PWR Primary Water Chemistry Guidelines

Volume 2, Revision 5

1002884-V2

June 2003

DRAFT
NON-PROPRIETARY VERSION

EPRI Project Manager
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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, 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.

Volume 2 of the PWR Primary Water Chemistry Guidelines covers startup and shutdown chemistry.

EPRI FOREWORD

This is the second consecutive issue in which a second volume of the PWR Primary Water Chemistry Guidelines focuses on startup and shutdown chemistry.

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:

- Ameren UE
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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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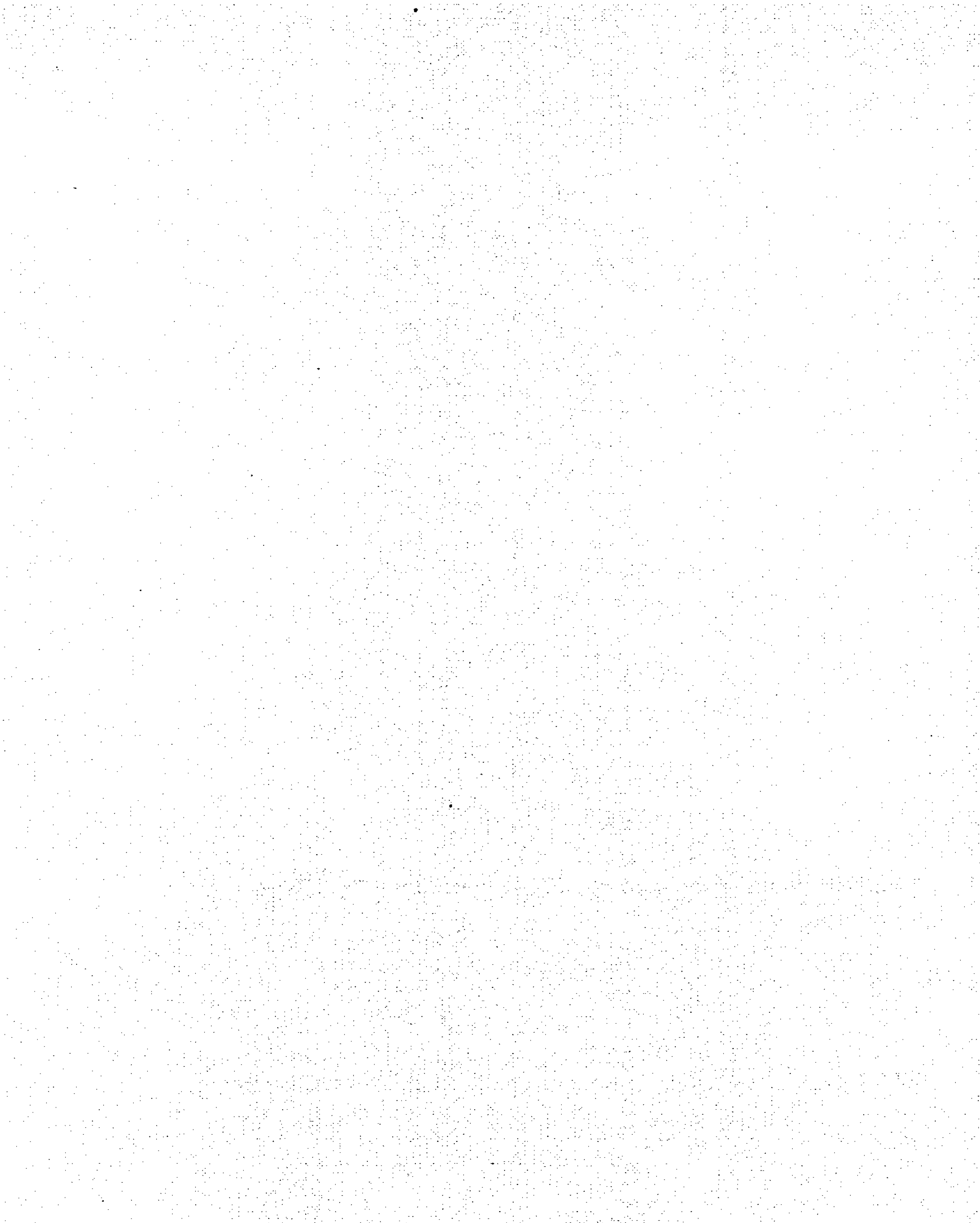

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3
PRINCIPLES OF CHEMISTRY CONTROL DURING SHUTDOWN

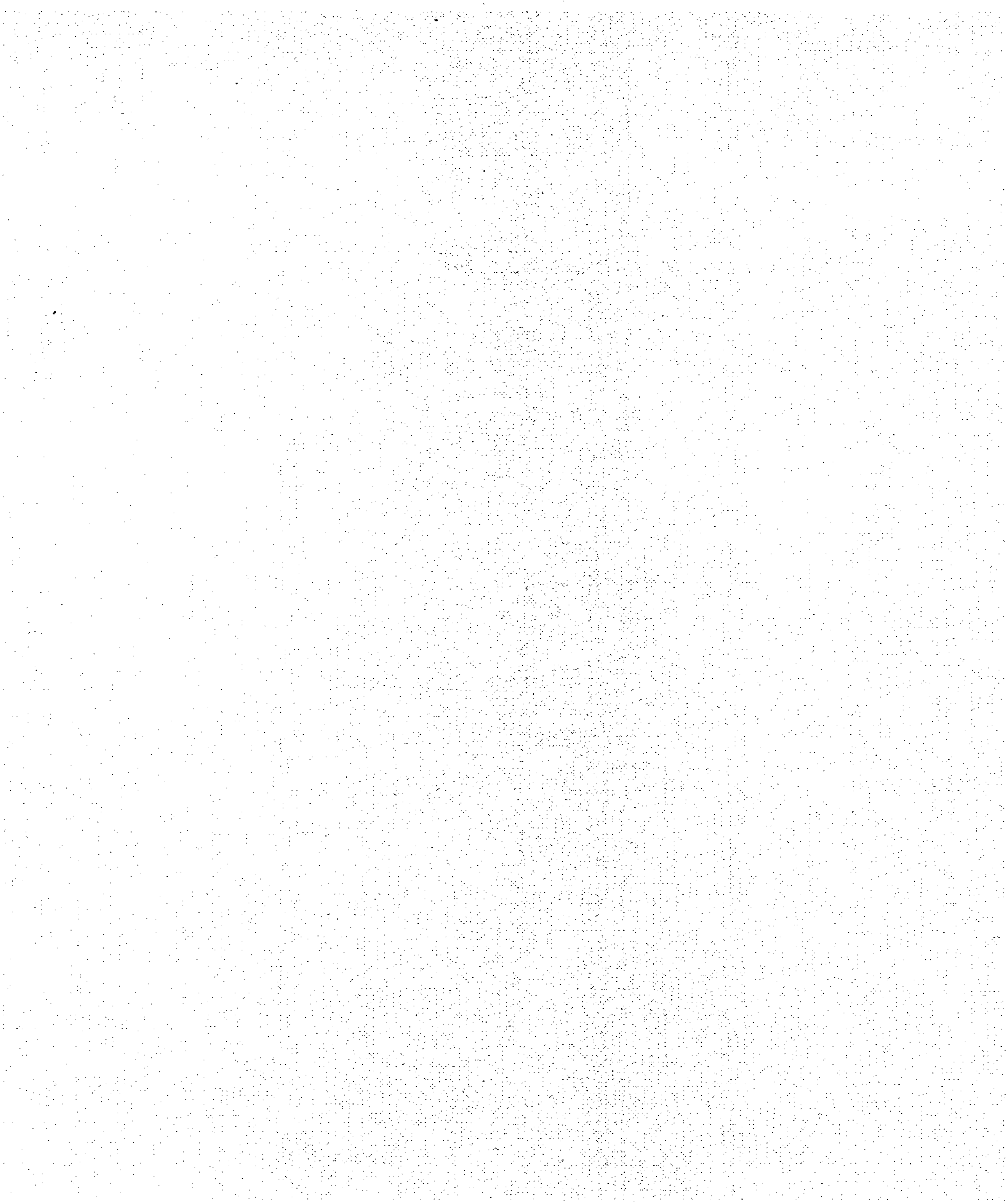
3.1 Shutdown Chemistry Controls

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



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3.2 Hydrogen Removal Practices

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3.2.2 Mechanical Degassing

3.2.3 Chemical Degassing

3.3 Activity Releases

3.4 RCS Oxygenation Practices

3.4.1 Introduction

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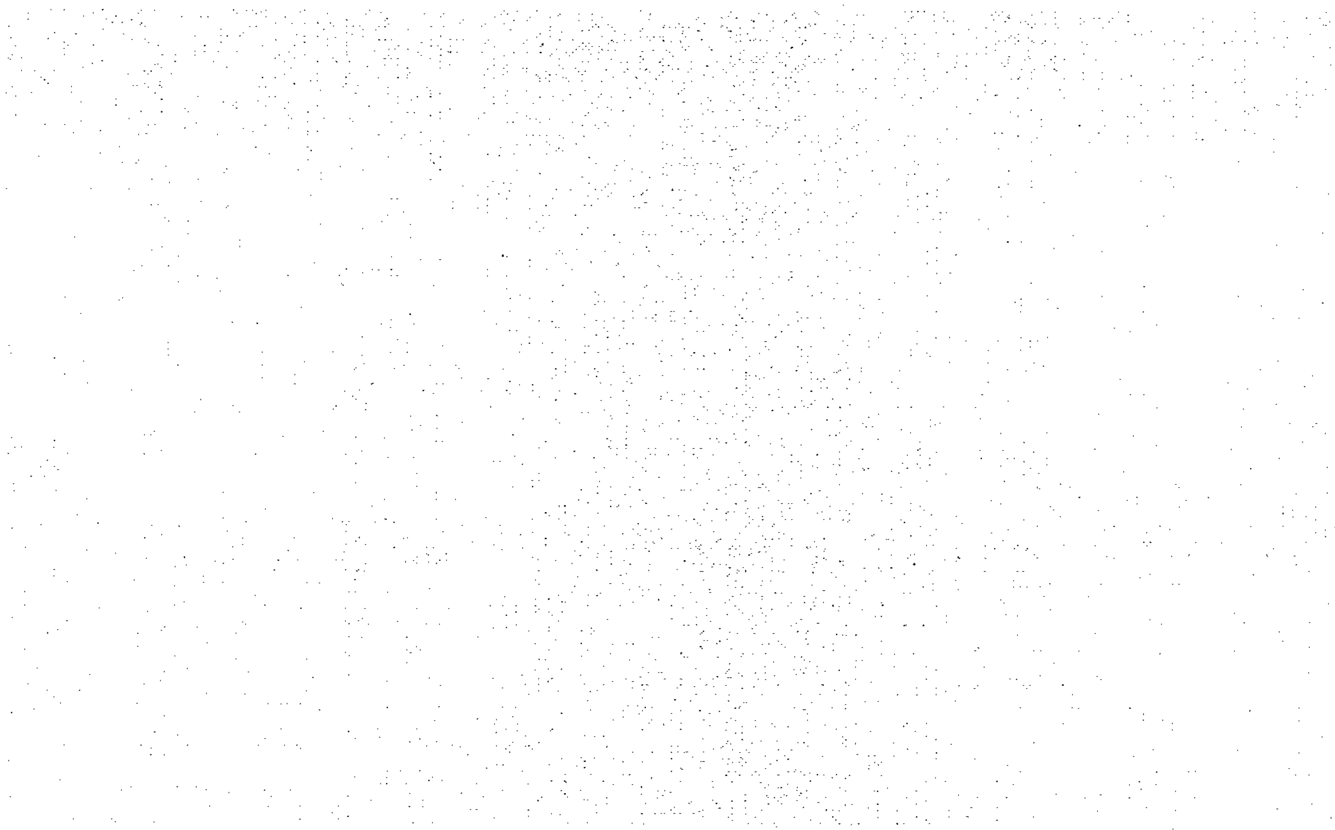
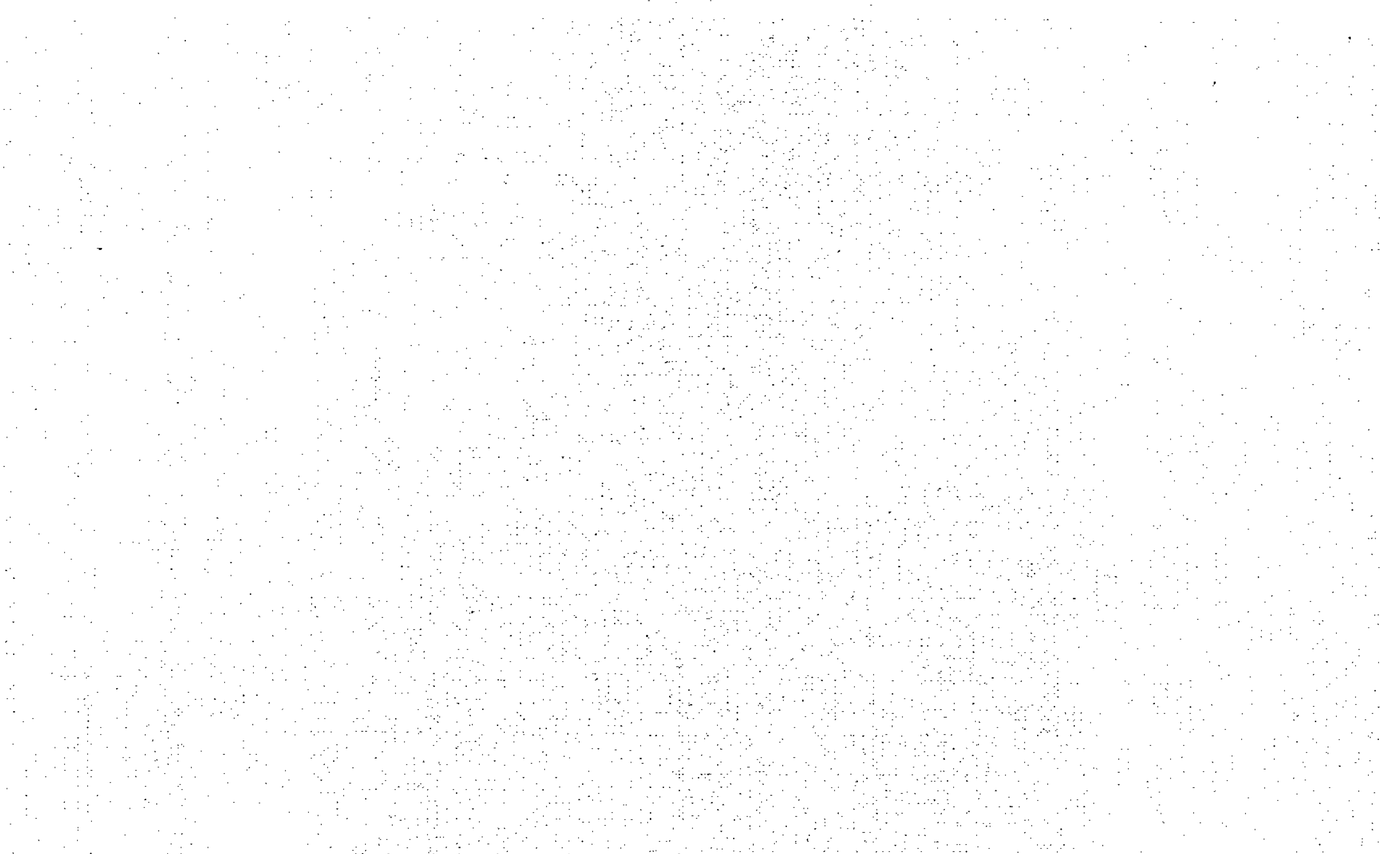
3.4.2.1 Introduction

3.4.2.2 Hydrogen Peroxide Qualification



3.4.2.3 Coolant Oxygenation Results



3.4.3 Control of Refueling Water Clarity by Hydrogen Peroxide Treatment

3.5 Fission Product Control During Shutdowns

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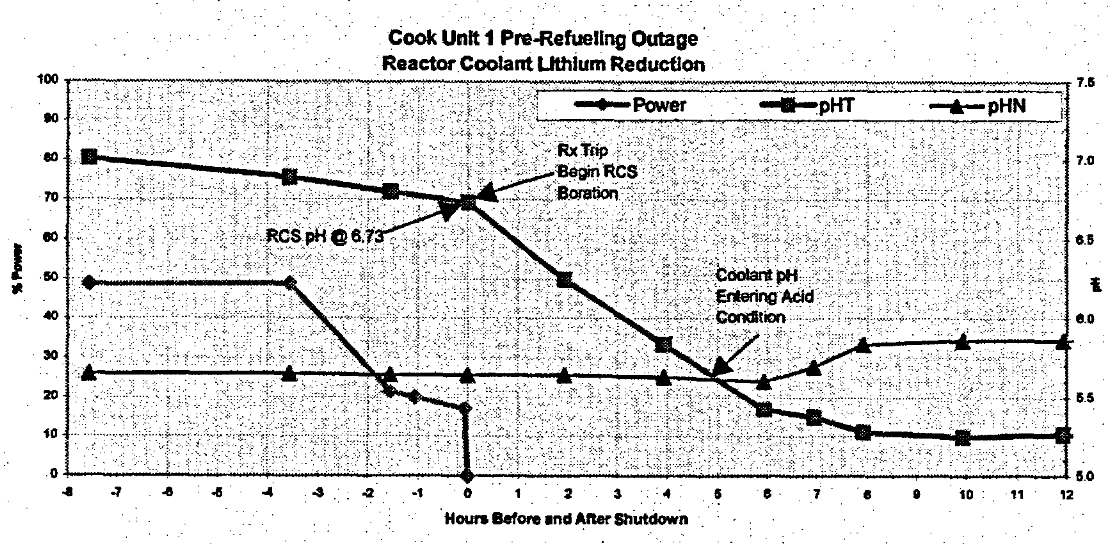
9. Increase to hourly after oxygenation. Once the cleanup is at the expected rate, sampling may be reduced to 1/4 hours.
10. Increase frequency when significant flow changes are expected.
11. Purification DF values should be calculated to determine removal efficiency for both particulate and soluble species.
12. VCT hydrogen analysis frequency can be relaxed once the system is oxygenated and stabilized. Particular attention should be given to hydrogen analysis following the collapsing of the pressurizer bubble.
13. Total and filtrate fractions for metals and corrosion product activities may be determined in place of non-filterable and filterable fractions.
14. Frequencies can be significantly reduced during draindown and throughout the shutdown. A default frequency of daily is recommended during this time frame.

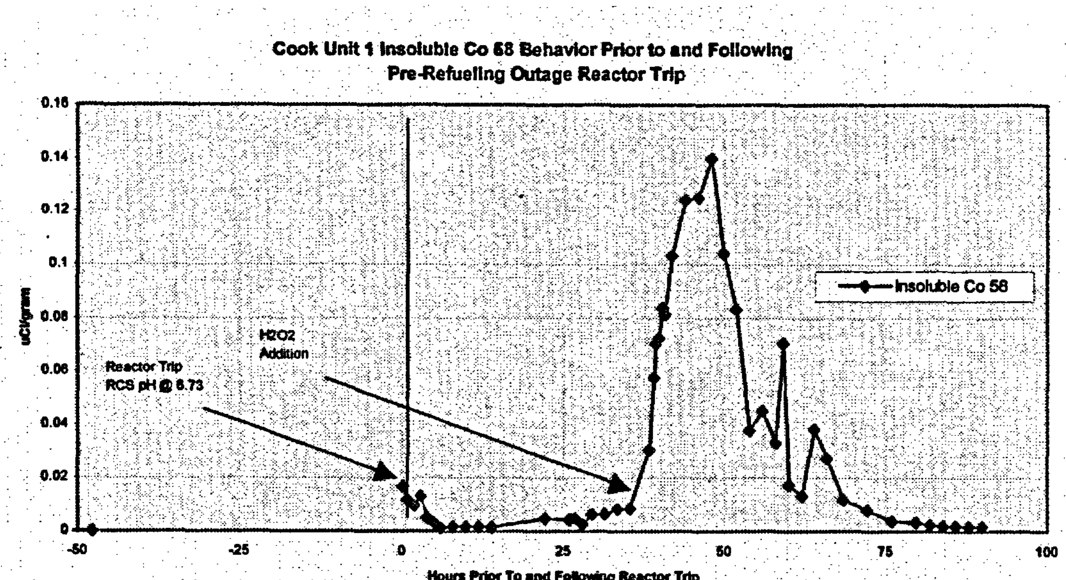
3.7 Utility Experience

3.7.1 D.C. Cook Pre-Refueling Shutdown RC Lithium / pH Reduction

The following chart is depicts a typical pre-outage reduction of lithium while at power at Cook Station Unit 1. In this instance the pH_T was reduced to 6.73 but the Mode 3 entry occurred prior to reaching the target pH.



The insoluble ^{58}Co behavior prior to and following the lithium reduction is depicted in the graph below. In this example, the reactor was tripped at approximately 17% power. The insoluble activity increase occurring immediately following the trip, from close to zero to about 0.02 µCi/gm, is indicative of the mechanical corrosion product release that occurs following any reactor trip scenario regardless of coolant pH.



4 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.

4.2 Corrosion Product Behavior During Heatup

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4.3.2.1 Mechanical Methods

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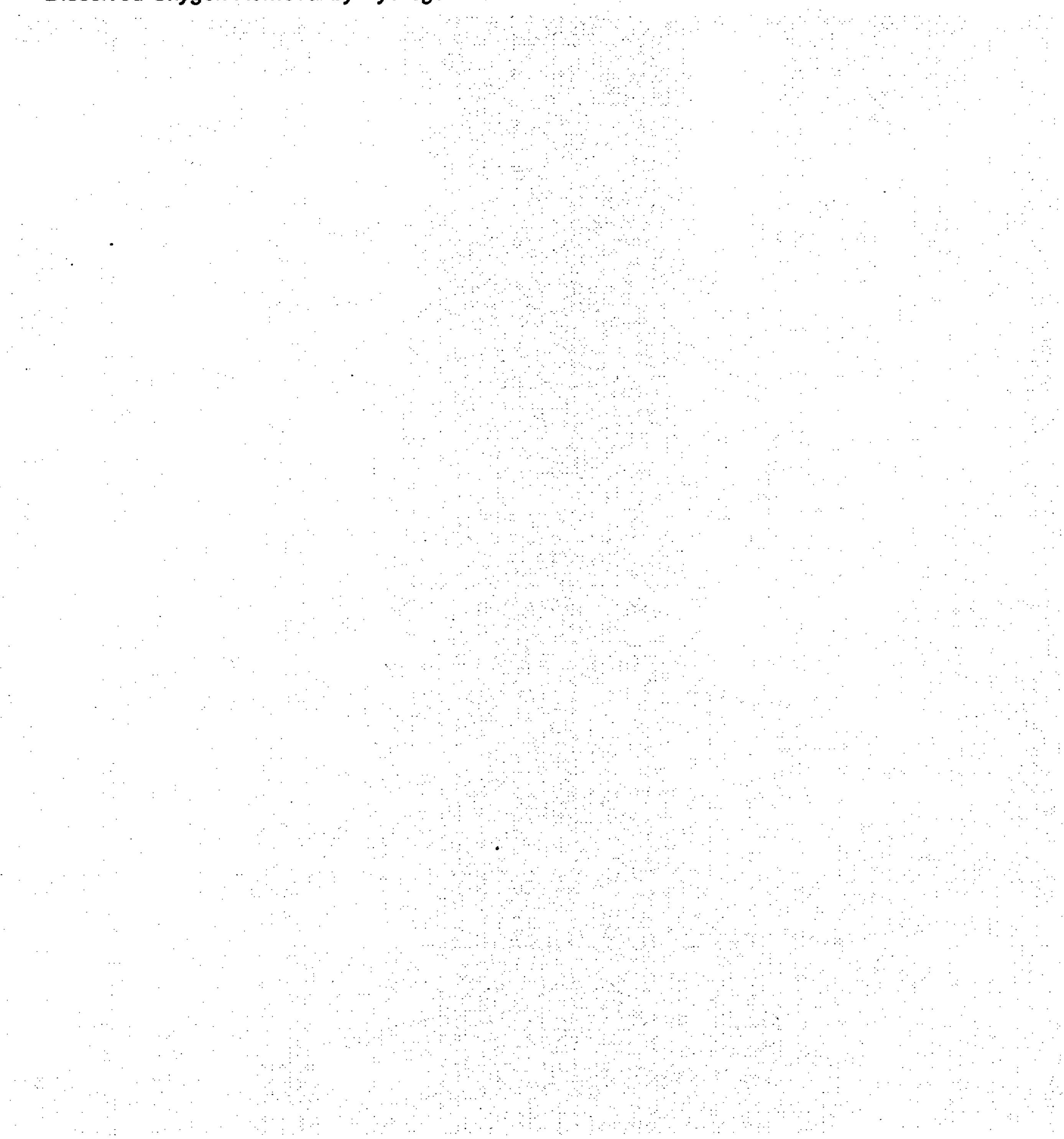
Dissolved Oxygen Removal by Hydrogen Addition



4.3.3 Pressurizer Oxygen Control

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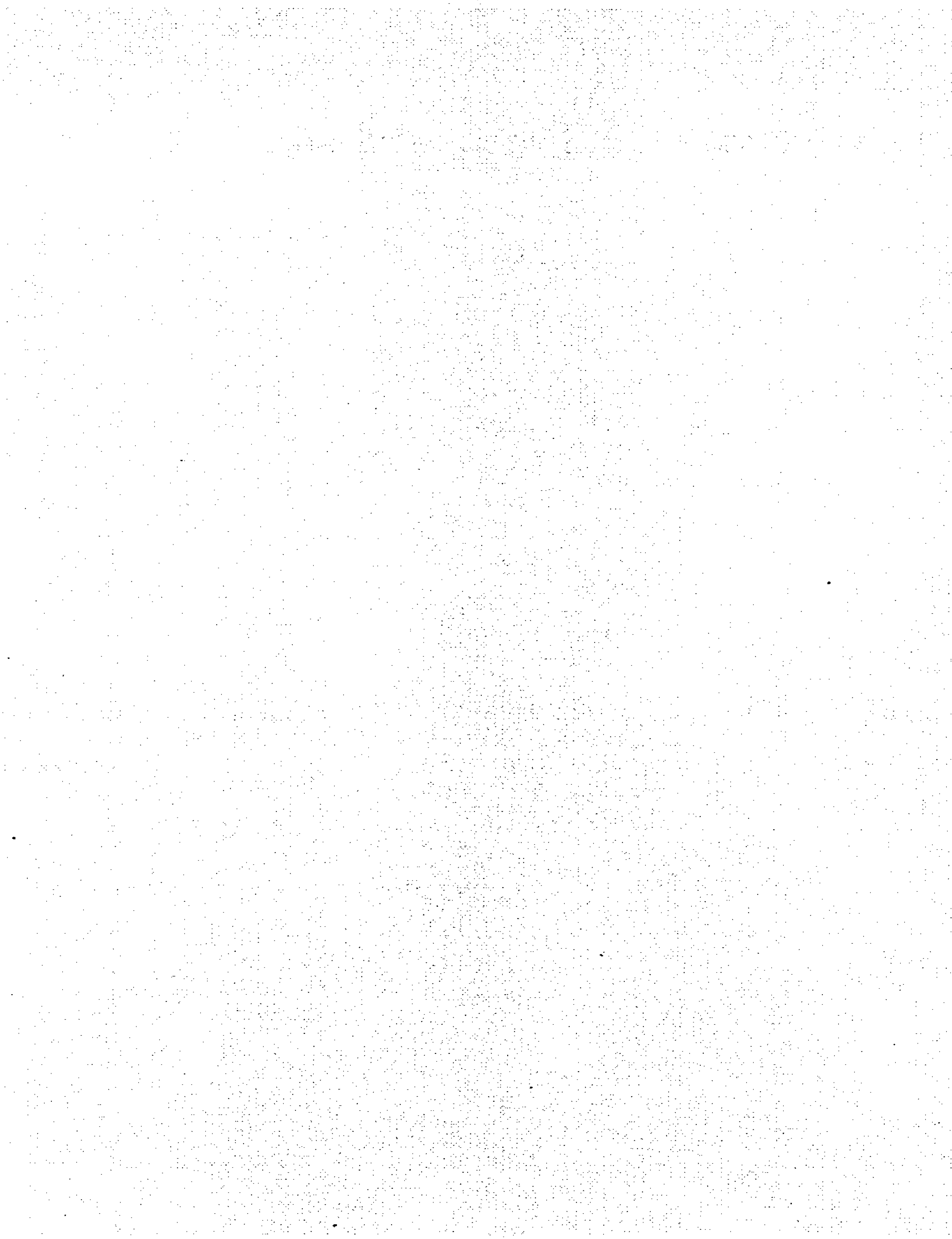

4.10 Example Utility Experience with Startup Chemistry

5
REFERENCES

A
EXAMPLE RCS MID-CYCLE SHUTDOWN CHEMISTRY DECISION LOGIC

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

References