B. 10 "BWR Water Chemistry: Effects on Materials Degradation and Industry Guidelines,"

by Robin L. Jones, Peter L. Andresen, and Christopher Wood

This background paper is comprised of an introductory section (Section A) that focuses specifically on the evolution of BWR water chemistry over time, and more specifically its effects on materials degradation. It is followed by a broader summary (Section B) based primarily on BWR Water Chemistry Guidelines that addresses such topics as chemistry effects on radiation build-up, fuel cladding corrosion, chemistry monitoring, and action level treatment of chemistry transients.

A. Effects on Materials Degradation

Introduction

Boiling water reactor (BWR) water chemistry is necessarily of high purity because boiling occurs on the fuel rods and the resulting steam directly drives the turbine; if high purity were not maintained then high concentrations of aggressive species would be formed on the heat transfer surface where boiling occurs. By contrast, pressurized water reactors (PWRs) have a primary system comprised of liquid water containing B, Li and H_2 that is pumped through tubing in several steam generators (the secondary system).

To understand the basics of BWR water chemistry, the water flow path must be clear, Figures B.10.1 and B.10.2). After the turbine, steam is condensed and demineralized, then returned as feed water. Feed water is heated to about 200°C, then it enters the pressure vessel, and its flow is distributed via feed water spargers, which are distributed near the inside diameter of the pressure vessel at an elevation somewhat above the top of the core (Figure B.10.1). Water is circulated through the core via jet pumps, with the average water molecule circulating about 7-10 times before becoming steam. A large pipe (the core shroud) separates the up-flow (in the core) from the down flow (in the annulus). In jet pump plants (all current US plants), the drive water is drawn from the annulus at an elevation below the bottom of the core, and flows through the recirculation piping and pumps, then flows back into the pressure vessel. In jet pumps, about one-third of the flow is drive water and two-thirds is drawn into the jet pump by the water jet. Thus, two-thirds of the water moves rapidly through most of the annulus region, and is exposed only briefly to the gamma field emanating from the core; the relevance of this factor is discussed later.

The bottom of the jet pumps seals into a ledge that blocks off the annulus region. The water flows into the bottom plenum (the bottom hemisphere of the reactor pressure vessel), then back up through the core. Advanced BWRs and some overseas designs use internal pumps and therefore have no recirculation piping.

BWR fuel rods (Figure B.10.3) are enclosed in "channels" or zirconium alloy wrappers around the fuel bundle (BWR fuel is comprised of an array of roughly 9 x 9 fuel rods = 81 total – the designs have evolved over time). About 90% of the water flows through the fuel channel, and 10% flows in the "bypass" regions between fuel bundles or around the periphery of the core along the inside of the shroud. The core inlet temperature is about 274°C, and about one-third of the way up the fuel the water temperature reaches 288°C and begins to boil. The volume fraction of steam ("steam quality") rises with elevation in the core. At the top of the core there is a dome or upper plenum at the top of which are steam separators, then steam dryers. The separators produce a rotating vortex flow, and the liquid water is centrifugally forced to the outside, where it is

routed outside the separator and falls on the top of the dome, then into the annulus. This 288 °C water is cooled by the ≈200°C feed water to 274°C. Thus, most structural materials (the vessel, the external piping, the outside of the shroud, the bottom plenum and the core support plate, etc.) are exposed to 274°C water.

The steam continues upward through the separators and steam dryer to the top dome of the reactor pressure vessel and out the main steam nozzle and piping to the turbine. The liquid content of the saturated steam is typically ≈ 0.1%. Thus, the upper half of the vessel internals is exposed to 288°C saturated steam, and all steam path surfaces are expected to have a water film.

While the condensate from the turbine is fully demineralized before returning to the reactor pressure vessel as feed water, the reactor water must also be cleaned up, because otherwise non-volatile impurities would concentrate because of boiling. The reactor water clean up system typically runs at 0.5 to 1% of the feed water flow rate, cooling the water before running it through demineralizers.

As water flows through the core and is exposed to ionizing radiation (esp. neutrons, which are slowed by their collisions with water (esp. H) and eventually reach "thermal" energies, at which point they are most effective in producing fission reactions), a wide variety of radiolysis products are produced. For simplicity, the primary species can be considered to be H_2 and H_2O_2. H_2 partitions to the steam phase, so the recirculated water is always oxidant rich. H_2O_2 decomposes to H_2O and O_2, and the relative proportions of O_2 and H_2O_2 changes with time and distance away from the core. Expressed as O_2, typical recirculation water has ≈ 200 ppb O_2 and ≈10 ppb H_2. It is helpful to note that O is 16 times heavier than H, but there are two H atoms in H_2O, so a stoichiometric balance is 2:1 H:O by atom ratio, but 1:8 H:O by weight. Thus, 10 ppb H_2 and 80 ppb O_2 represents a stoichiometric mixture.

In the core, some ^{16}O is transmuted to ^{16}N, which has a half-life of 7.13 seconds. In "normal water chemistry," the stable form of N is NO_3^-, which remains soluble. However, when sufficiently high H_2 is injected into BWRs, the stable form becomes NO_X (and eventually NH_3), which are volatile. Thus, rather than remaining in the recirculated reactor water as it decays, ^{16}N becomes volatile and can cause a large increase (up to (10X) in the turbine radiation level.

Apart from very slight consumption of H2O2 and O2 (e.g., by corrosion reactions) and some recombination of oxidants and H2, all of the radiolysis products eventually go up with the steam as H2 and O2. They are catalytically recombined in the off-gas system after the turbine and condenser.

SCC Mitigation by Water Purity Control

Control of water purity is particularly important in BWRs because the higher corrosion potential traditionally present creates a potential gradient in crevices and cracks which concentrates anionic impurities like Cl– and SO4= [1-7]. Until the late 1980s, many BWRs operated at solution conductivities between 0.3 and 0.8 (S/cm, which corresponds to 30 – 90 ppb of (usually acidic) impurities (these were often Cl– and SO4=, which are particularly damaging and were responsible for extensive cracking). Several plants had severe intrusions of impurities from seawater or release of resins into the reactor water, and experienced severe and immediate SCC. By the early 1990s (Figure B.10.4) the fleet average conductivity had decreased to (0.13 (S/cm, and it is cur-

rently (0.11 (S/cm, with much of the residual conductivity (theoretical purity water is 0.055 (S/cm) related to chromate (Cr in the oxide films of structural materials becomes soluble at high potential) and Zn ion (which is introduced into the feed water of most BWRs to control radiation build-up and provide some SCC initiation benefit). SiO2 is almost always present at higher levels (e.g., 100-500 ppb), but it ionizes only very slightly in 288(C water. It should be emphasized that chloride and sulfate have the largest effect on stress corrosion cracking; some ions, like chromate, nitrate and silicate anions have little effect on SCC unless their concentrations exceed 25 ppb, 100 ppb or 1000 ppb respectively [5-7].

A conductivity of 0.10 μS/cm represents only about 6 ppb Cl^- as HCl (1.7×10^{-7} N), and there is a limited value in striving for theoretical purity water because OH^- is present at 2.3×10^{-6} N in pure water; both logic and modern data support the idea that, when the "foreign" anions concentration is well below a tenth of the OH^- concentration, their role in carrying ionic current and thereby changing crack chemistry diminishes. However, SCC growth rates in autoclave outlet water of <0.065 μS/cm remain reasonably high at high potential, and crevice chemistry measurements show that a shift from acidic to alkaline crack/crevice chemistry occurs in pure water [3-6]. Thus, water purity alone cannot be used to reduce SCC to acceptable levels in BWRs.

SCC Mitigation by Hydrogen Water Chemistry

The presence of oxidants like H_2O_2 and O_2 in the water cause an increase in the corrosion potential of metals (Figure B.10.5). This in turn produces an aggressive crack chemistry that accelerates SCC growth rates (Figure B.10.6). The most effective way to mitigate SCC in BWRs is to modify the water chemistry by reducing the corrosion potential. Hydrogen Water Chemistry (HWC) does this by injecting H_2 into the feed water. H_2 levels above ≈500 ppb effectively suppresses radiolysis (PWRs use ≈3 ppm H_2), but such high levels are not economically achievable in BWRs because most of the H_2 is lost to the steam during each pass through the core (thus, the feed water would need to have 7-10 times more H_2, or ≈4 ppm).

However, the addition of some H_2 to the feed water is effective in reducing the oxidant levels and therefore the corrosion potential (Figure B.10.7) enough to effectively suppress stress corrosion cracking when the corrosion potential reaches a "protection potential" of -230 mV_{she} [8-9]. This decrease in corrosion potential occurs not by suppressing radiolysis but by gamma-radiation enhanced recombination in the annulus (or downcomer). The gamma level in the downcomer varies with reactor design, and some wide annulus plants have insufficient gamma radiation at the outside of the annulus (i.e., at the inside of the reactor pressure vessel) to produce very effective recombination – thus, the effectiveness of a given H_2 injection rate varies from plant-to-plant. In the best plants, HWC drops the oxidant levels from ≈200 ppb to < 1-2 ppb at the bottom of the annulus, which feeds the recirculation piping. However, since two-thirds of the jet pump flow is drawn from an area closer to the top of the annulus, the water that flows into the bottom plenum has a higher oxidant concentration. Thus, in "standard HWC" plants (where ≈300-500 ppb H_2 is injected into the feed water, which is diluted by 7-10X in the reactor water), the good plants achieve low corrosion potentials (e.g., < –300 mV_{she}) in the recirculation piping, along some of the outside of the shroud, and on the top surface of the ledge, but are not as effective in the bottom plenum where there are many structural welds and pressure vessel penetrations for the control rods and instrumentation tubes. (Figure B.10.8). No "standard HWC" plant is able to significantly lower the corrosion potential in-core.

Attempts to improve the coverage of HWC considered the obvious option of increasing the H_2 to higher levels. "Moderate HWC" plants inject about 5-10 times more H_2, e.g., ≈2 ppm H_2 in the

feed water. In many plants, this produces an adequately low corrosion potential in the bottom plenum and perhaps along the inside of the shroud (there are uncertainties in the measurements and models that make this less than certain). At such high H_2 levels, all plants see a large increase in "turbine shine" (^{16}N in the steam).

Note that once boiling occurs (essentially no boiling occurs in the bypass water outside of the fuel bundles), the H_2 level in the water drops significantly. Thus, components exposed to this water remain at high corrosion potential and remain unprotected from stress corrosion cracking (Figure B.10.8). Such components can include the top guide, the dome (upper plenum), the steam separators, the core spray piping and spargers, the feed water piping and spargers, and perhaps some area at the upper part of the core shroud. While there are a large number of feed water spargers distributed around the periphery of the core, there is also some concern for how quickly the H_2-rich feed water becomes thoroughly mixed with the core "over-flow" (recirculated) water, and therefore at which point down the outside the shroud a low corrosion potential is achieved. On the basis of an exhaustive qualification process for hydrogen water chemistry in the laboratory and in test reactors, all US BWRs now employ this technique for mitigating stress corrosion cracking in the components outlined in Figure B.10.8. However, a cautionary note is appropriate in that reduced corrosion potentials have been confirmed in a few locations in a limited number of operational BWRs. There is no direct confirmation of the benefit of HWC on SCC of BWR components due to the limited number of repeat inspections.

SCC Mitigation by NobleChem™

Rather than achieving a reduction in oxidant concentration in all of the reactor water, a novel technique (NobleChem™) was developed by GE in which all wetted surfaces could be made catalytic [10-13]. Metals such as Pt, Pd, Rh, Ru, Os and Ir are electro-catalytic; i.e., reactions (esp. H_2 and O_2 or H_2O_2 reactions) are dramatically accelerated. While these Pt-group metals can be added to alloys and used in thermal spray powders, the most efficient way to create catalytic surfaces is to introduce low concentrations of Pt salts (e.g., $Na_2Pt(OH)_6$) into BWR water, which results in Pt depositing on the surfaces of all wetted parts. Pt concentrations below 1% of a monolayer are adequate, and NobleChem™ application is performed at shutdown at ≈135°C. An "OnLine NobleChem™" is being developed that introduces Pt during full-power operation.

The development of electrocatalytic processes for improving the efficiency of the oxygen/ hydrogen recombination process and thereby extending the region of protection to the reactor core region (Figure B.10.9) has, like the hydrogen water chemistry process described earlier, been subject to years of qualification in the laboratory and test reactors. Currently the majority of US BWRs use, or are about to use, the NobleChem™ process (Figure B.10.10), in large part due to the fact that under the Noblechem process protection of the core internals from stress corrosion cracking can be achieved at lower feedwater hydrogen concentrations that do not give rise to accelerated ^{16}N offgas rates and increases in the main steam line radiation (Figure B.10.11). As with the hydrogen water chemistry, the benefit of NobleChem™ has only been confirmed in terms of reduced corrosion potentials in a few locations in a limited number of BWRs. There is no direct confirmation of the benefit of NobleChem™ on SCC of BWR components due to the limited number of repeat inspections. There are also some precautionary notes with respect to plant verification and inherent limitations to the effectiveness of NobleChem™. For instance:

- To achieve low corrosion potential at all locations of interest, H_2 must be in stoichiometric excess. Considering only O_2 (not H_2O_2), there must be two moles of H_2 per mole of

O_2, which translates to a ppb level of H_2 at least one-eighth of O_2. This is easily achieved at fairly low levels of H_2 injection to the feed water at all locations until boiling occurs. Thus, areas above the fuel channel (upper plenum, steam separators, core spray lines, etc.) are not protected. Additionally, there may be areas in the upper regions of the annulus where the (H_2-rich) feed water does not adequately mix with the core water, and stoichiometric excess H_2 might not exist in some local regions.

- Low corrosion potential does not translate to immunity to SCC. Indeed, higher yield strength materials (such as alloy 182/82 weld metal, irradiated stainless steel, cold worked stainless steel or alloy 600 – including regions of the weld heat affected zone – etc.) benefit less than, e.g., sensitized stainless steel, because cold work causes higher growth rates at both low and high corrosion potential (Figure B.10.6).

- If cracks grow extensive in between NobleChem™ applications, O_2 can get to areas of the crack flank that are not catalytic, so no catalytic benefit is observed [13]. This is a well-understood limitation, and where it has occurred in the operational reactors, it has been associated with a digression from operational procedure and the inadequate control of the hydrogen feed rate. OnLine NobleChem™ is under development and being demonstrated in plants to help resolve this concern.

Effects of Corrosion Potential on Corrosion Fatigue Initiation and Growth

The discussions above have mainly been associated with mitigating stress corrosion and irradiation assisted cracking of stainless steels and stress corrosion of nickel base alloys. In addition to these examples, there is a strong benefit of HWC and NobleChem™ on stress corrosion and corrosion fatigue crack initiation and growth in carbon and low alloy steels. Cracking in these systems is attributed primarily to the role of MnS inclusions, which readily (but not very rapidly) dissolve in high temperature water and affect crack growth by changing the crack tip chemistry. For many years it was assumed that stainless steels would behave in a similar fashion, and indeed they do from the perspective of crack growth, where the lowered corrosion potential makes the crack chemistry less aggressive. However, corrosion fatigue crack initiation is accelerated at low corrosion potentials, and this may result from the (≈5 times) higher general corrosion rate on stainless steels exposed to deaerated (or hydrogenated) high temperature water.

Other Chemistry Related Mitigation Approaches for Stress Corrosion Cracking

Zn Injection [9, 14-16] and *Insulated Protective Coatings* [17-19] are other methods that can mitigate SCC in BWRs. *Zn injection*, originally undertaken to reduce ^{60}Co absorption into the oxide on BWR piping and thereby increasing the maintenance dosage rates, also improves SCC initiation. It appears to be less effective on crack propagation, especially at high corrosion potential (where cation transport in cracks is resisted by the potential gradient). However, even at low corrosion potential, providing an adequate and continuing supply of Zn to the tip of a long, growing crack may be difficult.

Insulated protective coatings (ICP) depend on forming a dense or slightly porous layer on the surface that has very low electrical conductivity. The most attractive coating is ZrO_2, which can be deposited by various coating techniques, or formed in situ after creating a metallic Zr layer

on the surface, e.g., by wire arc or thermal spray techniques. IPC does not rely on H_2 injection or even the presence of H_2, but it is very unlikely that any technique can be developed to form effective, durable coatings in-situ as is done by NobleChem™.

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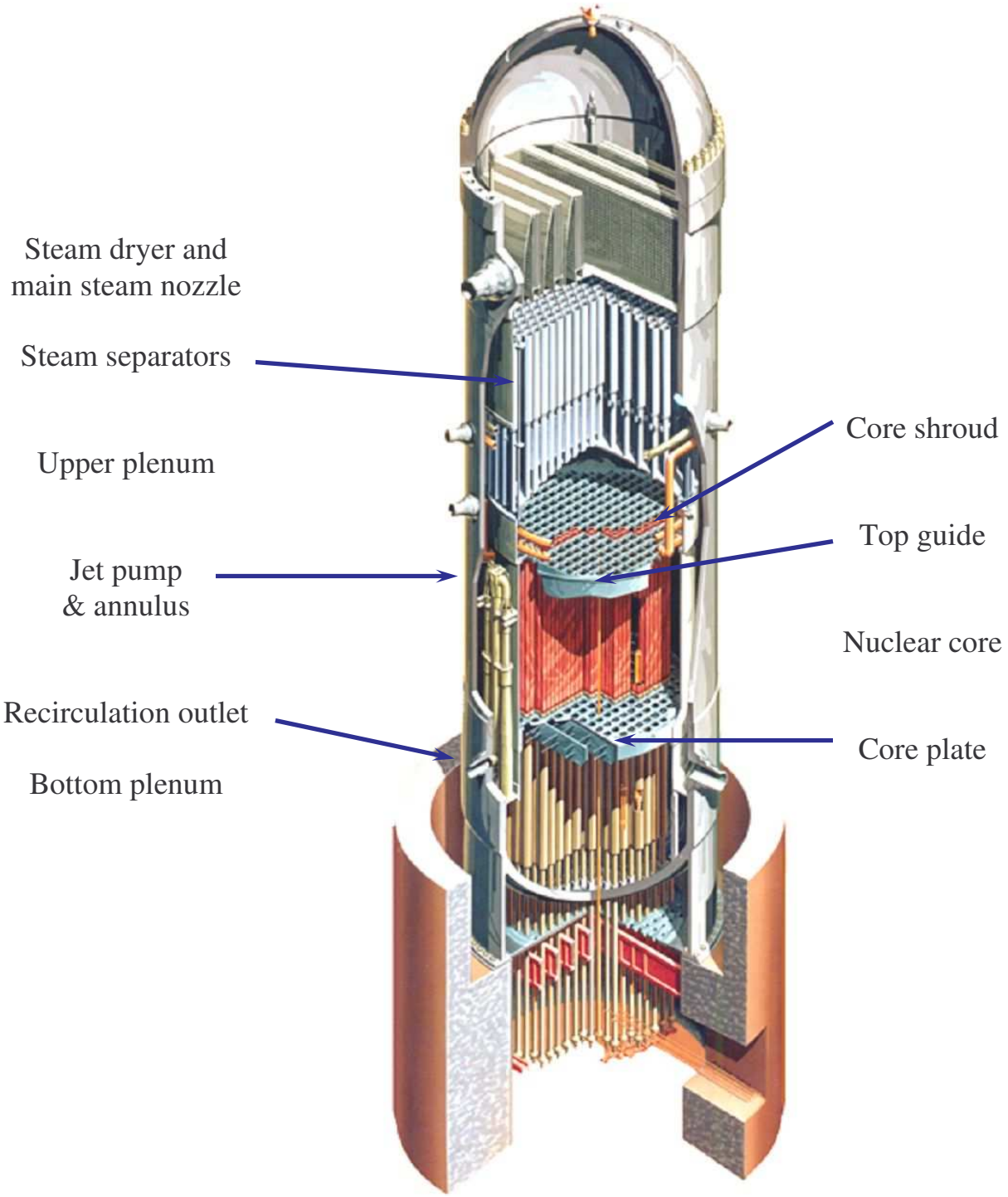

Figure B.10.1. Schematic of a BWR/6

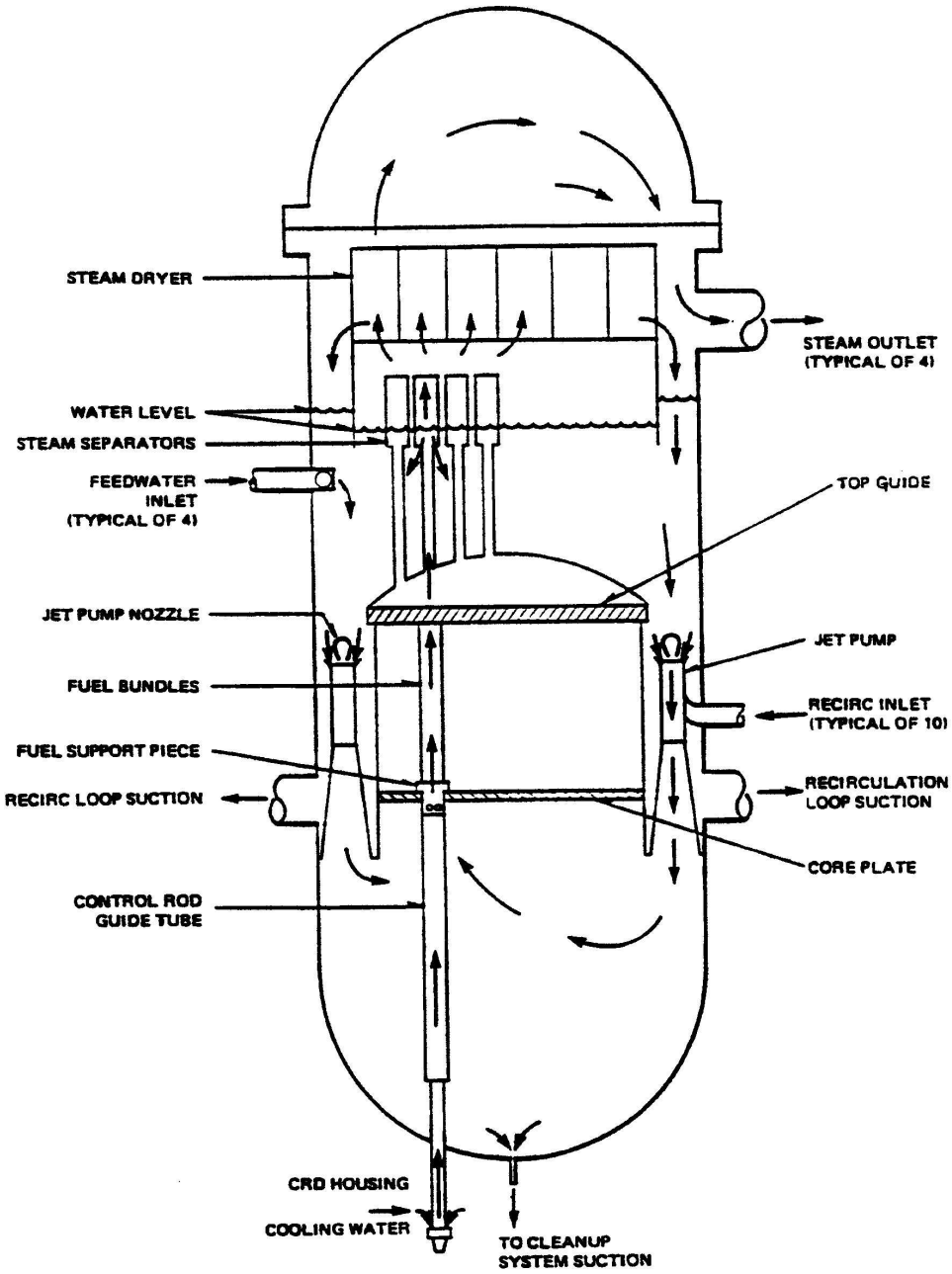

Figure B.10.2. Schematic of coolant flow path within BWR pressure vessel.

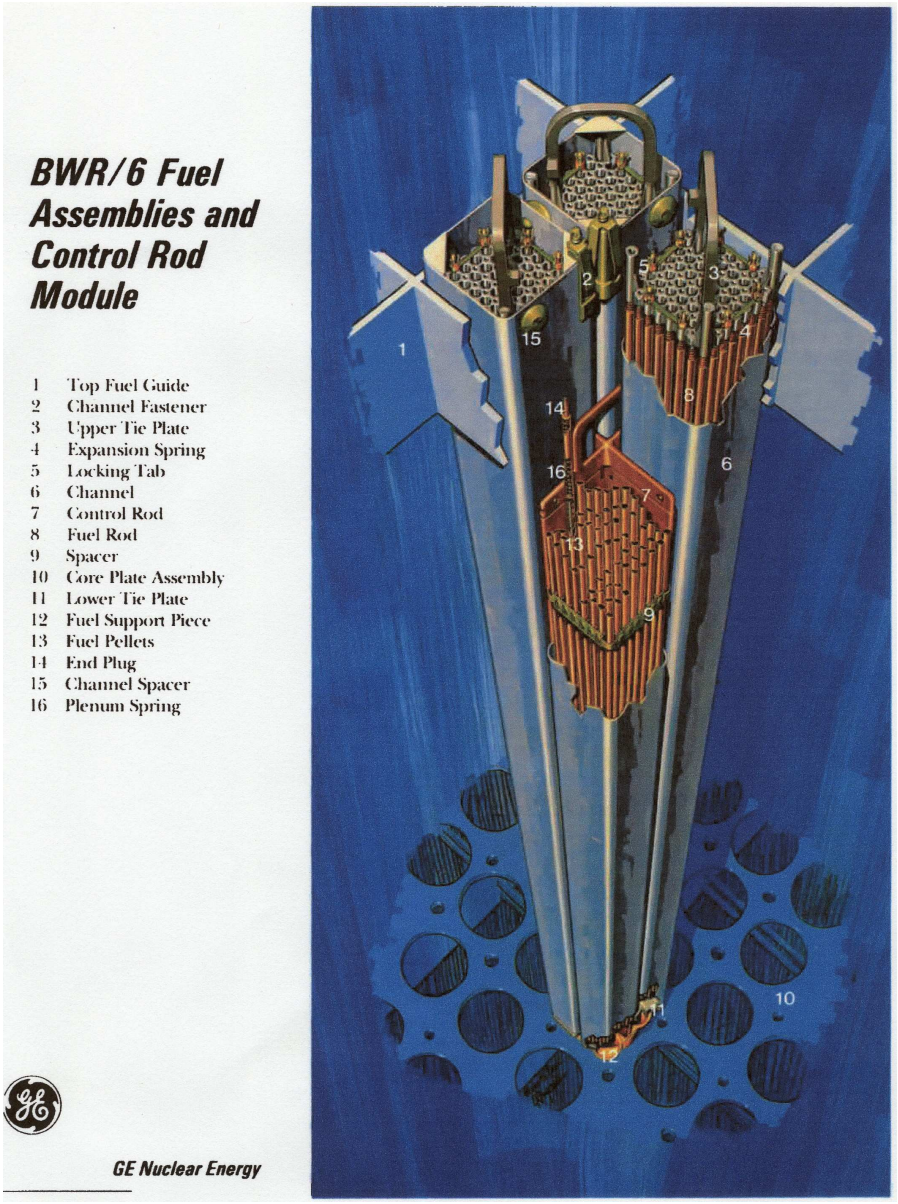

Figure B.10.3. Schematic of a BWR-6 fuel assembly, illustrating the relationship between the fuel channels and rods, and the different coolant flow paths inside and outside the fuel channels.

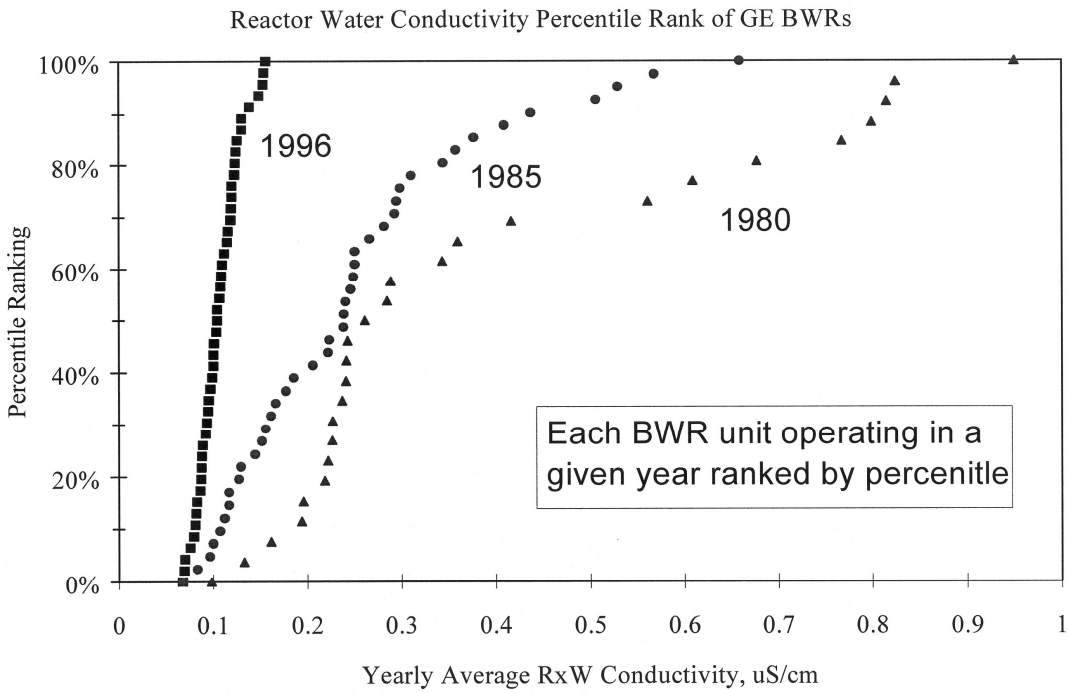

Figure B.10.4. Distribution in reactor coolant purity in the US BWR fleet at specific time periods.

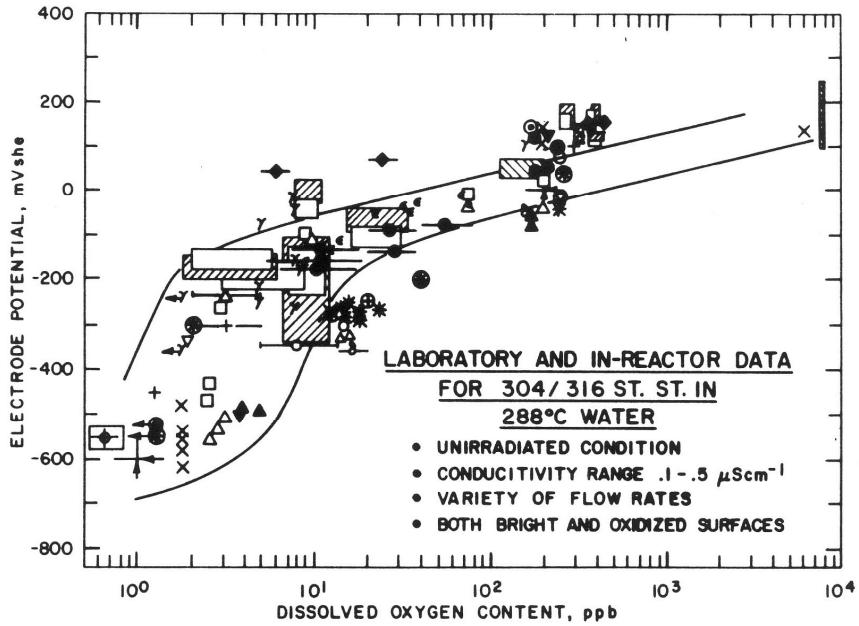

Figure B.10.5. Relationship between corrosion potential of 304 SS and dissolved oxygen content as a function of water temperature [2].

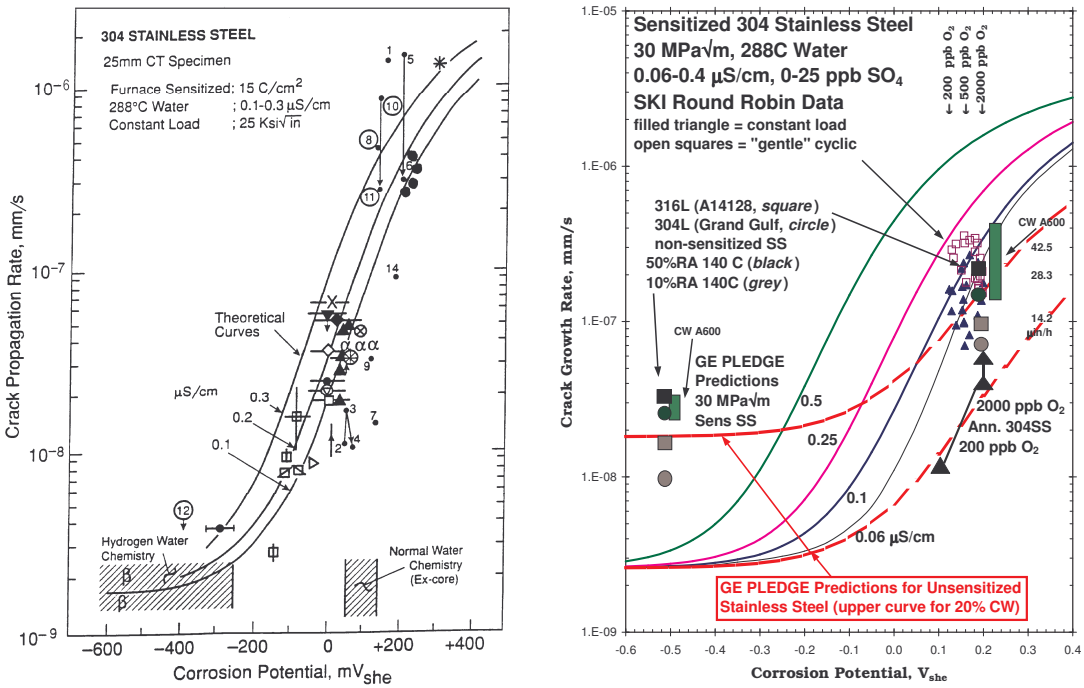

Figure B.10.6. SCC growth rate vs. corrosion potential for stainless steels tested in 288 °C high purity water containing 2000 ppb O_2 and 95 – 3000 ppb H_2.

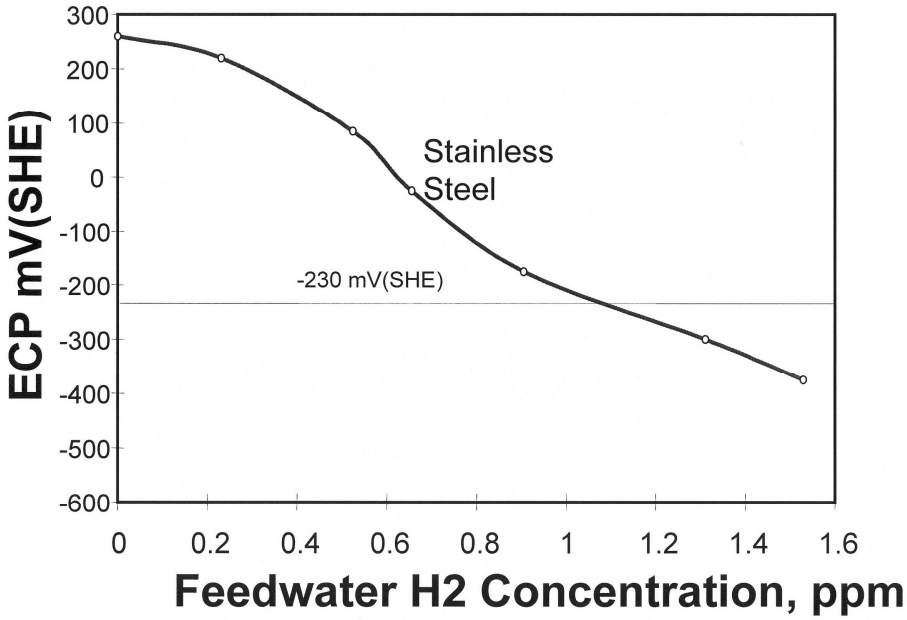

Figure B.10.7. Relation between corrosion potential and injected feedwater hydrogen content observed in feedwater line at a specific BWR.

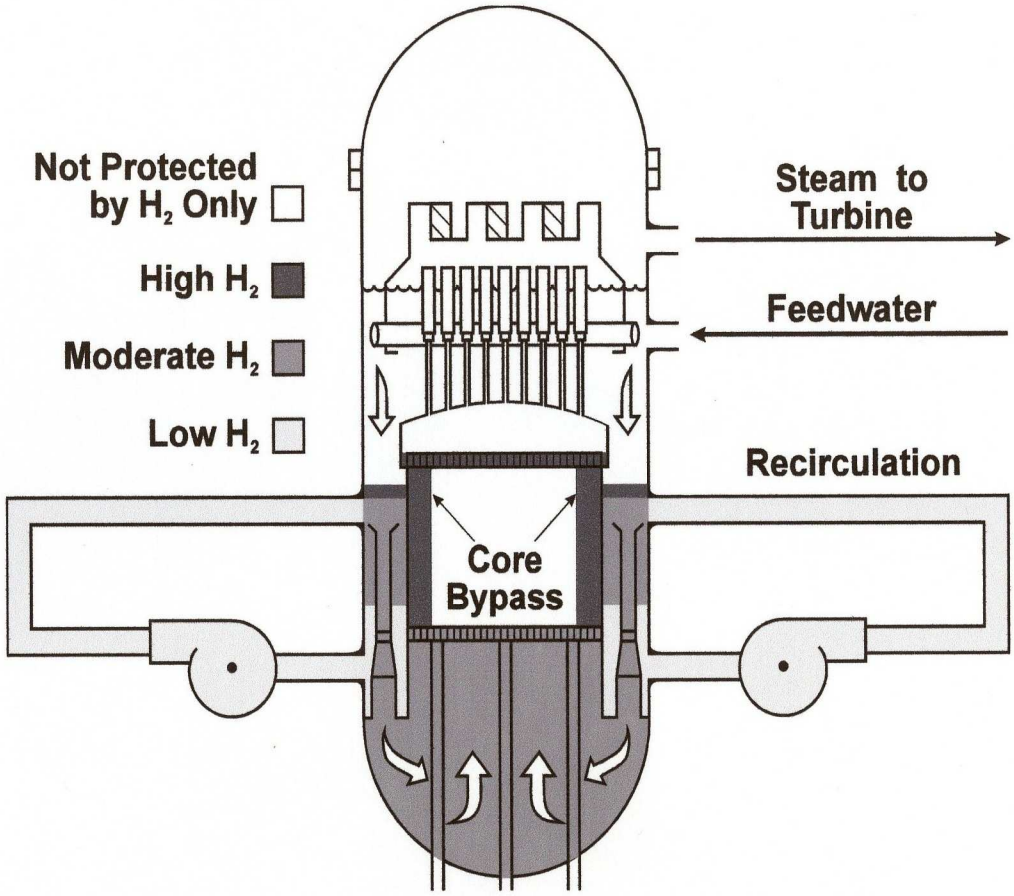

Figure B.10.8. Regions of the pressure vessel internals and recirculation piping protected by hydrogen water chemistry.

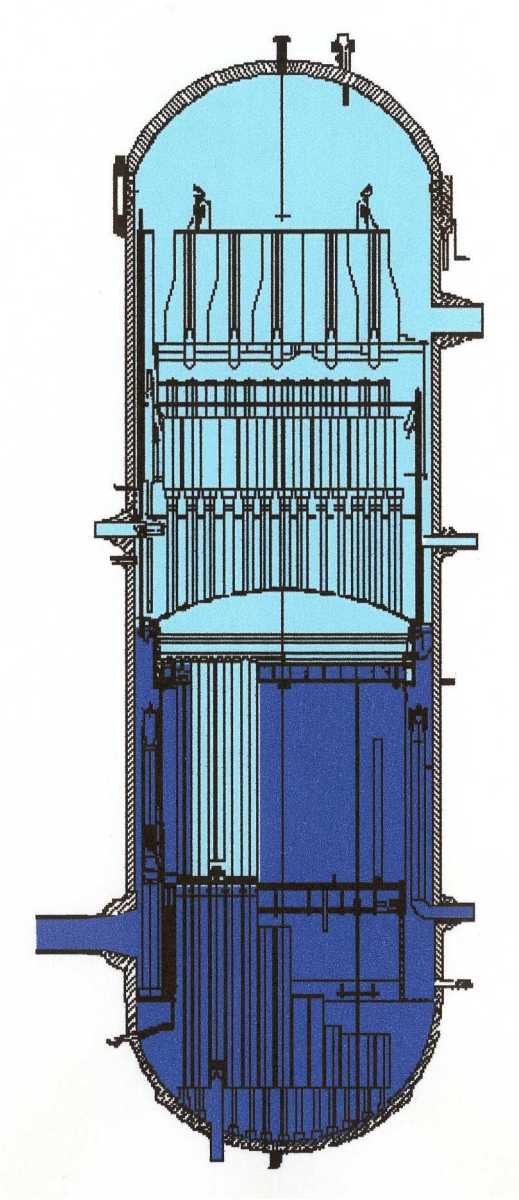

Figure B.10.9. Regions of the reactor core internals, colored dark blue, that are protected by NobleChem™ from stress corrosion cracking and irradiation assisted SCC.

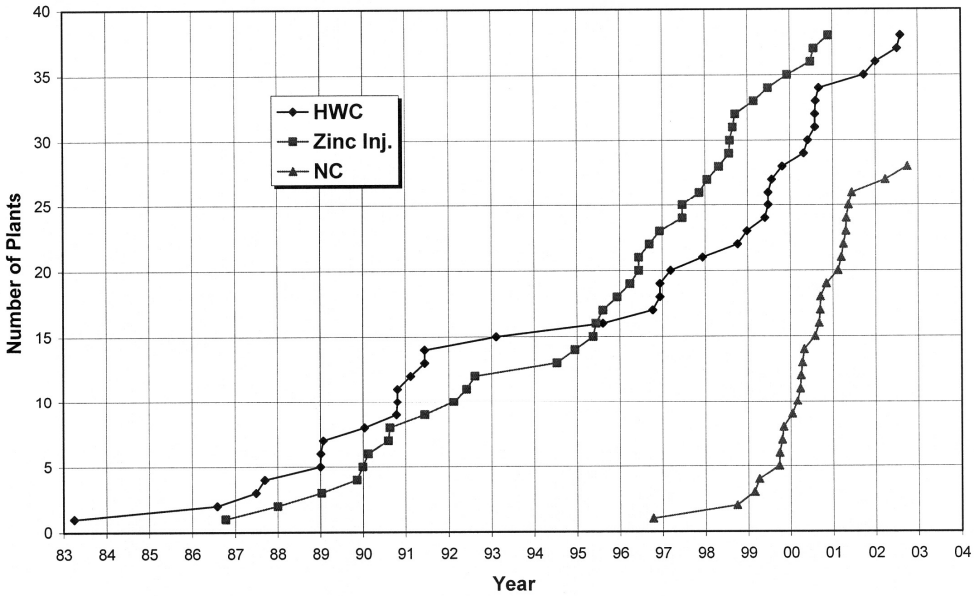

Figure B.10.10. Number of BWR plants transitioning to hydrogen water chemistry and NobleChem™ processes as a function of year.

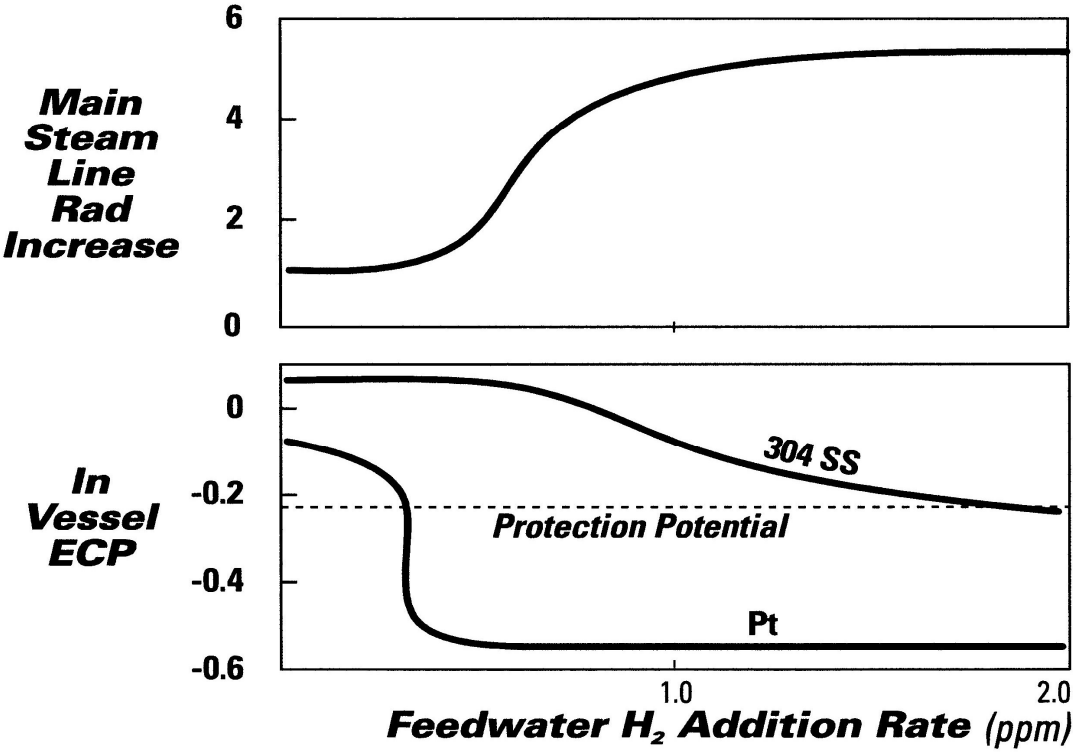

Figure B.10.11. Changes in corrosion potential and main steam line radiation increase as a function of feedwater hydrogen addition rate and the application of NobleChem™.

B. BWR Water Chemistry Guidelines

Introduction

The 2004 revision of the BWR Water Chemistry Guidelines continues to focus on intergranular stress corrosion cracking (IGSCC), which can limit the service life of susceptible materials and components in BWR water environments. In addition, the guidelines place increased emphasis on fuel performance concerns, in view of the increasing incidence of fuel failures since the last revision in 2000. Many plants have adopted noble metal chemical application (NMCA) in the past four years, and this document addresses the resultant issues with IGSCC mitigation, fuel performance and radiation fields.

This document provides proactive water chemistry recommendations for BWRs during all modes of operation. It summarizes the technical bases for all water chemistry alternatives and provides guidance on the development of plant-specific chemistry programs. The guidelines recommend tightening some limits, relaxing others, and implementing more cost-effective monitoring, which will improve protection against materials and fuel problems and also reduce the risks of loss of output from chemistry transients.

Background

The first edition of these guidelines focused on impurity control to reduce stress corrosion cracking and fuel degradation. Consideration of hydrogen water chemistry to reduce electrochemical potential was added subsequently, and noble metal chemical addition was considered in the latest revision, including the effects on radiation buildup. With fuel heat rates increasing, and examples of corrosion induced fuel failures in recent years, fuel/water chemistry interactions are now a central theme in the latest edition.

The BWR Water Chemistry Guidelines Committee and the Mitigation Committee of the BWR Vessel and Internals Program (BWRVIP) issued this document to provide proactive water chemistry guidance for mitigating IGSCC, maintaining fuel integrity, and controlling radiation fields. The BWR Fuels Focus Group of the Fuel Reliability Program has been closely involved in the development of this document to address the increased industry concern about fuel performance issues. It updates the *BWR Water Chemistry Guidelines - 2000,* providing an enhanced methodology for establishing site-specific BWR water chemistry control programs.

A committee of industry experts collaborated to review the available field and laboratory data on BWR water chemistry controls and their impact on plant operation, corrosion mechanisms, fuel performance and radiation fields. The committee included utility specialists, Nuclear Steam Supply System (NSSS) vendors and fuel vendor representatives, Institute of Nuclear Power Operation (INPO) representatives, consultants, and EPRI staff. The committee identified a range of water chemistry regimes from which utility personnel can select their site-specific program.

Key Points and Technical Issues

The content of this document is summarized below, with major changes from the 2000 revision noted:

Management Issues: Section 1. A recent policy of the U.S. nuclear industry commits each nuclear utility to adopting the responsibilities and processes on the management of materials aging issues described in "*NEI 03-08: Guideline for the Management of Materials Issues.*" Section 1 of the BWR Water Chemistry Guidelines specifies which portions of the document are "*Mandatory,*" *"Needed,"* or *"Good Practices,"* using the classification described in NEI 03-08.

Intergranular Stress Corrosion Cracking: Section 2 discusses the technical basis for water chemistry control of IGSCC. This Section has been updated with the latest information on the effects of impurities such as sulfate and chloride on crack growth rate and covers a wider range of electrochemical potential (ECP). The strong effect of copper ions on the effectiveness of hydrogen water chemistry (HWC) is detailed. The overall goal of demonstrating the effectiveness of mitigating IGSCC of piping and reactor internals using HWC and NMCA is discussed in detail, including the *Guidelines'* relationship to inspection relief programs contained in BWRVIP-62 and BWRVIP-75.

Some of the previous IGSCC concerns in BWRs have largely been resolved by replacing the impacted materials with more IGSCC-resistant materials or by performing simple repairs. However, there is a limit to what can be achieved by replacement and repair. For example, repair/replacement of internals below the core is expensive and could lead to premature shutdown and decommissioning in the worst cases. An aggressive mitigation strategy will reduce the probability of escalating repair costs.

For many BWRs, the best-available initial strategy is likely to be to adopt HWC-M (1.0-2.0 ppm hydrogen in feedwater) to protect components in the lower core region as soon as possible. This provides mitigation to plant components thought to be the most difficult to repair. Plant data should be used to optimize the hydrogen feed rates. For other BWRs, HWC-M may not be economically feasible and the implementation of NMCA will provide the IGSCC mitigation solution.

All utilities not currently using HWC-M or NMCA are recommended to conduct an updated economic analysis. If the analysis indicates that HWC-M or NMCA is cost-beneficial, it is recommended that they implement HWC-M or NMCA to protect components in the lower core and lower plenum region. However, additional fuel technical issues need to be assessed with NMCA implementation. NMCA has several benefits compared to HWC-M such as reduced hydrogen injection rate, operation with NWC dose rates, decreased personnel exposure during operation, elimination of increased localized shielding requirements and increased mitigation of components in the upper shroud annulus. On the other hand, HWC-M offers several benefits compared to NMCA such as no outage time for the "classical" NMCA application, no "crack flanking" concerns and no potential fuel crudding and corrosion issues.

Radiation Field Effects: Section 3. The discussion of the effects of NMCA and zinc injection on radiation fields has been updated with the most recent plant data. The discussion on control of feedwater iron has been strengthened, with the recognition that iron increases fuel crud formation and decreases the efficiency of zinc. The "desired range" recommendations for feedwater iron have been specified as 0.1 – 1.5 ppb for HWC and NMCA plants, and 0.5 – 1.5 ppb for normal water chemistry plants.

The technologies available to mitigate IGSCC via BWR water chemistry control can significantly affect both operating and shutdown dose rates. The injection of hydrogen into the feedwater at levels required for mitigation increases the main steam line radiation level by a factor of 5X and requires either increased shielding or changed operation modes or both. In addition, operation with feedwater hydrogen injection results in increased shutdown dose rates due to increased ^{60}Co uptake into the oxides formed under reducing conditions. Mitigation of the increased shutdown dose rates can be accomplished with feedwater zinc injection.

The NMCA method uses low feedwater hydrogen addition rates and operating dose rates are increased by only 10% or less. To mitigate the increased shutdown dose rates due to increased uptake of ^{60}Co into corrosion films, the reactor water ratio of soluble ^{60}Co to soluble Zn must be kept below 2.0×10^{-5} µCi/ml/ppb. Due to the nature of the restructuring of the corrosion films during initial operation during the first post NMCA cycle the resulting shutdown dose rates can be kept very low if this ratio is established early in the first post-NMCA cycle. For this reason, some plants may need to increase feedwater zinc concentrations. Increased zinc may also be desirable for a period following a chemical decontamination. However, because of fuel performance concerns, it is best to limit the average feedwater zinc concentration value (below 0.6 ppb for HWC and 0.4 ppb for NMCA plants) while establishing and maintaining this ratio. Feedwater iron input is also an important parameter to control shutdown radiation dose rates. A long-term goal of less than 1 ppb input is recommended with a minimum value of either 0.1 ppb or 0.5 ppb. Establishing this goal will make establishing the $^{60}Co(s)$/ Zn(s) ratio much easier when limiting feedwater zinc levels as suggested above.

Flow Accelerated Corrosion (FAC): Section 4. Flow-accelerated corrosion (also called flow-assisted corrosion and, misleadingly, erosion/corrosion) causes wall thinning of carbon steel piping, vessels, and components. The wall thinning is caused by an increased rate of dissolution of the normally protective oxide layer, (e.g., magnetite), that forms on the surface of carbon and low alloy steel when exposed to high velocity water or wet steam. The oxide layer reforms and the process continues. The problem is widespread in all types of conventional and nuclear power plants. Wall thinning rates as high as ~120 mpy (3 mm/year) have been observed. If the thinning is not detected in time, the reduced wall cannot withstand the internal pressure and other applied loads. The result can be either a leak or complete rupture.

The rate of wall loss (wear rate) of a given component is affected by the alloy composition, the pH at operating conditions, the liquid phase dissolved oxygen concentration, fluid bulk velocity, component geometry and upstream influences, fluid temperature and steam quality.

The effect of NMCA on the corrosion behavior of carbon steel in 550°F (288 °C) water containing various amounts of oxygen and hydrogen was examined and the data confirm that there is no adverse effect of NMCA on FAC. At low oxygen concentrations and a reducing environment, noble metal treatment of carbon steel surfaces raised the corrosion potential to values closer to the hydrogen/water reversible potential, suggesting that FAC of wetted carbon steel components will be reduced under these conditions.

Overall, due to the catalytic nature of noble metals, plants that undergo NMCA are able to inject lower amounts of hydrogen while still achieving SCC mitigation of the reactor vessel and internals (wetted regions). Plants with low HWC have higher reactor water oxygen contents when compared to moderate HWC plants. Typical reactor water oxygen levels with low HWC/NMCA plants have often been in the region of 30 to 80 ppb whereas under moderate HWC conditions, the reactor water oxygen is often less than 2 ppb. Consequently, there is less suppression of

radiolysis and a higher oxygen concentration in steam. In those regions of the steam cycle where moderate HWC causes an increase in FAC, there will be less of an increase with NMCA-HWC

Control of Chemistry for Fuel Integrity Concerns. Section 5 discusses water chemistry impacts on fuel integrity, and now includes a discussion of corrosion-related fuel failures. The need for control of feedwater zinc, iron and copper is discussed. Based on fuel integrity issues, quarterly average maxima for feedwater zinc of 0.6 ppb for HWC plants and 0.4 ppb for NMCA plants are recommended. A feedwater copper limit of <0.1 ppb is highly desirable for all plants. Given the industry trend of increasing fuel duty and the possibility of further chemistry modifications for plant system material protection, reducing the feedwater iron to <1.0 ppb should be considered at all plants.

Largely through improvement of cladding nodular corrosion resistance and vigilant utility efforts in maintaining good water purity, no industry-wide events relating to cladding corrosion fuel failure, with the exception of an isolated case, was reported throughout the decade of 1990-2000. However, the industry has experienced rapid changes in fuel designs and the water chemistry environment over the past decade. Higher efficiency fuel designs and operational procedures have been introduced to meet the needs for higher discharge burn-up, longer cycle lengths, and improved cycle economics. Increasing fuel duty can increase rates of deposition of crud and hideout of harmful chemical species if present. Water chemistry conditions that were acceptable in the 1990s may no longer provide adequate margin for maintaining fuel reliability. Thus, the rapid changes in fuel and chemistry have created highly challenging conditions for the industry to maintain the high fuel integrity achieved during the 1990s.

This Section reviews fuel cladding corrosion observations and assess the potential role of water chemistry and possible mitigation measures. The current state of knowledge of the effects of chemistry additives, hydrogen, zinc, NMCA, and impurities, such as Fe, Cu, electro-hydraulic control (EHC) fluid, etc., on fuel crud deposition and Zircaloy cladding corrosion is critically reviewed based on fuel surveillance results, fuel operation experiences, and simulation tests. Finally, recommendations on water chemistry conditions are provided with the aim of mitigating the future occurrence of fuel failures due to accelerated cladding corrosion.

Minimizing tenacious crud formation and preventing intrusion of potentially harmful chemical impurities are two key chemistry considerations to improve fuel operational margin and prevent fuel cladding corrosion-related issues. Each plant must optimize their reactor chemistry programs to maximize fuel performance and minimize the risks to reactor integrity and personnel dose.

BWR Water Chemistry Control: Section 6. Recognizing the increasing urgency of corrective actions with increasing impurity concentrations, the following rationale was used for establishing water chemistry control parameters, recommended operating limits, and recommended monitoring frequencies:

- Ingress of impurities into the RCS should be kept to a practical and achievable minimum.
- The oxidizing power of the reactor water should be maintained below a value at which both laboratory and specific reactor experience demonstrate that sensitized austenitic stainless steels and nickel-based alloys do not exhibit significant rates of IGSCC.

- Action levels should be based on quantitative information about the effects of the chemistry variables on the corrosion behavior of RCS materials, fuel performance and radiation field buildup. In the absence of quantitative data, achievable action level values should be specified.

- Action Levels and responses to exceeding Action Levels can vary with the approach to chemistry control, i.e., normal water chemistry (NWC), hydrogen water chemistry (HWC), or HWC following noble metal chemical application (NMCA).

- Recommended control, diagnostic and confirmatory parameters should be reliably measurable at the levels specified using currently available equipment and procedures.

- Monitoring frequencies should be established with the recognition that utility resources should be devoted to high-priority work.

This section comprises the recommendations for water chemistry control and diagnostic parameters, for start up, operation and shutdown. These now include separate tables for hydrogen water chemistry, HWC/ NMCA and normal water chemistry. The Action Level tables now address the possibility that IGSCC may be reduced with continued operation if the Action Levels are exceeded.

Recommended Goals for Water Chemistry Optimization: Section 7. This is a new section containing recommended goals for water chemistry optimization. These are “good practice” recommendations for targets that plants may use in optimizing water chemistry that balances the conflicting requirements of materials, fuel and radiation control. Significant time and expense may be required to meet these targets; thus efforts to achieve these goals should be considered in the context of the overall strategic plan for the plant.

Data Monitoring and Evaluation: Section 8. This Section discusses recommended chemistry surveillance. Recommendations from the 2000 revision of the *Guidelines* were reviewed. In support of the utilities’ need to reduce O&M costs, recommended surveillance and monitoring frequencies were reduced when such could be done without significant adverse impact on plant chemistry.

Appendix A discusses the effects of impurity transients on crack growth rates. It has been considerably enhanced, including two tables of documented BWR transients that have occurred during operation and shutdown, possible water chemistry responses to transients plus examples of decision trees for evaluating actions to minimize the detrimental effects on IGSCC.

Appendix B covers auxiliary systems.

Appendix C is new. It addresses calculations that may be made to correct the measured conductivity for the presence of ionic species that are benign toward system integrity.

Appendix D is a new appendix covering ultrasonic fuel cleaning.

Appendix E updates the appendix on the BWRVIA model in the 2000 revision.

References for B.10 Section B

[1] BWR Water Chemistry Guidelines, 2004 Revision. EPRI Report 1008192

[2] R.L. Jones, “Mitigating Corrosion Problems in LWRs via Chemistry Changes,” Power Plant Chemistry, November 2004, pp663-669

[3] R.L. Cowan, “Modern BWR Chemistry Operating Strategies,” International Conference on Water Chemistry of Nuclear Reactor Systems, San Francisco, October 2004