B.11 "PWR Primary Water Chemistry Guidelines,"

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Introduction

The fifth revision of the PWR Primary Water Chemistry Guidelines, published in 2003, describes an effective, state-of-the-art program from which a utility can develop an optimized program for their plant. The philosophy embodied in this document has generic applicability, but can be adapted to the particular conditions of the utility and the site. The detailed guidelines presented in Volume 1 on operating chemistry and in Volume 2 on startup and shutdown chemistry comprise a program that should serve as a model for the development of site-specific chemistry plans.

Ensuring continued integrity of RCS materials of construction and fuel cladding and maintaining the industry trend toward reduced radiation fields requires continued optimization of reactor coolant chemistry. Optimization of coolant chemistry to meet site-specific demands becomes increasingly important in light of material corrosion concerns in steam generator and reactor vessel penetrations, the movement toward extended fuel cycles, higher duty cores, increasingly stringent dose rate control, decreased refueling outage duration, and reduced operating costs. This document is the sixth in a series of industry guidelines on PWR primary water chemistry. Like each of the others in the series, it provides a template for development of a plant-specific water chemistry program.

Background

Historically, the guidelines focused on radiation field control while maintaining fuel and materials integrity. Thus a trend of gradual increase in recommended pH levels can be seen in successive revisions. With some plants increasing fuel duty, more attention is now been paid to water chemistry/fuel interactions, particularly crud deposition. Increasing pH is also beneficial in controlling crud buildup. The guidelines have always considered the small effects of chemistry on initiation of stress corrosion cracking of nickel-based alloys. Although chemistry effects are minor, one exception has been zinc injection, where a delay in crack initiation has been observed in laboratory tests. Recent crack growth data have also been considered, but again the influence of chemistry was found to be minor. The latest data shows a potential benefit from increasing hydrogen during operation, and this will be addressed in future editions, as will the possibility of mitigating low temperature crack propagation by adjusting shutdown procedures.

The *Guidelines* were prepared by a committee of experienced industry personnel through an effort sponsored by EPRI. Participation was obtained from chemistry, materials, steam generator, and fuels experts to ensure the Guidelines present chemistry parameters that are optimum for each set of operating and material conditions. Each EPRI-member utility operating a PWR participated in generation or review of these *Guidelines*. Therefore, this document serves as an industry consensus for PWR primary water chemistry control. In essence, it is a report from industry specialists to the utilities documenting an optimized water chemistry program.

Key Points and Technical Issues

The content of the 2003 revision is summarized below, with major changes from the previous revision noted:

Volume 1

Relative to Rev. 4 of these *Guidelines*, the major changes in Volume 1 of this document are as follows:

Management Responsibilities: Section 1. The U.S. nuclear industry established a framework for improving the reliability of steam generators, described in "*NEI 97-06: Steam Generator Program Guidelines"* Section 1 of the PWR Primary Water Chemistry Guidelines specifies which portions of Volume 1 *are* required in a "strategic water chemistry plan" to meet the intent of NEI 97-06. Volume 2 of these *Guidelines* addresses aspects of startup and shutdown chemistry practices which are not believed to impact SG tube integrity. Therefore, utilities need not meet the intent of Volume 2 to be in compliance with the NEI Initiative.

Technical Basis for Coolant Chemistry Control: Section 2 has been updated to include recent field experiences, laboratory test results and related investigations. Some of the key changes in Section 2 include:

- The quantitative discussion of the influence of water chemistry on primary water stress corrosion cracking (PWSCC) was updated to reflect recent data and a revised statistical evaluation of relevant test data. This evaluation indicates that use of the higher lithium levels required for constant elevated pH_T regimes (e.g., pH_T of 7.1 - 7.3 constant vs. earlier pH_T 6.9 constant or modified pH_T 6.9 regimes) results in little or no penalty in the characteristic time to PWSCC, and that any chemistry effect will be much smaller than the influence of material composition, stress or temperature. This conclusion is supported by plant experience where no significant effects of higher pH regimes have been observed at French, Swedish and U.S. plants that are experiencing PWSCC at low levels and have increased pH_T from 6.9 or 7.0 to 7.1 or higher. The discussion regarding the effects of hydrogen on PWSCC was revised to reflect recently published information that shows that the hydrogen concentration associated with the highest crack growth rate varies as a function of temperature.

- A brief discussion was added of recent test results regarding low temperature crack propagation (LTCP) in thick parts made from nickel-base alloys X-750, 82, 52, and 690, and how this cracking mode is affected by hydrogen levels in low temperature water.

- The discussion regarding the use of zinc in the field as an additive to mitigate PWSCC was updated. The discussion regarding use of zinc to reduce shutdown dose rates was updated to reflect the continuing encouraging results from both domestic and foreign plants. Even low levels of zinc added continuously are resulting in significant dose rate reductions in U.S. and German plants over multiple cycles. Approximately 20 PWRs are currently injecting zinc, mainly to control radiation fields, but plants using higher zinc concentrations are starting to see a reduction in PWSCC in steam generator tubing.

- An expanded discussion was included of the benefits of constant high pH regimes with regard to crud management, fuel deposits, and radiation dose rate. This discussion applies to all plants, but is especially relevant to plants with high duty cores where risks of fuel deposits and associated problems such as axial offset anomaly (AOA), or under-deposit clad corrosion failures are a concern.

- The review of the influence of the effects of primary water chemistry on corrosion of fuel cladding and on core performance was updated. The discussion emphasizes the importance of crud to corrosion of cladding, and discusses how increasing core duty increases the potential for crud deposition, cladding corrosion, and occurrence of axial offset anomaly (AOA). The review of fuel issues takes into account substantial industry experience with lithium concentrations up to 3.5 ppm, and use of lithium over 3.5 ppm for short periods of time. The review also reflects increased experience with use of zinc additions to the primary coolant, but indicates that use of zinc still demands successful completion of a field demonstration program for high duty cores. The review updates the evaluation of the effects of high silica on fuel performance, and indicates that increasing amounts of experience with silica levels of up to 3 ppm and even higher have been accumulated with no adverse effects.

Power Operation Chemistry Control Recommendations: Section 3 was revised to provide increased emphasis on the desirability of using a constant elevated pH_T (such as constant pH_T between 7.1 and 7.3) at all plants, but especially those with high duty cores, and to provide guidance with regard to making a transition to a constant elevated pH_T regime. Constant elevated pH_T has been shown to provide benefits in crud management, fuel deposits, AOA, and shutdown dose rates. The guidance also reflects the two potential concerns regarding high pH_T regimes that need to be considered: possible effects of higher lithium (e.g., over 3.5 ppm) on fuel cladding corrosion, and possible effects of higher lithium or pH on PWSCC. With regard to the effects of lithium on fuel, it was agreed to raise the level at which consideration of a fuel vendor review is indicated as being appropriate from 2.2 ppm to 3.5 ppm. Table 3-4, "Reactor Coolant System Power Operation Diagnostic Parameters (Reactor Critical)," was revised to add zinc as a diagnostic parameter. This reflects the Committee decision to recommend that all plants consider the use of zinc for its demonstrated dose reduction benefits.

Methodology for Plant-Specific Optimization: Section 4 was updated to reflect lessons learned from its use since it was first published in Revision 4. This mainly involved revising Table 4-1, “Chemistry Control Program Approaches,” to reflect the latest assessments of the positive and negative impacts of various options.

Appendix A “Calculation of pH_T and Data Evaluation methodology,” was modified to incorporate first order ionic strength corrections to 25°C values of pH and conductivity relevant to the spent fuel pool, and to include a discussion of thermodynamically predicted pressure and temperature effects on pH that are produced by the strong dependence of the ionization product of water on these variables.

Appendix B "Chemistry Control of Supporting Systems," was thoroughly reviewed and many corrections and improvements were incorporated. The changes made included additions to the descriptions of plant experiences, and some minor changes to the chemistry monitoring tables for the volume control tank, boric acid storage tanks, refueling water storage tank, and spent fuel cooling and cleanup system. Sulfate was added as a diagnostic parameter for the reactor water storage tank and for the spent fuel pool water.

Appendix C "Status of Enriched Boric Acid (EBA) Application," was updated to reflect industry experience of the past few years.

Appendix D "AOA and Ultrasonic Fuel Cleaning," that describes EPRI ultrasonic fuel cleaning technology and field experience demonstrating its promising role in ameliorating AOA and reducing dose rates was added.

Appendix E "Oxygen and Hydrogen Behavior in PWR Primary Circuits," was revised to incorporate a few minor improvements.

A new **Appendix F**, "Sampling Considerations for Monitoring RCS Corrosion Products," was added. It provides a description of typical PWR RCS letdown sampling systems and considerations, and includes descriptions of modern, high temperature, RCS hot leg particulate corrosion product sampling systems that can be used to provide improved monitoring of RCS particulates that are derived by re-entrainment of activated core deposits.

A new **Appendix G**, "Reactor Coolant Radionuclides," was added as an aid to chemistry staff and laboratory personnel for dealing with radionuclides and the potential significance of their trends during transient evolutions as well as trends from cycle to cycle.

A new **Appendix H**, "Definition of High Duty Core," was added to provide guidance with regard to the use and meaning of the high duty core index (HDCI) parameter, which is considered when evaluating effects of chemistry on fuel performance in cores with elevated local assembly steaming or core-wide subcooled nucleate boiling, as discussed in Section 2.4. The HDCI was defined and statistically tested against available cores that produced elevated steaming and/or AOA by the Robust Fuel Program specifically for this revision of the *Guidelines*.

Guidance in both Volume 1 and Volume 2 with respect to oxygen control in pressurizers was revised to reflect the interim guidance issued on August 31, 2001 by the Steam Generator Management Program. In addition, the guidance was expanded to cover control of oxygen during shutdowns, as well as during startups as addressed by the interim guidance.

Volume 2

This second volume of the PWR Primary Water Chemistry Guidelines focuses on startup and shutdown chemistry. As noted for the previous revision, the decision to cover startup and shutdown chemistry in a separate volume was made for two main reasons: (1) the increasingly large amount of information regarding shutdown and startup chemistry contained in the Guidelines warrants a separate volume, and (2) locating the startup and shutdown information in a separate volume separates it from the NEI Steam Generator Initiative requirements of Volume 1. This Volume 2 contains no specific requirements (with limited exceptions identified in Tables 4-2 and 4-3) which must be met by utilities to be in compliance with the NEI 97-06 Initiative.
The combined shutdown and startup chemistry coverage in this Volume 2 was updated from that in Revision 4 of the Guidelines to reflect new information and experience gained since issuance of that revision. Volume 2 continues to provide: (1) technical discussions regarding plant experiences with different types of shutdown and startup chemistries; and (2) tables of demonstrated options, together with their perceived benefits and possible negative impacts, for refueling and mid-cycle outages. Section 2 is modified to include the substantially new information since Revision 4 on the nature of fuel deposits and their role in activity transport for plants operating high duty cores. Sections 3 and 4 contain industry guidance for shutdown and startup, respectively, together with accompanying discussion and technical support.

Relative to Revision 4 (March 1999) of these Guidelines, the major changes made to Volume 2 are as follows:

1. Descriptions of the morphology and properties of the newly discovered fuel crud constituents bonaccordite and zirconium oxide were added to Section 2, as well as a discussion of how their largely insoluble nature affects shutdown chemistry strategies.

2. Discussions were added and expanded of methods for monitoring and controlling hydrogen and oxygen concentrations in the pressurizer during shutdowns and startups.

3. Discussion was expanded regarding the use of acid reducing conditions during mid-cycle outages in a manner that might reduce AOA in high duty cores.

4. Plant experience was described that shows strong benefits from using the maximum practical RCS cleanup flow during shutdowns. This experience indicates that modifying system designs to increase the maximum cleanup flow rate can be beneficial.

5. Discussion was expanded of the need and methods to maintain oxidizing conditions in the reactor water through flood-up in order to minimize activity release during that operation.

6. Oxygen control strategies (including hydrogen degassing on shutdown and oxygen removal on startup) appropriate to plants that maintain a two-phase pressurizer are offered that are consistent with material integrity goals for pressurizer materials.

7. A variety of experiences were described regarding use or non-use of reactor coolant pumps during shutdown, including when adding hydrogen peroxide.

8. A discussion was added regarding the benefits of using higher cross-linked resins.

9. Many changes were made to the startup and shutdown tables in Sections 3 and 4. These tables present the various options that are available, and their possible benefits and negative impacts. The changes reflect the experience gained since the last revision, including the topics noted above, and also reflect concerns that the industry must develop methods appropriate to PWR materials, temperature and stress intensities to assess the possibility of low temperature crack propagation (LTCP) in nickel-base alloys.

10. A new Appendix was added that details an example of the decision logic that chemists may find useful when deciding what options are consistent with cycle chemistry goals when faced with unplanned mid-cycle outages whose duration may not be known precisely at the point in time of shutting down the reactor.

References for B.11

[1] "PWR Primary Water Chemistry Guidelines," Revision 5, EPRI Report 1002884, Electric Power Research Institute, 2003.
[2] R.L. Jones, "Mitigating Corrosion Problems in LWRs via Chemistry Changes," Power Plant Chemistry, pp 663-669, November 2004.
[3] K. Fruzzetti, "A Review of EPRI PWR Water Chemistry Guidelines," International Conference on Water Chemistry of Nuclear Reactor Systems, San Francisco, October 2004.