Pressurized Water Reactor Primary Water Chemistry Guidelines

Volume 2, Revision 6

1014986

Final Report, December 2007

NON-PROPRIETARY

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PWR Primary Water Chemistry Guidelines Committee

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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, establish 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 these 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.

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 amount 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 (which generally require 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. This is the sixth revision of the *Guidelines* and considers the most recent operating experience and laboratory data. These *Guidelines* will be of interest to plant chemists, plant managers, chemical engineers, and engineering managers within utilities owning PWRs.

This is the third 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 revisions, 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 clearly separates it from the NEI requirements of Volume 1. This Volume 2 contains no specific requirements (with the limited exceptions identified in Tables 4-2 and 4-3, which are duplicates of Tables 3-6 and 3-7, respectively, in Volume 1 of these *Guidelines*) which must be met by utilities to be in compliance with the NEI 97-06 and NEI 03-08 Initiatives.

The combined shutdown and startup chemistry coverage in this Volume 2 was updated from that in Revision 5 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. Chapter 2 has been significantly modified to reflect a new understanding of shutdown chemistry. Specifically, nickel ferrite decomposition is now understood not to be a significant factor in shutdown chemistry. Likewise, Chapter 2 emphasizes that there is no inflection point in the transition from basic to acid conditions, i.e., there is nothing special about transitioning through pH-neutral. Chapters 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 guidance presented in Chapters 3 and 4 of Volume 2 comprise a program that should serve as a model for the development of site-specific chemistry programs.

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Relative to Revision 5 (2003) of these *Guidelines*, the major changes made to Volume 2 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
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
NMAC	Nuclear Maintenance Application Center
NSSS	Nuclear steam system supplier
NTU	Nephelometric turbidity units
PRT	Pressurizer 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
RCVRS	Reactor Coolant Vacuum Refill System
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
UFSAR	Updated Final Safety Analysis Report
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 shutdowns and startups. 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. Although some field data indicate a reduction in exposure rates following implementation of a controlled shutdown chemistry program, the primary purpose of such a program is to avoid problems such as increased radiation fields and extended outage schedules that may result from chemistry-related release of highly radioactive corrosion products during shutdown. Long-term radiation field reductions (normally less than 5%) may result from routine implementation of startup/shutdown chemistry controls, but in general these programs should only be expected to avoid potential problems given the state of the RCS and core present at EOC, not to achieve decontamination of ex-core surfaces.

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 steels, which constitute the greatest part of the primary system surface area (excluding the core), 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 chemical and physical mechanisms that continues to be studied.

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As a basis for establishing generic recommendations for a shutdown chemistry control program, the goal of the program was defined as follows (20):

"Prepare the plant for a refueling or mid-cycle outage in as short a time as possible without negatively impacting on shutdown dose rates or particulate contamination levels and associated contamination events."

Although outage exposure is a common assessment parameter, it is not specifically identified in the statement of goals since it is impacted by the scope and nature of outage activities. However, outage exposures should be minimized if shutdown dose rates and contamination levels are minimized.

The success of a particular shutdown chemistry control strategy depends not only on the strategy and operational practices during the shutdown evolution but also on the composition, physical nature and inventory of deposits on the core. The strategy outlined below in a series of principles has been successfully applied at numerous plants.

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Approaches to filling and venting the reactor coolant system, oxygen control, lithium control and hydrogen control should be assessed as part of the chemistry optimization program. The selected approaches can affect startup schedules and corrosion product and activity concentration variations. Site-specific chemistry program goals and outage considerations should drive startup process decisions.

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REFERENCES

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CEOG Mid-Cycle Shutdown Chemistry Decision Logic

(Continues on subsequent pages)

Linda Stevenson