Enclosure 4

PWR Primary Water Chemistry Guidelines:

Draft Revision 5

Non-Proprietary Version

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Volume 1, Revision 5

1002884-V1

June 2003

DRAFT
NON-PROPRIETARY VERSION

EPRI Project Manager
P. Frattini

EPRI • 3412 Hillview Avenue, Palo Alto, California 94304 • PO Box 10412, Palo Alto, California 94303 • USA
800.313.3774 • 650.855.2121 • askepri@epri.com • www.epri.com

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PWR Primary Water Chemistry Guidelines Committee

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CITATIONS

This report was prepared by

PWR Primary Water Chemistry Guidelines Committee

AECL
J. Sawicki

Ameren UE
G. Gary, E. Olson, J. Small

American Electric Power
K. Haglund, D. Kozin

AmerGen Energy
B. Walton

Arizona Public Service
J. Santi

Babcock & Wilcox
P. King

British Energy
J. C. Bates, K. Garbett, Consultant

Constellation Energy
E. Eshelman

Dominion Engineering
J. Gorman

Dominion Resources
E. Frese

Duke Energy
K. Johnson

Electricité de France
J-L. Belzic

Entergy
G. Dolese, D. Wilson

Exelon
R. Claes

First Energy
V. Linnenbom, S. Slosnerick

Florida Power & Light
C. Connelly

Framatome ANP
W. Allmon, L. Lamanna

GEBCO Engineering, Inc.
G. Brobst

INPO
R. Schirmer

iSagacity
J. Bates

Laborelec
E. Girasa, C. Laire

NMC
C. Jones, S. Lappegaard. J. McElrath

NPP Krsko
K. Fink

N. Atlantic Energy Serv. Co.
R. Litman, L. Michaud, G. Miller

NWT Corp.
S. Sawochka

Ontario Power Generation
K. Bagli

OPPD
T. Dukarski

Pacific Gas & Electric
C. Bowler

Progress Energy
N. Bach, P. Cross, E. Meyer, R. Thompson

PSE&G Nuclear LLC
J. Riddle

Ringhals
P.-O. Andersson, B. Bengtsson

Rochester Gas and Electric
G. Jones

South Carolina Electric & Gas
F. Bacon

Southern California Edison
J. Muniga

Southern Nuclear
F. Hundley, D. Rickertsen

STPNOC
D. Bryant, R. Ragsdale

TXU Energy
K. Cooper, B. Fellers, L. Wilson

TVA
D. Adams, D. Bodine

Westinghouse
A. Byers, J. Kormuth, S. Lurie, N. Vitale

WCNOC
J. Kuras, J. Truelove

ELECTRIC POWER RESEARCH INSTITUTE
P. Frattini, Chairman; J. Blok, B. Cheng, J. Deshon, K. Fruzzetti, J. Hickling, H. Ocken, R. Pathania, C. Wood

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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 2000.

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
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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
INTRODUCTION AND MANAGEMENT RESPONSIBILITIES

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.

2.2 Discussion of Chemistry Regimes

2.3 Materials Integrity in the Reactor Coolant System

2.3.1 Corrosion Modes of Structural Materials

2.3.2 Effects of Chemistry Parameters

2.3.2.1 PWSCC Mechanisms

2.3.2.2 Dissolved Oxygen

2.3.2.3 Dissolved Hydrogen – Effects at Operating Temperatures

2.3.2.4 Dissolved Hydrogen – Low Temperature Considerations

2.3.2.5 pH

2.3.2.6 Lithium

2.3.2.7 Analytical Evaluation of Effect of Lithium-pH History on PWSCC Susceptibility

2.3.2.8 Plant Experience Regarding Effects of Lithium and pH on PWSCC

2.3.2.9 Chloride

2.3.2.10 Fluoride

2.3.2.11 Sulfate

2.3.2.12 Organics

2.3.2.13 Zinc

2.4 Fuel Integrity Considerations

The zirconium alloy fuel rod cladding provides a barrier against the release of the radioactive fission products formed during operation. Maintaining cladding integrity, therefore, is a major objective of the plant operator and licensing authorities.

2.4.1 Chemistry Effects on Fuel Reliability

2.4.1.1 Cladding Corrosion

t

i

2.4.1.2 Fuel Crud Deposition

2.4.2 Effects of Chemistry Parameters

2.4.2.1 Dissolved Oxygen

2.4.2.2 Fluoride

2.4.2.3 Aluminum, Calcium, Magnesium, and Silica

2.4.2.4 Suspended Solids

2.4.2.5 pH

2.4.2.6 Lithium

2.4.2.7 Zinc

2.4.3 PWR Axial Offset Anomaly

2.5 Radiation Field Control

2.5.1 Sources of Radiation Fields

Shutdown radiation fields can be affected by numerous factors including operational chemistry control, plant configuration, materials of construction, surface finish, and time of operation (119, 120, 121, 122, 123).

2.5.2 Effects of Chemistry Parameters

2.5.2.1 Corrosion Product Release

2.5.2.2 Particulate Transport

2.5.2.3 Soluble Transport

2.5.2.4 Verification Tests and Plant Experience

2.5.2.5 Plant Data

2.5.2.6 Zinc

2.5.3 Summary

3
POWER OPERATION CHEMISTRY CONTROL RECOMENDATIONS

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.

3.2 Reactor Coolant System (RCS) pH Optimization

3.2.1 Operating Recommendations

3.2.2 Transition to Constant pH Operation

3.3 Control and Diagnostic Parameters

3.4 Guideline Recommendations

3.4.1 Goals

3.4.2 Corrective Actions

3.5 Definitions of Terms Used in the Guidelines

3.5.1 Plant Status

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

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

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.

4.2 Primary Water Chemistry Variables and Options

4.2.1 Program Objectives

4.2.2 Parameters Impacting Structural Integrity

4.2.2.1 Chloride/Fluoride/Sulfate

4.2.2.2 Dissolved Oxygen Control

4.2.2.3 Hydrogen

4.2.2.4 pH_T (Lithium Control Parameter)

4.2.2.5 Zinc

4.2.3 Parameters With Negligible Impact on Structural Integrity

4.2.3.1 Silica

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 SG Initiative Checklist

n
Negative Impacts
None
ɔact on fuel corrosion at er concentrations has not been well defined
: can be higher if depleted approach is used versus normal zinc

5
REFERENCES

A
CALCULATION OF PHT AND DATA EVALUATION METHODOLOGIES

1.0 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 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

Cc

y_1

y_2

y_3

y_5

l

fi

lo

y_6

y_7

y_8

y_9

p_1
p_2
p_3
p_4
p_5
p_6
p_7
p_8

u_1
u_2
u_3
u_4

3.0

4.0

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.

2.0 Letdown Purification System

2.1 System Description

2.2 Selection Criteria for Purification Filters and Ion Exchange Resins

2.3 Performance Monitoring

d be

ıre

e

2.4 Selected Industry Experiences

2.4.1 Resin Intrusions

2.4.2 Chloride Elution

2.4.3 Leachable Impurities

2.4.4 Boron/Power Excursions

2.4.5 Lithium Excursions/Power Effects

2.4.6 Shutdown Sulfate Increases

2.4.7 Makeup Water Contamination

3.0 Volume Control Tank

3.1 System Description

3.2 Chemistry Control and Technical Basis

3.3 Selected Industry Experiences

3.3.1 VCT Vapor Space Composition

4.0 Pressurizer

4.1 System Description

4.2 Chemistry Control and Technical Basis

4.3 Industry Experience

4.3.1 Corrosion Observations

4.3.2 RCS Hydrogen Control

4.3.3 Chloride Contamination

5.0 Boric Acid Storage

5.1 System Description

5.2 Chemistry Control and Technical Basis

5.3 Industry Experience

5.3.1 Silica Transport

5.3.2 Boric Acid Crystallization

5.3.3 Chloride Contamination

5.3.4 Magnesium Contamination

5.3.5 Sulfate Contamination

6.0 Refueling Water Storage Tank

6.1 System Description

6.2 Chemistry Control and Technical Basis

6.3 Industry Experience

6.3.1 Reactor Water Clarity

6.3.2 Resin Contamination

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

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

6.0 Fuel Cleaning Performance

7.0 Conclusions

8.0 References

E
OXYGEN AND HYDROGEN BEHAVIOR IN PWR PRIMARY CIRCUITS

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.

2.0 Radiation Chemistry

3.0 Minimum Hydrogen Concentrations at Full Power

4.0 The Effect of Voidage on Minimum Hydrogen Levels

4.1 Metal Ion Chemistry

5.0 Oxygen Ingress

6.0 Startup Deoxygenation

7.0 Spent Fuel Pool

8.0 Conclusions

9.0 References

F
SAMPLING CONSIDERATIONS FOR MONITORING RCS CORROSION PRODUCTS

1.0 Background on RCS Sampling Technology

2.0 Existing Sampling Practices

3.0 Continuous Corrosion Product Sampling

3.1 Background

3.2 Continuous Sampling and Analysis Methods

3.3 Conclusions

4.0 Augmented Reactor Coolant Corrosion Product Sampling at Diablo Canyon and Catawba (26)

5.0 References

G
REACTOR COOLANT RADIONUCLIDES

This appendix provides suggestions with regard to possible methods for use in monitoring radionuclides in the reactor coolant system.

1.0 Formation of Radionuclides in the RCS

1.1 Radionuclides Formed by Fission

1.2 Radionuclides Formed by Activation

2.0 Measurement of Radionuclides in the Reactor Coolant System

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

2.2 Identifying Unknown Gamma Ray Peaks

3.0 Expected Concentrations and Trends of RCS Radionuclides

3.1 Fission Products

3.2 Activation Product Trends

4.0 References

H
DEFINITION OF HIGH DUTY CORE

(A MEANS FOR EVALUATING THE PROPENSITY TO DEPOSIT CRUD ON FUEL ASSEMBLIES)

1.0 Background

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.

2.0 Definition

3.0 Methodology

4.0 Case Example

5.0 High Duty – Medium Duty – Low Duty

6.0 References