EPRI

Hydrogen Water Chemistry Effects on BWR Radiation Buildup

Volume 5: Executive Summary

Technical Report

Hydrogen Water Chemistry Effects on BWR Radiation Buildup

Volumes 2-5

Diverse laboratory experiments and a review of the most recent dose rate data from operating plants have identified key factors responsible for the increase in shutdown radiation fields at a number of BWRs following implementation of HWC. This information suggests strategies to minimize radiation field increases under HWC and to avoid possible problems during chemical decontamination.

INTEREST CATEGORIES

Radiation protection & exposure reduction
Operations & maintenance

KEYWORDS

Radiation buildup
Water chemistry
Reactor materials
BWR

BACKGROUND Currently, BWR utilities routinely use hydrogen water chemistry (HWC) to reduce the propensity of austenitic stainless steels to intergranular stress corrosion cracking. Significant increases in radiation fields have followed implementation of HWC at some plants. Also, some units experienced poor results in decontaminating piping following operation with HWC. To address various aspects of the problem, a tailored collaboration project was organized. An earlier interim report (EPRI TR-101463) evaluated relevant plant data and proposed areas for further investigation. Recent plant data and laboratory studies of cobalt release and deposition under NWC and HWC conditions were reported in TR-104605-V1. Companion Volumes 2-4 present detailed results from a wide range of laboratory and plant experiments, while Volume 5 serves as an Executive Summary.

OBJECTIVES

- To summarize recent results from projects that address the increase in fields associated with the implementation of HWC
- To identify operating strategies that BWR units can adopt that will minimize the increase in shutdown radiation fields and facilitate chemical decontamination

APROACH The results from corrosion release and activity deposition laboratory experiments, performed under NWC, HWC, and cycling conditions, and the chemistry and structure of films that form under cycling conditions were compiled and reviewed. Operating plant experience under HWC, including the on-line gamma spectroscopy measurements performed at Hope Creek, was also studied. The radiation buildup measurements at Monticello, Brunswick-2, and Duane Arnold were also considered.

The focus was to identify those areas that provided a general consensus about the factors responsible for activity buildup under HWC. Once this task was accomplished, the information was used to identify procedures that plant operators could utilize to mitigate undesirable effects.

RESULTS Chemical and structural changes occur in corrosion product films following the transition from NWC to HWC and from HWC to NWC. Chromium enrichment takes place under HWC and such films have a greater propensity to incorporate Co-60 than do films that form under NWC. Continued cycling between NWC and HWC aggravates this effect and increases radiation buildup. Therefore, plant operators should strive to keep hydrogen injection on-line and use a constant feed

rate. An optimum feedwater iron concentration of ~ 0.5 ppb will minimize shutdown dose rates. Minimizing reactor water cobalt also will decrease shutdown dose rates. This can be achieved by the use of depleted zinc oxide and by implementing a cobalt source reduction program. Achieving high chemical decontamination factors requires that the chromium-rich films forming under HWC be solubilized. This process can be accomplished by using a nitric permanganate preoxidation step, as is done in PWR decontaminations.

EPRI PERSPECTIVE Increases in dose rates on switching to HWC cannot be avoided, but this tailored collaboration project suggests that some operational procedures can minimize the increase. Earlier results from this project were used in developing the 1993 revision of the BWR Water Chemistry Guidelines (TR-103515). The new data will be used in preparing the 1996 revision of these guidelines.

EPRI contractors participated in this program, with their detailed results reported in Volumes 2-4 of this report. Volume 5 contains an Executive Summary of these findings. These projects addressed corrosion product sampling at Monticello and Brunswick 2 (TR-104605-V4); laboratory studies on the dissolution and deposition of simulated oxides that form during operation with NWC and HWC (TR-104605-V2); and monitoring of radiation fields at a number of BWR plants operating under HWC (TR-104605-V3).

PROJECT
RP3313-01, -02, -04
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ABSTRACT

Companion volumes issued by EPRI present detailed results from projects that address the issue of the increase in shutdown radiation fields when BWRs switch from normal water chemistry (NWC) to hydrogen water chemistry (HWC). These reports have been reviewed with the objective of summarizing steps that BWR plant operating personnel can implement to reduce adverse effects to a minimum. These measures include : controlling feedwater iron levels; maintaining the hydrogen injection rate; and minimizing reactor water cobalt. Steps that can be taken to ensure effective decontamination after operating under HWC are also summarized.

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CONTENTS

1. INTRODUCTION

Boiling water reactors (BWRs) use high purity water as the primary coolant. This water typically contains 200 ±50 ppb oxygen and 0 - 10 ppb hydrogen (i.e., normal water chemistry [NWC]). The high neutron flux in the reactor core causes radiolysis, which leads to oxidants (oxygen and hydrogen peroxide) being present in the primary system. These oxidants increase the susceptibility of structural alloys such as austenitic stainless steels and some nickel-base alloys to intergranular stress corrosion cracking (IGSCC) when other requisite factors, such as stress and a sensitized microstructure, are also present. Addition of hydrogen to the feedwater system has proved to be an effective technique to reduce the propensity of susceptible alloys to suffer IGSCC.

Some twenty BWRs worldwide now operate under hydrogen water chemistry (HWC), which leads to oxygen levels of <5 ppb and hydrogen levels ranging from 400 - 1600 ppb in the feedwater. One of the main adverse effects of using HWC has been an increase in shutdown dose rates. In some plants the increase on switching to HWC has been significant, but other plants have shown very minimal or no effect. Recently, some plants have found that decontamination after operation on HWC has yielded poor decontamination factors.

These undesirable effects, and the fact that higher levels of hydrogen might be added to reduce the susceptibility of core components to IGSCC, led a number of utilities to cosponsor a project to address this issue. The elements of the program included a preliminary review of shutdown dose rates in plants operating under HWC [1], which was updated in Volume 1 of this report [2]. Laboratory studies of corrosion release rates of BWR structural alloys operating under NWC and HWC and deposition of deposited activity in a loop operating under NWC, HWC, and cycling conditions also are described in Volume 1 as was characterization of corrosion product films formed in the laboratory under cycling conditions [2]. Laboratory studies of activity release from simulated spinel oxides were presented in Volume 2 [3]; on-line gamma spectroscopy at Hope Creek and a detailed assessment of radiation buildup at Monticello,

Brunswick-2, and Duane Arnold in Volume 3 [4]; and corrosion product sampling at the Monticello and Brunswick-2 plants in Volume 4 [5].

These projects have yielded fairly consistent results about the main factors responsible for the increase in shutdown radiation fields on implementing HWC, although differences remain in trying to explain some of the details. The objective of this document is to use the R&D findings to propose actions that plant operators can implement to reduce the undesired effects of HWC and increase the chances for effectively decontaminating piping systems after operating with HWC. These actions include [1] controlling feedwater iron levels; [2] maintaining the hydrogen injection rate; [3] minimizing reactor water cobalt; and [4] planning for effective chemical decontamination.

2. CONTROLLING FEEDWATER IRON LEVELS

Metal ions are released to the coolant from corroding surfaces in contact with the primary coolant. Colloids and particulates form when the saturation limit is reached. The released species deposit on the fuel surface as crud, where minor constituents are activated to form radioisotopes that are then released to the coolant in soluble or particulate forms. The main crud constituent, iron, serves as the "glue" for the other isotopes (Co-60 and Zn-65) that are responsible for the vast majority of shutdown radiation fields.

Optimizing the feedwater iron concentration represents a balancing act. The current BWR Water Chemistry Guidelines [6] calls for feedwater iron to be maintained at 0.1 - 0.5 ppb. High iron concentrations favor lower general area shutdown fields but increases the likelihood of deposition of insoluble particulates. Also, high iron levels will increase the inventory of natural or depleted zinc that has been used at some plants to address the increase in fields observed in switching to HWC. Some new Japanese plants have been designed with the capability to greatly reduce iron input. However, Co-58 and Co-60 levels in the coolant and on out-of-core surfaces were much higher than anticipated. The cause was found to be a change in the form of fuel crud from Fe_2O_3 in high-crud plants to NiO/CoO deposits in the very low iron plants. Japanese utilities found Co-58 and Co-60 reactor water concentrations could be decreased by controlling the iron-to nickel ratio in the feedwater to a value of 3-5. This results in the formation of fuel deposits $(Fe,Ni,Co)_3O_4$, with a lower solubility for transition metals, which is achieved by controlling feedwater iron to approximately 0.5 ppb. Another question that needs to be addressed is the optimum level of iron in the feedwater to keep radiation levels at a minimum. The prevailing view is that the optimum Fe/Ni ratio is 3:1.

3. MAINTAINING THE HYDROGEN INJECTION RATE

Loop experiments that measured deposited activity on austenitic stainless steel tubing specimens from soluble activation products injected under controlled conditions show that deposition rates of Co-60 are somewhat higher under HWC compared with NWC but increase dramatically when conditions are switched from NWC to HWC. These observations reflect the fact that HWC causes a change in the structure and chemistry of the films. The oxides that form under both NWC and HWC consist of different structures. These consist of a fine-grained inner layer, a second layer with intermediate-size grains and particles, and an outermost layer that contains large particles. The inner layer under both NWC and HWC consists of $[Fe_xCr_{1-x}]_3O_4$. Both the intermediate-size particles and the large-size particles in the outer layer consist of substituted Fe3O4 under HWC and α–Fe2O3 under NWC. The oxide that forms under HWC is thinner, is more highly enriched in Cr , and can incorporate larger amounts of Co-60, Zn-65, and other transition metal isotopes. Also, the kinetics of film formation plays a role in these effects. The switch from NWC oxides to HWC oxides takes longer to reach equilibrium than does the switch from HWC oxides to NWC oxides.

These observations suggest some measures for reducing the impact of implementing HWC. A HWC level required to mitigate IGSCC should be identified. Hydrogen injection should be implemented at this level, rather than approaching the target level in a step-wise manner. Inadvertent changes in reactor power level should be avoided to the extent possible, and operating strategies that lead to continuing power changes (i.e, load following) also should be avoided. Extended coastdowns at the end of a fuel cycle also should be avoided for similar reasons. While these proposals may not be implemented because they adversely affect fuel economics, if implemented they could prove effective in dealing with shutdown radiation fields.

To reduce cycling under HWC, a utility should first determine the factors responsible for cycling (i.e. RWCU pump maintenance, hydrogen injection system, feedwater pump, etc.). The utility may considering reviewing past events to determine the cause of HWC/NWC cycling. This review may provide

insights that can lead to recommendations for minimizing cycling. Such cycling may be a result of system components with high failure rates, which can be fixed with a minimal investment. Alternatively, cycling may be due to scheduled maintenance activities or routine testing that could be more effectively managed. Once the factors responsible for cycling are determined and corrective actions are implemented, plant management should ensure that all personnel understand the true cost of cycling. NWC/HWC cycling should be viewed as a long-term, high-cost element that should be used as a last resort and not as a short-term solution for routine testing or maintenance.

However, utilities should consider shutting off hydrogen injection about two weeks before shutdown if a decontamination is planned at the next shutdown. This suggestion is motivated by the view that restructuring from a HWC film to a NWC film is a relatively rapid process and may reduce shutdown fields. Also, the change in film chemistry associated with HWC that works against achieving effective decontamination factors is the higher levels of chromium. Cessation of hydrogen injection at the end of a fuel cycle after which a decontamination is planned may effectively leach chromium from the film, leading to a more effective decontamination. Cessation of hydrogen injection at the end of a fuel cycle in which no decontaminationis planned should not be implemented, because adverse affects that accompany film restructuring are likely to outweigh the benefits resulting from leaching of chromium from the film.

4. MINIMIZING REACTOR WATER COBALT

Because Co-60 is the main contributor to shutdown dose rates, measures that will reduce the release by corrosion and wear of cobalt will also reduce dose rates under both HWC and NWC. These measures include reducing the inventory of cobalt-base alloys by replacing control blades that contain cobalt-base alloys in the pins and rollers and replacing cobalt-base hardfacing alloys in plant valves using the approach suggested in Revision 1 of the Cobalt Reduction Guidelines [7]. ABB Combustion Engineering [8] and General Electric have developed equipment capable in providing in-situ replacement of pins and rollers in irradiated control blades. This technique for removing this cobalt source has been used at only a few BWRs, and recent assessments and plant experience suggests that the cobalt contribution from this component is fairly modest.

A more effective approach for lowering the concentration of reactor water Co-60 is through zinc injection. Marble et al. [9] have summarized recent experience in BWR plants using zinc. Reactor water Co-60 levels are reduced by about a factor of two to three. Use of depleted zinc oxide (DZO) reduces the impact of undesirable Zn-65 associated with natural zinc oxide. However, the high cost of DZO makes it desirable to perform a plant specific cost/benefit analysis. The high cost of DZO has led some plants with fairly low dose rates to abandon DZO and return to injecting natural zinc.

The effectiveness of zinc in lowering shutdown radiation fields is likely a result of two factors. Zinc readily substitutes for cobalt in fuel rod crud and in the oxide films that form on out-of-core surfaces. This leads to a factor of two to three lower Co-60 levels in the reactor water and reduces the sites available for incorporation of Co-60 in ex-core oxides. Also, soluble zinc reduces the general corrosion rate of reactor structural alloys.

5. PERFORMING EFFECTIVE CHEMICAL DECONTAMINATIONS

After switching to HWC the utility should plan to perform a chemical decontamination at the subsequent outage. Effective planning requires that the utility identify artifacts that can be examined by the prospective vendor that will provide the best available information about the oxide film chemistry that the decontamination solvent will encounter. The chemistry changes noted above (specifically the higher chromium content of the film) indicates that under HWC a film forms that resembles the Cr-rich films that form under the reducing conditions found in PWRs. As is done in PWR decontaminations, a preoxidation step should be used that will serve to solubilize the Cr-rich film. Evidence suggests that in Cr-rich films nitric permanganate (NP) is better than alkaline permanganate (AP) as a preoxidizing step and that in films with high nickel ferrite content LOMI performs better than citric acid or oxalic acid based reagents.

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