

Pressurized Water Reactor Primary Water Chemistry Guidelines

Volume 1, Revision 6

1014986

Final Report, December 2007

NON-PROPRIETARY

EPRI Project Manager
K. Fruzzetti

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This report describes research sponsored by EPRI.

This report describes research sponsored by the Electric Power Research Institute (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. EPRI, Palo Alto, CA: 2007. 1015018.

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 *Pressurized Water Reactor 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 in a pressurized water reactor (PWR).

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) and NEI 03-08 (Guideline for the Management of Materials Issues). The last revision of the PWR water chemistry 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 *Pressurized Water Reactor Primary Water Chemistry Guidelines, Revision 5*, published in 2003.

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 has retained a method for plant-specific optimization.

Results

Revision 6 of the *Pressurized Water Reactor Primary Water Chemistry Guidelines*—which provides guidance 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 5. This revision incorporates the terminology of NEI 03-08 and NEI 97-06 to distinguish between guidance elements that are “mandatory”, “shall”, and “recommended”. Chapter 5 of Volume 1 has been added to call attention to the elements within these guidelines that fall into these three classifications. The committee considers Volume 2 to be for information only and to be outside the framework of NEI 03-08 and NEI 97-06.

The revised Chapters 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. Both volumes of 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, adding zinc to minimize shutdown dose rates and mitigate PWSCC concerns, and ensuring that pH programs do not adversely impact 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 5. In particular, the discussion regarding removal of corrosion products during shutdown maneuvers was updated to reflect recent laboratory testing, reevaluation of fuel scraping deposit analyses, chemical thermodynamic considerations, and plant experience suggesting that reductive decomposition of nickel ferrite is not a major factor in shutdown chemistry.

The committee also updated the appendices to Volumes 1 and 2.

EPRI Perspective

This sixth revision of the *Pressurized Water Reactor Primary Water Chemistry Guidelines*, endorsed by the utility executives of the EPRI PWR Materials Management Program (PMMP), represents another step in the continuing use of proactive chemistry programs to limit or control degradation of steam generator tubes, fuel cladding, and other structural parts. This revision documents the increased consideration of state-of-the art water chemistry programs, taking into account 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

Fuel

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 seventh 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 (typically requiring 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 sixth 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
- AREVA NP Inc.
- Arizona Public Service
- British Energy
- CANDU Owner's Group
- Constellation Energy
- Dominion Resources
- Duke Energy
- Electricité de France (EDF)
- Entergy
- Exelon
- First Energy
- Florida Power & Light

-
- INPO
 - KEPCO
 - Laborelec (Belgium)
 - Nuclear Management Company (NMC)
 - Omaha Public Power District
 - Pacific Gas & Electric Company
 - Progress Energy
 - Public Service Electric & Gas
 - Ringhals (Sweden)
 - South Carolina Electric & Gas
 - Southern California Edison
 - Southern Nuclear Operating Co.
 - South Texas Project Nuclear Operating Company
 - Tennessee Valley Authority (TVA)
 - TXU Energy
 - Westinghouse Electric
 - Wolf Creek Nuclear Operating Corp.

This committee was significantly assisted in its work by C. Marks and J. Gorman of Dominion Engineering, Inc. and 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 guidance presented in Chapters 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. 5 of these *Guidelines*, the major changes in Volume 1 of this document are as follows:

Keith Fruzzetti, Chairman
PWR Primary Water Chemistry Guidelines Revision 6 Committee
EPRI Nuclear Power Group
December 2007

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
CT	Compact Tension
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
EFPY	Effective Full Power Years
EPRI	Electric Power Research Institute
EOC	End of cycle
EZ	Expansion Zone
HDCI	High duty core index
HUT	Holdup tank.
IFBA	Integral Fuel Burnable Absorbers
IGSCC	Intergranular stress corrosion cracking
INPO	Institute of Nuclear Power Operations
LTCP	Low temperature crack propagation
LTOP	Low temperature overpressure
MUT	Makeup Tank
NDE	Non-Destructive Examination
NEI	Nuclear Energy Institute
NSSS	Nuclear steam system supplier
NTU	Nephelometric turbidity units
NUPEC	Nuclear Power Engineering Corporation
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 <i>Guidelines</i> , 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.
RUB	Reverse U-bend
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
TS	Tube Sheet
TSS	Total suspended solids
VCT	Volume control tank. The term makeup tank (MUT) is used at some plants for the same tank.
WABA	Wet Annular Burnable Absorbers

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1

INTRODUCTION AND MANAGEMENT RESPONSIBILITIES

1.1 Introduction

The purpose of this document is to provide guidance 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 chemistry limits provided in these *Guidelines* 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.

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 re-affirmed this commitment by adopting Revision 1 in 2001 and Revision 2 in 2005. 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*. The focus of the NEI initiative is steam generator integrity. It recognizes that steam generators comprise a major portion of the primary system pressure boundary.

The U.S. nuclear power industry has more recently produced a policy that commits each nuclear utility to adopt the responsibilities and processes on the management of materials aging issues described in NEI 03-08, *Guideline for the Management of Materials Issues*. NEI 03-08 was established in May 2003, and the addenda to NEI 03-08, *Materials Initiative Guidance*, was issued in July 2005. The scope of NEI 03-08 extends to "PWR and BWR reactor pressure vessel, reactor internals and primary pressure boundary components", "PWR steam generators (SG)", and "nuclear fuels materials issues to the extent that they impact or are impacted by plant materials management strategies (e.g., chemistry/corrosion control strategies)". In addition, NEI 03-08 states, "as deliverables or guidelines are developed, actions should be classified as to relative level of importance: "mandatory" – to be implemented at all plants where applicable; "needed" – should be implemented whenever possible but alternative approaches are acceptable,

and “good practice” – implementation is expected to provide significant operational and reliability benefits, but the extent of use is at the discretion of the individual plant/utility.

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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2.2 Discussion of Chemistry Regimes

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2.3.2.1 PWSCC Mechanisms

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Variation in Crack Initiation Time vs. Boron Concentration for Fixed Lithium
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2.3.2.7 Plant Experience Regarding Effects of Lithium and pH on PWSCC

2.3.2.8 Chloride

2.3.2.9 Fluoride

2.3.2.10 Sulfate

2.3.2.11 Organics

2.3.2.12 Lead

2.3.2.13 Zinc

Figure 2-17

Number of New Tubes Affected by TSP PWSCC per Outage

Table 2-1
Calculated Factor of Improvement Due to Zinc Injection (TS EZ PWSCC)

Figure 2-18

- All SGs – TS EZ (WEXTEx) PWSCC (axial and circ.) – Tubes Affected

Figure 2-19

- All SGs – TS EZ (WEXTEx) PWSCC (axial and circ.) – Tubes Affected

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2.4.2 Effects of Chemistry Parameters

2.4.2.1 Dissolved Oxygen

2.4.2.2 Dissolved Hydrogen

2.4.2.3 Fluoride

2.4.2.4 Aluminum, Calcium, Magnesium, and Silica

2.4.2.5 Suspended Solids

2.4.2.6 pH

2.4.2.7 Lithium

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2.4.2.8 Zinc

2.4.3 PWR Axial Offset Anomaly

2.5 Radiation Field Control

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Variations in Iron Solubility from Core Inlet to Outlet as a Function of pH_T at 300°C (Boron = 600 ppm, H_2 = 35 cc/kg H_2O) (135)

Figure 2-28
Variations in Iron Solubility from Core Inlet to Outlet as a Function of pH_T at 300°C (Boron = 600 ppm, $\text{H}_2 = 0$ cc/kg H_2O) (135)

Figure 2-29
Variations in Nickel Solubility from Core Inlet to Outlet as a Function of pH_T at 300°C (B = 600 ppm, $\text{H}_2 = 35 \text{ cc/kg H}_2\text{O}$) (135)

Figure 2-30
Variations in Nickel Solubility from Core Inlet to Outlet as a Function of pH_T at 300°C ($B = 600$ ppm, $\text{H}_2 = 0$ cc/kg H_2O) (135)

2.5.2.4 Verification Tests

Figure 2-31
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2.5.2.5 Plant Data

Figure 2-32
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Figure 2-33
RCS Co-58 concentrations before and after implementing an elevated constant pH
program for

Figure 2-34
RCS Co-60 concentrations before and after implementing an elevated constant pH
program for

Figure 2-35
Average Hot and Cold Leg Channel Head Center Dose Rates for

Figure 2-36
Average Hot and Cold Leg Channel Head Center Dose Rates for

Figure 2-37
Average Loop Piping Dose Rates for

Figure 2-38
Average Loop Piping Dose Rates for

2.5.2.6 Effects of End-Of-Cycle Boron Concentration

2.5.2.7 Zinc

Figure 2-39
Cumulative Dose Rate Reduction Fraction vs Cumulative Zinc Exposure

2.5.3 Summary

2.6 Summary of Chemistry Considerations

As indicated in Section 2.1, the purposes of these 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.

Achievement of these objectives can be complex and, often times, plant specific. However, certain chemistry parameters are universal during power operation, including:

2.6.1 Considerations for pH (Lithium)

2.6.2 Considerations for Dissolved Hydrogen

2.6.2.1 Effect of Hydrogen on PWSCC

Figure 2-40

Comparison of initiation trend for H₂ dependency (at 330°C) with scaled inverse ratios of CGR data (at 338°C) obtained from Morton et al. (22) for Alloy 600. (1)

2.6.2.2 Effect of Hydrogen on Iron and Nickel Solubility in the RCS

2.6.2.3 Effect of Hydrogen on Iron and Nickel Solubility Through the Core

2.6.3 Conclusion of Chemistry Considerations

3

POWER OPERATION CHEMISTRY CONTROL

3.1 Introduction

3.2 Reactor Coolant System (RCS) pH Optimization

3.2.1 *Operation*

Figure 3-1
Schematic Representation of the PWR Primary Chemistry Optimization Problem

Table 3-1
Generic Principles for Optimization of Primary System pH⁽¹⁾

Figure 3-2
Variation of pH Due to Tolerance Band for Lithium as Function of Boron Concentration, for
Target pH_{300°C}

3.3 Control and Diagnostic Parameters

3.4 Guideline Philosophy

3.4.1 *Philosophy*

3.4.2 *Corrective Actions*

3.5 Definitions of Terms Used in the Guidelines

3.5.1 *Plant Status*

Table 3-2
Operational Status Modes

3.5.2 *Action Levels*

3.5.2.1 Action Level 1

3.5.2.2 Action Level 2

3.5.2.3 Action Level 3

3.6 Guideline Values for Chemistry Parameters During Power Operation

3.6.1 Reactor Coolant System Guidelines

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Reactor Coolant System Power Operation Control Parameters (Reactor Critical)

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Table 3-4
Reactor Coolant System Power Operation Diagnostic Parameters (Reactor Critical)

3.6.2 Special Considerations

3.6.2.1 Axial Offset Anomaly

3.6.2.2 Zinc Addition

3.6.2.3 Extended Fuel Cycles

3.6.2.4 Operation With Unusual Levels of Lithium

3.6.2.5 Chemistry Program Modification

3.6.3 Primary System Makeup Water

Table 3-5

Source Water for Reactor Makeup⁽¹⁾ Diagnostic Parameters -- All Modes

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

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Reactor Coolant System Cold Shutdown Control Parameters (Reactor <250°F (121°C))

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Reactor Coolant System Startup Control Parameters (Reactor Subcritical and >250°F (121°C))

Table 3-8
Reactor Coolant System Startup Chemistry Diagnostic Parameters (From Initiation of Continuous RCP Operation to Reactor Critical)

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 for documentation 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. Optimization of the primary water chemistry program is the process of developing a program which appropriately reflects the technical bases provided in Chapter 2 and the chemistry control guidance in Chapter 3 relative to approaches for insuring primary system pressure boundary and fuel cladding integrity and minimizing radiation fields. A review of the guidance provided for development of a Strategic Water Chemistry Plan for PWR secondary and the BWR water chemistry were also assessed during revision of this Chapter (216, 217).

4.2 Primary Water Chemistry Variables and Options

4.2.1 Program Objectives

As noted in Chapter 2, the purposes of the primary water chemistry control program is to:

- Ensure primary system pressure boundary integrity,
- Ensure fuel cladding integrity and achievement of design fuel performance, and
- Minimize out-of-core radiation fields.

4.2.2 Parameters Impacting Pressure Boundary or Fuel Cladding Integrity

4.2.2.1

4.2.2.2

4.2.2.3

4.2.2.4

4.2.2.5

4.2.2.6

4.2.3 Parameters With Negligible Impact on Pressure Boundary or Fuel Cladding Integrity

4.2.3.1 Organics

4.2.3.2 Suspended Solids

4.2.4 Chemistry Control During Shutdowns and Startups

4.2.4.1 Shutdown Chemistry Program

4.2.4.2 Startup Chemistry Program

4.3 Optimization Methodology

4.3.1 Optimization Process

4.3.2 NEI 03-08 and NEI 97-06 Checklist

Table 4-1
Key Design and Operating Parameters (EXAMPLE)

Table 4-2
Chemistry Milestones / Activities (EXAMPLE)

Table 4-3
Chemistry Control Program Approaches

Table 4-3
Chemistry Control Program Approaches (continued)

Table 4-3
Chemistry Control Program Approaches

5

MANDATORY, SHALL AND RECOMMENDED ELEMENTS

5.1 Introduction

Chapter 5 captures all of the specific elements contained within these *Guidelines* that are identified as mandatory, shall or recommended, consistent with NEI 03-08 and NEI 97-06. Each element is captured in Section 5.2, along with any needed supporting information related to the element. The Guidelines Revision 6 Committee evaluated and concurred with the inclusion of each element.

5.2 Mandatory, Shall and Recommended Elements

5.2.1 Mandatory Element

5.2.2 Shall Elements

5.2.3 Recommended Elements

6

REFERENCES

References

References

References

References

References

References

References

A

CALCULATION OF PHT AND DATA EVALUATION METHODOLOGIES

A.1 Calculation of pH_T

To provide a uniform basis for establishing a pH_T control program and for comparing observations at different plants, it is important that industry personnel employ similar expressions for pertinent chemical equilibria, e.g., the ionization of boric acid. The recommended relations are given below. Note that in all cases, the pH is defined and should be reported as the negative logarithm (to the base 10) of the molal concentrations of the hydrogen ion.

Figure A-1
Lithium-Boron Relationships for Various pH at 275°C

Table A-1
Relation of pH at 275°C to Lithium and Boron Concentrations

Table A-2
Relation of pH at 280°C to Lithium and Boron Concentrations

Table A-3
Relation of pH at 285°C to Lithium and Boron Concentrations

Table A-4
Relation of pH at 290°C to Lithium and Boron Concentrations

Table A-5
Relation of pH at 295°C to Lithium and Boron Concentrations

Table A-6
Relation of pH at 300°C to Lithium and Boron Concentrations

Table A-7
Relation of pH at 305°C to Lithium and Boron Concentrations

Table A-8
Relation of pH at 310°C to Lithium and Boron Concentrations

Table A-9

Relation of pH at 315°C to Lithium and Boron Concentrations

A.2 Low Temperature pH, Boron, Lithium Calculations and Data

Mathematical Development

Numerical Method Commentary

Table A-10
Variables and equations for solving the Li-B system

Table A-11
Constants used for Table A-10 equations

Table A-12
pH of Boric Acid - Lithium Hydroxide Solutions at 25°C

A.3 Data Consistency (pH at 25°C/Conductivity at 25°C/Boron/Lithium)

Table A-13
Equivalent Conductance of 25°C

Calculation of Equivalent Conductance of 25°C

Pentaborate conductivity contribution

Table A-14
Conductivity of Boric Acid - Lithium Hydroxide Solutions at 25°C

A.4 Verification and Validation of the EPRI ChemWorks™ Primary System pH Calculator

A.5 Temperature and Pressure Dependence of pH

Figure A-2
Lithium additions for historical “modified” chemistry control program illustrating difference calculated for $pH_{Tave=310^{\circ}C}$ vs. $pH_{Tref=300^{\circ}C}$

pH_{Tave} as a Convention

Pressure and Temperature Variations in pKw

A.6 References

B

CHEMISTRY CONTROL OF SUPPORTING SYSTEMS

B.1 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.

B.2 Letdown Purification System

B.2.1 System Description

B.2.2 Selection Criteria for Purification Filters and Ion Exchange Resins

B.2.3 Performance Monitoring

B.2.4 Selected Industry Experiences

B.2.4.1 Resin Intrusions

B.2.4.2 Chloride Elution

B.2.4.3 Leachable Impurities

B.2.4.4 Boron/Power Excursions

B.2.4.5 Lithium Excursions/Power Effects

B.2.4.6 Shutdown Sulfate Increases

B.2.4.7 Makeup Water Contamination

B.3 Volume Control Tank or Makeup Tank

B.3.1 System Description

B.3.2 Chemistry Control and Technical Basis

Table B-1
Solubility In Water For Various Gases (1)

Table B-2
Partial Pressure of Water Vapor at Various Temperatures

B.3.3 Selected Industry Experiences

B.3.3.1 VCT Vapor Space Composition

B.4 Pressurizer

B.4.1 System Description

B.4.2 Chemistry Control and Technical Basis

B.4.3 Industry Experience

B.4.3.1 Corrosion Observations

B.4.3.2 RCS Hydrogen Control

B.4.3.3 Chloride Contamination

B.5 Boric Acid Storage

B.5.1 System Description

B.5.2 Chemistry Control and Technical Basis

B.5.3 Industry Experience

B.5.3.1 Silica Transport

B.5.3.2 Boric Acid Crystallization

B.5.3.3 Chloride Contamination

B.5.3.4 Magnesium Contamination

B.5.3.5 Sulfate Contamination

B.6 Refueling Water Storage Tank

B.6.1 System Description

B.6.2 Chemistry Control and Technical Basis

B.6.3 Industry Experience

B.6.3.1 Reactor Water Clarity

B.6.3.2 Resin Contamination

B.6.3.3 Silica Control

B.6.3.4 Chloride / Fluoride Contamination Due to Freon Intrusion

B.7 Spent Fuel Pool Cooling and Cleanup System

B.7.1 System Description

B.7.2 Chemistry Controls and Technical Basis

B.7.3 Industry Experience

B.7.3.1 Failure of Bundle Top Nozzles

B.7.3.2 Silica Control

B.8 References

C

STATUS OF ENRICHED BORIC ACID (EBA) APPLICATION

C.1 Introduction

Boric acid is used in primary coolant of a PWR as a soluble reactivity control agent. Boron is referred to as a 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.

C.2 Summary of EPRI Studies

C.3 Plant Demonstrations of EBA

C.4 References

D

AOA AND ULTRASONIC FUEL CLEANING

D.1 Background

The evolving economics of electric generation provide some utilities with incentives to operate PWRs with higher fuel duty and longer cycles. Increased sub-cooled nucleate boiling in the upper fuel spans can be a consequence of core designs which are used to achieve this objective. 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), also referred to as crud induced power shift (CIPS).

Table D-1
Ultrasonic Fuel Cleaning Applications at PWRs through July 2007

D.2 Ultrasonic Fuel Cleaning Technology

D.3 System Description

Figure D-1
Schematic of EPRI's ultrasonic fuel cleaning system

D.4 Fuel Cleaning Efficacy

D.5 Full-Reload Cleaning Results

D.6 Fuel Cleaning Performance

Figure D-2

. Cycle 12 (no AOA) and Cycle 11 (with AOA)

D.7 Conclusions

D.8 References

E

OXYGEN AND HYDROGEN BEHAVIOR IN PWR PRIMARY CIRCUITS

E.1 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.

E.2 Radiation Chemistry

E.3 Minimum Hydrogen Concentrations at Full Power

Figure E-1
Concentrations of O_2 and H_2O_2 Around the Main Reactor Loop During Full Power
Operation. 25 cc/kg H_2 , 1800 ppm Boron. Two Transits Around the Main Circuit are
Shown. ()

Figure E-2
Steady-state O_2 and H_2O_2 Concentrations at 1800 ppm Boron, Corresponding to the Start of an 18 Month Fuel Cycle (pH(300°C) 6.9)

Figure E-3
Steady-state O_2 and H_2O_2 Concentrations at 0 ppm Boron, Corresponding to the End of an 18 Month Fuel Cycle (pH(300°C) 7.4)

E.4 The Effect of Voidage on Minimum Hydrogen Levels

E.4.1 Metal Ion Chemistry

E.5 Oxygen Ingress

Figure E-4
Concentrations of O_2 and H_2O_2 Around the Main Reactor Loop. 25cc/kg H_2 , 1800 ppm B, Full Power Operation, Oxygen Ingress from the CVCS. Two Transits Around the Main Circuit are Shown. ()

Figure E-5
Variation of O_2 and H_2O_2 Concentrations Through the Core for Different Hydrogen Levels,
 O_2 Ingress, 1 Day After Shut down, 177°C

E.5.1 Impact of Oxygen on Corrosion Product Transport

Table E-1
PWR Crud Incidents Attributable to Oxidizing Conditions (24)

E.6 Startup Deoxygenation

E.7 Spent Fuel Pool

E.8 Hydrogen Diffusion through the Steam Generators

E.8.1 Modeling Hydrogen Concentration Decreases

E.8.2 Equilibrium Hydrogen Concentration during Loss-of-Letdown

Figure E-6
Henry's Law Constant as a Function of Temperature

Figure E-7
Permeability of Hydrogen in Alloy 600

Figure E-8
Loss-of-Letdown at , Data and Model Predictions

Figure E-9
Loss-of-Charging at , Data and Model Predictions

E.9 Conclusions

E.10 References

F

SAMPLING CONSIDERATIONS FOR MONITORING RCS CORROSION PRODUCTS

F.1 Background to RCS Corrosion Product Sampling Issues

Figure F-1
Changes in Soluble Nickel and Cobalt Concentrations at Doel 1 due to Changes in Flow Rate

Figure F-2
RCS Particulate Concentrations at following Start-up after Refueling in 1995
caused by Control Rod Tests (Red – 0.5 to 1.0 μm , Blue – 1.0 to 5.0 μm)

F.2 RCS Hot Leg Sampling Practices

Figure F-3
Co-58 and Co-60 Concentrations at
Filtered RCS Hot Leg “Grab” Samples from Cycle 3 to Cycle 7 measured using

Figure F-4
Iron (Top), Nickel (Middle) and Cobalt (Lower) concentrations at . Particulate data
(>0.45 μm) in closed symbol, Soluble in open symbol, and Total concentrations in solid
line. IS=Integrated samples (200-300 liters during 3-4 days)

Figure F-5
Iron-59 (Top), Cobalt-58 (Middle) and Cobalt-60(Lower) concentrations at . Particulate data ($>0.45\ \mu\text{m}$) in closed symbol, Soluble in open symbol, and Total concentrations in solid line. IS=Intergrated samples (200-300 liters during 3-4 days)

F.3 CVCS Letdown Line Sampling

Figure F-6
Corrosion Product Radionuclide Concentrations at
Sample Panel **Measured using the CVCS**

F.4 Experience

Figure F-7
Elemental and Radionuclide Corrosion Product Concentrations at
15 Measured using either the RCS Hit-Leg or CVCS Sample Lines **in Cycles 13 to**

F.5 Analysis Methods

F.6 Conclusions

F.7 References

G

REACTOR COOLANT RADIONUCLIDES

G.1 Formation of Radionuclides in the RCS

Reactor Coolant Radionuclides

Table G-1
Radionuclides Found in the Reactor Coolant System and Potential Sources

Reactor Coolant Radionuclides

Table G-1
Radionuclides Found in the Reactor Coolant System and Potential Sources

Table G-2

Radionuclides Not Identified Directly by Gamma Spectroscopy or Determined by Other Means (Refer to Chart of Nuclides for Half Lives).

Reactor Coolant Radionuclides

Iodine Specific Activity (DEI-131)

\bar{E} – Average Disintegration Energy

G.1.1 Radionuclides Formed by Fission

Figure G-1
Fission Product Curve for Slow-Neutron Fissioning of U-235 (from Reference (1))

Reactor Coolant Radionuclides

Fuel Clad Intact

Table G-3
Theoretical and Actual Iodine Activity Ratios Relative to I-131 (No fuel defects).

Figure G-2
Example of Grid-to-Rod Fretting and RCS Radionuclides at

G.1.2 Fission Product Speciation

G.1.3 Radionuclides Formed by Activation

Reactor Coolant Radionuclides

Fuel Activation Products

Activation of Water

Tritium Production

Table G-4

Tritium Source Percentages for a High Duty PWR that Uses IFBA and WABA Rods
()

Reactor Coolant Radionuclides

Activation of Dissolved Species in Water

Corrosion Products

Reactor Coolant Radionuclides

Overall Activation Product Behavior

G.2 Measurement of Radionuclides in the Reactor Coolant System

G.2.1 Examples of Measurement of Radionuclides by Adjusting Sample/Counting Parameters

G.2.2 Identifying Unknown Gamma Ray Peaks

Reactor Coolant Radionuclides

Table G-5
Gamma Ray Peaks of Nuclides Which Can be Obscured

Table G-5(continued)
Gamma Ray Peaks of Nuclides Which Can be Obscured

Figure G-3

Activity Decay Curve. Two different radionuclides contributing at the same gamma ray energy. Note that after decay correction that the semi-log plots of both activities, individually, are straight lines.

Figure G-4
Noble Gas and Iodine Ratio Changes with a Tight Fuel Defect

G.3 Expected Concentrations and Trends of RCS Radionuclides

G.3.1 Fission Products

Figure G-5
Noble Gas and Iodine Concentrations for Tight Fuel Defect

Figure G-6
Noble Gas and Iodine Activities with an Open Fuel Defect

Figure G-7
Noble Gas and Iodine Ratios with an Open Fuel Defect

G.3.2 Activation Product Trends

Figure G-8
Changes in Corrosion Products and Lithium During CRDM Surveillance

G.4 References

Reactor Coolant Radionuclides