NUCLEAR ENERGY INSTITUTE

Alex Marion
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October 10, 2003

Dr. Brian W. Sheron
Associate Director for Project Licensing and Technical Analysis
Office of Nuclear Reactor Regulation
U. S. Nuclear Regulatory Commission
Mail Stop O5-E7
Washington, DC 20555

SUBJECT: Industry Steam Generator Management Project -- New Guidance

PROJECT NUMBER: 689

Dear Dr. Sheron:

The Steam Generator Management Project (SGMP) has issued revision 5 to its Pressurized Water Reactor Primary Water Chemistry Guidelines. Copies of this document are enclosed for your information. Your endorsement of this material is not requested.

The guidelines in Enclosure 1 contain proprietary information that is supported by the signed affidavit in Enclosure 2. The affidavit sets forth the basis on which the information may be withheld from public disclosure by the Commission and addresses with specificity the consideration listed in paragraph (b)(4) of Section 2.790 of the Commission's regulations. Accordingly, we respectfully request that the information, which is proprietary to EPRI, be withheld from public disclosure in accordance with 10 CFR 2.790. Copies of the non-proprietary version of the Primary Water Chemistry Guidelines are included in Enclosure 3.

If there are any questions on these matters, please contact me (202-739-8080 or email am@nei.org) or Jim Riley (202-739-8137 or jhr@nei.org).

Sincerely,

Alex Marion

Alex Marion

Enclosures

c: Ms. Louise Lund, NRC (w/o enclosure)
Mr. Emmett Murphy, NRC (w/o enclosure)
Mr. Ken Karwoski, NRC (w/o enclosure)
Mr. Brian Benney, NRC (w/ enclosure)

Enclosure 2

PWR Primary Water Chemistry Guidelines
Revision 5

Proprietary Affidavit

E L E C T R I F Y   T H E   W O R L D

EPRI

October 6, 2003

Document Control Clerk
U.S. Nuclear Regulatory Commission
OWN 11555 Rockville Pike
Washington DC, 20555

Subject: "PWR Primary Water Chemistry Guidelines: Volumes 1 and 2, Revision 5" FINAL EPRI Report 1002884, September 2003.

Gentlemen:

This is a request under 10CFR2.790(a)(4) that the NRC withhold from public disclosure the information identified in the enclosed affidavit consisting of EPRI owned Proprietary Information identified above (the "Report"). Copies of the Report and the affidavit in support of this request are enclosed.

EPRI desires to disclose the Report in confidence to the NRC as a means of exchanging information in support of generic regulatory improvements relating to NEI 97-06, "Steam Generator Program Guidelines." Further, EPRI welcomes any discussion with the NRC regarding the Report that the NRC desires to conduct.

The Report is for the NRC's internal use and may be used only for the purposes for which it is disclosed by EPRI. The report should not be otherwise used or disclosed to any person outside the NRC without prior written permission from EPRI.

If you have any questions about the legal aspects of this request for withholding, please do not hesitate to contact me at (650) 855-2340 Questions on the contents of the Report should be directed to James M. Benson of EPRI at (650) 855-2146.

Sincerely,

Warren J. Bilanin

Warren J. Bilanin
Director, Nuclear Power Sector

Enclosures (1)

Cc: Licensing
Jim Riley / NEI

AFFIDAVIT

RE: "PWR Primary Water Chemistry Guidelines: Volumes 1 and 2, Revision 5" FINAL EPRI Report 1002884, September 2003.

I, WARREN BILANIN, being duly sworn, depose and state as follows:

I am a Director at the Electric Power Research Institute ("EPRI") and I have been specifically delegated responsibility for the report listed above that is sought under this affidavit to be withheld (the "Report") and authorized to apply for their withholding on behalf of EPRI. This affidavit is submitted to the Nuclear Regulatory Commission ("NRC") pursuant to 10 CFR 2.790 (a)(4) based on the fact that the Report consists of trade secrets of EPRI and that the NRC will receive the Report from EPRI under privilege and in confidence.

The basis for withholding such Report from the public is set forth below:

(i) The Report has been held in confidence by EPRI, its owner. All those accepting copies of the Report must agree to preserve the confidentiality of the Report.

(ii) The Report is a type customarily held in confidence by EPRI and there is a rational basis therefor. The Report is a type, which EPRI considers as a trade secret(s) and is held in confidence by EPRI because to disclose it would prevent EPRI from licensing the Report at fees, which would allow EPRI to recover its investment. If consultants and/or other businesses providing services in the electric/nuclear power industry were able to publicly obtain the Report, they would be able to use it commercially for profit and avoid spending the large amount of money that EPRI was required to spend in preparation of the Report. The rational basis that EPRI has for classifying this/these Report(s) as a trade secrets is justified by the Uniform Trade Secrets Act, which California adopted in 1984 and which has been adopted by over twenty states. The Uniform Trade Secrets Act defines a "trade secret" as follows:

> "Trade secret" means information, including a formula, pattern, compilation, program, device, method, technique, or process, that:
>
> (1) Derives independent economic value, actual or potential, from not being generally known to the public or to other persons who can obtain economic value from its disclosure or use; and
>
> (2) Is the subject of efforts that are reasonable under the circumstances to maintain its secrecy.

(iii) The Report will be transmitted to the NRC in confidence.

(iv) The Report is not available in public sources. EPRI developed the Report only after making a determination that the Report was not available from public sources. It required a large expenditure of dollars for EPRI to develop the Report. In addition, EPRI was required to use a large amount of time of EPRI employees. The money spent, plus the value of EPRI's staff time in preparing the Report, show that the Report is highly valuable to EPRI. Finally, the Report was developed only after a long period of effort of at least several months.

(v) A public disclosure of the Report would be highly likely to cause substantial harm to EPRI's competitive position and the ability of EPRI to license the Report both domestically and internationally. The Report can only be acquired and/or duplicated by others using an equivalent investment of time and effort.

I have read the foregoing and the matters stated therein are true and correct to the best of my knowledge, information and belief. I make this affidavit under penalty of perjury under the laws of the United States of America and under the laws of the State of California.

Executed at 3412 Hillview Avenue, Palo Alto, being the premises and place of business of the Electric Power Research Institute:

October 6, 2003

Warren J. Bilanin

Subscribed and sworn before me this day: October 6, 2003

Nicole Alexandra Edraos, Notary Republic 10/6/03

October 6,2003

NICHOLE ALEXANDRA EDRAOS
Comm. # 1295461
NOTARY PUBLIC CALIFORNIA
expires Feb. 26, 2005

Enclosure 3

PWR Primary Water Chemistry Guidelines
Revision 5

Non - Proprietary Version

Pressurized Water Reactor Primary Water Chemistry Guidelines

Volume 1, Revision 5

1002884

Final Report, September 2003

NON-PROPRIETARY VERSION

EPRI Project Managers
P. Frattini
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Pressurized Water Reactor Primary Water Chemistry Guidelines

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DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

ORGANIZATION(S) THAT PREPARED THIS DOCUMENT

PWR Primary Water Chemistry Guidelines Committee

ORDERING INFORMATION

Requests for copies of this report should be directed to EPRI Orders and Conferences, 1355 Willow Way, Suite 278, Concord, CA 94520, (800) 313-3774, press 2 or internally x5379, (925) 609-9169, (925) 609-1310 (fax).

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This report describes research sponsored by EPRI.

The report is a corporate document that should be cited in the literature in the following manner:

Pressurized Water Reactor Primary Water Chemistry Guidelines: Volume 1, Revision 5, EPRI, Palo Alto, CA: 2003. 1002884.

REPORT SUMMARY

State-of-the art water chemistry programs help ensure the continued integrity of reactor coolant system (RCS) materials of construction and fuel cladding, ensure satisfactory core performance, and support the industry trend toward reduced radiation fields. These revised *PWR Primary Water Chemistry Guidelines*, prepared by a committee of industry experts, reflect the recent field and laboratory data on primary coolant system corrosion and performance issues. Volume 1 covers operating chemistry and Volume 2 covers startup and shutdown chemistry.

Background

EPRI periodically updates the PWR water chemistry guidelines as new information becomes available and as required by NEI 97-06, Steam Generator Program Guidelines. The last revision of these Guidelines identified an optimum primary water chemistry program based on then-current understanding of research and field information. This revision provides further details with regard to primary water stress corrosion cracking (PWSCC), fuel integrity, and shutdown dose rates.

Objective

To update the *PWR Primary Water Chemistry Guidelines, Revision 4*, published in 1999.

Approach

A committee of industry experts, including utility specialists, nuclear steam supply system and fuel vendor representatives, Institute of Nuclear Power Operations representatives, consultants, and EPRI staff, collaborated in reviewing the available data on primary water chemistry, reactor water coolant system materials issues, fuel integrity and performance issues, and radiation dose rate issues. From these data, the committee generated water chemistry guidelines that all PWR nuclear plants should adopt. Recognizing that each nuclear plant owner has a unique set of design, operating, and corporate concerns, the guidelines committee developed a methodology for plant-specific operation.

Results

Revision 5 of the *PWR Primary Water Chemistry Guidelines*, which provides recommendations for PWR primary systems of all manufacture and design, includes the following updates:

The Guidelines continue to emphasize plant-specific optimization of water chemistry to address individual plant circumstances. The committee revised guidance with regard to optimization to reflect industry experience gained since the publication of Revision 4. This revision continues to distinguish between prescriptive requirements and non-prescriptive guidance.

The revised Sections 2 and 3 of Volume 1 address the latest information on PWSCC of RCS materials, fuel cladding integrity and core performance, and radiation field control. The guidelines emphasize optimization of pH control programs with regard to maintaining system integrity, minimizing the potential for axial offset anomaly and excessive fuel deposits, use of zinc additions to minimize shutdown dose rates and mitigate PWSCC concerns, and ensuring that pH programs do not have adverse impacts on PWSCC or fuel cladding integrity.

The committee reviewed and revised shutdown and startup chemistry coverage in Volume 2 to reflect industry experience gained in this area since issuance of Revision 4. In particular, the technical basis for corrosion product transport and activity transport control were updated with the significant results of studies of fuel deposits from cores with significant local assembly steaming or core-wide high duty commensurate with axial offset anomaly.

The committee also updated or added several appendices to Volumes 1 and 2. These include new sections on RCS sampling, ultrasonic fuel cleaning technology, radiochemistry, definition of a high duty core index, and mid-cycle shutdown/startup decision logic.

EPRI Perspective

This fifth revision of the *PWR Primary Water Chemistry Guidelines*, endorsed by the utility executives of the EPRI Steam Generator Management Project, represents another step in the continuing use of proactive chemistry programs to limit or control degradation of steam generator tubes and other structural parts. This revision documents the increased consideration of state-of-the art water chemistry programs to help ensure the continued integrity of reactor coolant system (RCS) materials of construction and fuel cladding, ensure satisfactory core performance, and support the industry trend toward reduced radiation fields. These revised *PWR Primary Water Chemistry Guidelines* reflect the recent field and laboratory data on primary coolant system corrosion and performance issues, which PWR operators can use to update their primary water chemistry programs.

Keywords

PWRs
Water chemistry
Primary water stress corrosion cracking
Guidelines
Reactor coolant system

ABSTRACT

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 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.

EPRI FOREWORD

Chemistry optimization of pressurized water reactor (PWR) primary systems in recent times has been complicated by the demands of longer fuel cycles (i.e., higher initial boron concentrations), increased fuel duty (more subcooled boiling) and material/fuel corrosion concerns. Current utility concerns focus on minimizing costs without sacrificing materials integrity or safety. These *Guidelines* provide a template for a responsive chemistry program for PWR primary systems and the technical bases/supporting information for the program. It is the fifth revision of the *Guidelines* and considers the most recent operating experience and laboratory data. The *Guidelines* will be of interest to plant chemists, plant managers, chemical engineers, and engineering managers within utilities owning PWRs.

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.

Special acknowledgment is given to the following organizations for submitting first-hand experience through committee participation:

- Ameren UE
- American Electric Power
- AmerGen Energy
- Arizona Public Service
- Atomic Energy of Canada, Ltd.
- Babcock & Wilcox
- British Energy
- Constellation Energy
- Dominion Resources
- Duke Energy
- Electricité de France
- Entergy
- Exelon
- First Energy

- Florida Power & Light
- Framatome ANP
- INPO
- Laborelec (Belgium)
- NPP Krsko
- Nuclear Management Corporation (NMC)
- Omaha Public Power District
- Ontario Power Generation
- Pacific Gas & Electric Company
- Progress Energy
- Public Service Electric & Gas
- Ringhals (Sweden)
- Rochester Gas and Electric
- South Carolina Electric & Gas
- Southern California Edison
- Southern Nuclear Operating Co.
- South Texas Project Nuclear Operating Company
- Tennessee Valley Authority
- TXU Energy
- Westinghouse Electric
- Wolf Creek Nuclear Operating Corp.

This committee was significantly assisted in its work by J. Gorman of Dominion Engineering; G. Brobst of GEBCO Engineering; J. Bates of iSagacity; K. Garbett, consultant; H. Sims of AEA Technology; R. Litman, consultant; S. Sawochka of NWT Corporation. In addition, the Committee would like to acknowledge the support and input of fuel specialists from EPRI-member utilities.

This document is intended to be a set of guidelines which describe 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 Sections 3 and 4 of this volume and of Volume 2 on startup and shutdown chemistry comprise a program that should serve as a model for the development of site-specific chemistry plans.

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

Paul L. Frattini, Chairman
PWR Primary Water Chemistry Guidelines Revision Committee
EPRI Nuclear Power Group
March 2003

ACRONYMS

AOA	Axial offset anomaly
BAST	Boric acid storage tank
BOC	Beginning of cycle
BRS	Boron recovery system.
BTRS	Boron thermal regeneration system
BWR	Boiling water reactor
CVCS	Chemical and volume control system. The term makeup system (MU) is used at some plants for the same system.
DEI	Dose equivalent iodine-131
DF	Decontamination factor
DHC	Debye-Huckel limiting slope
DRP	Discrete radioactive particle
$\bar{E}$	E-bar, average disintegration energy
EBA	Enriched boric acid
ECP	Electrochemical potential
EPRI	Electric Power Research Institute
EOC	End of cycle
HDCI	High duty core index
HUT	Holdup tank.
IGSCC	Intergranular stress corrosion cracking
INPO	Institute of Nuclear Power Operations
LTCP	Low temperature crack propagation
LTOP	Low temperature overpressure
NEI	Nuclear Energy Institute
NSSS	Nuclear steam system supplier
NTU	Nephelometric turbidity units
PRT	Pressurized relief tank
PWR	Pressurized water reactor
PWSCC	Primary water stress corrosion cracking
RCP	Reactor coolant pump
RCS	Reactor coolant system. For purposes of these *Guidelines*, the RCS includes the pressurizer.
RFO	Refueling outage
RHR	Residual heat removal system. The terms decay heat (DH) system and shutdown cooling (SDC) system are used at some plants for the same system.
RWST	Refueling water storage tank. The term borated water storage tank (BWST) is used at some plants for the same tank.
SCC	Stress corrosion cracking

SFP	Spent fuel pool system. The term spent fuel cooling (SFC) system is used at some plants for the same system.
STP	Standard temperature and pressure
TOC	Total organic carbon
TSS	Total suspended solids
VCT	Volume control tank. The term makeup tank (MUT) is used at some plants for the same tank.

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1.1 Introduction

The purpose of this document is to provide recommendations on primary chemistry control to continue to maximize the long-term availability of PWR plants. The nuclear power industry has compiled an excellent performance history in maintaining PWR primary system component integrity. In addition, primary water chemistry control can and has been effectively used to control radiation field buildup on ex-core surfaces.

It is important that all levels of utility management understand that operation outside the recommended chemistry limits can increase the probability of reduced unit availability. Such losses may be limited by controlling the magnitude and frequency of abnormal reactor coolant system (RCS) chemistry conditions. A principal goal has been to minimize corrosion of RCS components. Effectively implementing these *Guidelines* will support this goal, thereby maximizing the cumulative availability of the unit. In addition, the US nuclear power industry established a framework for increasing the reliability of steam generators by adopting NEI 97-06, *Steam Generator Program Guidelines*, and has re-affirmed this commitment by adopting Revision 1 of NEI-97-06. This initiative adopted EPRI's Water Chemistry Guidelines, including this document, as the basis for an optimized chemistry program. Specifically, the initiative required that US utilities meet the intent of the *EPRI PWR Primary Water Chemistry Guidelines*.

1.2 Generic Management Considerations

1.3 Communication and Training

1.4 Outage Planning and Coordination

2
TECHNICAL BASIS FOR THE NEED TO CONTROL THE COOLANT CHEMISTRY IN PWRS

2.1 Introduction

The purposes of PWR primary coolant chemistry guidelines are:

- To assure primary system pressure boundary integrity,
- To assure fuel-cladding integrity and achievement of design fuel performance, and
- To minimize out-of-core radiation fields.

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3.1 Introduction

In this section, chemistry control recommendations intended to serve as industry-consensus guidelines are presented. These recommendations are based on current technical understanding and industry experience. For less restrictive site-specific modifications to control parameters in these *Guidelines*, plant chemistry personnel must produce a written technical justification that addresses the relevant regulatory, fuel warranty, and safety implications of such modifications (see Section 4).

3.2 Reactor Coolant System (RCS) pH Optimization

3.2.1 Operating Recommendations

3.2.2 Transition to Constant pH Operation

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[illegible]

3.7 Control and Diagnostic Parameters, Frequencies, and Limits for Startup Chemistry

4 METHODOLOGY FOR PLANT-SPECIFIC OPTIMIZATION

4.1 Introduction

The purpose of this section is to provide a framework for plant chemistry personnel to develop an optimized primary chemistry program considering plant design, materials of construction, fuel design and cycle length, corrosion degradation history, regulatory commitments, fuel vendor warranty requirements, etc.

The recommended approach recognizes that nuclear power plants must consider a variety of issues in developing a primary water chemistry program and that these issues must be dealt with on a plant specific basis.

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To provide a uniform basis for establishing a pH_T control program and for comparing observations at different plants, it is mandatory that industry personnel employ similar expressions for pertinent chemical equilibria, e.g., the ionization of boric acid. The recommended relations are given below.

2.0 Low Temperature pH, Boron, Lithium Calculations and Data

3.0 Data Consistency (pH at 25°C/Conductivity at 25°C/Boron/Lithium)

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5.0 Temperature and Pressure Dependence of pH

6.0 Monitoring for Fuel Reliability

7.0 Primary-to-Secondary Leak Monitoring

8.0 References

B
CHEMISTRY CONTROL OF SUPPORTING SYSTEMS

1.0 Introduction

Chemistry control practices in systems that interface with the reactor coolant system are discussed below. Specifically, selected system designs, the rationales for chemistry control, possible impacts on reactor coolant chemistry and industry experiences where impacts on RCS chemistry have been observed are discussed. Suggestions are provided on chemistry and radioactivity parameters to be monitored and the frequency of monitoring.

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6.3.3 Silica Control

6.3.4 Chloride / Fluoride Contamination Due to Freon Intrusion

7.0 Spent Fuel Pool Cooling and Cleanup System

7.1 System Description

Normal makeup for the spent fuel pool comes from the RWSTs, with alternate makeup paths from the Boron Recycle System holdup tanks via the transfer canal, or from the demineralized water system. An emergency source of makeup can come from the condensate storage tanks or the service water system.

7.2 Chemistry Controls and Technical Basis

7.3 Industry Experience

7.3.1 Failure of Bundle Top Nozzles

7.3.2 Silica Control

8.0 References

C
STATUS OF ENRICHED BORIC ACID (EBA) APPLICATION

1.0 Introduction

Boric acid is used in primary coolant of a PWR as a soluble reactivity control agent. Dissolved boric acid is referred to as a soluble poison or chemical shim because the ^{10}B isotope has a high cross section for absorbing thermal neutrons. However, natural boron contains only 20 atom percent of the ^{10}B isotope. The remaining 80% is ^{11}B, which has a much smaller cross section for thermal neutron absorption. Enriching natural boric acid with ^{10}B can reduce the concentration of boric acid in the coolant while retaining the required reactivity control.

2.0 Summary of EPRI Studies

3.0 Plant Demonstrations of EBA

4.0 References

D
AOA AND ULTRASONIC FUEL CLEANING

1.0 Background

The evolving economics of electric generation requires PWRs to operate with higher fuel duty and longer cycles. Sub-cooled nucleate boiling in the upper fuel spans is a consequence for such aggressively driven cores. Thermodynamic and hydraulic factors favor deposition of corrosion products on the boiling surfaces of the fuel, resulting in axially non-uniform deposition on high-duty fuel. Axially variable distribution of boron compounds in these fuel deposits is an important cause of axial offset anomaly (AOA).

2.0 Ultrasonic Fuel Cleaning Technology

3.0 System Description

4.0 Fuel Cleaning Efficacy

5.0 Full-Reload Cleaning Results

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1.0 Summary

Oxygen and hydrogen behavior in a PWR primary circuit are linked by the radiolysis reactions occurring in the core to the extent that they cannot normally co-exist in the coolant, other than upstream of the core. In normal operation and during shutdown the important aspects are – (1) what is the minimum hydrogen level to suppress radiolysis in the water phase in the core, (2) will sub-cooled nucleate boiling on fuel assemblies in the core deplete the hydrogen in the water phase below this minimum hydrogen concentration and (3) what is the effect of oxygen ingress into the RCS.

The concentrations of oxygen, hydrogen, hydrogen peroxide and other species in a PWR primary circuit are controlled by approximately 50 radiolytic and thermal reactions, all of which occur simultaneously as the coolant circulates around the circuit. The rate constants of these reactions are known over the full operating temperature range of the primary circuit and the behavior can be modeled with reasonable confidence. This appendix describes the overall behavior and is based on (1) and (2), which model oxygen/hydrogen concentrations in a typical Westinghouse 4-loop PWR.

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Plants with high fluid temperatures and high surface heat flux at the fuel clad have a portion of the total heat transfer to the coolant occur by sub-cooled nucleate boiling (SNB). Although favorable for thermal efficiency, the combination of high temperature and SNB leads to more severe duty on the fuel, and surface boiling is known to enhance the formation of corrosion product deposits (crud) on the cladding surface.

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Pressurized Water Reactor Primary Water Chemistry Guidelines

Volume 2, Revision 5

1002884

Final Report, September 2003

NON-PROPRIETARY VERSION

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REPORT SUMMARY

State-of-the art water chemistry programs help ensure the continued integrity of reactor coolant system (RCS) materials of construction and fuel cladding, ensure satisfactory core performance, and support the industry trend toward reduced radiation fields. These revised *PWR Primary Water Chemistry Guidelines*, prepared by a committee of industry experts, reflect the recent field and laboratory data on primary coolant system corrosion and performance issues. Volume 1 covers operating chemistry and Volume 2 covers startup and shutdown chemistry.

Background

EPRI periodically updates the PWR water chemistry guidelines as new information becomes available and as required by NEI 97-06, Steam Generator Program Guidelines. The last revision of these Guidelines identified an optimum primary water chemistry program based on then-current understanding of research and field information. This revision provides further details with regard to primary water stress corrosion cracking (PWSCC), fuel integrity, and shutdown dose rates.

Objective

To update the *PWR Primary Water Chemistry Guidelines, Revision 4*, published in 1999.

Approach

A committee of industry experts, including utility specialists, nuclear steam supply system and fuel vendor representatives, Institute of Nuclear Power Operations representatives, consultants, and EPRI staff, collaborated in reviewing the available data on primary water chemistry, reactor water coolant system materials issues, fuel integrity and performance issues, and radiation dose rate issues. From these data, the committee generated water chemistry guidelines that all PWR nuclear plants should adopt. Recognizing that each nuclear plant owner has a unique set of design, operating, and corporate concerns, the guidelines committee developed a methodology for plant-specific operation.

Results

Revision 5 of the *PWR Primary Water Chemistry Guidelines*, which provides recommendations for PWR primary systems of all manufacture and design, includes the following updates:

The Guidelines continue to emphasize plant-specific optimization of water chemistry to address individual plant circumstances. The committee revised guidance with regard to optimization to reflect industry experience gained since the publication of Revision 4. This revision continues to distinguish between prescriptive requirements and non-prescriptive guidance.

The revised Sections 2 and 3 of Volume 1 address the latest information on PWSCC of RCS materials, fuel cladding integrity and core performance, and radiation field control. The guidelines emphasize optimization of pH control programs with regard to maintaining system integrity, minimizing the potential for axial offset anomaly and excessive fuel deposits, use of zinc additions to minimize shutdown dose rates and mitigate PWSCC concerns, and ensuring that pH programs do not have adverse impacts on PWSCC or fuel cladding integrity.

The committee reviewed and revised shutdown and startup chemistry coverage in Volume 2 to reflect industry experience gained in this area since issuance of Revision 4. In particular, the technical basis for corrosion product transport and activity transport control were updated with the significant results of studies of fuel deposits from cores with significant local assembly steaming or core-wide high duty commensurate with axial offset anomaly.

The committee also updated or added several appendices to Volumes 1 and 2. These include new sections on RCS sampling, ultrasonic fuel cleaning technology, radiochemistry, definition of a high duty core index, and mid-cycle shutdown/startup decision logic.

EPRI Perspective

This fifth revision of the *PWR Primary Water Chemistry Guidelines*, endorsed by the utility executives of the EPRI Steam Generator Management Project, represents another step in the continuing use of proactive chemistry programs to limit or control degradation of steam generator tubes and other structural parts. This revision documents the increased consideration of state-of-the art water chemistry programs to help ensure the continued integrity of reactor coolant system (RCS) materials of construction and fuel cladding, ensure satisfactory core performance, and support the industry trend toward reduced radiation fields. These revised *PWR Primary Water Chemistry Guidelines* reflect the recent field and laboratory data on primary coolant system corrosion and performance issues, which PWR operators can use to update their primary water chemistry programs.

Keywords

PWRs
Water chemistry
Primary water stress corrosion cracking
Guidelines
Reactor coolant system

ABSTRACT

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 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.

Volume 2 of the PWR Primary Water Chemistry Guidelines covers startup and shutdown chemistry. In an era of ever shortening refueling outages, a primary goal of shutdown chemistry becomes minimizing the time from breaker trip to reactor vessel head lift while maintaining appropriate cautions to ensure safety. Shutdown chemistry evolutions can often become critical path depending on their relative success at reaching corrosion product transport and activity transport goals. Plant degassing procedures, forced oxidation results, and pressurizer oxygen control are but three important issues impacting on those goals. In an analogous way, the startup chemistry plan should strive to achieve power ascension in a minimum of time while still ensuring safety as well as meeting corrosion product transport goals that might impact core performance in the new cycle.

EPRI FOREWORD

Chemistry optimization of pressurized water reactor (PWR) primary systems in recent times has been complicated by the demands of longer fuel cycles (i.e., higher initial boron concentrations), increased fuel duty (more subcooled boiling) and material/fuel corrosion concerns. Current utility concerns focus on minimizing costs without sacrificing materials integrity or safety. These Guidelines provide a template for a responsive chemistry program for PWR primary systems and the technical bases/supporting information for the program. It is the fifth revision of the Guidelines and considers the most recent operating experience and laboratory data. The Guidelines will be of interest to plant chemists, plant managers, chemical engineers, and engineering managers within utilities owning PWRs.

This is the second consecutive issue in which a 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.

Volume 2 was 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. 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 startup and shutdown chemistry control. This document is intended to be a set of guidelines which describes an effective, state-of-the-art program from which a utility can develop an optimized water chemistry plan 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 Sections 3 and 4 and Volume 2 comprise a program that should serve as a model for the development of site-specific chemistry programs

Special acknowledgment is given to the following organizations for submitting first-hand experience through committee participation:

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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.

Paul L. Frattini, Chairman
PWR Primary Water Chemistry Guidelines Revision Committee
EPRI Nuclear Power Group
March 2003

ACRONYMS

AOA	Axial offset anomaly
BAST	Boric acid storage tank
BOC	Beginning of cycle
BRS	Boron recovery system.
BTRS	Boron thermal regeneration system
BWR	Boiling water reactor
CVCS	Chemical and volume control system. The term makeup system (MU) is used at some plants for the same system.
DEI	Dose equivalent iodine-131
DF	Decontamination factor
DHC	Debye-Huckel limiting slope
DRP	Discrete radioactive particle
$\bar{E}$	E-bar, Average disintegration energy
EBA	Enriched boric acid
ECP	Electrochemical potential
EPRI	Electric Power Research Institute
EOC	End of cycle
HDCI	High duty core index
HUT	Holdup tank.
IGSCC	Intergranular stress corrosion cracking
INPO	Institute of Nuclear Power Operations
LTCP	Low temperature crack propagation
LTOP	Low temperature overpressure
NEI	Nuclear Energy Institute
NSSS	Nuclear steam system supplier
NTU	Nephelometric turbidity units
PRT	Pressurized relief tank
PWR	Pressurized water reactor
PWSCC	Primary water stress corrosion cracking
RCP	Reactor coolant pump
RCS	Reactor coolant system. For purposes of these *Guidelines*, the RCS includes the pressurizer.
RFO	Refueling outage
RHR	Residual heat removal system. The terms decay heat (DH) system and shutdown cooling (SDC) system are used at some plants for the same system.
RWST	Refueling water storage tank. The term borated water storage tank (BWST) is used at some plants for the same tank.

SCC	Stress corrosion cracking
SFP	Spent fuel pool system. The term spent fuel cooling (SFC) system is used at some plants for the same system.
STP	Standard temperature and pressure
TOC	Total organic carbon
TSS	Total suspended solids
VCT	Volume control tank. The term makeup tank (MUT) is used at some plants for the same tank.

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This volume of the *PWR Primary Water Chemistry Guidelines* describes the technical basis and specific recommendations for chemistry control of reactor coolant during shutdown and startup. Industry experience continues to indicate that appropriate control of reactor coolant chemistry during plant shutdowns and startups can help control or reduce localized high radiation areas, personnel exposures, and refueling water turbidity problems.

2 TECHNICAL BASIS FOR RCS CHEMISTRY CONTROL DURING HEATUP AND COOLDOWN

2.1 Corrosion Product Behavior in the RCS

2.1.1 General Considerations

Metallic materials exposed to water in the RCS owe their corrosion resistance to a protective layer of chemically stable metal oxide that is formed in the operating environment. Although corrosion rates are very low for Alloys 600, 690, and 800 and stainless steel, which make up the greatest part of system surface area, metal oxidation products are released from such surfaces and are transported throughout the system.

The process by which corrosion and activation products are transported within the RCS involves a complex set of interacting chemical and physical mechanisms that continues to be studied.

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2.8 Mid-cycle Outages

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PRINCIPLES OF CHEMISTRY CONTROL DURING SHUTDOWN

3.1 Shutdown Chemistry Controls

3.1.1 General Principles

Three global shutdown chemistry strategies have been used successfully prior to peroxide treatment:

- High temperature acid reducing conditions
- Low temperature acid reducing conditions
- No acid reducing conditions

3.1.2 Shutdown Options Based on Recent Experience Requiring Plant-Specific Technical Justification

3.1.3 Evaluation of Shutdown Chemistry Data

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PRINCIPLES OF CHEMISTRY CONTROL DURING STARTUP

4.1 Post Refueling Startup and Mid-Cycle Chemistry Management Issues

Strategic decisions such as the method of filling and venting the reactor coolant system, the methods of oxygen control, the impacts of placing RCPs in operation, the timing of lithium additions and hydrogen controls should be developed for each plant as part of the chemistry optimization program.

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The chemistry options for shutdown in midcycle outages are discussed in Sections 2 and 3 of this volume.

References

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