of metal corrosion, and thus advantages of hydrazine.

Given that the crud on most of the fuel surface is likely to be in an oxidized state, the addition of hydrazine to the RPV during heatup and low power operation may induce some crud restructuring, similar to that observed when starting hydrogen injection. The conditions would be similar to those in BWRs that start hydrogen injection at low power ($\leq$5%), when there is little or no boiling to strip hydrogen from solution in the core. Crud releases from the fuel would be cleaned up by the RWCU system, so RWCU availability is required. Re-deposition of released crud should not be significant assuming RWCU is in service to support cleanup of any crud transient prior to power operating conditions (>10% power).

Based on PWR experience with hydrazine injection into the primary system during startup, reactions that change the crud from an oxidized to reduced form are indicated to be slow. Differences between BWR and PWR conditions must be considered, but crud restructuring with hydrazine injection is not expected to have a large impact on the release of crud or activated corrosion products. Appropriate monitoring for such changes should be performed during the initial plant demonstration.

## 5.2 Fuel Reliability

The impact of hydrazine injection into the BWR reactor coolant on the fuel needs to be considered. No direct chemical attack of the Zircaloy-2 cladding is expected from hydrazine, ammonia or organic acids as long as conductivity stays below Action Level 1 (<0.3 µS/cm). Many years of PWR experience with hydrazine injection into the primary system have revealed no fuel issues associated with hydrazine use with Zircaloy-4 and Zircaloy-5 cladding. Bounding studies should be considered for the BWR, although no fuel issues associated with hydrazine use are expected.

Laboratory test results reported in the literature concluded that adding hydrazine to the coolant would have little influence on the corrosion of Zircaloy-2 fuel cladding material used in BWRs based on weight gain, oxide film thickness and hydrogen pickup measurements [2]. The test program was based on addition of nitrogen and ammonia, the decomposition products of hydrazine, to supercritical water containing the test specimens with and without gamma irradiation.

A review of INPO SOER 03-02 will be required for a plant implementing hydrazine injection. For the lead plant, a fuel surveillance program will also likely be required. Details of the fuel surveillance program would have to be developed in conjunction with the EPRI Fuel Reliability Program.

## 5.3 Noble Metal Surface Integrity

The noble metals durability with hydrazine injection is being evaluated in loop tests. Noble metal surfaces currently undergo the change from oxidizing to reducing conditions, and the reverse, when HWC is placed in service and secured. Based on the results of the loop tests, the need to pull and analyze plant coupons as part of a plant demonstration should be considered.

## 5.4 Resin

The hydrazine reaction products with oxygen are innocuous: $N_2$ and $H_2O$. Excess hydrazine will be decomposed to ammonia and nitrogen during heatup (>400 °F), although the rate and stoichiometry of the decomposition reaction are not quantitatively predictable. Decomposition may be abetted by decay heat radiation from the fuel. Ammonia will be removed by either the RWCU system or (with steaming to the condenser) by the condensate polishers. Ammonia will tend to increase the pH of reactor water, depending on its concentration and the concentration of other ions in solution. Residual core radiation may cause some decomposition of ammonia to nitrogen and hydrogen, which would be desirable. Ammonia may also undergo oxidation reactions to produce nitrite and nitrate anions.

The impact of ammonia, nitrate and nitrite on RWCU resin utilization, and perhaps changes in operating procedures for the cleanup systems to handle the additional ionic loading, should be considered. While copper, zinc, nickel, cobalt and chromium form cationic complexes with ammonia, such complexes are not expected to form to a large extent until the pH increases above about 8.5. The effects of the increase in pH from ammonia on the ion exchange performance for chloride or sulfate will have to be considered. Although these anions have high selectivities relative to hydroxide, the equilibrium capacity for chloride may be affected depending on the hydroxide concentration in solution [3]. Silica removal capacity may decrease, which should be considered in operation of the RWCU system. The ammonium ion will also compete with cation resin sites for sodium, so the equilibrium capacity for sodium should be considered [4]. Most BWRs have only filter demineralizers for cleanup in the RWCU system, but three U.S. BWRs have deep bed demineralizers, either alone or downstream of filter demineralizers. The management of the resins used should be considered. Plants with RWCU filter demineralizers backwash and precoat with fresh resin routinely, so application of fresh precoats for use during hydrazine injection should be straightforward and not represent a significant additional burden. Plants with RWCU deep beds typically replace the resin bed used in the previous operating cycle with the new bed prior to startup from a refueling outage. RWCU deep beds are typically not replaced prior to startup from a mid-cycle planned or forced outage.

The impact of hydrazine present in letdown from the reactor to the condenser or radwaste during heatup and early startup evolutions should be considered. This includes any impacts on condensate polisher resin or radwaste processing for recycle or discharge. As startup progresses and steam flow becomes significant, the impact of hydrazine and ammonia carryover on condensate polisher resin utilization should be considered. The ion exchange impacts will be similar to those for RWCU and will be dependent on the plant-specific condensate polishing system configuration, particularly whether deep bed demineralizers or filter demineralizers are available.

## 5.5 Main Steam

Hydrazine injection is being considered to lower ECP under Startup/Hot Standby conditions (>200 F, power $\leq$10%). The MSL (Main Steam Line) dose rates are very low at <10% power, and even at power <30% under NWC MSL dose rates are <20% of those at full power operation. Therefore, even if hydrazine injection caused the bulk water to be highly reducing, with a hydrogen to oxidant molar ratio of ~6, the resulting MSL radiation levels are not expected to be high, and would be very unlikely to reach full power levels. The high rate of core flow to steam flow during low power operation would tend to retain more of the volatile ammonia compounds and the low velocity at which steam flow progresses through the balance of plant would result in more reduction by N-16 decay between the reactor vessel nozzles and downstream components.

The injection chemicals and reactions products may carry over into steam lines and drains. The effects of these chemicals on downstream components and materials should be evaluated.

## 5.6 Offgas

Nitrogen is produced by the hydrazine reactions with oxygen and hydrogen peroxide. Nitrogen and hydrogen are produced by the hydrazine decomposition reaction. The potential for explosive gas mixtures must be considered.

The additional gas flow to the offgas system does not appear to pose a potential problem, since even with ppm levels of hydrazine in reactor water the gas release rates from the reactor vessel are unlikely to exceed a fraction of that at full power. This should be confirmed on a plant-specific basis.

If significant hydrogen is being generated by hydrazine and ammonia decomposition while the MVP (Mechanical Vacuum Pump) is in service, the effect on hydrogen concentration in the MVP system will need to be evaluated. Most plants have a limit on the maximum allowable hydrogen concentration in the MVP system because it isn’t designed to be explosion proof. The maximum power level at which the MVP can be in service, which is typically about 5%, must be considered in the evaluation. Existing and projected concentrations of hydrogen in the MVP piping should be evaluated and measured during the demonstration of this process.

If SJAE’s and the Offgas system are in service during hydrazine injection, the rate of hydrogen generation from hydrazine/ammonia decomposition will need to be estimated to assure that it is <40% of the air inleakage rate (1 SCFM $O_2$/5 SCFM Air x 2 SCFM $H_2$/SCFM $O_2$ = 0.4 SCFM $H_2$/SCFM Air). This is also not expected be a problem for plants that installed an augmented offgas system. Such plants were originally designed with the SJAE outlet flow at full power routed to a hold-up pipe to allow time for radioactivity decay.

Potential effects of poisoning of the recombiner catalyst with ammonia generated from hydrazine decomposition should be considered [1], particularly for plants that must operate the recombiner system at low power levels. Although unlikely, since simple volatile chemicals will most likely be reversibly removed, it should be considered on a site-specific basis for the catalyst in use.

## 5.7 FAC

FAC (Flow Accelerated Corrosion) effects should be considered if hydrazine is injected into carbon steel piping, resulting in low concentrations of dissolved oxygen. Potential flow accelerated corrosion effects should be evaluated considering the injection location, flow velocity and temperature. Since hydrazine is routinely injected into the PWR secondary system, in which carbon steel piping and materials are used, PWR experience should be reviewed.

The CRD system contains carbon steel piping. If hydrazine injection into the CRD system is pursued, FAC effects in this system would have to be considered.

The RWCU piping is constructed of carbon steel at several plants. This piping is exposed to low dissolved oxygen concentrations during normal operating conditions with hydrogen injection in service. If hydrazine is injected into the RWCU piping during heatup/early startup, the RWCU piping would be exposed to low dissolved oxygen concentrations earlier in the startup than previously experienced, prior to placing HWC in service. This is not expected to have a significant impact on the RWCU piping.

With hydrazine injection into RWCU, the section of feedwater piping at and downstream of the RWCU return could be exposed to low dissolved oxygen conditions prior to initiating flow through this piping from the condensate/feedwater flow path. For this to occur, the hydrazine injected would have to be sufficient to consume most of the oxygen in the reactor recirculation system suction stream. The velocity would be low in the feedwater piping section with only RWCU providing flow. FAC effects on this piping section should be evaluated if the RWCU system is selected as a hydrazine injection point. PWR experience with hydrazine injection in carbon steels systems should be evaluated.

## 5.8 Impact on ECP

ECP must be reduced at lower temperatures values that provide IGSCC mitigation. Measurements should be corrected for pH and temperature. Reliable ECP measurements are being made in loop tests, along with corrections for pH. The relevance of -230 mV (SHE), which is the criterion used for mitigation at operating temperature, needs to be considered at temperatures between 200 $^{o}$F and 500 $^{o}$F. At these intermediate temperatures, hydrazine injection should reduce the ECP to a value that is shown to provide mitigation for NMCA treated or untreated surfaces.

The ability to make meaningful ECP measurements in a plant demonstration should also be considered. Very few plants have in-situ ECP measurements. Sample lines to the ECP electrodes in the NMMS have noble metal deposits, resulting in consumption of oxidants, hydrazine and hydrogen in the sample line upstream of the electrodes. If representative ECP measurements are not available in a demonstration plant with NMCA, the ratio of reducing agent to oxygen in the reactor coolant sample may have to be related to autoclave ECP and possibly crack growth rate test results as the basis for mitigation.

## 5.9 Reactor Water Conductivity

Reactor water conductivity will increase in proportion to the concentration of hydrazine and ammonia present. If the starting reactor water is slightly alkaline due to the presence of zinc, the conductivity impact of the weak bases hydrazine and ammonia will be somewhat muted because ionization will be suppressed. Acidic decomposition products if present in significant quantity relative to ammonia would tend to neutralize the alkalinity and reduce conductivity. Conductivity action levels may be exceeded depending on the concentration of hydrazine required to achieve mitigation.

## 5.10 Reactor Water pH

Reactor water pH will increase in proportion to the concentration of hydrazine and ammonia present. If the starting reactor water is slightly alkaline due to the presence of zinc, the pH impact of the weak bases hydrazine and ammonia will be somewhat muted because ionization will be suppressed. The pH at temperature is the important parameter to allow estimation of the influence of pH on ECP.

## 5.11 Zinc Injection

The effects of hydrazine on zinc deposition on surfaces or the potential removal of deposited zinc from surfaces should be considered. PWR experience with zinc injection to the reactor coolant containing 1 – 2 ppm ammonia has not resulted in problems with zinc deposition or removal due to zinc complexes with ammonia. Any zinc-ammonia complexes that may form in the BWR are cationic, so removal from solution will occur by cation exchange in the RWCU system.

## 5.12 Copper Transport

For plants with copper-alloy condensers and condenser tubes, the presence of low levels of ammonia in the condenser could have a modest impact on copper transport. With hydrazine injection, ammonia may be transported to the condenser through letdown from RWCU and, when there is significant steam flow, from carryover with the steam. However, the rate and stoichiometry of formation of ammonia from hydrazine decomposition reactions is not precise. Injection of hydrazine in PWR primary systems during startup has resulted in significantly less ammonia generation than would be expected from reaction rates and stoichiometry reported in the literature.

Limerick 1 and Limerick 2 are two units that could benefit from chemical injection during heatup and startup since hydrogen injection is not started until power increases to about 50%. These units also have copper-alloy condenser tubes, so it is important to consider the effects of hydrazine injection on corrosion and copper transport to other systems. In a demonstration of hydrazine injection, hydrazine and ammonia concentrations in the condenser should be monitored and limits on the concentrations of these species should be established.

Hydrazine injection should not be considered for an initial demonstration at a plant with copper-alloy condenser tubes and condensate filter demineralizers, due to the potential for increased copper transport to the reactor. Plants with deep bed condensate demineralizers should have sufficient ion exchange capacity available to remove any additional copper that may be released. The potential impact of hydrazine injection at a plant with copper alloy RHR heat exchanger tubes should also be considered, in the event that RHR in shutdown cooling mode is invoked during or following hydrazine injection.

## 5.13 Materials Compatibility

Fuel cladding and carbon steel materials were addressed previously in this section. Hydrazine and its decomposition products are not corrosive to stainless steel and nickel based alloys. Based on extensive PWR primary and secondary operating experience with hydrazine injection, no materials compatibility issues are expected. Compatibility with BWR metallic and non-metallic materials in systems that would come into contact with hydrazine will be evaluated.

## 5.12 References

1. BWRVIP-156: BWR Vessel and Internals Project, Generic Guidelines for Improvement In HWC System Availability. EPRI, Palo Alto, CA. 1011706.
2. Hidetoshi Karasawa, Kazushige Ishida, Yoichi Wada, Masao Endou, Yoshitaka Nishino, Motohiro Aizawa, Motomasa Fuse, Eiichi Kadoi and Hideki Takiguchi, “Hydrazine And Hydrogen Co-injection to Mitigate Stress Corrosion Cracking of Structural Materials in Boiling Water Reactors, (III) Effects of Adding Hydrazine on Zircaloy-2 Corrosion,” Journal of Nuclear Science and Technology, Vol. 43, No. 10, p. 1218-1223 (2006).
3. PWR Primary Water Chemistry Guidelines: Volume 2, Revision 5, EPRI, Palo Alto, CA, 2003. TR-105714-V2R5.
4. Condensate Polishing Guidelines for Pressurized Water Reactor and Boiling Water Reactor Plants – 2004 Revision, EPRI, Palo Alto, CA: 2004. 1002889.

# 6
# DEMONSTRATION PLANT CONSIDERATIONS

## 6.1 Demonstration Plant Characteristics

The initial demonstration plant must have performed NMCA, and should have a minimum of one operating cycle with HWC+NMCA and DZO injection. The effects of crud restructuring should have subsided by that point. It is preferable not to demonstrate chemical injection at a plant that performed a classic NMCA during the shutdown for the same outage to avoid introducing too many changes at one time. Performing hydrazine injection during a startup after a classic NMCA can be reconsidered after a successful demonstration.

To assure sufficient noble metal availability to catalyze the surface reactions, the residual noble metals deposition on the durability monitoring coupons or representative vessel internal artifacts should meet criteria established by General Electric based on the projected residual at the time of the chemical injection demonstration.

To limit potential crud effects, the feedwater iron concentration during at least the past cycle should preferably be within the EPRI recommended range of 0.1 ppb – 1.0 ppb. Cycle average feedwater zinc should be <0.4 ppb so that crud spallation is not expected due to DZO injection. The selected plant should not have a recent history of corrosion related fuel failures or anomalies.

The demonstration plant should not have a high cobalt source term to reduce the potential for high Co-60 releases during startup. The feedwater copper concentration should be <0.05 ppb to minimize the potential for high copper release from surfaces.

The demonstration plant should also have acceptable points available for chemical injection. The selected plant should include jet pumps in the recirculation system.

It would be highly desirable if the demonstration has existing in-situ ECP reference electrodes, or had them in the past and consider installing new ones for this process demonstration. The typical locations have been, RWCU piping flange or tap, recirculation flange, bottom head drain flange or in-core monitoring sensor modification.

## 6.2 Data Availability

### *6.2.1 Baseline Data*

Approximately three cycles of condensate, feedwater and reactor water chemistry data should be evaluated for the demonstration plant. Most of the data are available in the EPRI BWR Chemistry Monitoring Database, but any key data gaps will have to be filled. Data from at least one startup without chemical injection should be evaluated to provide a baseline against which changes with chemical injection can be compared. Any previous ECP data from in-situ and external measurements should be obtained.

### 6.2.2 Baseline Data

For the plant startup when chemical injection for ECP reduction will be demonstrated, a preliminary listing of data to be collected is given below:

Startup Milestones (date/time of each milestone)

Operational milestones during reactor pressure vessel leak test and startup (pump starts/stops, systems in service/out of service, etc,)

Plant Computer Data (hourly or more frequently)

Reactor Thermal Power

Reactor Temperature (from initial heatup)

Reactor Pressure (from initial heatup)

CRD Flow (including Recirculation Pump and RWCU Pump seal flows if provided by CRD)

Final Feedwater Temperature (when feedwater flow commences)

Reactor Recirculation Pump and Core Flow

RWCU Flow (letdown and return to feedwater)

Feedwater Flow (after feedwater flow commences)

Hydrogen Flow (when hydrogen injection starts)

Main Steam Line Radiation Levels

Offgas Radiation Monitor Levels

Mechanical pump flow rate

Offgas flow rate

Chemistry On-line Data (hourly or more frequently)

Reactor water sample lineup to the reactor water sample panel should include RWCU Inlet and Reactor Recirculation (if available). Online parameters include:

Reactor Water Conductivity

Reactor Water Dissolved Oxygen

Reactor Water Dissolved Hydrogen

RWCU Effluent Conductivity

Feedwater Dissolved Oxygen (when there is feedwater flow)

Feedwater Conductivity (when there is feedwater flow)

Condensate Dissolved Oxygen

Condensate Conductivity

Reactor Water pH (if available)

Reactor Water Anions (online if available)

Reactor Water Cations (online if available)

Chemistry Grab Sample Data (baseline prior to injection and every 4 hours during injection)

Reactor Water Conductivity

Reactor Water Anions

Reactor Water Cations (including ammonium)

Reactor Water Gamma Isotopics (soluble and insoluble)

Reactor Water Metals (soluble and insoluble)

Condensate Anions

Condensate Cations (including ammonium)

Condensate Hydrazine and Ammonia

Mechanical Vacuum Pump hydrogen and oxygen gases (if representative sample point is available)

ECP

ECP monitoring would allow a direct measure the effects of chemical injection on ECP reduction in the demonstration plant. All available ECP measurements should be logged, include those from any available in-reactor, BHD, RWCU or recirculation piping probe and those from the NMMS, although such external ECP measurements will be affected by platinum and rhodium deposits in the sample line. The need to install in-situ ECP electrodes should be considered and identified early in the demonstration planning process.

Prior to the demonstration, electrodes to be used should be confirmed to be functioning properly. The NMMS system may not be available during the reactor hydrostatic pressure test and the heatup phase of startup. Available ECP measurements during key phases of chemical injection, including heatup and early startup under reducing and oxidizing conditions, should be logged.

## 6.3 Startup Evolutions

A detailed safety evaluation will be needed to support the demonstration. The startup procedure of the demonstration plant will be reviewed in detail. Detailed operational data and operator logs of the previous startup from the last refueling outage should be reviewed and the timing to reach key milestones should be determined to obtain a baseline.

The hydrazine demonstration should be targeted for the startup from a refueling outage to allow sufficient time for planning and coordination, unless performing the demonstration during startup from a planned maintenance outage is available and preferred by the station. During most maintenance outages, the reactor vessel head is not removed, in which case a pressure leak test would normally not be performed.

The specific outage schedule, scope and duration should be reviewed to make sure there would be no potential for conflict with or adverse impact on hydrazine injection during startup. Design or procedure changes that may affect the startup evolution during the hydrazine injection demonstration should be identified and their impact considered. If injection during the reactor pressure vessel leak test will be included in the scope of the demonstration, the leak test boundaries should be evaluated to assure that there would be no conflicts with the injection scheme or monitoring plan.

## 6.4 Preferred Injection Point and Injection System Requirements

A plant-specific feasibility study is needed for the plant selected for the demonstration of chemical injection. Based on a preliminary evaluation, it appears that injection directly into the reactor recirculation loops or into the RWCU effluent is viable, although each has advantages and disadvantages. For plants that flood up via core spray, injection into this system while filling for the reactor vessel pressure leak test may also be practical. The preferred injection point or points must be determined based on the scope of the demonstration, plant-specific layout, accessibility to the tie-in location and outage-specific conditions.

Details of the injection skid (or skids) design should be developed to meet the requirements of the demonstration objectives and plant requirements. The need for process signals to the injection skid, such as for use as permissives to allow injection or to trip the injection pumps and isolate the skid, must be determined.

# 7
# CONCLUSIONS AND RECOMMENDATIONS

## 7.1 Conclusions

Loop test results summarized in this report support the feasibility of using hydrazine injection during the BWR heatup and early startup to substantially lower the ECP of surfaces on which noble metals are deposited and on untreated (prefilmed) stainless steel. The noble metal durability after exposure to hydrazine after laboratory simulated repeated BWR startup and shutdown evolutions is being tested. Based on these preliminary results, chemical injection during the reactor pressure leak test and in the heatup and low power portions of the startup process (Startup/Hot Standby conditions) is concluded to be feasible. Recommendations for future work are discussed below.

## 7.2 Recommendations for Future Work

1. Complete the laboratory test program to evaluate the effects of hydrazine, carbohydrazide, hydrogen and methanol on the ECP of NMCA treated and untreated stainless steel specimens at BWR startup conditions in the absence of gamma radiation. The test program includes measurements to assess the durability of NMCA treated surfaces following simulated BWR startup and shutdown evolutions with chemical injection. The test work is being conducted by NWT Corporation. A detailed report will be published in 2008.
2. Assess the effects of hydrazine and other chemicals on the durability of noble metals deposits on reactor piping and internal component surfaces. Loop testing described above to evaluate the durability in the laboratory can be used as input to the assessment.
3. Perform a literature review to compile information on reactions of chemicals being considered for injection to reduce ECP during BWR startups. Pertinent information includes overall reactions and stoichiometry, and reaction mechanisms, products and kinetics.
4. To the extent practical, the quantity and rate of hydrazine injection should be bounded during heatup and as reactor power is increased. The rate of hydrazine reactions with oxidants and decomposition after injection should be considered as temperature increases during heatup to normal operating temperature and as gamma flux increases as reactor power is increased. Consider performing additional laboratory tests as needed to support these estimates. Such estimates will be useful in sizing the injection equipment.
5. The chemical injection process during Startup/Hot Standby should be reviewed and calculations should be performed to assure no significant risk of the formation of explosive gas mixtures. The maximum hydrogen concentration at which the mechanical vacuum pump can be operated must be considered.
6. Bounding estimates should be made of the increase in ionic loading on RWCU and condensate polishing system ion exchange resins from hydrazine injection for the various

phases of injection. This will support plans for estimating the quantity of and requirements for resins to be used.

7. Review available BWR crud and activated corrosion products transport data in the BWR Chemistry Monitoring Database for NMCA plants that start hydrogen injection at low power (approximately 3% – 5%). This can be used as a basis to assess the effects of reducing conditions in the core during startups with chemical injection to reduce ECP. Since boiling is not significant at low power, hydrogen should remain in the coolant and reducing conditions should be achieved at surfaces in higher elevations of the core than at full power operating conditions.
8. Industrial safety and environmental impacts of hydrazine, carbohydrazide and methanol use in a BWR plant must be considered. PWR experience with the use of hydrazine and carbohydrazide should be reviewed. Chemical storage, use of containers and piping, use in reactor and turbine buildings, effects on balance of plant systems, potential for combustion in auxiliary systems, health hazards and fire hazards are among the items to be considered.
9. Review PWR operating experience with hydrazine injection into carbon steel systems to assess the impact on FAC. Since hydrazine is routinely injected into the PWR secondary system, in which carbon steel piping and materials are used, PWR experience should be reviewed.
10. A plant-specific feasibility study is needed for the plant selected for the demonstration of chemical injection. Injection point(s), the capability to measure ECP and the use of other acceptance criteria must be addressed.
11. Develop the detailed process requirements for a BWR hydrazine injection system. This would include equipment sizing, instrumentation and controls, all functional requirements of components, and materials of construction.

## Export Control Restrictions

Access to and use of EPRI Intellectual Property is granted with the specific understanding and requirement that responsibility for ensuring full compliance with all applicable U.S. and foreign export laws and regulations is being undertaken by you and your company. This includes an obligation to ensure that any individual receiving access hereunder who is not a U.S. citizen or permanent U.S. resident is permitted access under applicable U.S. and foreign export laws and regulations. In the event you are uncertain whether you or your company may lawfully obtain access to this EPRI Intellectual Property, you acknowledge that it is your obligation to consult with your company's legal counsel to determine whether this access is lawful. Although EPRI may make available on a case-by-case basis an informal assessment of the applicable U.S. export classification for specific EPRI Intellectual Property, you and your company acknowledge that this assessment is solely for informational purposes and not for reliance purposes. You and your company acknowledge that it is still the obligation of you and your company to make your own assessment of the applicable U.S. export classification and ensure compliance accordingly. You and your company understand and acknowledge your obligations to make a prompt report to EPRI and the appropriate authorities regarding any access to or use of EPRI Intellectual Property hereunder that may be in violation of applicable U.S. or foreign export laws or regulations.

## The Electric Power Research Institute (EPRI)

The Electric Power Research Institute (EPRI), with major locations in Palo Alto, California; Charlotte, North Carolina; and Knoxville, Tennessee, was established in 1973 as an independent, nonprofit center for public interest energy and environmental research. EPRI brings together members, participants, the Institute's scientists and engineers, and other leading experts to work collaboratively on solutions to the challenges of electric power. These solutions span nearly every area of electricity generation, delivery, and use, including health, safety, and environment. EPRI's members represent over 90% of the electricity generated in the United States. International participation represents nearly 15% of EPRI's total research, development, and demonstration program.

Together…Shaping the Future of Electricity

© 2007 Electric Power Research Institute (EPRI), Inc. All rights reserved. Electric Power Research Institute, EPRI, and TOGETHER…SHAPING THE FUTURE OF ELECTRICITY are registered service marks of the Electric Power Research Institute, Inc.

*Printed on recycled paper in the United States of America*

1016206

**Electric Power Research Institute**
3420 Hillview Avenue, Palo Alto, California 94304-1338 • PO Box 10412, Palo Alto, California 94303-0813 • USA
800.313.3774 • 650.855.2121 • askepri@epri.com • www.epri.com