

Radiation Field Control Manual

**WARNING:**

Please read the License Agreement on the back cover before removing the Wrapping Material.

Effective December 6, 2006, this report has been made publicly available in accordance with Section 734.3(b)(3) and published in accordance with Section 734.7 of the U.S. Export Administration Regulations. As a result of this publication, this report is subject to only copyright protection and does not require any license agreement from EPRI. This notice supersedes the export control restrictions and any proprietary licensed material notices embedded in the document prior to publication.

Technical Report

Radiation Field Control Manual

1003390

Final Report, December 2004

EPRI Project Manager
D. Hussey

DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

THIS DOCUMENT WAS PREPARED BY THE ORGANIZATION(S) NAMED BELOW AS AN ACCOUNT OF WORK SPONSORED OR COSPONSORED BY THE ELECTRIC POWER RESEARCH INSTITUTE, INC. (EPRI). NEITHER EPRI, ANY MEMBER OF EPRI, ANY COSPONSOR, THE ORGANIZATION(S) BELOW, NOR ANY PERSON ACTING ON BEHALF OF ANY OF THEM:

(A) MAKES ANY WARRANTY OR REPRESENTATION WHATSOEVER, EXPRESS OR IMPLIED, (I) WITH RESPECT TO THE USE OF ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT, INCLUDING MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, OR (II) THAT SUCH USE DOES NOT INFRINGE ON OR INTERFERE WITH PRIVATELY OWNED RIGHTS, INCLUDING ANY PARTY'S INTELLECTUAL PROPERTY, OR (III) THAT THIS DOCUMENT IS SUITABLE TO ANY PARTICULAR USER'S CIRCUMSTANCE; OR

(B) ASSUMES RESPONSIBILITY FOR ANY DAMAGES OR OTHER LIABILITY WHATSOEVER (INCLUDING ANY CONSEQUENTIAL DAMAGES, EVEN IF EPRI OR ANY EPRI REPRESENTATIVE HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES) RESULTING FROM YOUR SELECTION OR USE OF THIS DOCUMENT OR ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT.

ORGANIZATION(S) THAT PREPARED THIS DOCUMENT

EPRI

ORDERING INFORMATION

Requests for copies of this report should be directed to EPRI Orders and Conferences, 1355 Willow Way, Suite 278, Concord, CA 94520. Toll-free number: 800.313.3774, press 2, or internally x5379; voice: 925.609.9169; fax: 925.609.1310.

Electric Power Research Institute and EPRI are registered service marks of the Electric Power Research Institute, Inc. EPRI. ELECTRIFY THE WORLD is a service mark of the Electric Power Research Institute, Inc.

Copyright © 2004 Electric Power Research Institute, Inc. All rights reserved.

CITATIONS

This report was prepared by

Principal Investigators

D. Hussey

C. Wood

Additional work and assistance provided by

R. Asay, Radiological Solutions, Inc.

C. Bergmann, Westinghouse

J. Blok, EPRI

D. Bradbury, Bradtec Decon Technologies

D. Chapman, Westinghouse

N. Delse, EPRI solutions

P. Frattini, EPRI

J. Fox, Duke Power

K. Fruzzetti, EPRI

R. Kohlmann, Radiological Solutions, Inc.

H. Miller, Exelon

H. Ocken

R. Pucci, FENOC

C. Repass, Exelon

R. Rodriguez-Gilroy, PPL

P. Saunders, Suncoast Solutions

B. Thompson, Exelon

J. Underwood, TVA

T. Walters, Southern Nuclear

This report describes research sponsored by EPRI.

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

Radiation Field Control Manual, EPRI, Palo Alto, CA: 2004. 1003390

REPORT SUMMARY

The EPRI Radiation Management Program is dedicated to reducing nuclear power plant worker personnel exposure by developing practices and technologies to increase the radiation protection of the worker, and to implement methods to reduce radiation fields. The nuclear power industry has recently implemented the RP2020 Initiative to promote positive radiation protection trends. Control of radiation fields is crucial to one of the initiative goals of reducing exposure. This manual provides the current state of technology available to the industry to reduce out-of-core radiation fields.

Background

Previous editions of the EPRI Radiation Field Control Manual described available technologies. Recently, the industry has developed several new techniques for radiation field control and reduction. The technologies attack the problem by either reducing the radiation source term generated, preventing the deposition of existing active material in the ex-core surfaces of the plant, or removing the source term from the system. This manual updates earlier editions, describes the general methods used for each of these approaches, and provides insights and industry experiences to optimize existing plant resources.

Objective

To provide a comprehensive review of radiation field control options for utility engineering, chemistry and radiation protection managers and technicians, with sufficient background information to serve as a training aid for new staff.

Approach

The project team consulted utility radiation protection specialists, consultants and research organizations to develop a detailed review of current technology and utility experiences in implementation. The EPRI project team held a workshop to discuss each area of radiation field control, and compiled the comments into the manual.

Results

This manual discusses the origin of radiation fields, and provides an overview of the countermeasures used to reduce or prevent them. It outlines source term reduction techniques by reviewing the materials issues (including hard-faced valve replacement strategies, valve maintenance practices, preconditioning of replacement components, and the use of low-cobalt materials), improvement of plant chemistry practices for both PWRs and BWRs (including the use of zinc injection), and the removal of activity from system via chemical decontamination and ultrasonic fuel cleaning.

The nuclear industry has made advances in all areas of radiation field control, and many plants have already successfully implemented them. Utilities have refined methods for selecting valves with low-cobalt hard-facing, and updated valve maintenance to include a novel use of x-ray fluorescence for cobalt-59 detection. This report evaluates industry experience with low-cobalt steam generator tubing.

This report presents a review of components that may contribute to source term, and supplements the information with the methods used by the Brown's Ferry Unit 1 restart team to eliminate cobalt from the system. The report also updates the effects of surface preconditioning using electropolishing and stabilized chromium, including a presentation of the results from several plants that applied stabilized chrome to their manway seal plates.

This manual also updates the chemistry chapters to reflect the most recent versions of the EPRI chemistry guidelines. It discusses the effects of operating and shutdown PWR chemistry on radiation fields and the effects of normal and depleted zinc injection in primary coolant. The report also includes a discussion of BWR coolant and the results of the combination of noble metals application, depleted zinc oxide injection, and hydrogen water chemistry. The project team presents recommendations for implementation of these technologies.

The report also includes a review of chemical decontamination methods and plant experiences. The project team presents the field reduction effects of ultrasonic fuel cleaning on PWRs, and a discussion of the potential for similar benefits from BWR ultrasonic fuel cleaning.

EPRI Perspective

This Radiation Field Control Manual provides the industry with a resource that informs new and experienced radiation protection managers and technicians, chemistry personnel, and management about the industry standards and requirements for radiation field control. It also discusses current radiation field control practices and technologies.

Several technologies introduced recently to address materials and fuels issues have produced significant reductions in radiation fields. These include zinc injection to control primary water stress corrosion cracking, noble metal application in BWRs to control intergranular stress corrosion cracking (in conjunction with zinc injection) and ultrasonic fuel cleaning to control crud-induced local flux depression in PWRs. This manual highlights these promising developments. EPRI will update the manual periodically, therefore allowing industry a resource to share knowledge and common experiences.

Keywords

Radiation field control

Source term reduction

Chemistry

ALARA

Surface preconditioning

CONTENTS

1 INTRODUCTION	1-1
Radiation Field Control Technical Initiatives in the Industry RP2020 Strategic Plan	1-1
Radiation Exposure Trends.....	1-1
Radiation Field Control Overview.....	1-5
Economic and Performance Incentives for Implementing a Dose Reduction Program.....	1-6
Worker Health and Safety	1-6
Regulatory Compliance	1-7
Outage and Task Performance	1-7
Litigation	1-8
Decontamination and Shielding.....	1-8
License Extension and Life of Plant Performance	1-9
Radioactive Waste.....	1-9
Summary of Cost Considerations.....	1-10
Program Direction and Focus.....	1-11
Document Objectives	1-12
2 RADIATION FIELDS: ORIGINS, REGULATIONS, AND COUNTERMEASURES.....	2-1
Radiation Basics	2-1
Radiation Properties	2-1
Radiation Dose Measurement and Terminology	2-2
Quantification of Radioactive Materials	2-3
Time, Distance, and Shielding.....	2-3
Radiation Field Measurements in Nuclear Plants: Historical Background	2-5
Origin of Radiation Fields	2-8
Exposure Regulations	2-11
Techniques for Controlling Radiation Fields.....	2-12
Reducing the Source Material	2-13
Controlling Activation and Transport	2-13

Controlling Out-of-Core Deposition	2-14
Decontamination.....	2-15
Available Radiation Field Control Techniques and On-Going EPRI R&D	2-15
Radiation Field Control Strategy	2-16
Radiation Field Control Benefits Derived from Technologies Implemented for Alternate Reasons	2-17
Efficiency Improvement for Existing Techniques.....	2-18
Integrate Radiation Field Control Techniques	2-18
Key Considerations - Radiation Fields: Origins and Countermeasures	2-18
References	2-19
3 COBALT SOURCE REDUCTION	3-1
Introduction	3-1
Limiting Impurity Levels of Cobalt in Structural Alloys.....	3-2
Eliminating In-Core Cobalt Sources	3-4
Eliminating Ex-Core Cobalt Sources	3-5
Turbine Buckets.....	3-5
Jet Pumps.....	3-5
Pumped Forward Heater Drains	3-6
Cobalt Contribution from Valve Maintenance Activities.....	3-6
Debris Description.....	3-6
Target Valves.....	3-7
Foreign Material Exclusion	3-7
Maintenance Activity Preparation	3-7
Post-Maintenance Cleaning	3-8
Inspection	3-8
Alternative Repairs	3-8
Alternatives to Cobalt-Base Hardfacing Alloys.....	3-9
Delcrome 910	3-9
F-20	3-9
NOREM	3-9
Loop Tests of Valves with NOREM Trim	3-11
Compilation and Evaluation of NOREM Test Results: Implications for Valve Applications	3-12
Industry Experience of Valves with NOREM Trim	3-13

Cobalt Reduction in Siemens-Designed PWRs	3-14
Cobalt Reduction in Atomic Energy of Canada CANDU Reactors	3-16
Logic Tree for Implementing a Valve Replacement/Refurbishment Program	3-16
Identification of RCS Contact Valves	3-17
Candidate Valve Identification and Prioritization	3-17
Cobalt Release Estimation	3-17
Evaluation of Various Cobalt Sources in Westinghouse Designed Plants	3-19
Evaluation of Plant Dose Rates	3-19
Evaluation of ⁶⁰ Co Released during Refueling Shutdowns in Ringhals PWRs	3-20
Low Cobalt Tubing Summary and Conclusions	3-23
Key Considerations – Cobalt Source Reduction	3-24
References	3-25
4 PRECONDITIONING SURFACES OF REPLACEMENT COMPONENTS	4-1
Introduction	4-1
Electropolishing Basics	4-1
Electropolished Steam Generator Channel Heads	4-3
Introduction	4-3
Evaluation Techniques	4-5
Results of Evaluations	4-6
Plants that Replaced Steam Generators	4-6
Plants with Electropolished Channel Heads Since Startup	4-9
Electropolished Steam Generator Channel Heads - Summary and Conclusions	4-10
Electropolishing of Reactor Water Cleanup Pump (RWCU) for FENOC's Perry Plant	4-11
Evaluating Alternatives to Electropolishing	4-11
Doel Coupon Experiments	4-12
Performance of SCrP-Treated Components in PWRs	4-14
Recontamination of Manway Seal Plates (Diaphragms)	4-14
Catawba-1 Dose Rates	4-15
Catawba-1 Specific Activity Measurements	4-17
Electropolishing of Temporary Reactor Vessel Cover and Test Plates at TVA's Sequoyah	4-18
Dose Rate Measurements from Other SCrP-Treated Diaphragms	4-21
Performance Data from Other SCrP-Treated Components	4-23

Diablo Canyon Residual Heat Removal (RHR) System Piping	4-24
V C Summer Radiation Monitor Housing.....	4-26
Performance of SCrP-Treated Components in BWRs	4-26
Monticello RWCU Test Piping	4-26
Barsebäck Tubing Tests.....	4-27
Peach Bottom 2 and 3 RWCU Test Piping.....	4-28
Other Applications of SCrP	4-29
Valve internals	4-29
Pump elements.....	4-30
Jet Pumps.....	4-31
Other Surface Modification Opportunities	4-32
Electropolishing of Tubing Components - Zircaloy Fuel Rod Cladding and Alloy 690 SG Tubing	4-32
Key Considerations – Preconditioning Surfaces of Replacement Components.....	4-33
References	4-34
5 PWR PRIMARY COOLANT CHEMISTRY	5-1
Discussion of Chemistry Regimes.....	5-2
Effects of Chemistry Parameters.....	5-4
Corrosion Product Release	5-5
Particulate Transport	5-5
Soluble Transport	5-6
Verification Tests and Plant Experience	5-7
Plant Data.....	5-8
Uncoordinated Versus Coordinated Chemistry Operation.....	5-8
Modified Versus Coordinated Chemistry Operation.....	5-9
Elevated Lithium Versus Coordinated Chemistry Operation.....	5-10
Comparison of Radiation Field Trends as a Function of Coolant Chemistry	5-10
Effects of Startup and Shutdown Chemistry.....	5-11
Shutdown Chemistry Activity Releases.....	5-13
Source Term Control.....	5-15
Recent Events	5-16
Zinc Addition to the Primary Coolant.....	5-16
Zinc Addition History.....	5-16
Relationship of Dose Rate Reduction with Zinc Exposure	5-19

EPRI PRIMARY chemWORKS™ MODULES.....	5-21
Primary System pH Calculator	5-22
Primary System Shutdown Chemistry Calculator.....	5-23
Key Considerations – PWR Primary Coolant Chemistry.....	5-24
References	5-26
6 BWR COOLANT CHEMISTRY	6-1
Introduction	6-1
BWR Coolant Treatment Options.....	6-1
Hydrogen Water Chemistry	6-1
Natural and Depleted Zinc Oxide Addition	6-2
Noble Metals Chemical Addition.....	6-4
Radiation Field Buildup on Out Of Core Surfaces.....	6-4
HWC Effect on ¹⁶ N Radiation Increase in Main Steam Line	6-4
NMCA and the ¹⁶ N Radiation Increase in the Main Steam Line.....	6-6
⁶⁰ Co Transport Processes in the BWR Primary System	6-9
Effects of HWC on ⁶⁰ Co Transport.....	6-12
The Effects of Depleted Zinc Oxide (DZO) Addition.....	6-20
NMCA and Shutdown Dose Rates	6-21
Correlation of Shut Down Dose Rates with Reactor Water ⁶⁰ Co(s)/Zn(s) Ratio.....	6-22
Insoluble ⁶⁰ Co Impact on Shut Down Dose Rates.....	6-23
Summary of NMCA Shutdown Dose Rate Findings	6-24
Control of Iron Input.....	6-24
Basis for Feedwater Iron Control – Activity Transport	6-27
Soluble Transport.....	6-27
Insoluble Transport	6-28
Activity Transport Summary	6-31
Corrosion and Corrosion Product Deposits	6-31
High Iron Levels	6-31
Low Iron Levels	6-32
Plant Design Factors Impacting Iron Control	6-33
Summary on Control of Iron Input.....	6-36
Key Considerations – Recommended Goals for BWR Water Chemistry Optimization	6-36
Final Feedwater Goals	6-36
Reactor Water Goals	6-37

Specific Recommendations for Plants Using NMCA (Developed from recommendations in 2003 NMCA Application Guidelines, BWRVIP-118)	6-39
References	6-41

7 SYSTEM AND COMPONENT DECONTAMINATION.....7-1

Decontamination Processes.....	7-3
CAN-DEREM	7-3
CITROX	7-4
LOMI	7-5
LOMI Compared to Regenerative Organic Acid Processes	7-7
LOMI-2.....	7-8
CORD	7-10
Oxidation Processes	7-12
Alkaline Permanganate (AP)	7-12
Nitric Permanganate (NP)	7-12
Permanganic Acid (HP)	7-13
Cleanup Following Oxidation Step	7-14
Decontamination Corrosion Issues	7-14
CAN-DEREM	7-14
CITROX	7-16
LOMI	7-16
CORD	7-18
BWR Decontamination	7-19
Effects of BWR Hydrogen Water Chemistry (HWC) and Zinc on Decontamination	7-19
Background.....	7-19
Plant Experience.....	7-20
Effects of BWR Noble Metal Chemical Addition	7-21
PWR Decontamination	7-22
Effects of Zinc Addition on Decontamination in PWR Plants.....	7-22
Decontamination Using Hydrolasing and Flushing.....	7-22
Experience with Full System Decontaminations	7-23
Decontamination Wastes	7-25
Current Situation.....	7-25
Mixed Waste Issues	7-26
Key Considerations – System And Component Decontamination	7-26

References	7-27
8 ULTRASONIC FUEL CLEANING	8-1
History and Status	8-1
Ultrasonic Fuel Cleaning for PWRs	8-2
Ultrasonic Fuel Cleaning for BWRs	8-2
Crud Removal Characteristics	8-3
General Description of Fuel Cleaning Equipment	8-3
Technical Issues	8-6
Mitigating AOA	8-6
Shutdown Dose Reduction with Fuel Cleaning	8-7
Fuel Cleaning Efficiency	8-9
PWR Fuel Cleaning Efficiency	8-9
BWR Fuel Cleaning Efficiency	8-12
Waste Considerations	8-14
Crud Capture Media	8-14
Crud Characteristics	8-14
Key Considerations – Ultrasonic Fuel Cleaning	8-16
A EXELON COBALT REDUCTION PROGRAM SUMMARY	A-1
B BROWN’S FERRY UNIT 1 RESTART SOURCE TERM REDUCTION INITIATIVES	B-1
Introduction	B-1
Overview	B-1
Cobalt in Perspective	B-1
What is Cobalt?	B-2
Replacements for Stellite®?	B-2
Where is the Cobalt?	B-2
How Do We Reduce Cobalt?	B-3
Action Plan Status	B-3
Summary	B-4
C SOUTHERN NUCLEAR HWC DIAL DOWN DECISION TOOL	C-1
D SUMMARY OF REFERENCES	D-1
Chapter 2: Radiation Fields: Origins, Regulations, and Countermeasures	D-1

Chapter 3: Cobalt Source Term Reduction	D-1
Chapter 4: Preconditioning Surfaces of Replacement Components	D-1
Chapter 5: PWR Primary Coolant Chemistry	D-2
Chapter 6: BWR Coolant Chemistry.....	D-3
Chapter 7: System and Component Chemical Decontamination	D-3

LIST OF FIGURES

Figure 1-1 Radiation Exposure at U.S. Nuclear Power Plants.....	1-2
Figure 1-2 Comparison of US and International PWR Exposure Data	1-3
Figure 1-3 Comparison of US and International BWR Exposure Data	1-3
Figure 1-4 Radiation Exposure and Power Generation at U.S. Nuclear Power Plants Since 1991	1-4
Figure 1-5 Radiation Exposure at U.S. Nuclear Power Plants with Trend to 2007	1-5
Figure 2-1 Electromagnetic spectrum	2-1
Figure 2-2 Decay of Radiation Field Strength as a Function of Distance	2-4
Figure 2-3 Westinghouse Steam Generator SRMP Location Map	2-5
Figure 2-4 Westinghouse Piping SRMP Location Map	2-6
Figure 2-5 Combustion Engineering SRMP Location Map	2-7
Figure 2-6 BRAC radiation sampling points for typical BWR recirculation piping	2-8
Figure 2-7 Corrosion Products in PWR Primary Circuit Are Activated in Core and Deposited on Out-of-Core Surfaces	2-9
Figure 2-8 BWR Contamination Results from Activation of Corrosion Products in the Feedwater	2-10
Figure 2-9 Schematic Diagram of Deposition on Out-of-Core Surfaces	2-10
Figure 2-10 Crud Growth Model for BWRs	2-11
Figure 2-11 Techniques to Control Radiation Fields.....	2-13
Figure 3-1 Stellite Valve Seat Damage	3-1
Figure 3-2 Typical Jet Pump Beam.....	3-6
Figure 3-3 Schematic for Implementing a Cobalt Reduction Program for Nuclear Plant Valves	3-18
Figure 3-4 ⁶⁰ Co Released during Refueling Shutdowns in the Ringhals PWRs.....	3-22
Figure 4-1 Comparison of “As-Received” and Electropolished Surfaces (28" elbow).....	4-2
Figure 4-2 Average SG Channel Head Dose Rate in the Ringhals 2 Plant	4-5
Figure 4-3 Buildup Reduction Factors for Chromium-Coated Coupons Exposed at the Doel 2 PWR	4-13
Figure 4-4 Dose Rate Comparison of Catawba-1 Diaphragms (I-690T) Before and After Stabilized Chromium Pretreatment	4-17
Figure 4-5 Co-58 Dose Rate and Activity, SG Cold Legs at Catawba-1	4-18
Figure 4-6 Coupon Contamination Levels – Mechanical Polish	4-19
Figure 4-7 TRVC Coupon Contamination Levels – Electropolished	4-20

Figure 4-8 TRVC Coupon Contamination Levels – Electropolished and Preoxidized	4-20
Figure 4-9 TRVC Coupon Contamination Levels – SCrP Treatment.....	4-21
Figure 4-10 Dose Rate Buildup of Monticello RWCU Piping After Treatment with SCrP	4-27
Figure 4-11 Dose Rate Buildup for Barsebäck Tubing Tests.....	4-28
Figure 4-12 Valve Body Following Application of SCrP	4-30
Figure 4-13 RWCU Pump Casing following Application of SCrP	4-31
Figure 4-14 Jet Pump Following Application of SCrP	4-32
Figure 5-1 Schematic of the Problems with Optimizing RCS pH Control.....	5-2
Figure 5-2 Schematic of Coordinated Chemistry at pH _T 7.1 Consistent with Lithium Below 3.5 ppm (at 300°C)	5-4
Figure 5-3 Variation with pH of Average Activities of Co-60 and Co-58 on Steam Generator Tubing at the End of MIT in-Pile Loop Tests.....	5-8
Figure 5-4 Steam Generator Channel Head Dose Rates (Comparison of Trends of Plants in Group 3 - Plant Startup after 1981) Data for Four Plants are Shown as Three-Year Moving Mean	5-11
Figure 5-5 Relationship of Dose Rate Reduction and Cumulative Zinc Exposure.....	5-21
Figure 5-6 Boron-Lithium Control Band Chart	5-22
Figure 5-7 SMART ChemWorks Displays Real-Time Boron, Lithium, and pH(t) Data on Plant Specific Boron-Lithium Control Charts.....	5-23
Figure 5-8 Example of an Output Chart from the Primary Shutdown Chemistry Calculator	5-24
Figure 6-1 Laboratory Results Showing the Uptake of ⁶⁰ Co by Type 304 Stainless Steel Under NWC, HWC, NWC + Zn, HWC + Zn and NMCA Treated Type 304 Under HWC +Zn Conditions (4-22).....	6-3
Figure 6-2 Main Steam Line Radiation Monitor Activity Increase as a Function of Feedwater Hydrogen Concentration	6-5
Figure 6-3 Main Steam Line Radiation Response at Duane Arnold Before and After NMCA.....	6-7
Figure 6-4 EC P Response of NMCA Treated Plants at Low Hydrogen Addition Levels.....	6-8
Figure 6-5 Main Steam Line Radiation Monitor Response at Peach Bottom 2 in First Post NMCA Fuel Cycle	6-8
Figure 6-6 Schematic Diagram of ⁶⁰ Co Isotope Creation, Transport and Deposition.....	6-11
Figure 6-7 Correlation Between Soluble ⁶⁰ Co Concentration in Reactor Water and Recirculation Pipe Dose Rates	6-12
Figure 6-8 Potential Source of HWC-Related ⁶⁰ Co	6-13
Figure 6-9 A schematic cross sectional view of the corrosion film growing on a stainless steel surface in BWR reactor water.....	6-14
Figure 6-10 Laboratory Tests Showing the Effect of Switching from NWC Oxidizing Conditions (200 ppb O ₂ + 25 ppm H ₂) to HWC Reducing Conditions (<1 ppb O ₂ + 150 ppm H ₂) on the ⁶⁰ Co Uptake on Type 304 and 316 Stainless Steel.....	6-15
Figure 6-11 Schematic Representation of ⁶⁰ Co Incorporation into Corrosion Film under NWC Conditions.....	6-16

Figure 6-12 Schematic Representation of ⁶⁰ Co Incorporation into Corrosion Film under HWC Conditions.....	6-16
Figure 6-13 Schematic of ⁶⁰ Co Incorporation in Corrosion Film Under HWC Plus Zinc Conditions	6-17
Figure 6-14 Summary of Range of Vessel ECP Measurement Made Under NWC, HWC and NMCA plus Low Hydrogen Conditions.....	6-18
Figure 6-15 Schematic of ⁶⁰ Co Incorporation into the Corrosion Film under NMCA plus Low Hydrogen plus Zinc Conditions.....	6-18
Figure 6-16 Pre and Post NMCA ⁶⁰ Co Behavior at Duane Arnold (Note that there have been two NMCA applications at Duane Arnold)	6-22
Figure 6-17 Comparison of measured BRAC dose rates versus cycle median ratio of RW ⁶⁰ Co (s)/RW Zn(s) for 1st post NMCA cycle BWRs. (Data available as of April 30,2003)	6-23
Figure 6-18 Reactor Water Zn/Feedwater Zn Ratio for Low Feedwater Iron Plants on HWC or HWC/NMCA with DZO Injection	6-26
Figure 6-19 2003 Average Feedwater Total Iron	6-26
Figure 6-20 Data Excluding Highest Dose Rate Plant Showing Effect of Low FW Iron (<1 ppb) (Data Available as of 6/30/04).....	6-28
Figure 6-21 BHD Dose Rates vs. Insoluble ⁶⁰ Co.....	6-29
Figure 6-22 Brunswick 1 Reactor Water Insoluble ⁶⁰ Co vs. Feedwater Iron	6-30
Figure 6-23 Brunswick 1 BRAC Results	6-30
Figure 7-1 Typical Portable Hydrolasing Unit	7-23
Figure 8-1 Schematic of EPRI's ultrasonic fuel cleaning system.....	8-5
Figure 8-2 South Texas Ultrasonic Fuel Cleaning Equipment	8-5
Figure 8-3 STP Transducer Basket Insertion into Reflector Housing	8-6
Figure 8-4 Callaway CVCS Heat Exchanger Pre- and Post-Cleaning Dose Rate Trends.....	8-8
Figure 8-5 Callaway Steam Generator Channel Head Pre- and Post-Cleaning Dose Rates	8-8
Figure 8-6 Time Required for Ultrasonic Fuel Cleaning STP2 Data	8-10
Figure 8-7 Callaway - Cleaning Efficiency Based on Isotopics.....	8-11
Figure 8-8 Callaway - Cleaning Efficiency Based on Mass Removal	8-12
Figure 8-9 DAEC Fuel Cross-Section Showing Crud and Areas of Delamination	8-13
Figure 8-10 Quad Cities Assembly YJA 230, Before and After Ultrasonic Cleaning. Second Span, Between First and Second Spacers.	8-14
Figure 8-11 Activity increase on Fuel Cleaning Crud Capture Filters – STP2	8-15

LIST OF TABLES

Table 1-1 Radiation Field Incurred Cost Factors	1-10
Table 1-2 Radiation Field Avoided Cost Elements	1-11
Table 2-1 Half Value and Tenth Value Layers for Co and Cs.....	2-4
Table 2-2 Radiation-Field Reduction Techniques Available (A) and Under Development (UD) in 2004.....	2-16
Table 2-3 Related EPRI Radiation Exposure Control Research and Reports	2-16
Table 3-1 Seat Leakage of Gate Valves with NOREM HF – EdF Test Results.....	3-12
Table 3-2 Stellite Surface Areas in Siemens PWRs (m ²).....	3-15
Table 3-3 Approximate Effect of Various Cobalt Sources on Plant Dose Rates.....	3-20
Table 3-4 Amounts of ⁶⁰ Co Released (Curies) During Refueling Shutdowns in the Ringhals PWRs	3-21
Table 3-5 Average and Normalized ⁶⁰ Co Activities (Curies) Released by Categories	3-23
Table 4-1 Replacement or Original Steam Generators Electropolished by Fin-Tech, Inc.	4-4
Table 4-2 Approximate Effect of Various Source Reduction Techniques on Plant Dose Rates	4-7
Table 4-3 Summary of Certain SG Channel Head Center and Tubesheet Average Dose Rates (R/h) and Ratios in Plants Before and After SGR and a no-SGR Plant.....	4-7
Table 4-4 Normalized After/Before SGR Ratio to Estimate Electropolishing Effect.....	4-8
Table 4-5 Plants Treating SG Manway Seal Plates Using SCrP	4-15
Table 4-6 Average Dose Rates of I-690T Manway Diaphragms at Catawba-1	4-16
Table 4-7 Performance of PWR Manway Diaphragms Following Application of SCrP	4-23
Table 4-8 Other SCrP Applications.....	4-24
Table 4-9 Activity Buildup on RHR System Test Spools at Diablo Canyon 2 (After Restart)	4-25
Table 4-10 Activity Buildup on RHR System Test Spools at Diablo Canyon 2 (After Exposure for Two Fuel Cycles)	4-25
Table 4-11 Activity Buildup on RHR System Test Spools at Diablo Canyon 2 (After Exposure for Three Fuel Cycles)	4-26
Table 5-1 Summary of Plants Implementation Parameters for PWR Plants Operating with Zinc Addition	5-18
Table 5-2 Zinc Exposure and Shutdown Dose Rate Reduction.....	5-20
Table 6-1 General Principles for Iron Control at Low Levels (Below 0.5 ppb)	6-31
Table 6-2 Types of Condensate Polishing Systems for US and Swedish BWRs	6-35

Table 6-3 Summary of Recommended Goals for Final Feedwater.....	6-37
Table 6-4 Summary of Recommended Goals for Reactor Water	6-38
Table 7-1 US BWR plants under HWC using chemical decontamination since 1994.....	7-2
Table 7-2 The CAN-DEREM Concept	7-4
Table 7-3 The LOMI Concept	7-6
Table 7-4 Typical Process Conditions for LOMI Decontaminations.....	7-7
Table 7-5 The CORD/UV Concept.....	7-11
Table 7-6 Summary of oxidation steps used for decontamination	7-13
Table 7-7 Summary of Materials Compatibility Data for the CORD Process.....	7-19
Table 8-1 Refueling Outage Worker Dose Trend, Callaway.....	8-9
Table 8-2 Measurements Required for Waste Characterization.....	8-16
Table 8-3 Most Prevalent Isotopic Composition of Fuel Crud, STP2.....	8-16

1

INTRODUCTION

Radiation Field Control Technical Initiatives in the Industry RP2020 Strategic Plan

A long term initiative currently being undertaken jointly by the industry with direct support from NEI, INPO, and EPRI is to develop a strategic plan (RP2020) to promote positive trends in radiation protection (RP) events. The focus of the strategic planning effort is to “reshape radiological protection at nuclear power plants to continue a positive trend of performance and significantly reduce costs.” A strong focus of the R&D portion of the RP2020 plan is related to technical radiation field control initiatives.

One of the most fundamental and critical program elements is the need to communicate the current state of radiation field control technology and related industry experience to the appropriate plant staff. Senior management, Chemistry, Radiation Protection, Operations, Engineering, and Reactor Fuels staff members need to understand the available processes and their impact on plant radiation fields. More importantly, it is necessary that a station researches, understands, and effectively communicates the impact that the implementation of one or more individual processes can have on overall radiation field controls – prior to implementation. This Radiation Field Control Manual is designed to be part of this communication strategy.

The RP2020 effort also identified the strong need to “fill in the gaps” with new technologies for field reduction. Technology advancements related to surface modification and decontamination are in development, and existing techniques are often demonstrated on new components. International utilities are demonstrating reductions in collective exposures because of the implementation of new cobalt-free alloys. As part of the RP2020 plan, priority for field reduction technical research and implementation has been acknowledged. New technologies, high duty cores and a host of related technological advancements will be evaluated. Additionally, ongoing projects sponsored by EPRI in areas such as remote monitoring technology, component surface modification, and primary chemistry control continue to identify and support implementation of advanced exposure management options.

Radiation Exposure Trends

Electric utility efforts to reduce worker exposure focus on four primary areas: [1] reducing maintenance requirements by controlling corrosion-related damage, [2] minimizing radiation field task time (e.g., using remote monitoring and robotics), [3] worker awareness and ownership, and [4] radiation field reduction.

Introduction

As a direct result of these successful efforts, occupational exposures have shown a decreasing trend since the early 1980s (Figure 1-1), and the rate of decline has continued through the present.

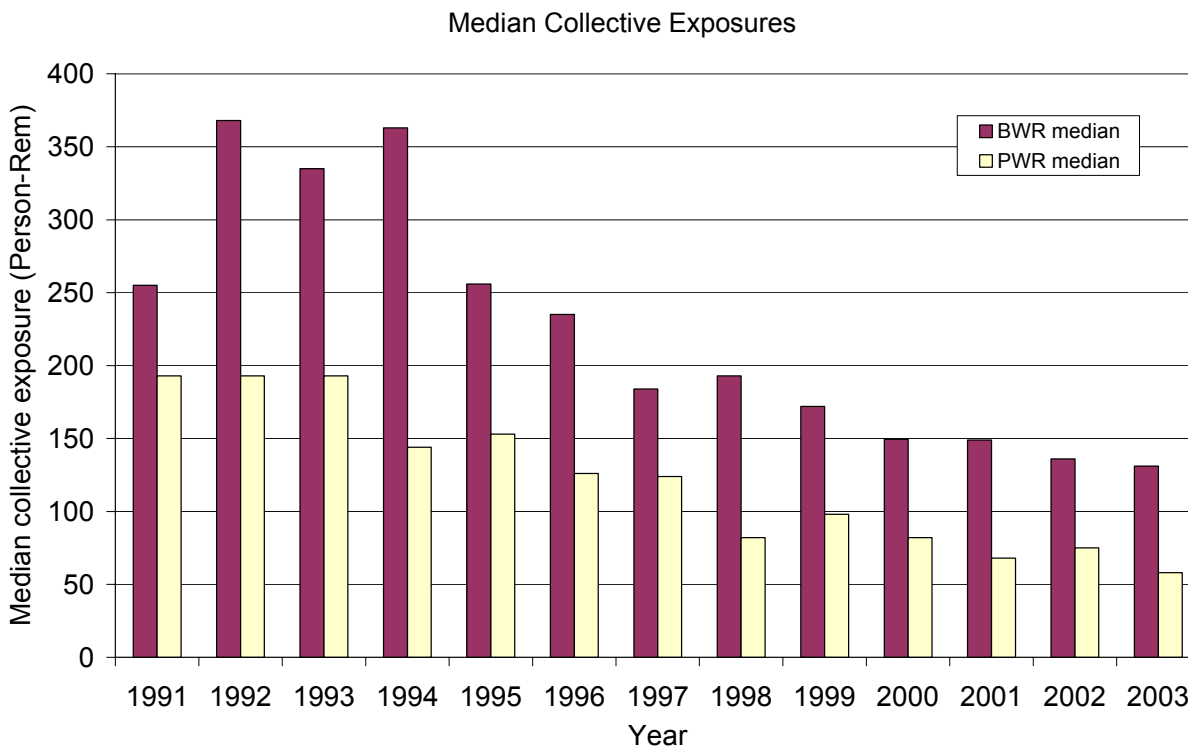


Figure 1-1
Radiation Exposure at U.S. Nuclear Power Plants

The annual electric generation from U.S. nuclear plants has increased nearly every year, with the current electrical output increasing 19% since 1991. Figure 1-2 and Figure 1-3 show broadly similar trends internationally. The radiation exposure as a function of power generation at U.S. nuclear power plants has decreased every year since 1991, with a 64% decrease between 1991 and 2002, but increased in 2003 as a result of repair/replacement work at a few plants. This resulted in an increase in total collective exposure and a slight reduction in power generation (Figure 1-4).

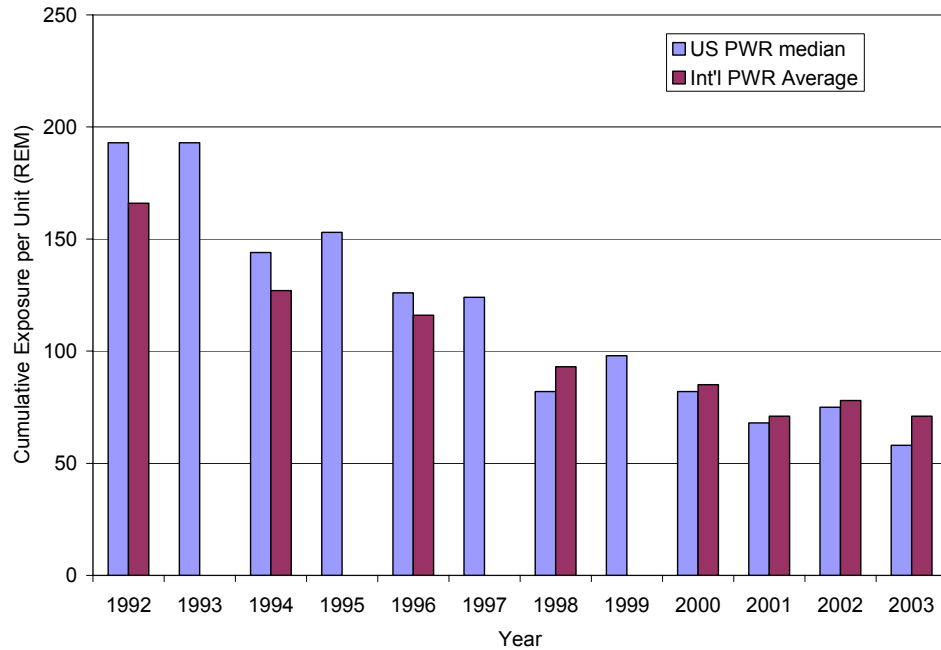


Figure 1-2
Comparison of US and International PWR Exposure Data

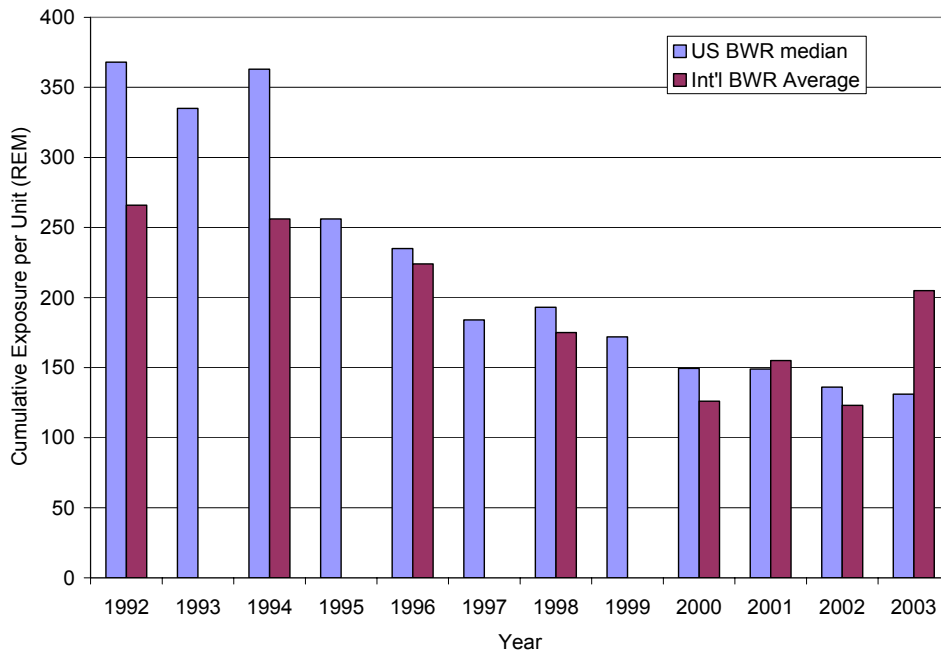


Figure 1-3
Comparison of US and International BWR Exposure Data

Introduction

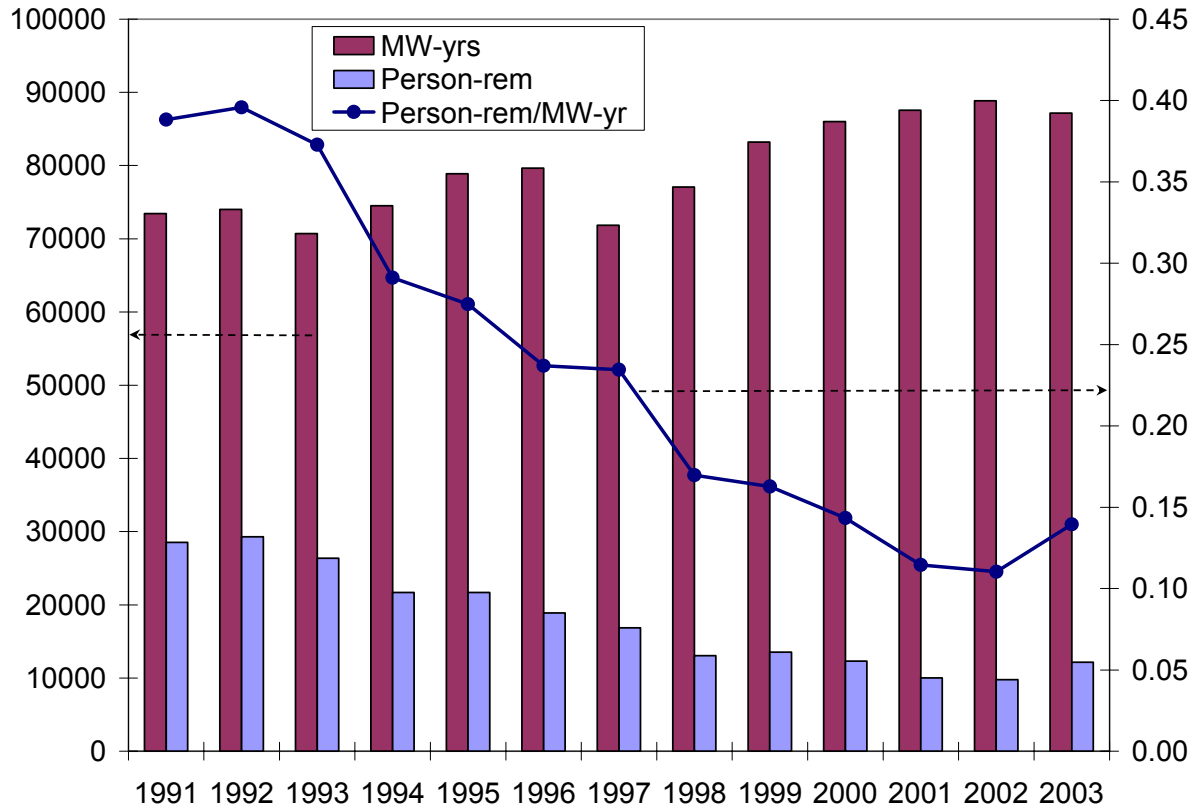


Figure 1-4
Radiation Exposure and Power Generation at U.S. Nuclear Power Plants Since 1991

Although the industry performance trends are positive, challenges remain including aging plants with material wear and replacement issues, increased power output, shorter outages, and the appropriate technology and experience transfer to new employees related to the increase in average workforce age. Additionally, utilities are currently challenged by the industry's (INPO governance) administrative exposure goal of 2 Rem per individual per calendar year and the 2005 cumulative exposure per unit goals of 65 Rem (PWR) and 120 Rem (BWR). Figure 1-5 captures PWR and BWR projections through 2007 based on the current U.S. performance and its associated rate of improvement.

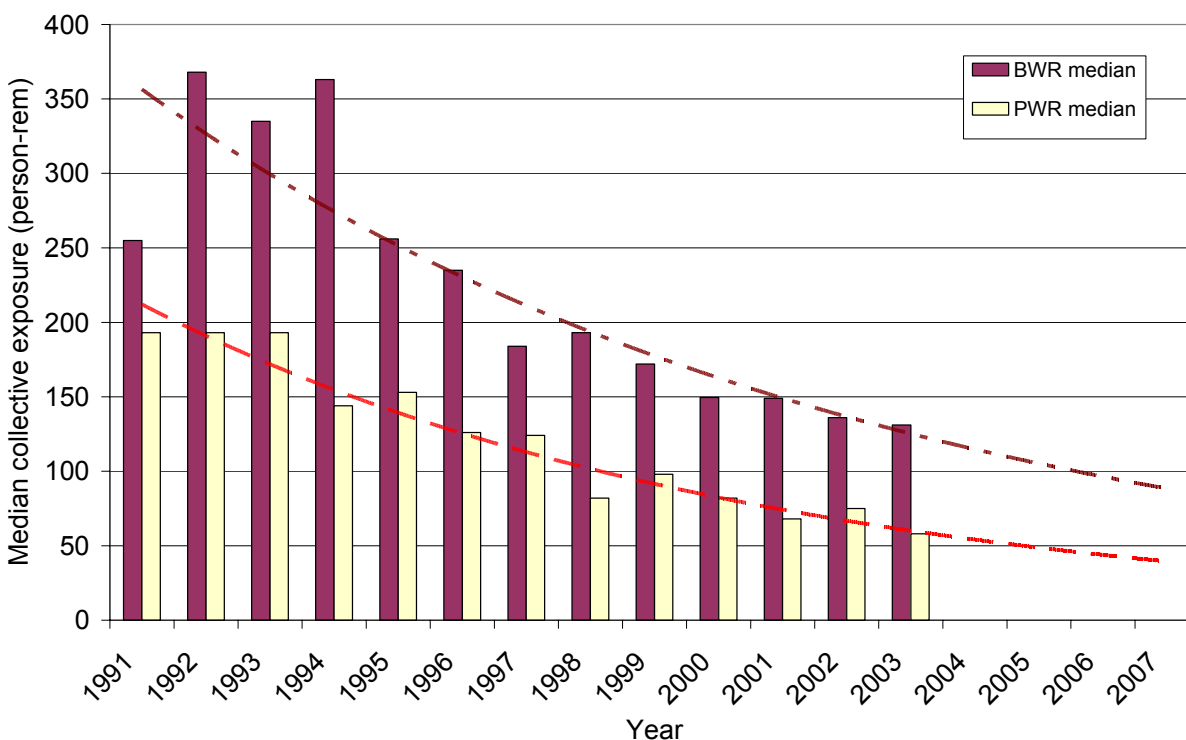


Figure 1-5
Radiation Exposure at U.S. Nuclear Power Plants with Trend to 2007

Further, as a result of international acceptance of the ICRP 2 Rem per individual per calendar year limit, which is averaged over 5 years, the USNRC is evaluating a revision to regulatory limits to reflect that value. In support of these challenges, EPRI continues to investigate and promote radiation field control technologies to identify cost effective tools and strategies for continued industry exposure reduction.

Radiation Field Control Overview

The success of exposure reduction actions is directly impacted by plant radiation field intensity, which is directly impacted by research and implementation of advanced radiation field control technologies. ^{60}Co is typically the primary source of radioactivity in BWR plants, and ^{58}Co is the primary source PWR plants because of the activation of ^{58}Ni . Cost-effective actions can be taken to avoid the presence of ^{59}Co (the precursor to ^{60}Co) or to ensure that released ^{59}Co is not allowed to migrate to the reactor core for activation. In those reactor designs where cobalt sources have been minimized (e.g., the Swedish BWRs and the Siemens Konvoi PWRs), dose rates and personnel exposure are very low. Several key examples of proven radiation field reduction techniques include:

- non-cobalt hardfacing alloy as valve trim
- low-cobalt Inconel 690 tubing for replacement steam generators
- low-cobalt 304 stainless steel (SS) for in-core components and replacement piping in BWRs

Introduction

- improved chemistry control during operation and implementation of improved startup and shutdown chemistry control programs
- zinc injection for PWRs
- improvements to hydrogen water chemistry (HWC), zinc injection, and Noble Metals Chemical Application (NMCA) for BWRs
- improvements in the use of chemical decontamination techniques for sub-system and full system applications
- ultrasonic fuel cleaning for fuel crud removal for PWRs and BWRs
- electropolishing and stabilized chromium coatings to precondition replacement components

Implementation of these techniques should involve consideration of materials and fuel performance issues.

Economic and Performance Incentives for Implementing a Dose Reduction Program

To optimize a site radiation field control program, utility management must maintain a vision that balances various perspectives. The vision of an effective program should include the following perspectives: Customer (public), Employee Safety (long term health effects related to personnel exposure), Financial (profitability, insurance, and investor risk), Innovation and Learning (technology), and Internal Business (O&M, capital).

There are significant regulatory, economic, and personnel-related incentives for reducing radiation fields and, as a result, collective exposure. Two of the most significant financial benefits are related to improved capacity factor and worker efficiency. Additionally, establishing and maintaining processes and controls that result in low plant radiation fields will reduce the economic impact of future regulatory and administrative reductions to individual exposure limits and improve gap analyses related to INPO points. Many utilities have developed monetary incentive programs for the station staff that are based on INPO and/or regulatory exposure performance.

The following sections contain a brief overview of how a dose reduction program impacts both business and operational performance.

Worker Health and Safety

Radiation exposure and occupational dose limits are technical, personal health (medical) issues. Although scientific controversy exists about the effects of radiation and whether a threshold exists below which incurred radiation has no effect, the radiation level to which plant personnel are exposed is a constant source of concern and oversight. Optimizing radiation field control programs can assist a plant with creating a work environment that facilitates reductions to, and leveling of, personnel exposure. Lower radiation fields will allow work to be performed more

efficiently and will not require the “best” workers to repeatedly perform high exposure tasks due to stay time constraints.

Regulatory Compliance

Since the 1990’s, there has been heightened industry interest in reducing the annual cumulative exposure at both the individual person and plant levels. This issue was addressed by the Nuclear Regulatory Commission (NRC) in the 10CFR20—Standards for Protection Against Radiation. The standards are summarized by the ALARA definition, found in NRC 10CFR20.1003—Definitions.

“ALARA (acronym for "as low as is reasonably achievable") means making every reasonable effort to maintain exposures to radiation as far below the dose limits in this part as is practical consistent with the purpose for which the licensed activity is undertaken, taking into account the state of technology, the economics of improvements in relation to state of technology, the economics of improvements in relation to benefits to the public health and safety, and other societal and socioeconomic considerations, and in relation to utilization of nuclear energy and licensed materials in the public interest.”

This definition specifically recognizes the importance of economic considerations when addressing the concept of ALARA and is consistent with the concerns faced by utilities. A specific economic incentive for developing and maintaining a successful radiation field control and ALARA program is the mitigation of the potential for regulatory compliance enforcement actions. Personnel overexposure, off-standard liquid effluent activity, and controlling access to high radiation areas all present challenges related to their management and the potential for regulatory financial judgments. Eliminating or reducing the activity available to create undesirable conditions will reduce the financial regulatory risk.

Historically, ALARA program optimization has been supported by several key industry organizations including the NRC, INPO, EPRI, the World Association of Nuclear Operators (WANO), and American Nuclear Insurers (ANI). The adequacy of individual exposure reduction programs and the identification of opportunities for improvement are addressed by those organizations during nuclear facility inspections and evaluations. The magnitude of cobalt contribution to plant occupational exposure, and the NRC’s ALARA mandate to reduce such exposure wherever it is deemed technically and economically practical, emphasizes the importance of developing and implementing a formal radiation field reduction program.

Outage and Task Performance

Scheduling and performing outage work at nuclear power plants is a complex task. Most recently outage schedule compression initiatives have further complicated, and made more significant, the impact of outage work efficiency. A large number of outage tasks require access near plant systems and areas that contain radioactivity, which results in exposure to plant personnel. ⁶⁰Co is typically the primary source of radioactivity in BWR plants and ⁵⁸Co is the primary source PWR plants. Cost-effective actions can be taken to avoid the use of ⁵⁹Co (the precursor to ⁶⁰Co) or to ensure that released ⁵⁹Co is not allowed to migrate to the reactor core where it can become

Introduction

activated. In those reactor designs where cobalt sources have been minimized (i.e., the Swedish BWRs and the Siemens Konvoi PWRs), dose rates and personnel exposure are very low. Repair and replacement of components during plant outages provide utilities with an ongoing opportunity to reduce the ^{59}Co inventory.

The presence of radioactivity complicates the planning and performance of outage activities. Outage planners must consider the existence and expected magnitude of radiation fields during any required activity. Considerations that impact outage duration, quality, and cost include [1] the selection of the most qualified individuals, which reduces their availability for more significant tasks, [2] design, installation, and removal of temporary shielding, [3] high radiation area worker stay time limits, [4] the resources required to develop and perform heightened training exercises including increased usage of expensive mock-ups, [5] development of remote tools, [6] increased manpower requirements, [7] use of personnel protective equipment (PPE) that restricts worker productivity, [8] increased regulatory and quality assurance oversight, and [9] increased radwaste processing and disposal costs. These considerations reduce the flexibility of outage schedule compression and staff deployment, and increase the time and costs.

Litigation

There is a potential indirect impact on nuclear liability premium from claims activity. The costs associated with defending nuclear liability claims are factored into the overall premium on an actuarial basis. As the average age of the industry workforce increases, there is a growing worker consciousness of long term radiation health related issues. There is also global risk management experience that suggests that achieving compliance with applicable regulations does not always offer protection from claims alleging bodily injury caused by the nuclear energy hazard. Proactive management of radiological fields serves to strengthen a plant's ability to demonstrate that reasonable actions have been taken to protect both workers and the general public.

The term that describes this concept is *risk minimization*. In brief, risk minimization uses proactive, contemporary, systematic risk minimization principles that are not necessarily regulatory driven to address the control of radioactive materials that may present risk from plant systems, structures or property. Risk minimization also considers the plant staff's and public's perception of risk, which often is more significant than the scientific basis for the risk as determined by measurement and computational methodologies used today. For example; it is known that a curie of cobalt-60 presents a markedly more significant biological impact than does a curie of tritium. Many people, however, do not differentiate between these isotopes with regard to the level of concern and perception of harm caused by different radioactive constituents at nuclear facilities.

Decontamination and Shielding

Decontamination – The use of decontamination processes impacts radiation field control programs in several ways. Using in-situ processes will reduce the source term and radiation fields and is a proven element of many station's radiation field control program. However, the recurring financial burden associated with decontamination processes may render that option less

than cost effective. Also, as noticed by Quad Cities experiences, the exposed surfaces may recontaminate quickly. In most instances, immunizing the need for decontamination by controlling activity generation at the source should result in a more cost-effective, long term solution.

Shielding – Shielding requirements are directly proportional to the radiation field. There are many cost factors related to both temporary and permanent installations including:

- Design and planning
- Fabrication
- Staging and installation
- Removal
- Decontamination
- Access restrictions to work area
- Equipment interface
- Component or structure reinforcement to facilitate load bearing requirements

Reducing radiation field intensity using source reduction controls will result in a direct reduction of shielding related costs.

License Extension and Life of Plant Performance

As noted earlier, the majority of utilities have aggressively pursued reductions in individual and cumulative exposures. Most of the nuclear plants in the United States complete their original licensed life in the decade between 2005 and 2015. Considerable work on license extension is in progress, and it is already evident that there are significant economic incentives for exposure control related to that effort. Consider that additional inspections and some component replacement is required in order to extend existing plant licenses, and they will be required periodically over the extended life of the unit. In these scenarios, lower radiation fields will provide a more efficient work environment and reduce the impact of corrosion products on waste disposition; these factors can produce significant economic benefits.

Radioactive Waste

The future of low-level waste burial in the United States remains uncertain; as of mid 2004 the Barnwell disposal site is expected to restrict access in 2008, and some plants have already begun on-site storage of all, or at a minimum their Class B & C, wastes. Waste handling, transport, volume reduction, and disposal costs continue to increase and historically are dependent not only upon the volume of material to be buried but also the radioactivity content. Reducing the concentration of radioactivity that is available for deposition on or entrapment in removed components or that is deposited on liquid system cleanup resins and filters is highly desirable. Although component and system decontamination methods exist to reduce the radiation levels to levels acceptable by individual LLW repositories, the cost of such activities can significantly

Introduction

increase the O&M cost burden and does not reduce the volume of radioactive waste requiring disposal (and in fact can increase the volume related to generated media and consumables).

The preferred approaches are to reduce the amount of radioactive material created and to minimize deposition on or in nuclear plant components. Control of the amount of cobalt and corrosion products that are available for activation is a critical strategy for limiting recurring LLW disposal costs. As stated previously, radioactive waste shipments represent an insurance liability exposure to the general population and property while in transit. That liability exposure is proportional to the volume, activity and distance shipped. ANI currently uses activity (curies) shipped for evaluating waste disposition impact on a station's ERF, therefore it follows that reductions in waste activity should result in direct reductions to liability premiums.

Summary of Cost Considerations

Table 1-1 and Table 1-2 capture the fundamental cost factors that should be included in analyses of radiation field technology or strategy revisions. Numerous other site or application specific factors may exist and should be included as appropriate. Note that several factors (i.e., decontamination) may be presented as both avoided and incurred costs.

Table 1-1
Radiation Field Incurred Cost Factors

<i>Incurred Cost Elements</i>	<i>Key Considerations</i>
Cost to implement alternate radiation field controls	Benchmarking and validation, design, planning, equipment, material, fabrication, installation, testing, staff resources, contracted services, routine maintenance, operation and analysis, consumables, generated waste
Decontamination	In-situ system or component decontamination to reduce source term.

Table 1-2
Radiation Field Avoided Cost Elements

Avoided Cost Elements	Key Considerations
Worker health and safety	Quality of life, efficiency, future litigation, staff morale
Regulatory action	Enforcement penalties, personnel exposure, high radiation area access control, liquid effluent activity, increased oversight – frequency and level of detail
Task performance	Efficiency, quality, crew rotation frequency, shielding interference
Litigation	Risk minimization through defensible programs
Insurance premium	Liquid effluent ERF, risk minimization, reduced liability
Decontamination	In-situ system or component decontamination to reduce source term, elimination of need for decontamination using alternate source term controls
Shielding	Temporary or permanent installations, work access restriction, design, fabrication, planning, staging, installation, removal, and decontamination
License extension	Additional inspection requirements, component replacement, longer period of plant operation and maintenance
Radioactive waste	Volume due to activity buildup and/or corrosion degradation necessitating replacement, hot spot flush slurry processing, spent media activity levels and related shipping, volume reduction and disposal costs
Exposure “cost”	Utility/site cost per person-Rem

Program Direction and Focus

The most successful programs are supported by significant senior management to provide focus and direction related to the desired program endpoint. Middle and lower tier managers require educated, clear, and achievable direction related to program expectations and the resources to attain those expectations.

In order to understand the unique challenges related to all aspects of radiation field control management, it is strongly recommended that all managers review this document completely.

The document is intended for use by both senior and line managers, with particular emphasis on the Chemistry, RP, Operations, Engineering, and Fuels and Material Management disciplines. Each section of the report addresses the recommended owners for specific program attributes. One recommended approach for document application that has been successfully used for similar products is outlined in the following steps.

1. Define the impacted utility organizations at both the site and corporate level using the recommended process owners contained in the document.
2. Distribute the document to those organizations for review.

Introduction

3. Assemble a multi-discipline utility focus group from the reviewing organizations to assess all options and identify opportunities. The most successful stations use this critical step to ensure interdisciplinary issues are identified, discussed in detail, and resolved in an efficient manner.
4. Construct a project configuration and implementation plan that includes actions, priorities, and goals.
5. Select three or four “primary” indicators to track at the management level to ensure the program’s status is clearly communicated and that the team remains focused on success. Additional “secondary indicators” can be tracked at a lower level.

Document Objectives

The primary purpose of this document is to provide a description of the technologies used to prevent or alleviate radiation fields in both PWRs and BWRs, and provide references for more detailed investigation of individual technologies. The emphasis is on proven, available technology, with some discussion of EPRI research and development. Specifically, it is intended to provide plant radiation source mitigation information, and is not intended for identifying mechanisms for reducing individual worker’s exposure. For example, it does address cobalt reduction and fuel cleaning, but does not address the use of temporary shielding, specialized tooling, or remote monitoring technology. Those program aspects are addressed in other available EPRI and industry documents.

This document also references the latest versions the EPRI PWR and BWR Water Chemistry guidelines; it does not completely replicate the spectrum or level of detail found in those documents.

The technical and reference information provides a ready resource that can be used for educating future generations of process owners. This supports industry succession planning, off-setting the loss of experienced staff members and their undocumented in-depth process knowledge.

2

RADIATION FIELDS: ORIGINS, REGULATIONS, AND COUNTERMEASURES

Radiation Basics

This section discusses briefly the properties of radiation, radiation exposure dose measurement and terminology, and the quantification of radioactive materials. More information is available from a variety of radiation protection reference documents and professional organizations.

Radiation Properties

Radiation is energy that travels in waves, and yet also exhibits properties of particles. The physical definition of radiation by analogy to observable phenomena is not possible. Although scientists cannot define exactly what radiation is; its properties and behavior have been studied extensively. The properties of radiation are determined by its energy, which is directly related to its frequency and inversely related to its wavelength. All radiation energies and wavelengths are found on the electromagnetic spectrum, shown below in Figure 2-1.

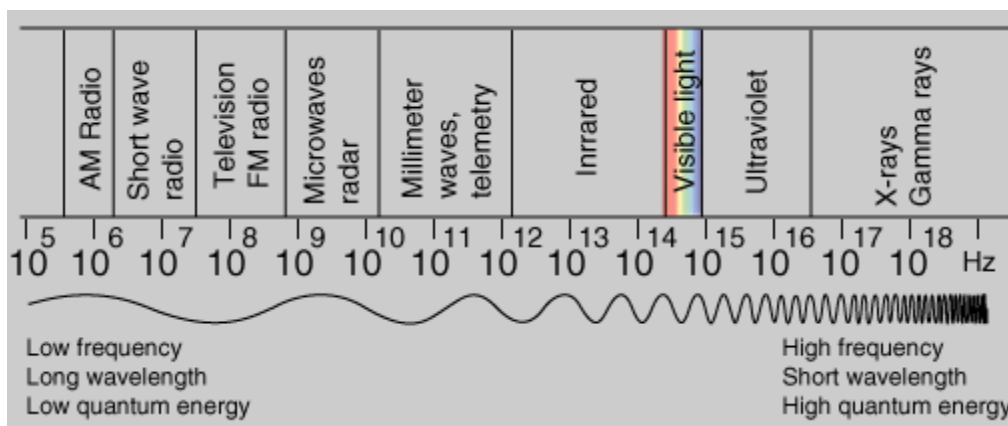


Figure 2-1
Electromagnetic spectrum

Radiation may be classified into non-ionizing and ionizing radiation. Ionizing radiation may remove electrons from atoms, which may cause chemical reactions that lead to cell mutations and health concerns such as cancer. The radiation of concern is in the X-ray and gamma ray wavelengths, radiation from ultraviolet and larger wavelengths are non-ionizing.

Typically, ionizing radiation is classified into two categories (although there are many forms): particle radiation and electromagnetic radiation. Particle radiation typically refers to alpha and beta particles, while electromagnetic radiation refers to X-ray and gamma radiation. Note that although alpha and beta radiation are defined as particles, they still exhibit wave properties.

Alpha particles are essentially stripped helium nuclei, i.e. two protons and two neutrons. They are very short range particles and are easily shielded; they cannot penetrate human skin or paper. However, they can be ingested, inhaled or introduced through open wounds. Examples of alpha emitting nuclides are radium, radon, uranium, and thorium.

Beta particles are either electrons or positrons (positive electrons). They are short range particles that may penetrate several feet of air or human skin, and may cause skin damage if high levels are left on the skin for extended periods of time. Some pure beta emitters include strontium-90, carbon-14, and tritium.

Gamma radiation is electromagnetic energy. It has high energy and very long range penetration properties. It passes through tissue, clothing and air with little energy loss; dense materials such as lead or tungsten are required to shield it effectively. Some gamma emitting nuclides include iodine-131, cesium-137, cobalt-60, and radium-226.

Neutron radiation results from electrically neutral particles whose mass is roughly the same as a proton. It interacts with matter over an extremely short range and can be effectively shielded using dense materials such as concrete, steel, or water. Neutron exposure is reactor power dependent and is therefore not addressed as a radiation field control technique. However, in the context of this manual it is most significant in its role in interacting with and activating formerly non-radioactive materials such as the conversion of cobalt-59 to cobalt-60.

Radiation Dose Measurement and Terminology

In United States power plants, *radiation absorbed dose*, *dose equivalent*, and *exposure* are measured and stated in rad, rem, and Roentgen (R). The units represent the amount of energy absorbed per gram of material. The familiar SI prefixes are used to denote smaller values; milli- (abbreviated m) for $1/1000^{\text{th}}$, micro (abbreviated μ) for $1/1,000,000$. International plants use the SI radiation units, gray (Gy) for absorbed dose, and sieverts (Sv) for equivalent dose. The conversions between SI and US units are:

$$\begin{aligned}1 \text{ gray (Gy)} &= 100 \text{ rad} \\1 \text{ Sv} &= 100 \text{ rem} \\1 \text{ rad} &= 0.01 \text{ Gy} = 10 \text{ mGy} \\1 \text{ rem} &= 0.01 \text{ Sv} = 10 \text{ mSv}\end{aligned}$$

Exposure (dose) is classified as external radiation exposure and internal radiation exposure. External dose is acquired when the whole body or extremity is inserted into a radiation field. Internal dose occurs when the radiation emitter is ingested, inhaled, or incorporated into the skin. The most commonly used personnel exposure or exposure rate units used in the U.S. are fractions of a Rem and Rem/hr (fraction of Sv and Sv/hr).

Radiation counting systems count the disintegrations per minute, abbreviated 'dpm,' to indicate the number of nuclide atoms that have decomposed.

Activity measurements in power reactors typically involve large dpm values therefore the activity is converted to Curies with one microcurie (1.0 μCi) being equal to 2,220,000 dpm. The SI equivalent for disintegrations is the becquerel (Bq), which is one disintegration per second. Conversions between the two units are below:

37 GBq = 37 billion Bq = 1 Curie
1 MBq = 1 million Bq = ~ 27 microcuries
1 GBq = 1 billion Bq = ~ 27 millicuries
1 TBq = 1 trillion Bq = ~ 27 Curies

Quantification of Radioactive Materials

The mass of a nuclide alone does not indicate the radioactivity. Each radionuclide has a *specific activity*, expressed as curies per unit mass, and a half-life, or the amount of time required for half of the atoms in a mass of a nuclide to decay. For example, uranium-238, which has a 4.5 billion year half-life, has a very small specific activity of $3.31\text{e-}7$ Ci/g, while cobalt-60, with a half-life of 5.3 years, has a specific activity of 1,132 Ci/g.

The nuclear industry commonly uses curies (or becquerels) of activity as a shorthand notation of the mass of a specific radionuclide. This is practiced because the radiation emitted from the nuclide has a specific energy (and therefore wavelength and frequency) that allows classification of the nuclide, and can readily be measured to determine the nuclide mass with great accuracy.

Time, Distance, and Shielding

The first principles of radiation field control are the intelligent application of time, distance, and shielding. Each is discussed briefly below.

Time has two applications in field control. First, the less time spent in a radiation field, the less energy is absorbed by the person, and less exposure is acquired. Therefore, efficient planning of tasks in radiation fields is mandatory to prevent unnecessary exposures. Second, as stated previously, all radionuclides have a half-life, and many of the nuclide half-lives are very short (e.g., minutes, hours). Therefore, if a task can be scheduled to take advantage of short half-life nuclide decay, the exposure will be reduced because the field has been reduced without expending resources.

Distance—Radiation field intensity decays as a function of the inverse of the square of the distance. For example, the energy absorbed per unit time from a radiation field at two meters from the source is one-fourth the energy absorbed from the same field at a one meter distance from the source. The concept is shown below in Figure 2-2. As can be seen from the figure, small distances away from the field source reduce the field strength dramatically.

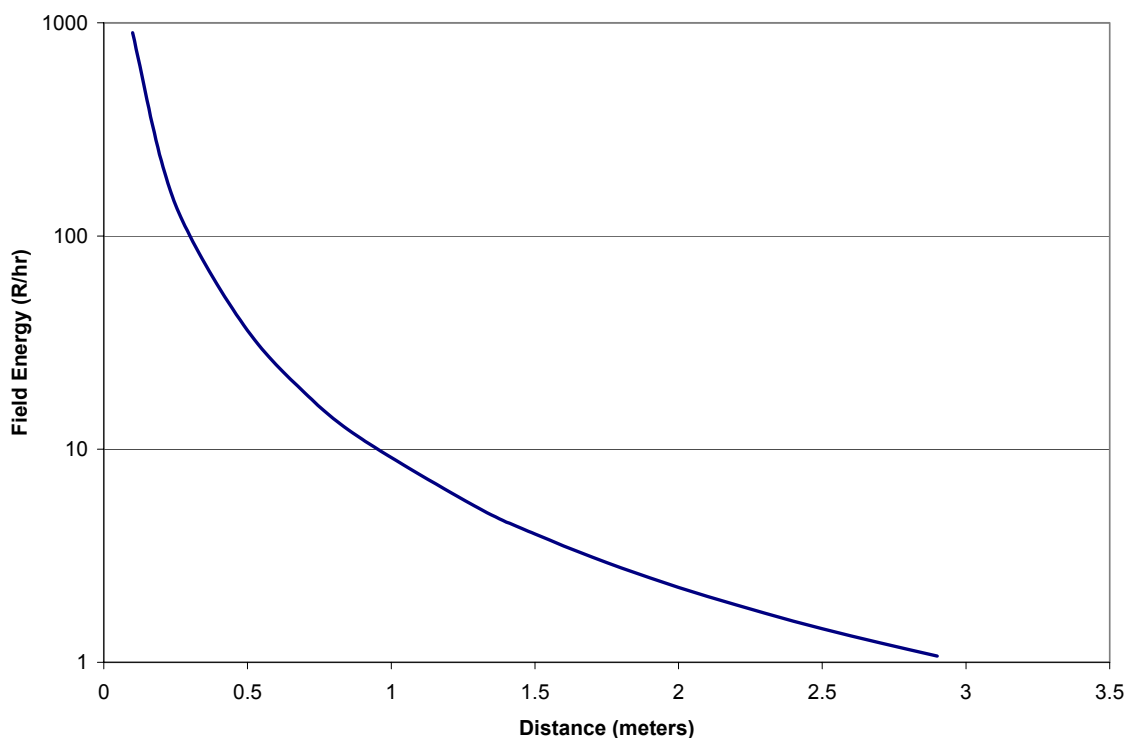


Figure 2-2
Decay of Radiation Field Strength as a Function of Distance

Shielding—It is relatively easy to shield against alpha and beta particle radiation with protective clothing and respiratory equipment, however, gamma radiation requires a very dense substance such as lead or concrete to block the penetration of the radiation. Temporary and permanent shielding are typically used when work must be performed in radiation fields generated by nuclides that have a relatively long half-life or where work will be performed over extended periods of time. Half-value layers and tenth-value layers represent the thickness of a material that must be present to reduce the radiation field to 1/2 and 1/10th of their original values. Table 2-1 shows examples of cobalt-60 and Cs-137 half and tenth value layers for three common materials.

Table 2-1
Half Value and Tenth Value Layers for Co and Cs

Nuclide	Half Value Layer (cm)			Tenth Value Layer (cm)		
	Lead	Iron	Concrete	Lead	Iron	Concrete
Cs-137	0.65	1.6	4.8	2.1	5.3	15.7
Co-60	1.2	2.1	6.2	4.0	6.9	20.6

Radiation Field Measurements in Nuclear Plants: Historical Background

Studies of the processes causing the growth of ex-core radiation fields have been carried out in several countries over the past 40 years. EPRI work on radiation-field buildup started more than 20 years ago and covers the various phases of plant construction and operation. More recently, EPRI studies have placed increasing emphasis on technology transfer through capturing utility experiences and lessons learned in reports, guidelines, and seminar proceedings.

Initially, the focus was on data collection and evaluation, continuing work started by NSSS vendors, notably General Electric with its BWR Radiation Assessment and Control (BRAC) program, and Babcock & Wilcox, Combustion Engineering and Westinghouse with what became the Standard Radiation Monitoring Program (SRMP). Data evaluation continued with the cobalt source identification programs in conjunction with General Electric, Westinghouse, and Combustion Engineering.

BRAC Point surveys are performed at BWRs to monitor and trend Reactor Recirculation Piping exposure rates. Once data are collected, they are forwarded to a vendor and EPRI for comparisons with historical station information and with other BWR industry BRAC values. A BRAC value is normally the average of Recirculation Pump Suction and Discharge Piping dose rates.

Examples of standardized radiation measurement points are shown in Figure 2-4 and Figure 2-3 for Westinghouse plants and Figure 2-5 for Combustion Engineering units. Figure 2-6 shows the BRAC sample points on the recirculation system of a typical BWR plant.

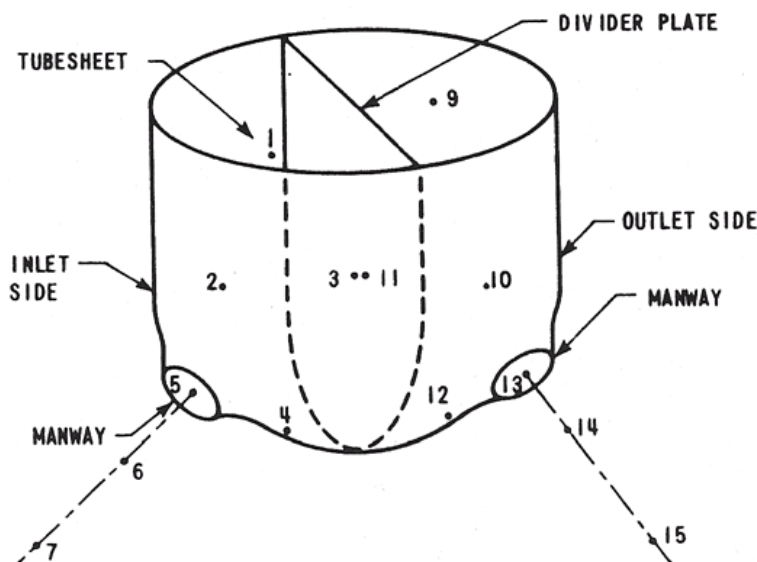


Figure 2-3
Westinghouse Steam Generator SRMP Location Map

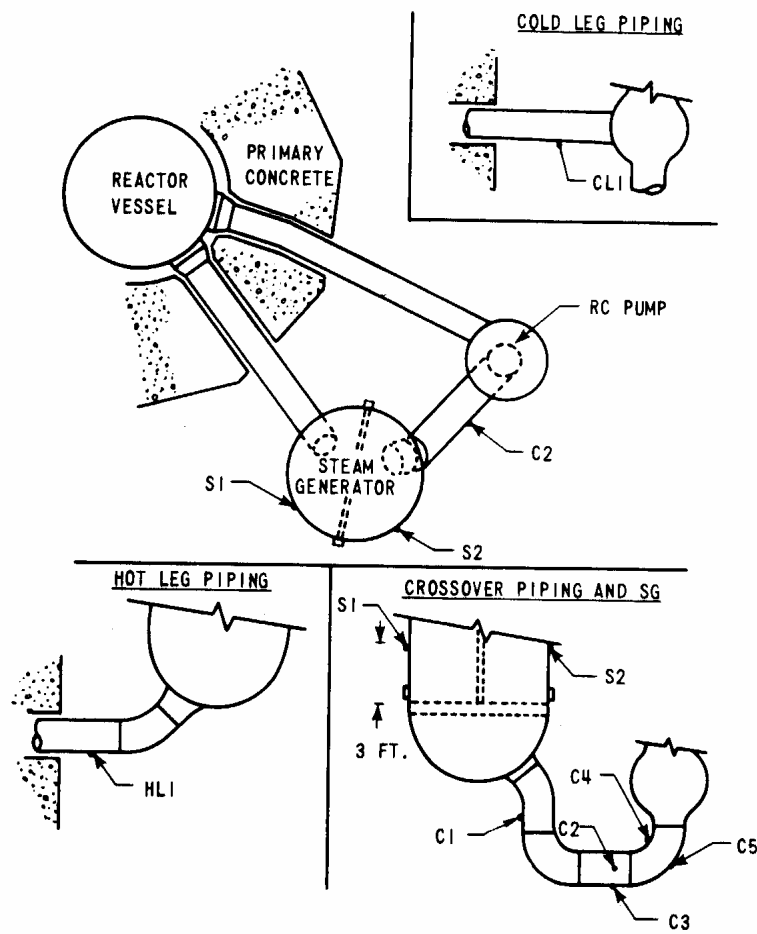


Figure 2-4
Westinghouse Piping SRMP Location Map

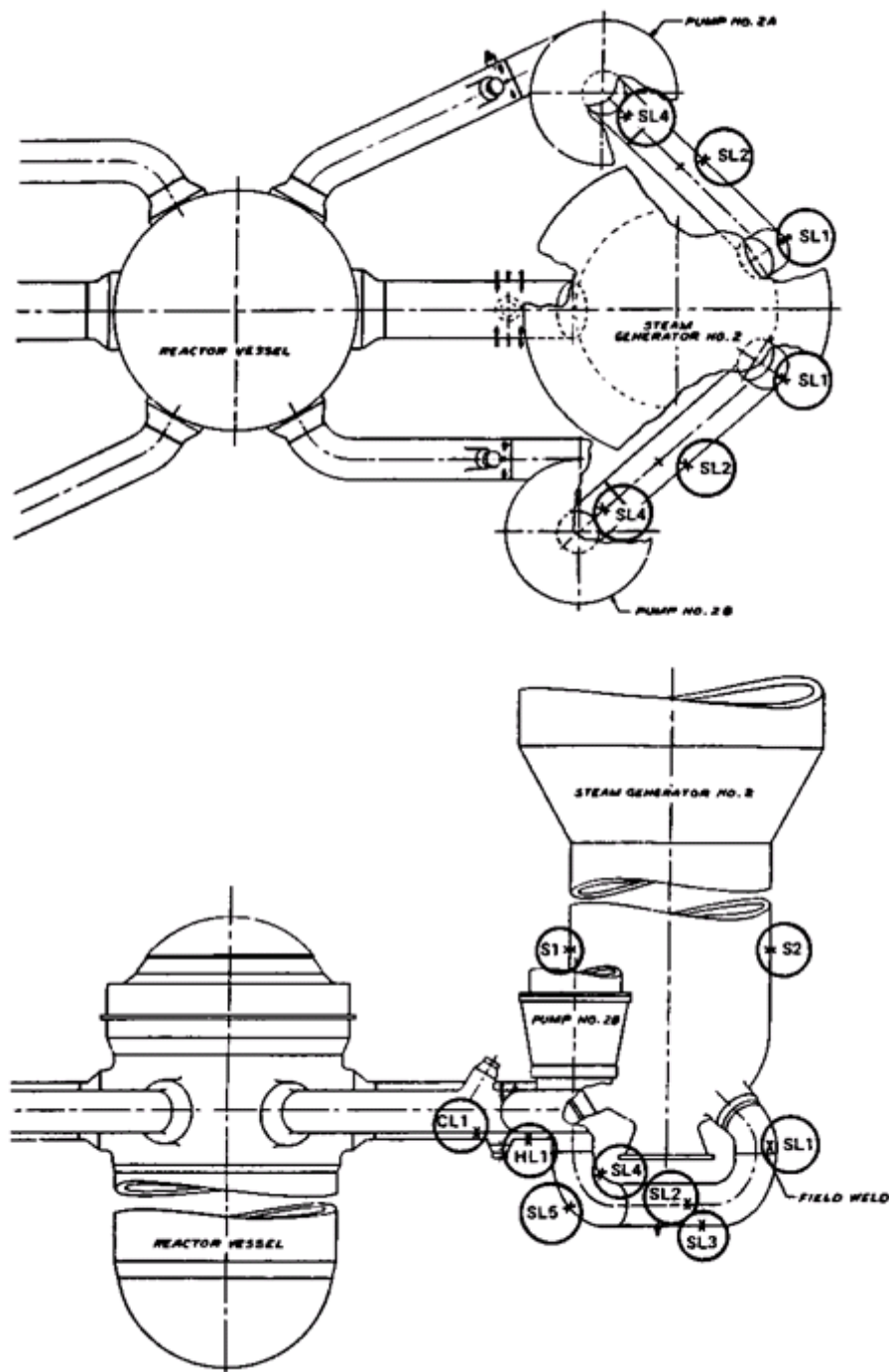


Figure 2-5
Combustion Engineering SRMP Location Map

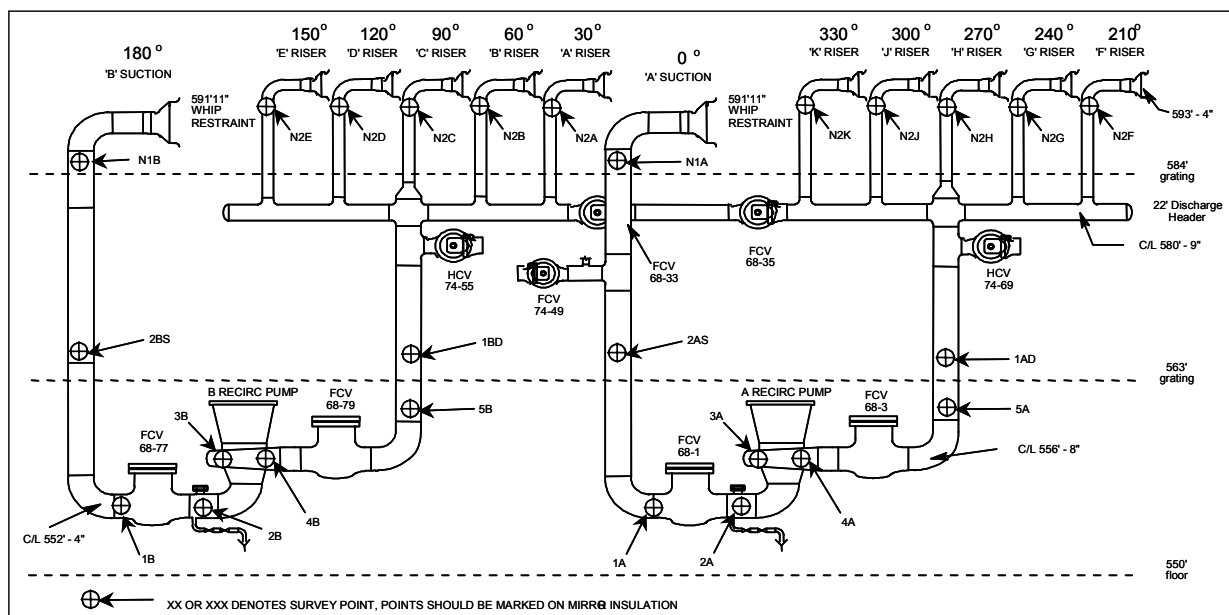


Figure 2-6
BRAC radiation sampling points for typical BWR recirculation piping

From these studies potential techniques for radiation-field reduction were identified and the necessary development work performed. The next stage involved laboratory loop testing and field testing with, in some cases, full-scale plant demonstrations. Throughout the process basic research work continued, with the objective of improving understanding of the fundamental processes. A large portion of the data and evaluation work is available through EPRI's website, www.epri.com.

Origin of Radiation Fields

Non-radioactive corrosion products form as a result of oxidation of primary system materials. Corrosion products are formed by the release of metal-oxide ions, colloids, and particles generated from the general corrosion of materials in contact with the coolant water. Corrosion products are typically comprised of iron and nickel oxides with small amounts of manganese, chromium, and traces of cobalt. Some of these corrosion products are released and are transported by the coolant and redeposit throughout the primary system. Other metal and metal-oxide wear products are created during operation or maintenance of the plant. Wear products are formed as a result of operating plant equipment, such as control rod drive mechanisms in PWRs, control blades in BWRs, reactor coolant pumps, and valves. Wear products can also result from debris-induced fretting of the fuel and from component maintenance, such as grinding or lapping of valves. These materials are also released into the bulk coolant and redeposit throughout the primary system.

These metallic non-radioactive corrosion and wear products are present as soluble, colloidal or particulate species that pass through the core and deposit on the fuel rod surfaces by precipitation, adsorption, or particle deposition. They become radioactive by absorbing fast or thermal neutrons in the reactor core. Re-entrainment in the coolant is a result of thermal,

hydraulic, chemical, redox potential or solubility changes in the primary system or erosion. Activation products then redeposit on ex-core components resulting in increased radiation fields and personnel exposure.

Fission products are produced by the fissioning of uranium inside the fuel assembly and are released from inside the fuel cladding into the reactor coolant through a defect in the cladding. Both radioactive fission products and activation products contribute to plant radiation fields. However, fission products from failed fuel rarely contribute to long-term radiation-field buildup, especially since fuel failure rates have decreased significantly over the years. The focus of this manual is to provide information describing currently accepted practices to minimize the activation, transport and deposition of corrosion and wear products in the primary system.

The primary long-term source of radiation fields in nuclear power plants is cobalt-60. In PWR plants, cobalt-58 also is a significant source, especially early in life. Cobalt-60 is formed as a result of neutron absorption by cobalt-59, which is the only isotope present in naturally occurring cobalt. Cobalt-58 is formed from the neutron bombardment of nickel-58, which is the isotope present as 68% of naturally occurring nickel. nickel-58 is a primary alloying constituent in PWR steam generator tubing and BWR core support structures and is a minor element in other reactor coolant primary pressure boundary materials. Cobalt is an impurity in these materials, usually present at levels of a few tenths of a percent. However, cobalt is the major constituent in hardfacing materials, such as Stellite™, used in valve seats, pump journals (bearing surfaces), and other components that require outstanding wear resistance.

Figure 2-7 and Figure 2-8 show the main transport processes that lead to corrosion product activation in PWRs and BWRs, respectively. Although corrosion of pressure boundary materials does not result in degradation of the properties of the materials, release of metal ions or metal-oxide particles to the coolant is responsible for a large proportion of the radiation fields on out-of-core surfaces.

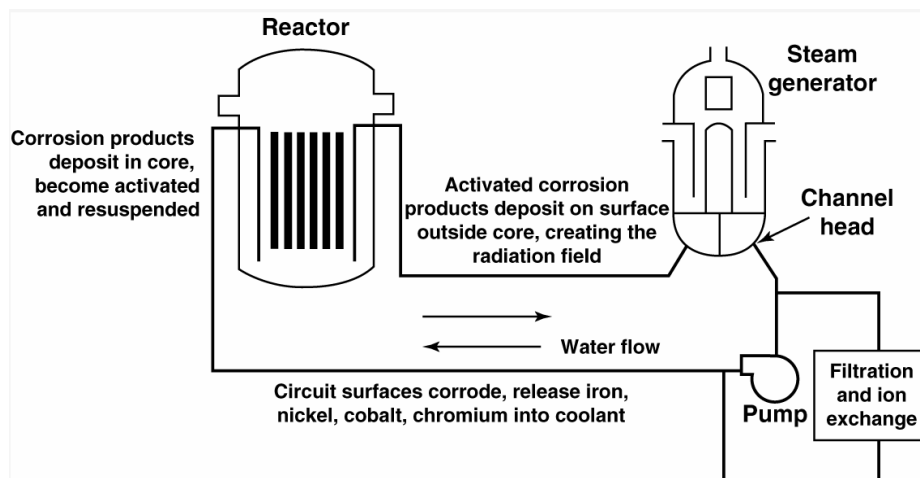


Figure 2-7
Corrosion Products in PWR Primary Circuit Are Activated in Core and Deposited on Out-of-Core Surfaces

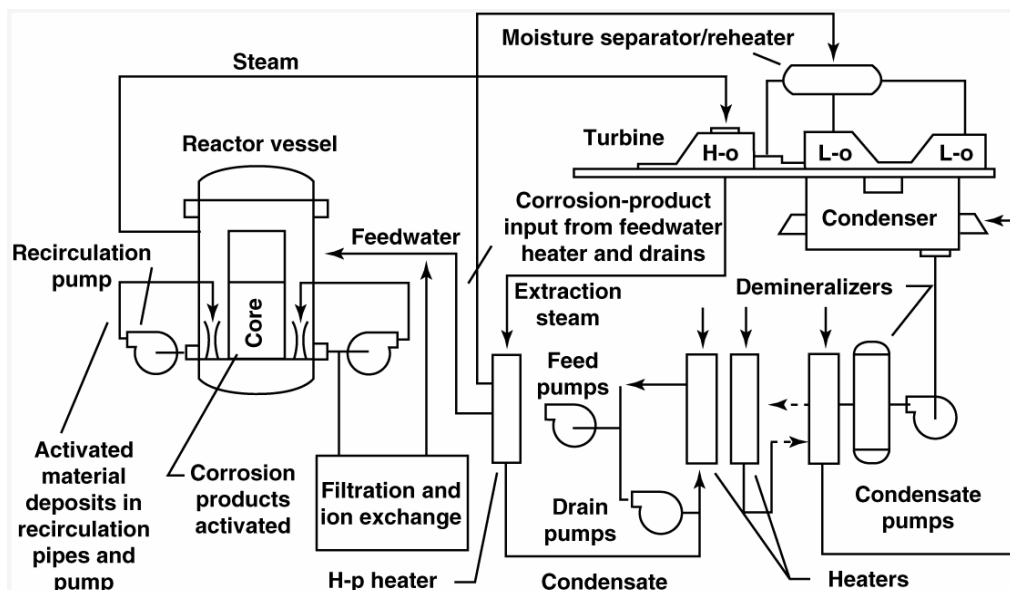


Figure 2-8
BWR Contamination Results from Activation of Corrosion Products in the Feedwater

Primary coolant cleanup systems in LWRs are relatively ineffective for removing activity compared to the decay of corrosion products on out-of-core surfaces. Radiation fields tend to buildup over a few years before an equilibrium level is reached following initial startup, chemistry regime changes, or system/component decontamination.

Consideration of the deposition process on out-of-core surfaces gives clues to the most effective methods for controlling buildup of activity. Out-of-core surfaces in contact with reactor coolant will pick up particles, colloids and ions. These will be incorporated in the growing film which exists on these surfaces as shown in Figure 2-9 and for the BWR case only in Figure 2-10.

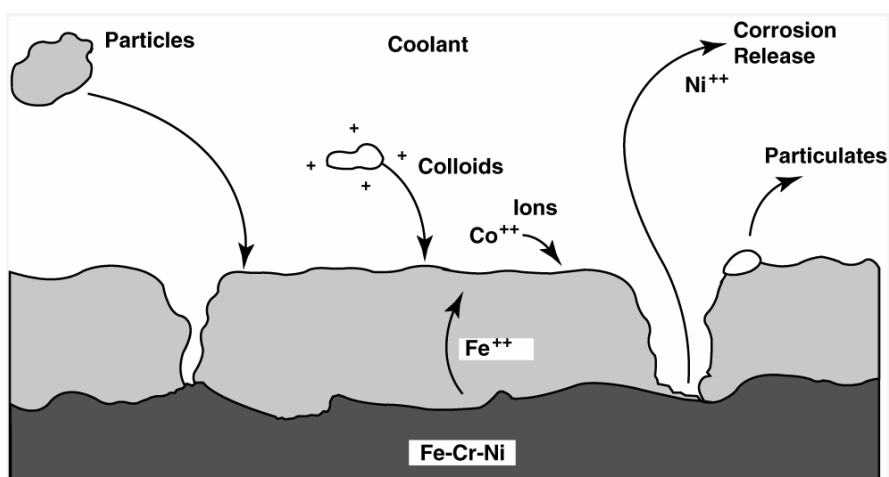


Figure 2-9
Schematic Diagram of Deposition on Out-of-Core Surfaces

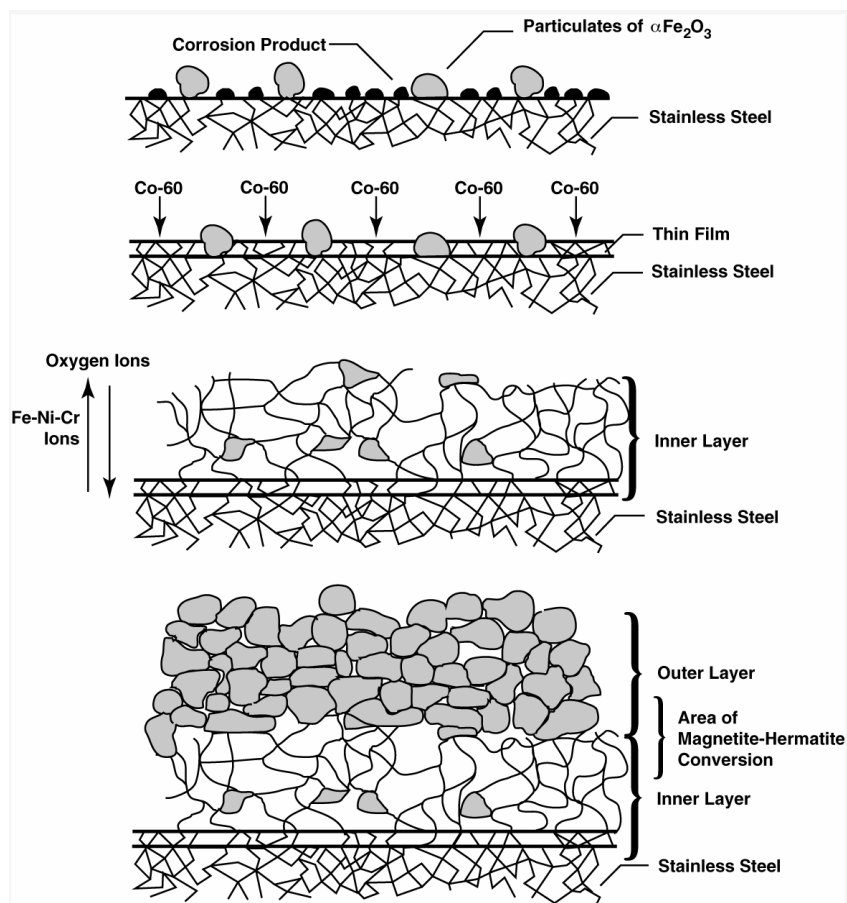


Figure 2-10
Crud Growth Model for BWRs

Corrosion products are released from the base metal, some of which are retained in the growing oxide film, while others are released directly to the coolant itself. During the early stages of corrosion, very little cobalt-60 is available for incorporation since there has been little opportunity for its generation on the fuel surface. As the growth of this film proceeds, cobalt-60 is now available and will be incorporated into the film.

Exposure Regulations

Compliance with regulatory requirements is an obvious and essential element of a radiation field control program. Currently, radiation workers in commercial nuclear plants are subject to regulations governing their allowable exposure to ionizing radiation. In the U.S., Subpart C of 10CFR20 imposes occupational dose limits for adults as follows, except for planned special exposures:

- (1) An annual limit, which is the more limiting of--
 - (i) The total effective dose equivalent being equal to 5 rems (0.05 Sv); or
 - (ii) The sum of the deep-dose equivalent and the committed dose equivalent to

any individual organ or tissue other than the lens of the eye being equal to 50 rems (0.5 Sv).

(2) The annual limits to the lens of the eye, to the skin of the whole body, and to the skin of the extremities, which are:

- (i) A lens dose equivalent of 15 rems (0.15 Sv), and
- (ii) A shallow-dose equivalent of 50 rem (0.5 Sv) to the skin of the whole body or to the skin of any extremity.

The International Council of Radiation Protection (ICRP) has set planned occupational exposure limits considerably lower than the current United States limits. The current limits are outlined below:

The limits for adult workers from the Basic Safety Standards (SS-115) are:

1. an effective dose of 20 mSv (2 rem) per year averaged over five consecutive years;
2. an effective dose of 50 mSv (5 rem) in any single year;
3. an equivalent dose to the lens of the eye of 150 mSv (15 rem) in a year;
4. an equivalent dose to the extremities (hands and feet) or the skin of 500 mSv (50 rem) in a year.

Techniques for Controlling Radiation Fields

Radiation field control techniques include reducing the source term, controlling out-of-core deposition, controlling the transport and activation of corrosion and wear products, and removing deposited activity from component surfaces by the use of chemical and mechanical decontamination. Many successful plant control programs feature actions that utilize all four aspects of radiation-field control.

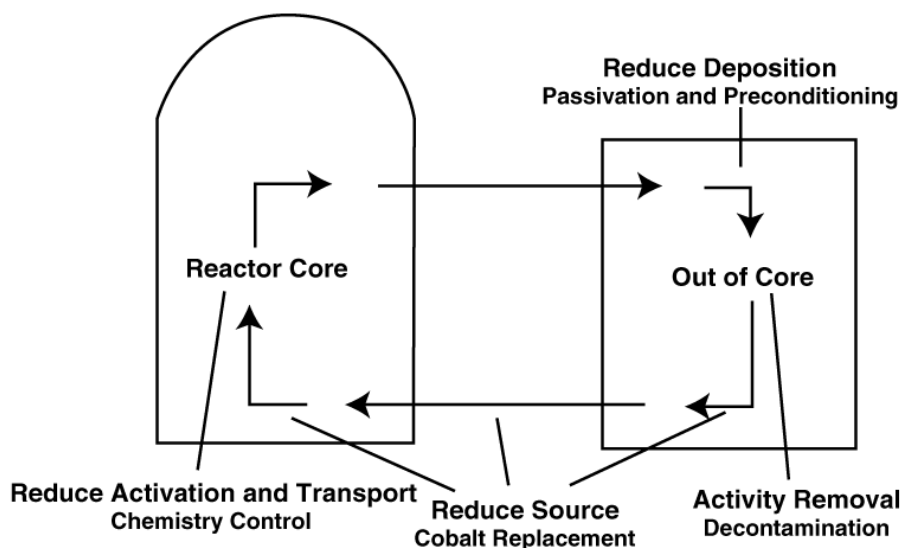


Figure 2-11
Techniques to Control Radiation Fields

Reducing the Source Material

Reduction of the amount of cobalt in components that can release corrosion and wear products to the reactor core has been shown to be an effective method for reducing out-of-core radiation fields. Extensive guidance addressing cobalt reduction has been made available through EPRI and other industry sources. Many utilities have developed formal programs whose goal is to avoid the use of cobalt-base materials wherever possible. It has been demonstrated that numerous cobalt-free alloys with appropriate characteristics are available to replace the cobalt-base alloys previously used as hardfacing materials. Cobalt-free or reduced cobalt materials have undergone extensive testing programs and are now being introduced and used with increasing frequency in numerous applications throughout the industry with acceptable results. Also, a structural alloy with good wear resistance such as 400 grade stainless steel may be used in some applications where a cobalt-base hardfacing alloy previously had been used. Controlling the cobalt impurity level in structural alloys used in replacement components is discussed in Chapter 3.

Ultrasonic fuel cleaning is a new technology that is used to remove the source from the reload fuel. The application of the technology was intended to reduce Axial Offset Anomaly (AOA). Also known as Crud Induced Power shift (CIPS), but the dose reductions observed were an ancillary benefit. More details are provided in Chapter 8.

Controlling Activation and Transport

A strong correlation has been found between the absence of radiation hot spots in crud traps and good water chemistry. The value of primary chemistry regimes tailored to reduce shutdown fields such as zinc injection has been demonstrated in both BWRs and PWRs. For example, the discovery that concentrations of ~5 - 10 ppb zinc in BWR reactor water reduce the release of

soluble corrosion products and also inhibits the deposition of cobalt-60 has resulted in its use at many BWR plants, reducing activity values by as high as 50%.

Injection of natural zinc leads to the generation of zinc-65 by capture of a thermal neutron. Zinc-65 contributes to shutdown radiation fields and to solid and liquid low level waste stream activity levels, so depleted zinc oxide (DZO) is the preferred additive. DZO is depleted in ^{64}Zn to avoid formation of ^{65}Zn .

Historically, PWR chemistry control programs addressing radiation field reduction focused primarily on the control of coolant pH (i.e., the relative concentrations of lithium and boron) and the solution corrosion potential (i.e., the relative concentration of dissolved hydrogen and oxidizing species) chemistry during power operating conditions. However, the industry has expanded the focus of chemistry control by instituting new programs which support the goal of radiation field reduction by diminishing the transport to and deposition of corrosion products on in-core surfaces. Recent developments in the areas of shutdown and startup chemistry control, research and testing of chemical additives, such as zinc, to the coolant, and potential alternate chemistry control programs using enriched boric acid are now becoming the central focus of chemistry improvements. Details for controlling transport and activation are discussed in Sections 5 and 6.

Controlling Out-of-Core Deposition

Preconditioning - Preconditioning of primary system surfaces, either before plant startup or before installing replacement components, can significantly reduce the deposition rate of activated corrosion products. Surface modification by mechanical and electrochemical polishing plus chemical preoxidation has been applied to develop a passive oxide film before the surfaces is exposed to reactor coolant. Preconditioning the surfaces of new or replacement components has been established as a practical, cost-effective method to reduce radiation fields. Examples of major component replacements are steam generators in PWRs and primary recirculation piping in BWRs. Also, numerous smaller components are routinely replaced (e.g., pumps, valves, small bore piping and manway diaphragms). Proven methods for surface preconditioning are discussed in Section 4.

Filtration and Ion Exchange – Historically, the use of filtration and ion exchange has proven to be marginally effective for reducing the concentration of activity available for deposition in primary systems. The low flow rate and vessel media capacities for the vast majority of installed cleanup systems in both BWR and PWR applications had proven to be less than adequate for the volume of liquid requiring treatment, resulting in poor turnover ratios (time required to completely process one full system volume). However, at a minimum the available capacity should be optimized through careful research and application of available media types and configurations.

Recent advancements in both filtration and ion exchange media have improved the overall effectiveness of these systems. Several advanced cleanup media and media use strategies are currently being demonstrated in the U.S. with reported performance improvement. However, at the time of publication much of the data required for validation was not available for evaluation and inclusion in this document.

More importantly, the time that cleanup systems remain in service at full flow during reactor shutdown crudburst cleanup operations should be maximized. The success of that cleanup effort is a primary factor in determining activity deposition, and outage, and to a lesser extent post startup, radiation field intensity.

Decontamination

Radiation field control by specific component or system decontamination has been widely applied by U.S. and European nuclear plants. In 1991, the LOMI process was qualified for full system decontamination (FSD) applications in BWRs, for both fuel-removed and fuel-in-place, but to date there have been no field applications. The AP/LOMI and AP/CAN-DEREM processes were also qualified in 1991 for FSD applications in PWRs with the fuel removed. This work culminated in an FSD at Indian Point 2 in February 1995. Work to qualify PWR FSD applications with the fuel in place is completed. A nitric permanganate (NP) preoxidation step has been shown to be effective in conjunction with LOMI in addressing the chromium-rich oxides that form under typical PWR primary conditions and in BWRs operating under HWC.

Component and subsystem chemical decontamination is an integral part of many BWR station's radiation field control strategy. Several stations schedule and use the above processes on a routine basis, resulting in at least temporary relief from elevated activity levels. As a result of lower radiation fields and subsystem isolation issues, in-situ decontamination of components and subsystems is employed on a less frequent basis in PWR stations. Industry decontamination experience and decontamination processes and issues are discussed in Section 7.

Available Radiation Field Control Techniques and On-Going EPRI R&D

Many techniques are now available for application and have shown great success in reducing radiation fields and occupational exposure. The techniques that are available or are now under development are shown in Table 2-2. Table 2-3 lists some relevant EPRI reports.

Table 2-2
Radiation-Field Reduction Techniques Available (A) and Under Development (UD) in 2004

Technique	PWR	BWR
Chemical decontamination	A	A
Elevated pH primary chemistry	A	N/A
Zircaloy fuel grids	A	A
Cobalt-free pins and rollers for replacement control blades	N/A	A
Electropolishing and pre-oxidation of replacement components	A	A
Valve maintenance procedures to minimize cobalt debris	A	A
Structural alloys with low cobalt for replacement parts	A	A
PWR and BWR zinc injection	A	A
Zinc injection using DZO or Zinc acetate	A	A
In-situ replacement of control blade pins and rollers	N/A	A
Cobalt-free hardfacing for valves	A	A
Stabilized chromium process for preconditioning components	A	A
Cost effective application of enriched boric acid	UD	N/A
Noble metal chemical addition radiation field evaluation	N/A	A
Plant-specific optimum feedwater iron recommendations	N/A	A
Ultrasonic fuel cleaning	A	A
Reactor shutdown and startup field control optimization	UD	UD
Advanced cleanup system media and strategies	UD	UD

Table 2-3
Related EPRI Radiation Exposure Control Research and Reports

Topic	EPRI Report Number or Status
Effective Personnel Exposure Control in Shortened Refueling Outages: Final Report: Review of Remote Monitoring Systems	1003686
Development of a Successful Reactor Cavity Decontamination Plan, Electric Power Research Institute, Palo Alto, CA: 2004.	TR-1009576
ALARA Planning and Scheduling	In Progress. Target completion December 2005
Scaffolding Program Management for Dose Reduction	TR-1003392
Stabilized Chromium Process: Final Report	TR-1003374
BWR Dose Reduction Using Depleted Zinc Oxide, Including Effects of Noble Metal Chemical Addition	TR-1003127

Radiation Field Control Strategy

The first section of this report identified regulatory and economic incentives for nuclear utilities to implement substantive field reduction programs, and this chapter has presented information addressing the development of current radiation control measures. EPRI continues to support the basic research that has led to many of the current advancements in radiation control technology, and the subsequent field tests and plant demonstrations that have documented the benefits of new technology. This strategy has proven to be valuable to utilities. Their aggressive implementation of these technologies and techniques coupled with other site specific initiatives have resulted in average annual per unit collective radiation exposures that are at historical lows; 75 person-rem at PWRs and 136 person-rem at BWRs in 2002. However, this is not a time for complacency.

With utilities challenged by deregulation, reductions in operating costs, and aging plants and workforces, the issue of maintaining this desirable exposure reduction trend must be addressed.

From a utility perspective, this is an opportune vantage point; it is much easier to maintain fields low than to implement a range of programmatic controls to drive fields down from higher levels. As the plants age it is clear that increasing special maintenance activities, such as dealing with replacement of critical BWR and PWR large components, will result in increased exposure.

Radiation Field Control Benefits Derived from Technologies Implemented for Alternate Reasons

PWR zinc injection was originally demonstrated in loop tests for purposes of radiation field control. However, the initial application at Farley had the objective of reducing stress corrosion cracking of nickel-base steam generator tubing. A reduction in radiation fields was observed even though zinc was injected only for about one half of the fuel cycle, but this reduction was partially offset by an increase in zinc-65. Farley has reintroduced zinc, and other PWRs have followed. Based on the success of zinc injection in reducing BWR radiation fields, it was expected that a significant reduction in PWR radiation fields would follow.

The costs/benefits of using enriched B-10 boric acid are being re-evaluated, with the primary motivation being the shutdown margin for mixed-oxide (MOX) fuels. The high temperature deposits on fuel that result in local flux depression [Axial Offset Anomaly (AOA)] are attributed to boron concentration in the corrosion product buildup. Reducing release of corrosion products from the steam generator tubing can be achieved by raising pH, but there are limits imposed by fuel corrosion concerns at elevated lithium levels. The higher enrichment of B-10 increases the effectiveness of boric acid as a neutron poison. This lowers the required concentration of boric acid, and therefore less lithium is needed to balance the acidity. Enriched boric acid is expensive, but may be justified if it mitigates AOA and increases the possibility of extending fuel discharge burnups. Raising the pH is also known to reduce general corrosion rates and should therefore also lower out-of-core radiation fields.

Noble Metal Chemical Addition (NMCA) is used at over 20 BWRs to increase the effectiveness of hydrogen water chemistry in controlling reactor internals cracking. NMCA requires significant preparation and planning before application; refer to the BWR Water Chemistry Guidelines for the recommended program. Plants using NMCA after several months of zinc injection and hydrogen water chemistry have observed significant radiation field reductions. Adverse field trends have been observed with plants with high feedwater iron and cobalt sources that implemented NMCA before the BWR Water Chemistry Guidelines recommendations were available.

Ultrasonic fuel cleaning in PWRs may allow the conservation of one or more new fuel assemblies in high-duty cores. This is possible because the burnup rate of the first and second burned assemblies is increased with the reduced crud loading on the fuel cladding. The savings obtained by conserving one or more assemblies should justify the purchase and application of the technology. Significant reductions in out-of-core radiation fields have been reported by PWR plants utilizing fuel cleaning for other reasons. This technology has been successfully applied at a BWR and continues to be refined for improved results and efficiency.

Efficiency Improvement for Existing Techniques

Several developments in the LOMI chemical decontamination process are being made, with the objective of reducing ion-exchange requirements for radwaste processing. Recycling the picolinic acid is one method that looks feasible and could result in significant waste processing and disposal costs.

Stabilized chromium coatings are very effective at reducing radiation-field buildup, particularly in reducing chemistry environments. Methods of applying these coatings in a cost-effective manner to complex geometries, especially valve internals, have been developed and demonstrated. The results of these efforts will be available following in plant at power application of the components.

Integrate Radiation Field Control Techniques

The best example of integrating techniques is the combination of HWC, zinc injection, and decontamination in BWRs. The most economical solution to the increase in dose rates observed at most BWRs when raising hydrogen levels is a chemical decontamination at the first outage after starting HWC followed by the use of depleted zinc to minimize recontamination.

A second example includes an aggressive cobalt reduction program combined with an aggressive hot spot flushing campaign, ultrasonic fuel cleaning, and chemical decontamination. Eliminating sources of cobalt contamination followed by removal of historical ^{60}Co will result in significant reductions to radiation fields.

Key Considerations - Radiation Fields: Origins and Countermeasures

A synopsis of the key topics of this chapter.

1. Industry wide consistency in radiation field measurements facilitates more accurate data tracking, trending, and benchmarking.
2. Understanding the mechanisms of radiation field origins will improve analyses and implementation of field reduction options.
3. The level of effort to comply with exposure regulations is directly related to the intensity and quantity of radiation fields.
4. An effective cobalt reduction program will reduce the inventory of radioactive material without compromising plant operability.
5. Preconditioning is a proven, effective method for reducing out of core activity deposition. It can be applied to both simple and complex geometries.
6. In-situ component or system decontamination will remove activity and is a cost effective option for plants with high radiation fields.
7. Several relatively new processes that produce a side benefit of reduced radiation fields have been applied, proven, and continue to be developed, including ultrasonic fuel cleaning and alternate chemistry regimes such as NMCA.
8. Integration of multiple exposure reduction options can enhance the overall benefit derived.

References

- 2-1. C. A. Bergmann and R. L. Bencini. Evaluation of PWR Radiation Fields: 1991-1996. Palo Alto, CA: Electric Power Research Institute, February 1997. TR-107566.
- 2-2. BWR Water Chemistry Guidelines - 2004 Revision. Palo Alto, CA: Electric Power Research Institute, December 2004. TR-103515-R3
- 2-3. Development of a Successful Reactor Cavity Decontamination Plan, 1009576

3

COBALT SOURCE REDUCTION

Introduction

Because the long-lived ^{60}Co isotope is a key contributor to shutdown dose rates, elimination of its sole precursor isotope, ^{59}Co , is one of the most effective approaches for reducing shutdown radiation fields in BWRs. A “typical” BWR ^{59}Co corrosion/erosion rate is on the order of several hundred grams per year. Cobalt is found as an impurity in the structural alloys used in the primary system of light water reactors. Cobalt is also the major constituent of the wear-resistant hardfacing alloys (e.g., the StellitesTM) that are used to provide wear and corrosion resistance to critical components such as valves, PWR control rod drive mechanisms, and the pins and rollers used in the earliest BWR control blades provided by General Electric. Figure 3-1 illustrates the magnitude of stellite contribution from valve seat damage during normal operations. The volume of material is significant in light of the impact grams of material can have on radiation field buildup.



Figure 3-1
Stellite Valve Seat Damage

The first step in the activation process is the release of cobalt-59 into the reactor coolant by corrosion and/or wear of cobalt-bearing alloys. Early EPRI-sponsored assessments of cobalt sources showed that the cobalt release rates from both structural alloys and hardfacing alloys were comparable, so an effective radiation control program must address both facets of the problem. Because component replacement is very costly, opportunities to implement source

Cobalt Source Reduction

term reduction technologies are typically limited to components that must be refurbished or replaced for reasons other than exposure control. Clearly, the most significant opportunities lie in the development and construction of the next generation of advanced reactors. Careful material and process evaluations for advanced nuclear plant designs could result in significant advancements in radiation field controls.

Limits on cobalt impurity levels in structural alloys used in nuclear power plants and the substitution or elimination of cobalt-base hardfacing alloys used in the primary circuit of LWRs have been reviewed. One of EPRI's roles in this area is the development and implementation of the wear-resistant iron-base hardfacing alloy designated NOREM. The other main development in this area is the significant reduction in the use of cobalt-base hardfacing alloys in the newest generation of Siemens-designed PWRs, the KONVOI plants. A summary of the evaluations performed by Siemens staff on a number of candidate iron-base hardfacing alloys will be provided. A comparison of the dose rate trends at the KONVOI plants with those at the earlier designs clearly demonstrates the benefits of lowering the cobalt inventory. Limited information is available regarding the use of alternative cobalt-free alloys in CANDU reactors.

Limiting Impurity Levels of Cobalt in Structural Alloys

A properly designed change to plant design should result in no extra contribution to a site's current exposure performance, or should make solid recommendations for minimizing or managing the exposure contribution. Utilities need formal processes and procedures in place that ensure their material and component suppliers and site staff responsible for materials or designing modifications are aware of the importance cobalt elimination or reduction. Formal training coupled with procurement specifications, written and verbal communications, and procurement checklists should be developed and implemented to ensure long term success. The costs related to these considerations should be included in the overall repair or replacement cost analysis.

Industry Experience: At the Browns Ferry site, all engineers are required to attend engineering specific ALARA training. The formal training class is conducted for new engineers and is also included in continuing training that is provided on a routine basis. The station has also developed an extensive Engineering review checklist that is procedurally required to be used for all modifications and for procurement specifications, including:

1. The design eliminates the use of cobalt (stellite) -containing materials for parts or components (e.g., valve trim, seats, pins, etc.) that could be in a flow path leading to the core.
2. The design maximizes cobalt removal from systems that interface with the RCS.

Following completion by the lead engineer, the document requires a signature from an ALARA-trained design or system Engineer, followed by a detailed review and approval signature from an ALARA staff member. The queries contained in the checklist force the responsible engineer to address opportunities for long-term reductions in cumulative site exposure, and similarly to address issues that may result in increased exposure.

Personnel should also be made aware of fact that significant levels of impurities are present in materials manufactured using conventional melting practices employed by metal fabricators. Cobalt impurity levels should be less than 500 ppm in stainless steels and less than 200 ppm in Inconels for all nuclear replacement components. There is little cobalt present in the zirconium-base Zircaloy alloys used for fuel rod cladding and in some fuel spacer grids, with the cobalt content of Zircaloy typically less than 50 ppm.

Industry Experience: Plant Hatch evaluated all valves and assigned a priority for low cobalt alloy replacement. The priority is based on recurring maintenance, communication with the reactor vessel, outage use, accident use, and valve type. Each valve is then evaluated individually for acceptable low cobalt alternatives using EPRI guidance. (4-1, 4-2)

Clearly, additional benefits can be realized if replacement components are supplied with lower cobalt impurity levels.

Industry Experience: In 1993 Niagara Mohawk specified and purchased stainless steel for replacement control blades with cobalt contents below 150 ppm and less than 250 ppm for local power range monitors. In addition to lowering the potential for released cobalt to contribute to shutdown radiation fields, the utility also noted the lower cobalt content would lead to lower activation levels, thereby lowering low level waste disposal costs.

The Ni-base Alloy 690 tubing used in PWR replacement SGs can readily be supplied with an average cobalt content of less than 150 ppm and a maximum value of 200 ppm for any one heat.

Laboratory investigations confirm that cobalt-base hardfaced (HF) alloys provide the highest resistance to adhesive (galling) wear. However, this attribute is only necessary in valve designs where metal surfaces are in intimate contact under high stress. Therefore, the use of cobalt-base HF alloys should be limited to large gate valves, with hardenable martensitic 400 series alloys or iron-base HF alloys specified for globe, swing check, and flow control valves. The primary degradation mechanism in these valves is corrosion and/or cavitation-erosion damage, and many cobalt-free alloys are available that can provide this attribute.

Utility personnel should also be aware of the importance of not only placing cobalt impurity limits on the structural alloys used for in-core reactor components but also placing limits on the cobalt content of materials used to fabricate such components. The cobalt content of nickel plate used to fabricate in-core components should be <50 ppm and of braze material less than 500 ppm.

The Borselle staff's observations prompted Westinghouse review differences in the channel head dose rate trends for Westinghouse-designed PWRs that had changed from Inconel to Zircaloy grids within the first four cycles of operation (D. C. Cook 1, Prairie Island 1 and 2, and Kewaunee) and others that either did not change from Inconel to Zircaloy grids or changed in later cycles (Beznau 1 and 2, Beaver Valley 1, Farley 1, Indian Point 2, and North Anna 2). Westinghouse reported that channel head dose rates for the first group of plants leveled out at 5 to 7 R/hr, while the comparable steady-state values for the second group were about a factor of three higher. The steam generator shell dose rates for these two groups show similar variations, but in this case the difference in steady-state values is about a factor of two. Crud transport

Cobalt Source Reduction

computer calculations suggested radiation levels should be only about 20% lower in plants that begin operation with Zircaloy fuel grids compared with those that begin operation with Inconel grids. With the available evidence from Borselle, an investigation was undertaken to estimate the cobalt impurity concentration that could have been present in the nickel plating used to fabricate Inconel fuel grids manufactured by Westinghouse. This study showed that the cobalt concentration in the nickel plating could have ranged from 0.04 to 1.3% for grid spacers fabricated from the late 1960s to early 1978.

Industry Experience: The Borselle plant staff concluded that a significant fraction of the high radiation levels observed in the steam generator channel head could be attributed to ^{60}Co that formed from cobalt that was present as an impurity in the nickel plating used in the manufacture of the Inconel fuel grid spacers. They estimated that the nickel used to plate the Inconel had cobalt impurity concentrations exceeding 1%. Subsequently, the staff implemented new cobalt impurity levels both for fuel elements and for processes involved in their fabrication. Examples of these limits include: cobalt limits in the nickel used as anode materials for the pre- and main Ni plating baths were lowered from 100 ppm for the ninth reload to 50 ppm thereafter; low cobalt nickel salts were specified for the nickel plating baths; Inconel with cobalt less than 200 ppm was specified for spacer grid straps for the 12th reload; stainless steel with less than 240 ppm cobalt was specified for control rod guide tubes purchased for the 11th reload; old tubes with 800 ppm cobalt were rejected; and solder materials with cobalt levels under 100 ppm were specified for use in the 9th and subsequent reloads.

Eliminating In-Core Cobalt Sources

Elimination of in-core sources of cobalt-base HF alloys is critical to reducing shutdown dose rates. EPRI data have shown that such sources contribute more to shutdown dose rates than identical amounts of cobalt-59 released from an ex-core source. Establishing low limits for cobalt impurity levels in the structural alloys used in replacement components, especially those that will be irradiated in the reactor core (e.g., fuel assembly components and BWR control blades) will help to reduce the quantity of in-core cobalt. The limits should also be placed on materials used to fabricate in-core components, such as the alloys used to braze fuel spacer grids.

Cobalt-base alloys in the pins and rollers of BWR control blades are an example of an in-core source with a high specific ^{60}Co activity. The most effective way to eliminate this source is to accelerate replacement of BWR control blades with new ones containing cobalt-free pins and rollers even if such a changeout may not be justified based solely on source reduction considerations.

Industry Experience: At Southern Nuclear Operating Company's Hatch-2 unit all cobalt bearing control blades were removed by 1997. Four to five years later, the station experienced the lowest shutdown dose rates as measured at any U.S. BWR, although other factors, including good chemistry control, contributed to this excellent performance.

Similarly, one factor contributing to the historic low shutdown dose rate values reported in Swedish BWRs is that cobalt-base alloys were never used in the pins and rollers of control

blades installed in these plants. Elimination of in-core sources at the newer Siemens-designed KONVOI PWRs has played a key role in reducing shutdown radiation fields.

Eliminating Ex-Core Cobalt Sources

Cobalt sources are not limited to surfaces exposed to reactor water. Several specific ex-core sources are discussed in this section of the document including low pressure turbine buckets, jet pumps, and valves. The focus of this information is on source elimination or reduction; it does not elaborate on the nuances related to when a material is “in-core” or “ex-core”.

Turbine Buckets

Industry Experience: As discussed in Appendix A, the Quad Cities Exposure Reduction Challenge Board identified the Stellite buckets in the low pressure turbine as a major cobalt contributor. The Challenge Board findings suggested that the turbine buckets released up to 3 grams/month of ⁵⁹Co to the reactor, and subsequently the blades were replaced with flame hardened blades.

Jet Pumps

Several stations including Susquehanna and LaSalle have experienced failures related to jet pump wedges and restrainer brackets. Slip joint leakage (and possibly other factors) led to excessive vibration and subsequent damage. LaSalle station replaced their damaged jet pump wedges with low cobalt alloys. Similarly, as part of their Unit 1 restart effort, Browns Ferry has approved jet pump inner mixer wedge replacement using X-750 alloy. Figure 3-2 is a photo of an actual jet pump beam assembly.

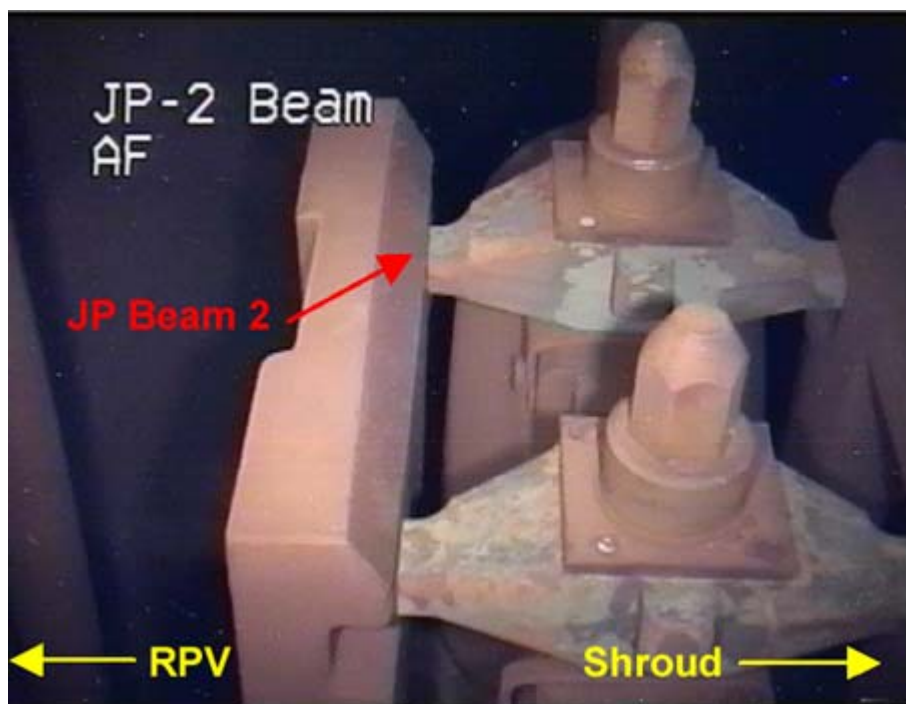


Figure 3-2
Typical Jet Pump Beam

Pumped Forward Heater Drains

In BWRs, pumped forward heater drains result in a portion of the reactor feedwater bypassing the condensate purification system. The bypass flow transports iron and other corrosion products directly to the reactor. This increases the volume of material available for irradiation, contamination and subsequent deposition on both in and out of core surfaces.

Cobalt Contribution from Valve Maintenance Activities

Valve maintenance activities can generate significant amounts of debris containing cobalt. This debris invariably results from seat repair activities such as grinding. This particulate material can result in significant radiation fields. Much of the debris can be controlled by close attention to barrier type and use, clean-up techniques and tools, and close out inspection quality. Reducing the potential for cobalt introduction may be improved through the use of non-cobalt seat replacements, whole valve replacements, or using flanged valves that can be repaired away from the system opening.

Debris Description

The quantity of material removed from valve seat faces by grinding depends on the severity of the damage to the face. Typically, 25 to 250 microns of Stellite can be removed during repairs; however, in extreme cases, 500 microns or more may be taken off to correct seat leakage. The

weight of the material removed is a function of the valve size, type, and design, and the density of the hard facing. Representative weights of material ground off are ½ gram from a 2-inch (DN50) valve to an extreme value of 50 grams from a 24-inch (DN600) main steam isolation valve (MSIV). Values in the 9 to 18 gram range are more typical for the MSIV. The size of the debris typically ranges from 4 to 40 microns with a median length of 10 microns. Particles of this size can be kept in suspension, due to molecular motion of water, and can circulate throughout the plant for long periods.

To minimize the cobalt contribution, plants should ensure that valve maintenance activities involving seat repair are controlled in such a manner as to ensure control of material and efficient removal of debris. The following recommendations are intended to complement foreign material exclusion (FME) programs.

Target Valves

Valves with Stellite seats in systems that flow directly to the reactor such as BWR feedwater, RHR, CVCS, RWCU, etc. are the greatest contributors. Discussions with plant maintenance personnel indicate that valves most frequently worked in these systems included

- Feedwater control valves
- RHR check valves
- Valves required to be local leak rate tested (LLRT) under the 10CFR50 Appendix J program.

Industry Experience: At least one station exempts Appendix J valves from their cobalt reduction program because of the significance of LLRT failure potential.

Other systems that do not directly communicate with the reactor (e.g. BWR main steam), can also contribute cobalt depending on system removal rates as well as the amounts resulting from maintenance. For example larger valves, (e.g., the BWR main steam isolation valves) create large amounts of debris that may not be removed in the condenser and condensate polishers.

Foreign Material Exclusion

Maintenance Activity Preparation

Several steps should be taken to reduce the potential for cobalt introduction before valve seat repairs begin. After all fluids are drained from the valve, the cavity is wiped down to remove loose dirt, corrosion byproducts, and other debris, and then allowed to dry. This will facilitate post-work cleanup and minimize debris becoming entrapped in the corrosion film on the valve interior. The valve runs should be blocked to prevent debris from migrating into the pipes. Baffles or inflatable dams are recommended for this purpose. Sometimes the use of a protective film that can be peeled off after the repair is finished may be considered. The film will reduce the number of crevices and surface irregularities in which debris can be trapped inside the valve. Another approach is to use a paper with an adhesive on one side in appropriate locations near the grinding activity. The net results will be better cleaning efficiencies and lower cobalt input.

Post-Maintenance Cleaning

The most effective means of limiting cobalt input from in-place valve seat maintenance, aside from replacement of the cobalt-based seating material, is post-work cleaning. Following seat grinding, the valve should be cleaned as thoroughly as possible to meet ANSI N45.2.1 Class B cleanliness standards. Class B is the high level of cleanliness applicable to reactor coolant systems, components, and other items.

Industry Experience: The BFN 1 chemistry organization obtains samples from the worked component and uses energy dispersive X-ray fluorescence (XRF) spectrometry for a rapid empirical analysis of elemental cobalt-59. That information is used to verify that the station's post maintenance component cleanliness standards are met.

Vacuuming is the most effective and quickest method to remove the grinding debris. Sixty percent removal rates have been reported in two tests. By using micro tool attachments such as crevice wands and brushes, it is possible to clean the runs and other difficult-to-reach places in the valve. Commercially available HEPA vacuums are designed specifically for this type of task, which reduces the potential for contamination spread via the vacuum exhaust. Additionally, routing the exhaust into existing building vents will further reduce contamination.

The grinding debris can also be wiped out; tack cloth approved for contact with system surfaces is an efficient wiping technique, with a 37 % removal rate in a one-time test. Wiping the valve with a lint-free cloth and an approved solvent greatly increases the effectiveness of cleaning by wiping. This technique includes demineralized water, alcohol, or other approved solvents. The solvent should not be volatile (creating airborne contamination) and must be compatible with the station's chemical control program and NSSS vendor specifications. Some plants reported the use of the spray foam used for decontamination. The wiping should be thorough with sufficient effort applied to remove as much of the debris as possible. If a film was applied prior to commencing maintenance activities, applying a second overlay coating of the film after repairs but prior to cleanup will seal the debris between the two layers facilitating more efficient debris removal.

Inspection

Independent verification is the preferred method to monitor the cleaning procedures. The criteria of ANSI N45.2.1 (3-7) should be used. Visual inspections should be made with adequate lighting and mirrors or other devices, when necessary. Wipe tests should also be made, using clean, white, lint-free cloths. Further cleaning is required when the valve fails either the visual or wipe inspection test. Procedures should include a signoff sheet to document the inspection.

Alternative Repairs

Cobalt input can also be reduced by decreasing the amount of in-place valve seat grinding. The use of valves with replaceable seats should be considered. This is also an ideal time to replace the cobalt seat material and eliminate the cobalt corrosion by-product contribution. Some plants replace smaller valves entirely rather than repair them. Although this is done as an economic

measure and is not specifically aimed at cobalt reduction, it results in a reduction of cobalt input to the system. Another option is to use a flanged valve that permits removal, shop repair and reinstallation, which facilitates a significant portion of the post maintenance cleanup and minimizing the chance of cobalt debris entry.

Alternatives to Cobalt-Base Hardfacing Alloys

Evaluations of new cobalt-free HF alloys and their subsequent use in nuclear power plant components have been supported mainly by EPRI and Siemens. Appendix A and B contain examples of Exelon procedures for identifying cobalt contribution and prioritizing replacement efforts. This section will provide recent information about various evaluations and plant applications of EPRI's NOREM HF alloy and will also summarize information available in the open literature about the use of such alloys in Siemens-designed PWRs and in Atomic Energy of Canada-designed CANDU reactors.

Delcrome 910

Samples were fabricated from two different heats of Delcrome 910 and were evaluated for their friction and galling behavior by the tribology group at Battelle Columbus Laboratories for the CANDU Owner's Group (COG). The tests indicated acceptable wear and corrosion; however, higher coefficients of friction were noted.

F-20

EPRI is currently evaluating an alternative low-cobalt iron-based alloy developed in Sweden by Durloc in conjunction with Uppsala University. The current trade name of the alloy is F-20. The alloy is applied to surfaces using a computer-assisted laser welding technique. Preliminary tests indicate promise; however, complete test results will not be available before the end of 2004.

NOREM

EPRI's goal in supporting the development of new Cobalt-free wear-resistant alloys was to provide an alternative to the long-established Cobalt-base StellitesTM for nuclear valve applications.

After successful results were obtained with the alloys that were eventually trademarked under the NOREM name, additional wear tests were performed and other attributes needed for the proposed plant applications were evaluated. These attributes included measurements of other types of wear resistance, such as cavitation-erosion wear and adhesive wear, (again using test procedures specified by ASTM) and of corrosion resistance under simulated LWR operating conditions. Application of HF alloys to nuclear valve components relies on various welding techniques, and an extensive program was implemented to address issues associated with NOREM welding.

After favorable results were obtained from the initial laboratory evaluations, NOREM was used as the valve trim in small 6" gate valves that were stroked (opened and closed) under controlled conditions designed to simulate the operating conditions typically found in the primary circuit of LWRs. The first of these tests were performed at AECL and then at Electricité de France (EDF). The main goal of these tests was to measure valve leak rates (a more direct measure of hardfacing performance than can be obtained from the pin-on-plate galling wear tests) after a specified number of stroking cycles. At the conclusion of the test the performance of the valve trim was further evaluated by using optical and electron microscopy.

The NOREM alloy was then thoroughly evaluated in a series of laboratory and industrial trials. The results of these tests were documented in detail in several reports (3-1, 3-2), and the summaries of the tests are given below.

Wear and Fracture Toughness Measurements—Galling wear measurements were performed using button and block specimens. All of the HF alloys were tested as self-mated couples in water at ambient temperature. NOREM 02 appears to have the optimum balance of galling wear resistance and fracture toughness values for the iron-base hardfacing alloys studies here.

Coefficient of Friction and Galling Threshold Measurements—EPRI developed a methodology for predicting gate valve thrust requirements under flow and differential pressure conditions. From the series of tests performed on the two NOREM variants, it was concluded that temperature, contact stress, stroke length and contact area under loaded conditions play an important role in establishing the frictional and galling response of the alloys. The combination of intermediate temperatures and long stroke lengths appeared to be most conducive to the onset of galling. The only HF alloy that exhibits similar responses in both pin-on-plate and the Batelle Columbus Laboratories (BCL) sliding wear tests is Stellite 6.

Localized HF Repair Techniques—The HF alloys used to provide wear and corrosion protection to critical surfaces pose a challenge when these alloys must be repaired in the field after components suffer degradation following service. Utilities must either replace the hardfaced component or go through a time-consuming and difficult repair procedure. Valve vendors and service organizations have developed in-situ repair procedures using high preheats and proprietary welding procedures. However, the repair effort does not always meet expectations and the owner must then replace the component.

Successful repair practices were developed for stainless steel, carbon steel, and chrome-moly, but the details of the procedure differed for each alloy. The results were reviewed, and HF repair guidelines were developed. Consult reference 3-2 for the detailed procedures.

Evaluation of Manual Plasma Welding (PTAW) with Powder HF Alloys—All repair welds were conducted with the Stellite MicroStar system using the manual PTAW process in the flat position. NOREM 02A could readily be used to repair welds on stainless steel pipe mockups with full depth cavities and no preheat. Full depth cavities on the carbon steel pipe mockup were difficult to repair, but success was achieved using Anval powder and high 450°F preheat. Repair of circular patch welds on plates was difficult to achieve in all circumstances. Cracks often occurred at the initiation of the arc and in some cases even with the application of preheat. No significant improvements were found after the plates were stress relieved. NOREM applied over

a stainless steel 309L butter layer on the carbon steel plate was readily repaired with a 200°F preheat. Successful repair welds were accomplished with shallow repairs requiring a single pass at 400°F and 200°F preheats. Anval powder was found to be more “welder friendly” and provided better results than the Praxair powder.

Corrosion Measurements—AECL performed corrosion evaluations of the NOREM hardfacing alloys as part of the post-exposure of valve seats and discs that were used in the valve loop tests and no indications of corrosion-induced degradation were found (3-2). The performance of NOREM in all of these environments was deemed to be acceptable.

Limited evaluations of the corrosion resistance of NOREM following exposure to chemical decontamination solvents have been performed. The corrosion film thickness formed on coupons exposed to the five-step CAN-DEREM™ process was somewhat smaller than those that formed on Stellite 6 coupons that were exposed to the same conditions.

Loop Tests of Valves with NOREM Trim

EDF tested a 6” gate valve under typical PWR operating conditions (3-1). The valve was initially stroked 860 times in ambient temperature (70°F) water. The loop temperature was then raised and the valve stroked for 1500 cycles, opening at a differential pressure of 155 bar (15.5 MPa) and closing at a nominal flow rate of 2.5 m/s at a temperature of 285°C (545 °F). The friction coefficient was continuously monitored. Leak rates were measured after 50, 500, 1000, and 1500 cycles.

After cycling at ambient temperature, the measured leak rate was 3.8 cm³ per hr at 170 bar. There was no galling or significant abrasion of the NOREM surfaces. After cycling at elevated temperature, the valve again showed no evidence of galling. However, the measured leak rates were somewhat higher than the value established by EDF as the acceptable limit for a 6” gate valve. The high leak rates were reported to be the result of damage (“scratches”) on the downstream seating surfaces that apparently resulted from abrasion that occurred shortly after testing began at elevated temperature. Some “healing” of the damage took place with continued stroking as demonstrated by the fact that lower upstream to downstream leakage rates were measured after 1500 cycles than after 50 cycles (Table 3-1). EDF continues to view NOREM as holding promise to serve as a replacement for Stellite 6 and tests of other valves with NOREM are taking place.

Table 3-1
Seat Leakage of Gate Valves with NOREM HF – EdF Test Results

Test Condition	Strokes	Differential Pressure (bar)	Up to downstream Leak Rate (liter/hr)	Down to Upstream Leak Rate (liter/hr)
Cold (35 C)	860		3.8	1.2
Hot (285 C)	50	170	80	2
Hot (285 C)	500	170	40	1.26
		260	2500	0.35
Hot (285 C)	1000	170	250	0.5
		260	360	0.4
Hot (285 C)	1000	170	45	1.0
		260	85	1.5

Compilation and Evaluation of NOREM Test Results: Implications for Valve Applications

An evaluation of all available information was undertaken in 1999 to identify the acceptable range of conditions for specifying NOREM as an alternative to the Cobalt-base Stellite HF alloys. One motivation for undertaking this review was to provide utility personnel responsible for performing 10 CFR 50.59 evaluations with a roadmap for documenting that an Unresolved Safety Question (USQ) does not exist when specifying NOREM as a substitute for Cobalt-base HF alloys in replacement valves and in-valve repairs. This review confirmed the response of NOREM was equivalent to, or better than, the response of Cobalt-base Stellite HF alloys in all wear and corrosion evaluations as well as weldability assessment, with two exceptions:

1. In sliding wear tests performed at BCL (reference EPRI report TR-109655), NOREM responded more poorly than in earlier evaluations of the alloy. Galling was seen at loads as low as 10 ksi at 200 degrees F and the coefficient of friction (COF) was rather high. Stellite 6 offered superior performance based on measurements of friction coefficients and galling resistance performed on specimens characterized by large contact areas and long stroke lengths.
2. Leak rates were higher than a standard specified by EdF in measurements performed on a 6" gate valve that had been stroked under simulated PWR operating conditions.

Note: The results suggest that caution is appropriate when specifying NOREM HF alloy for use in some gate valve applications.

Gate valves can easily experience line and point contact loads much higher than 15 ksi in applications where the valve must stroke under DP conditions. A primary concern surrounds NOREM use in gate valves where design and service conditions can lead to large contact areas between two surfaces hardfaced with NOREM. Until further field experience is available, coolant flow rates, contact stresses, and leak rate requirements should be reviewed carefully with the valve manufacturer if NOREM is proposed for use in gate valves larger than 6".

No USQ exists if NOREM is specified as a substitute for Cobalt-base HF alloys in nuclear plant stop and swing check valves, globe valves, and butterfly valves of any size. Also, no problems are anticipated if NOREM is used to repair a gate valve disc and Stellite is used for the valve seat.

Industry Experience of Valves with NOREM Trim

NOREM trim has been applied in several nuclear applications.

Grand Gulf Nuclear Station performed the first field repair of an installed valve at a nuclear power plant using the NOREM alloys beginning in 1995. The research was extensive; the details are described in reference (3-2).

Comision Federal de Electricidad (Laguna Verde) applied NOREM to the seats and discs of four 4" gate valves and one 12" gate valve. The valves were inspected during the first outage following their installation, and NOREM performance was satisfactory. The utility has indicated it plans to use NOREM to repair other valves.

Taiwan Power Co. (KuoSheng) replaced a 20" double disc gate valve with NOREM on the disc and Stellite on the seat ring in 1995. The valve is in the recirculation system and operates at 1650 psi at a flow rate of 32,550 gpm. This valve was disassembled and inspected at the May 1998 outage and NOREM performance was reported as "good."

Exelon's Byron station installed a 3-inch 900# CF8M double disc gate valve in February of 2002 to increase RCS letdown flow. These valves will be cycled twice per refueling outage (once during system startup and once during system shutdown). There are no long-term performance data on these components. Also at Byron, 2 inch 600# WCB split wedge gate valves have been used in a plant modification to supply alternate cooling water to the charging pumps. There have been no indicated failures of these valves, which were installed in Oct. of 2001.

Dominion Engineering installed a 4" gate valve with NOREM trim in the recirculation spray system in March of 1996 at its North Anna Station. The system is designed for 150 psig at a design temperature of 285°F. The system working pressure is 130 psig and the working temp is 130°F. There have been no internal inspections or reported problems with this valve since it was installed.

Two-inch double disc gates valves with NOREM were placed in service at Entergy's River Bend BWR in April 1999 in the RWCU suction line. Although these valves have not been inspected since their installation, there have been no reported problems since the valves were installed.

EdF has purchased check and globe valves with NOREM trim from the Velan Valve Co. (France) for use in the primary circuit of their nuclear plants, but performance results have not yet been obtained.

Cobalt Reduction in Siemens-Designed PWRs

Since the introduction of its first plants in 1982, subsequent generations of Siemens-designed PWRs have incorporated design and operational features to lower shutdown dose rates. One of the principal design changes that was implemented to reach this goal has been a reduction in the inventory of high cobalt Stellite™ HF alloys. The alloys selected for use in the KONVOI plants were chosen based on the results obtained from an extensive evaluation of the metallurgy (microstructure), wear (including friction coefficients), corrosion resistance, mechanical properties, and “weldability” of various candidate alloys.

The reported results of this evaluation (3-2) are based on testing of three iron-base alloys, Everit 50, Antinit DUR 300, and Cenium Z 20. Wear tests were performed both at ambient and elevated temperatures. Corrosion evaluations were performed under simulated BWR and PWR coolant chemistry conditions in test rigs that permitted alloy responses to be evaluated under no-flow, low-flow and high flow conditions. Siemens staff also devoted considerable efforts to identifying the specific load parameters faced by HF alloys used in various plant applications so that these requirements could be compared with the measured property profiles of the candidate replacement alloys. The key factors were deemed to be the normal force, the areas of the contacting surfaces, the total sliding length and sliding velocity, the allowable minimum clearance, and the operating environment. Antinit DUR 300 was selected for use in many of the in-plant applications in the KONVOI design, although it did not provide the highest wear resistance in the laboratory evaluations.

The report describes the reductions in the cobalt inventory associated with each generation of Siemens plants and has correlated shutdown dose rate trends with the reductions in cobalt sources. In the first three-loop PWRs, the Stellite inventory was variable but high and there was no effort to use cobalt-free alternatives in any applications. In the first standard four-loop plants the total Stellite area in contact with the primary coolant was 11.46 m². In later four-loop units this value was lowered to 8.08 m² and then to 2.44 m². In the latest KONVOI design this value has been reduced further to 1.80 m², with the largest remaining use of Stellite being in the control rod drive mechanisms. In the evolution of these designs the in-vessel cobalt inventory dropped from 1.52 m² to 0.02 m² and the valve inventory from 5.6 m² to 0.56 m². Also, cobalt-base HF alloys are no longer used in the main coolant pumps. The locations and surface areas of components with Stellite are shown in Table 3-2.

Radiation fields measured on main coolant pipework and on the channel head hot leg at Siemens PWRs show the benefits realized from lower cobalt inventories. Pipework radiation fields at KONVOI plants are less than 0.2 mSv/h and on the channel head they are less than 10 mSv/h. The values were reached within the first cycle of operation and remained constant through the third operating cycle. Measurements of deposited activity values were converted into percentage contributions of the various deposited isotopes. The contribution of ⁶⁰Co to dose rates in the KONVOI plants is now so low that it is no longer the dominant contributor to shutdown fields (⁵⁸Co contributed from 50 to 75% of the fields over the first two operating cycles). Total coolant concentration data (soluble plus insoluble) for the main radionuclides were expressed as cycle-average values. The ⁶⁰Co coolant concentration trends are similar to those found for shutdown radiation fields and ⁶⁰Co activity deposition. Compared to the early designs with high Cobalt inventories, the ⁶⁰Co levels at the KONVOI plants are four to five times lower.

Table 3-2
Stellite Surface Areas in Siemens PWRs (m²)

Component	3-loop units GKN-1, KKG CNT	4-loop units (standard) KKG-BAG KWG	4-loop units (Stellite reduced) KKP-2	4-loop units (Stellite reduced) KBR	KONVOI KKI-2 KKE GKN-2
Control rod drive assemblies	Y	1.22	1.22	1.22	1.22
In-vessel components	Y	1.52	0.02	0.02	0.02
Main coolant pumps (a)	Y	2.92	1.04	0	0/0.3 (b)
Valves	Y	5.8	5.8	1.2	0.56
TOTAL	variable	11.46	8.08	2.44	1.80/2.10

Notes

Y Denotes Stellite is present but areas vary from plant to plant

a KSB pumps installed at KKG, KKG-BAG, KWG, KBR, KKI-2, and KKE (Stellite mainly on impeller edge); Andritz pumps installed at GKN-1, CNT, KKP-2 and GKN-2 (Stellite mainly on shaft in radial bearing)

b Stellite used only at GKN-2

The progressive elimination of Stellite in Siemens PWRs enables one to assess the relative contribution of different Stellite sources on radiation fields. A comparison of the results for the different designs suggests that Stellite HF is the main source of ⁶⁰Co in the coolant and on primary system surfaces. Because the KONVOI plants retain Stellite in the control rod drive mechanisms (CRDMs), the results suggest that the primary source of ⁶⁰Co in the Siemens PWRs is cobalt released from other sources. This conclusion is consistent with results reported by Westinghouse staff in their evaluation of cobalt sources. Measurements of CRDM wear in a test designed to simulate 20 years of plant operation, together with estimates of corrosion release rates, showed that cobalt release from CRDMs is less than 10% of the total inventory released from the representative three-loop and four-loop plants (Beaver Valley and Trojan). It was also noted that because the position of the CRDMs is above the reactor vessel and the intricate coolant pathway to some of the high cobalt parts, some of the released high-cobalt corrosion and wear products would be trapped in the CRDM parts, a hypothesis that is supported by radiation surveys indicating crud is trapped in some CRDM parts. A similar assessment of cobalt sources in Combustion-Engineering-designed PWRs concluded that CRDMs account for approximately 50% of the released cobalt, but this assessment was based on estimated values of Stellite wear rates, rather than on direct measurements of CRDM wear.

In the intermediate Siemens designs, the main improvement was the virtual elimination of cobalt from in-vessel components. Cobalt was eliminated from the control rod alignment pins, the grid plate centering bolts, the hold down plates of the upper core support, and the centering bolts of the upper core support. The substitute material used for the first item was a Cr₃C₂/CrNi-binder and for the other items Antinit DUR 300. The total reduction in area of Cobalt-base alloys as a result of these substitutions was approximately 1.16 m². The ⁶⁰Co contribution to radiation fields was a factor of 3 to 6 times lower after four cycles than in the earliest designs even though there

Cobalt Source Reduction

was only a 30% reduction in the total cobalt inventory. In a later intermediate design, Stellite also was eliminated from the main coolant pumps and valves that are subjected to lesser duty. The radiation field data suggest these changes provided little extra benefit.

In the KONVOI design, Stellite was eliminated in medium duty valves, such as the pressurizer spray valves and purification system flow control valves. Eliminating these Stellite sources has further reduced radiation fields by approximately 50%, compared with fields measured at “intermediate” design PWRs. Although this reduction is significant, the further improvement was only about 15 to 25% of the reduction in radiation fields that was achieved by eliminating the in-vessel sources of Stellite.

Cobalt Reduction in Atomic Energy of Canada CANDU Reactors

No limit was placed on the use of Stellite in Atomic Energy of Canada’s early CANDU designs, and the alloy was used extensively in Pickering Nuclear Station (PNS) Units 1 to 4. The single exception was in the main heat transport circulating pumps, where the original bearing sleeve that was hardfaced with Stellite was replaced with Type 420 stainless steel prior to startup. Cobalt-free alternatives to Stellite were available for the later PNS Units 5 to 8 and these alloys were used in a number of valve applications. The Ni-base alloy Deloro 50 was used in large isolating valves, such as steam generator and main pump isolation valves. Other Ni-base alloys, Colmonoy 4 and 5, were used for a large number of drain and vent valves, and Type 440C stainless steel was selected for use in feed and bleed valves. Subsequent evaluations showed that these Ni-base hardfacing alloys suffered significant corrosion-induced degradation in service, especially in neutral and acidic conditions. Current AECL specifications require forged, hardenable stainless steel alloys, such as 17 4PH, Type 440C, or Type 410, in the seat rings and plugs of globe and flow control valves. NOREM is specified for use in swing check valves because of its good corrosion resistance under all CANDU chemistry conditions, and galling is not a concern in these valves because there is no sliding contact. The cobalt-base Stellites are still specified for use in gate valves. The Fe-base Delchrome 910 alloy is being evaluated as a potential substitute for Stellite.

Logic Tree for Implementing a Valve Replacement/Refurbishment Program

The realization that many valve functions do not require cobalt-base HF alloys and the increasing availability of valve types and sizes with cobalt-free hardfacing alloys by valve vendors supplying the nuclear power industry suggest that the use of cobalt-base HF alloys as the default value for all valve trim is not appropriate. An approach for selecting appropriate valve trim for nuclear power plant valves was developed in the last revision of the Cobalt Reduction Guidelines – Revision 1, which was developed with the assistance of utility and valve vendor personnel.

The recommended approach for implementing a cobalt reduction program is shown schematically in Figure 3-3, which addresses all the issues and concerns that have been identified in this chapter. The approach assumes that replacement of valves or valve parts will not be performed only to lower the cobalt source term. Rather, cobalt reduction should be pursued only as an adjunct to other work that is required to restore the valve to meet specifications. It is assumed there is evidence of shortcomings in the valve’s performance. (e.g., the valve fails a

mandated leak rate test or there is some other evidence the valve is not meeting its design requirements). Appendix A contains example procedures for contribution estimating and prioritization.

Identification of RCS Contact Valves

The first step in addressing valve material impact on the cobalt reduction program is to identify those valves that are in contact with reactor coolant systems and sub systems. As discussed previously, opportunities exist for valves outside the primary system boundaries to contribute to the cobalt source term through erosion, carryover, and incorporation in recycled liquid wastes. This evaluation should capture not only the system and valve nomenclature, but also the type of valve (gate, globe, swing check, etc.), manufacturer, serial number, and the operational environment to which the valve is exposed, i.e., flow rate and cyclic duty.

Candidate Valve Identification and Prioritization

Some utilities have implemented cobalt reduction programs using a systematic approach that estimates cobalt releases from many or all primary system valves by using published estimates of Stellite wear and corrosion release rates. This is not the most effective approach to address this issue. Because valve refurbishing or replacement typically occurs during plant outages to address issues other than source term reduction, the replacement rate will be low. The initial focus should be on eliminating Stellite from those valves that historically have been found to be in need of refurbishing. This approach streamlines the process for identifying replacement candidates and likely serves to focus on those valves that are indeed the largest contributors of released cobalt to the primary circuit.

Cobalt Release Estimation

One result supported by field experience of this road map is that the use of cobalt-base HF alloys is not necessary to achieve satisfactory valve performance in some valve designs. An early EPRI study reported wear measurements on a number of components following service in commercial LWRs. These measurements established that BWR feedwater check valves are a large source of released cobalt. After one year of service at Vermont Yankee, the measured cobalt released from feedwater regulator valve “A” was about 30.4 grams and from valve “B” approximately 8.0 grams. Vermont Yankee used costly decontamination operations in 1979, 1981, and 1983 to lower shutdown dose rates at each of its then yearly refueling outages. Vermont Yankee then replaced the cobalt-base HF previously used in these valves with cobalt-free Type 440C stainless steel valves at the 1981 outage. After each of the next two operating cycles, measurements showed that wear of these new feedwater valves was negligible. Measurements performed at the

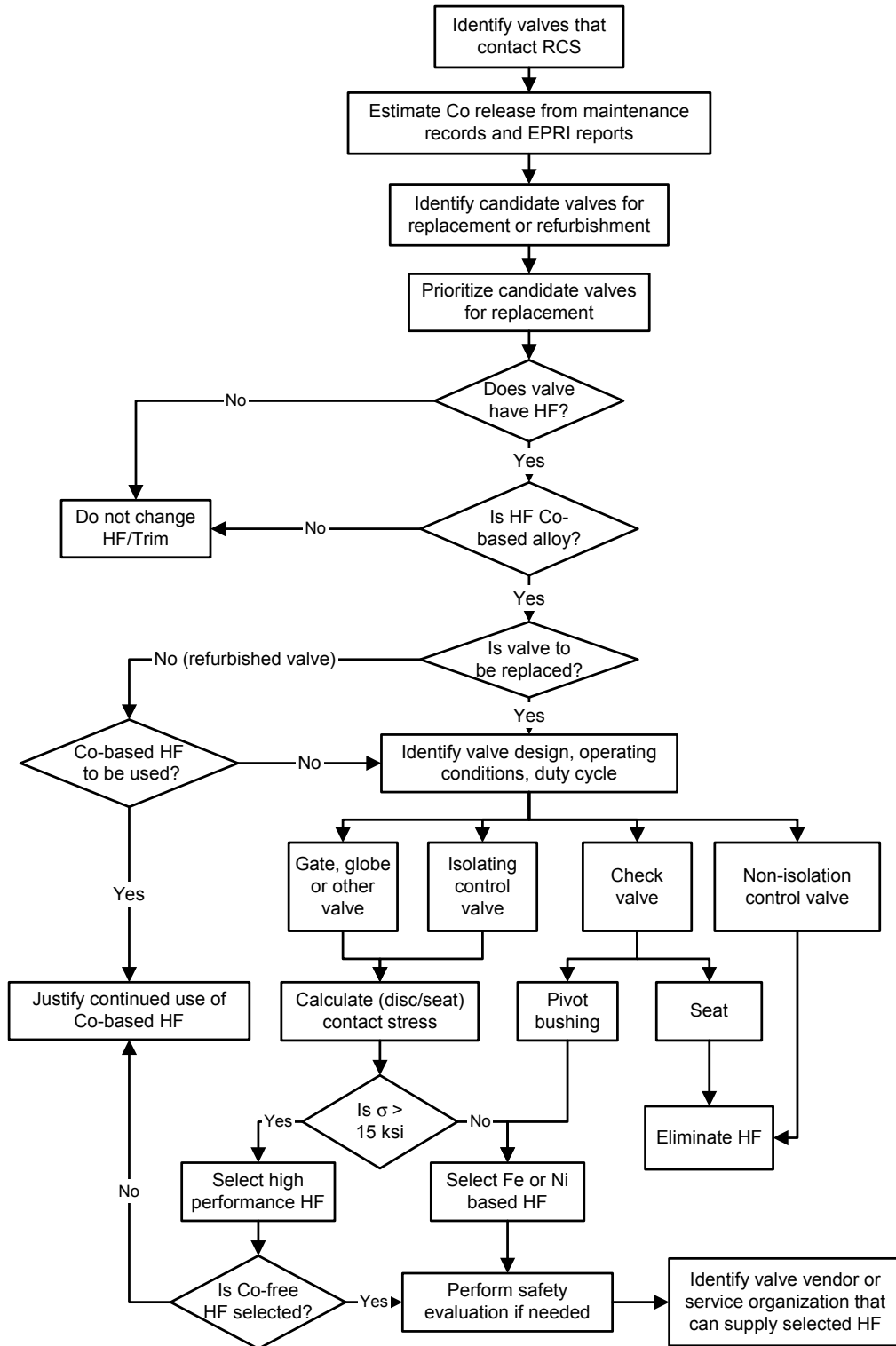


Figure 3-3
Schematic for Implementing a Cobalt Reduction Program for Nuclear Plant Valves

1983 outage showed that maximum wear of the 440C stainless steel was less than 10 microns and the maximum wear after the second fuel cycle of operation was less than 25 microns. This contrasts with the 1.5 millimeters of wear that was measured after operation for one fuel cycle when the valve earlier contained Stellite hardfacing. Utility personnel concluded that replacement of these stainless steel valves would not be needed for at least ten years. The use of these cobalt-free valves is one of the factors that have contributed to the dramatic drop in shutdown dose rates at Vermont Yankee, from its high value of almost 1200 mR/hr in 1983 to its current value of about 100 mR/hr in 2002.

Evaluation of Various Cobalt Sources in Westinghouse Designed Plants

The influence and effect of various cobalt input sources can be made in two ways: (1) an evaluation of the direct effect on plant dose rates and, (2) a review of the amounts of ^{60}Co and ^{58}Co released during refueling shutdown chemistry evolutions. This section summarizes the results of prior direct evaluation studies of the effects of various cobalt sources in Westinghouse designed plants and presents the trends in the amounts of ^{60}Co released during refueling shutdowns in the Ringhals PWRs.

Evaluation of Plant Dose Rates

Early evidence of the effect of cobalt sources on PWR plant dose rates was first reported on wherein the dose rate trends in the Borselle PWR plant were evaluated. It was found that the cobalt impurity content of the nickel plating used in the Inconel fuel grids manufacturing process was as great as 1%. Since the fuel grids are in a high fuel flux, the activated cobalt presented a potentially large source of ^{60}Co that could be released into the primary reactor coolant system. A check of the cobalt content of the nickel plating used in Westinghouse fuel grids also found that the cobalt content could have been greater than 1% for a period of time. Subsequently, the effect of various cobalt sources on the dose rate trends in Westinghouse designed plants were evaluated (refs. 3-3 and 3-5) and the results are summarized below.

The effect on dose rates of the following cobalt sources were evaluated: (1) use of high cobalt impurity nickel plating in the Inconel fuel grids, (2) replacement of low cobalt impurity Inconel fuel grids with no-cobalt impurity Zircaloy fuel grids, and (3) use of low cobalt impurity Alloy 690 tubing in replacement steam generators. The trend of the dose rates and the absolute value of dose rates in the plants as measured at three locations in the plant were used in the evaluation. The results of the evaluation, summarized in Table 3-3, show the approximate effect of the factors on plant dose rates:

Table 3-3
Approximate Effect of Various Cobalt Sources on Plant Dose Rates

<i>Cobalt Source</i>	<i>Dose Rate Fraction Reduction of Low Cobalt Sources</i>
High vs. Low Cobalt Impurity Fuel Grid Nickel Braze	0.80
High vs. Low Cobalt Fuel Grids (Inconel vs Zircaloy)	0.72
High vs. Low Cobalt Impurity SG Tubing	0.70
Overall Reduction	0.40

The evaluation also included the effect of changing the operational coolant chemistry from a varying pH to a constant pH. It was found that constant pH operation could account for another reduction factor of 0.86, or a combined overall reduction of 0.35 for the low cobalt and chemistry factors. The validity of these estimates was confirmed (Ref. 3-5) in that the average steam generator channel head dose rates in plants that have replaced steam generators and have had all of the source reduction techniques applied (4R/h) were about one-third of the average dose rate in plants that did not have any of the reduction techniques (12 R/h), because the steam generator represents about 85% of the RCS corroding surface, steam generator replacement (SGR) is essentially equivalent to operating with a new plant with respect to dose rate trends.

These results indicate that on the average the combined magnitude of the effects is reasonable. It is noted that the factors are based on the average of plant dose rates by categories. Inspection of the data from individual plants shows variations from the mean, suggesting that other factors influence the dose rates in certain plants or that the magnitude of the above factors can vary among plants.

Evaluation of ^{60}Co Released during Refueling Shutdowns in Ringhals PWRs

The amount of ^{60}Co released during refueling shutdown chemistry evolutions is expected to be an indirect measure of the amount of cobalt generated and transported during the fuel cycle. Data from the Ringhals 2, 3, and 4 plants were reviewed because a considerable amount of data is available before and after SGR (ref.3-6). It should be noted that the Ringhals units operated at elevated pH for several cycles.

The Ringhals data are of interest since they reflect plants that have had varying sources of cobalt as follows:

- Ringhals 2 had Inconel fuel grids that were contaminated with high cobalt impurity nickel grid plating and were subsequently replaced with low cobalt impurity nickel grid plating during a several cycle period. The plant also replaced steam generators with low cobalt Alloy 690 tubing.

- Ringhals 3 had Inconel fuel grids that were contaminated with high cobalt impurity nickel grid plating and were subsequently replaced by no-cobalt Zircaloy fuel grids during a several cycle period. The plant also replaced steam generators with low cobalt Alloy 690 tubing.
- Ringhals 4 had Inconel fuel grids that were primarily not contaminated with high cobalt impurity nickel grid plating and were subsequently replaced with no-cobalt Zircaloy fuel grids during a several cycle period. The plant has not replaced steam generators.

Table 3-4 lists the ^{60}Co released during refueling shutdowns cycle with pertinent notes. Figure 3-4 shows the radiocobalt release trends in the three Ringhals plants. Items that could influence the trends such as SGR and changes to low cobalt fuel grids are noted in Figure 3-4.

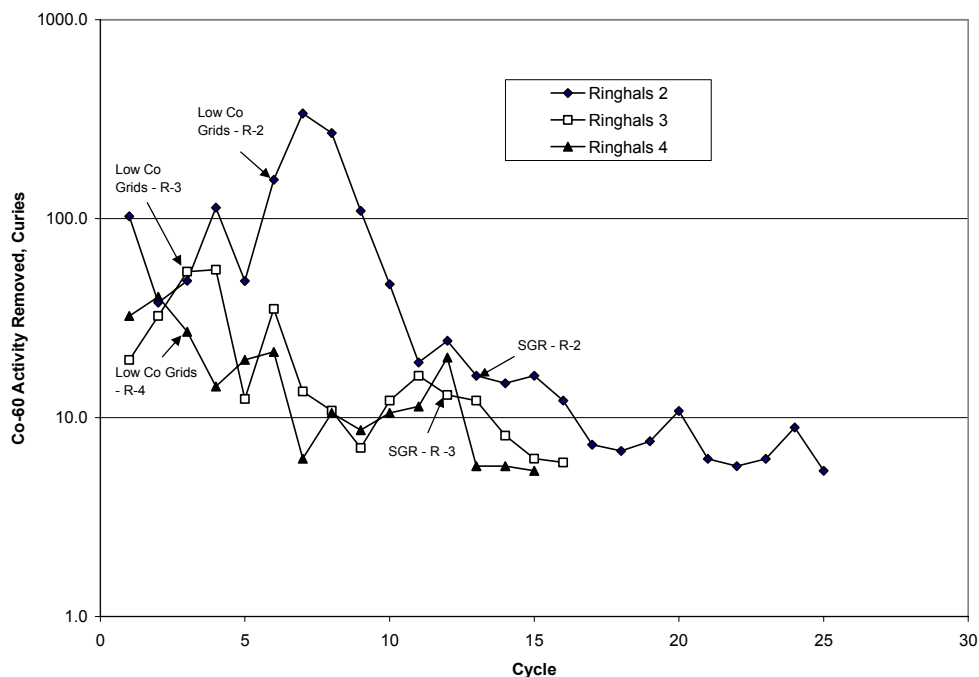
Table 3-4
Amounts of ^{60}Co Released (Curies) During Refueling Shutdowns in the Ringhals PWRs

<i>Ringhals 2</i>			<i>Ringhals 3</i>			<i>Ringhals 4</i>		
<i>Cycle</i>	<i>Year</i>	<i>Ci</i>	<i>Cycle</i>	<i>Year</i>	<i>Ci</i>	<i>Cycle</i>	<i>Year</i>	<i>Ci</i>
1	1977	102.7	1	1984	19.5	1	1984	32.4
2	1978	37.8	2	1985	32.4	2	1985	40.5
3	1979	48.6	3 ⁽¹⁾	1986	54.1	3 ⁽¹⁾	1986	27.0
4	1980	113.5	4	1987	55.4	4	1987	14.3
5	1981	48.6	5	1988	12.4	5	1988	19.5
6 ⁽¹⁾	1982	156.8	6	1989	35.1	6	1989	21.4
7	1983	337.8	7	1990	13.5	7	1990	6.2
8	1984	268.9	8	1991	10.8	8	1991	10.5
9	1985	109.5	9	1992	7.0	9	1992	8.6
10	1986	46.8	10	1993	12.2	10	1993	10.5
11	1987	18.9	11	1994	16.2	11	1994	11.4
12	1988	24.3	12 ⁽²⁾	1995	13.0	12	1995	20.0
13 ⁽²⁾	1989	16.2	13	1996	12.2	13	1996	5.7
14	1990	14.9	14	1997	8.1	14	1997	5.7
15	1991	16.2	15	1998	6.2	15	1998	5.4
16	1992	12.2	16	1999	5.9			
17	1993	7.3						
18	1994	6.8						
19	1995	7.6						
20	1996	10.8						
21	1997	6.2						
22	1998	5.7						
23	1999	6.2						
24	2000	8.9						
25	2001	5.4						

⁽¹⁾ Change grid nickel plating specification to low cobalt or change to no cobalt (Zircaloy) grids

⁽²⁾ Steam generator replacement (SGR) with low cobalt tubing

Cobalt Source Reduction

**Figure 3-4** **^{60}Co Released during Refueling Shutdowns in the Ringhals PWRs**

Inspection of the trends in Figure 3-4 and Table 3-4 indicates an effect on the amount of ^{60}Co released as follows:

- In Ringhals 2 and 3 the activity released first increased after the change to the low cobalt fuel grids and then decreased. This indicates a residual effect of the high cobalt impurity plating which is expected due to the long ^{60}Co half-life and the fact that changes take place over a three cycle period. A similar effect is not seen in Ringhals 4 indicating the fuel grids were not contaminated with the high cobalt plating.
- In Ringhals 2 and 3 the activity released tended to level off until the steam generators were replaced. They then continued to decrease after the replacement indicating the combined effect of the low cobalt Alloy 690 tubing and a possible lower corrosion release rate of the tubing relative to the Alloy 600 tubing used before replacement.
- The decreasing trend in the Ringhals 4 activity released indicates a lower corrosion release rate of the RCS materials with time of operation.

The average of the amounts of ^{60}Co released by several categories was calculated to reduce the variation in the values and further define and quantify differences among the categories. The average and normalized results are given in Table 3-5. The results were normalized to the average after seven or more cycles of operation after the change to the low cobalt material because by this time the residual effect should be minimal.

Table 3-5
Average and Normalized ^{60}Co Activities (Curies) Released by Categories

<i>Category Description</i>	<i>Amount Released during Shutdown</i>			<i>Normalized Amount Released</i>		
	R - 2	R - 3	R - 4	R - 2	R - 3	R - 4
Before Change to Low cobalt Mat'l	70.3	25.9	36.5	1.63	1.68	3.48
3 Cycles after Change to Low cobalt Mat'l	254.5	40.6	20.3	5.90	2.64	1.93
4+ Cycles after Change but before SGR	43.1	15.4	10.5	1.00	1.00	1.00
After SGR – Low cobalt Tubing	9.0	8.1	--	0.21	0.53	--

Inspection of the results in Table 3-5 suggests the following:

- The cobalt contamination was the greatest in Ringhals 2 as indicated by highest average activity after change to the low cobalt materials. Ringhals 3 had an intermediate contamination and Ringhals 4 had the lowest or none. Note that the average is the greatest three cycles after the change to the low cobalt material indicating the residual effect of the cobalt contamination due to the long ^{60}Co half-life.
- The low average amount of ^{60}Co released after SGR in Ringhals 2 and 3 reflects use of the low cobalt tubing.
- The decreasing trend in Ringhals 4 indicates the effect of the change to the Zircaloy grids and a decreasing corrosion release of RCS materials with time.
- The overall trends show that actions to reduce cobalt input into the RCS are reflected in the amounts of ^{60}Co released during shutdowns. Assuming that shutdown releases represent cobalt activation during a fuel cycle, lower plant dose rates should result from the cobalt reduction actions. Inspection of the SG channel head dose rates in the plants before SGR replacement (3-5) shows an approximate correlation in that the dose rates are in the same order as the average absolute released values, namely, highest in Ringhals 2 and lowest in Ringhals 4.

Low Cobalt Tubing Summary and Conclusions

- Evaluation of dose rates in over 70 nuclear plants showed that factors relative to cobalt input into a nuclear plant can be quantified. The results indicated that a combination of cobalt source reduction actions could result in dose rates 60 % lower than the dose rates if no actions were taken.
- Inspection of the overall trends in the amounts of ^{60}Co released during refueling shutdowns in the three Ringhals PWRs show that actions to reduce cobalt input into the RCS are reflected in the amounts of ^{60}Co activity released during the shutdown. Assuming that shutdown releases represent cobalt activation during a fuel cycle, lower plant dose rates should result from the cobalt reduction actions. Inspection of the SG channel head dose rates in the three

plants before SGR replacement show an approximate correlation in that the dose rates are in the same order as the average absolute released values, namely, highest in Ringhals 2 and lowest in Ringhals 4.

Key Considerations – Cobalt Source Reduction

A synopsis of the most important aspects of this chapter.

This review and summary of recent progress to address control of cobalt sources suggests that the most effective measures that a utility can implement to achieve success in lowering the inventory of cobalt sources include:

1. Establish low limits for cobalt impurity levels in the structural alloys used in replacement components, especially those that will be irradiated in the reactor core (e.g., fuel assembly components and BWR control blades). Such limits should also be placed on materials used to fabricate in-core components, such as the alloys used to braze fuel spacer grids.
2. Identify and eliminate historical inventory of cobalt laden valves and components. Consider transfer of those materials to utility fossil stations as part of an asset recovery plan.
3. Focus on eliminating in-core sources of cobalt-base alloys. BWR utilities should accelerate replacement of any control blades containing cobalt-base pins and rollers, and low pressure turbine buckets.
4. Laboratory investigations confirm that cobalt-base HF alloys provide the highest resistance to adhesive (galling) wear, but this attribute is only necessary in valve designs where metal surfaces are in intimate contact under high stress. Therefore, the use of cobalt-base HF alloys should be limited to large gate valves.
5. Specify the use of the hardenable martensitic 400 series alloys or iron-base HF alloys for use in globe, swing check, and flow control valves. The primary degradation mechanism in these valves is corrosion and/or cavitation-erosion damage, and many cobalt-free alloys are available that can provide this attribute. The successful use of Type 440C stainless steel in feedwater check valves at Vermont Yankee and its widespread use in CANDU reactors illustrate this point.
6. Proceduralize a site specific version of the success roadmap shown in Figure 3-3 to establish an effective approach for identifying target valves for cobalt replacement. Ensure the process remains focused on those valves that have historically required refurbishing during plant outages.
7. For cobalt-bearing valves that are subject to valve maintenance, plant maintenance procedures and training should incorporate “good practices” that can minimize release of cobalt to the coolant after plant restart.

References

- 3-1. Compilation and Evaluation of NOREM Test Results: Implications for Valve Applications: Generic Background Information for 10 CFR 50.59 Evaluations: EPRI, Palo Alto, CA: 1999. TR-109343.
- 3-2. Performance of NOREM™ Hardfacing Alloys, EPRI, Palo Alto, CA: 1999. TR-112993.
- 3-3. BWR Water Chemistry Guidelines - 2004 Revision. Palo Alto, CA: Electric Power Research Institute, December 1996. TR-103515-R3.
- 3-4. Perock, J. D. and Bergmann, C. A., “Evaluation of PWR Radiation Fields: 1986-1990”, EPRI TR-100306, April 1992.
- 3-5. Bergmann, C. A., and Bencini, R. L., “Evaluation of PWR Radiation Fields: 1991-1996”, EPRI TR-107566, February 1997.
- 3-6. Aronsson, P. et. Al., “Dose Rate Trends in Swedish LWRs”, paper in *Proceedings: 1999 Radiation Control Seminar*, EPRI , Palo Alto, CA: 1999. TR-114003.
- 3-7. ANSI N45.2.1, Cleaning of Fluid Systems and Associated Components During Construction Phase of Nuclear Power Plants

Acronyms

GKN-1	Neckarwestheim-1		KKE	Emsland
KKG	Gosgen		GKN-2	Neckarwestheim-2
CNT	Trillo		TEM	transmission electron microscopy
KKG-BAG	Grafenrheinfeld		ASTM	American Society for Testing and Materials
KWG	Grohnde		USQ	unresolved safety question
KKP-2	Philippsburg-2		HF	hardfacing
KBR	Brokdorf		TGS	threshold galling stress
KKI-2	Isar-2			

4

PRECONDITIONING SURFACES OF REPLACEMENT COMPONENTS

Introduction

Preconditioning of the surfaces of replacement components can significantly reduce recontamination rates, as well as reduce the cobalt release rate. The nature of primary component surfaces affects the ability of the passive oxides that form on them to incorporate the activated corrosion products, primarily ^{60}Co , ^{58}Co , and ^{65}Zn , that are responsible for occupational radiation exposure. Surface roughness, surface chemistry, and even surface residual stresses play a role in determining the amount of activity pickup. It was recognized early that electropolishing might lower activity pickup simply by reducing the total surface area in contact with the primary coolant. Another approach to reducing the build-up of radioactivity is to effectively film or coat components that contact the primary coolant. Such coatings could serve two main functions: [1] they form a diffusion barrier against the outward migration of cobalt that is present as an impurity in reactor construction materials, which is desired because the release of cobalt to the coolant is the first step leading to its activation, and [2] coatings may render the surface less susceptible to the incorporation of radioisotopes following their formation in the reactor core. Replacement of primary system components affords utilities an opportunity to specify a surface treatment that is designed to lower the incorporation of activated corrosion products.

Comprehensive programs to develop effective preconditioning techniques have been successful, and the two most widely used surface modification techniques now used in US nuclear power plants are electropolishing (EP) and a chromium coating and passivation technique that is designated the “Stabilized Chromium Process (SCrP).” This chapter will review these processes, summarize the experiments that suggested their value in reducing activity pickup, describe the performance of components with treated surfaces that have been placed in service in commercial reactors (i.e., report measured recontamination rates), and finally discuss possible new applications of these techniques.

Electropolishing Basics

Electropolishing (EP) is the electrochemical removal of microscopic irregularities from metal surfaces. The process involves the controlled anodic dissolution of metallic surfaces using an electrolyte and a cathode suitably shaped to accommodate the geometry of the component. The electrolyte used is typically orthophosphoric acid with additions of either sulfuric or chromic acid. Direct current is applied to the system in the presence of the electrolyte that has been heated to $\sim 100^{\circ}\text{F}$ to 140°F . The applied current and application time are the key variables that affect the amount of metal removed. Under an applied potential, surface peaks are associated

Preconditioning Surfaces of Replacement Components

with higher current densities than adjacent regions, so electropolishing removes these undesirable features faster than it attacks smoother surfaces. On a microscopic scale the electropolished surface is smooth and free of folds, asperities, discontinuities or general roughness. A typical electropolished stainless steel surface is compared to a mechanically polished surface in Figure 4-1. Small components to be electropolished are placed in the tank containing the electrolyte. Electropolishing of larger components is achieved by designing a cathode that brings the electrolyte to a portion of the surface and then moving this cathode over the surface area.



Figure 4-1
Comparison of “As-Received” and Electropolished Surfaces (28\" elbow)

EP has been shown to provide the following advantages for surfaces of components that have been placed in service in nuclear power plants and in other industrial applications: Surface roughness is reduced significantly, thus lowering the chances for subsequent deposition of activated corrosion products and particulates. The smoother surface also facilitates particulate deposit removal using simple surface cleaning methods such as hydrolasing. In addition, surface area is reduced by as much as a factor of seven, which has several benefits such as lowering the chances for both subsequent corrosion release and deposition, decreasing contact surface area, which improves heat transfer to entrained fluids while reducing surface friction and drag. Corrosion resistance can also be increased because of chromium enrichment of the surface and the removal of surface contaminants that may promote corrosion.

An early EPRI study showed that EP lowered radioactivity buildup on electropolished manway seal plates that were exposed in the Chinon 1 PWR by about a factor of five. More recent work confirmed that significant benefits are achieved in terms of reductions in both corrosion and corrosion release for electropolished surfaces compared with “as-received” surfaces. The activity was lowered 30-90% for Inconel samples exposed in a high temperature test loop. This study also showed that cold working of metal surfaces as a result of sandblasting or grinding was more detrimental than could be explained solely by changes in surface area. It was also concluded that EP led to the formation of a more protective film, which may be one factor that contributed to the reduction in corrosion release rates.

When electropolishing was first considered for treating nuclear power plant components in the early 1980's there was concern that the process might promote intergranular stress corrosion cracking (IGSCC). This concern arose because electropolishing is often used to etch grain boundaries of metal specimens that are to be investigated by optical microscopy, and grain boundary attack may often be a precursor of IGSCC. EP was qualified for BWR applications by electropolishing a 12-inch diameter Type 316 nuclear grade pipe, including welds and an elbow, and varying a range of conditions (temperature, current density, and time) that would encompass the process parameter variations experienced in a typical plant application. The pipe was then sectioned for metallographic examination. Test specimens were prepared and then subjected to constant extension rate testing and crevice bent beam tests in simulated BWR water chemistry. No intergranular attack (IGA) was found and susceptibility to IGSCC was not increased. Indeed, the evaluation showed that electropolishing removed IGA that formed during fabrication of the pipe and the improved surface finish that accompanies electropolishing most likely increased long term resistance to IGSCC by reducing residual surface stresses.

Qualification of electropolishing required more extensive evaluations for PWR steam generators because three main structural alloys are used. These qualification programs used prototypical materials and weld overlay processes employed by SG fabricators. A significant number of test plates were electropolished by using a wide range of process variables to establish that the allowable parameters did not degrade the metallurgical properties of the weld clad overlay, the Inconel divider plate material, and the Inconel 182 weld metal that joins the divider plate to the Type 309 stainless steel channel head overlay. The electropolished specimens were prepared using both the standard welding process and other repair processes. This led to varying amounts of ferrite in the specimens, a variable of concern. Other programs evaluated the response of Inconel 600 and Inconel 182 weld test samples to electropolishing. These evaluations all confirmed that electropolishing was benign, and there was no basis for concluding that it may adversely affect the corrosion performance or structural integrity of an electropolished component when it was used in a nuclear power plant. Details of the projects that served to qualify electropolishing for PWR applications of nuclear plant applications are presented in EPRI reports.

The first large-scale application of electropolishing BWR reactor components was performed on replacement piping and reactor water cleanup piping spools that were installed at the Monticello and Cooper plants. The earliest nuclear plant application of electropolishing at a PWR was the replacement of the SG channel head components installed at the Electricité de France (EDF) Nogent plant. Measurement of the recontamination rates at these plants suggest that electropolishing of nuclear components typically reduces activity pickup by 50-80% compared with an as-machined surface.

Electropolished Steam Generator Channel Heads

Introduction

Results from activity deposition studies indicate that electropolishing of steam generator (SG) channel head surfaces should result in lower channel head dose rates. Table 4-1 lists data concerning the U. S. plants that have had new or replacement electropolished steam generators.

Table 4-1
Replacement or Original Steam Generators Electropolished by Fin-Tech, Inc.

<i>Utility</i>	<i>Plant</i>	<i>No. of SG's</i>	<i>Manufacturer</i>	<i>Year</i>
Nuclear Mgmt. Co.	Palisades	2	CE	1990
Dominion Energy	Millstone 2	2	B&W	1991
TVA Nuclear	Watts Bar 1 ⁽¹⁾	4	W	1992
SCE&G	VC Summer	3	W	1994
RG&E	Ginna	2	W	1994
Duke Power	McGuire 1 & 2	8	BWI	1996
Duke Power	Catawba 1	4	BWI	1996
F P&L	St. Lucie 1	2	BWI	1997
Exelon Generation	Byron 1	4	BWI	1997
Exelon Generation	Braidwood 1	4	BWI	1997
Progress Energy	Shearon Harris	3	W	1998
Reliant Energy	S. Texas Project 1 & 2	8	ENSA	1999-2001
SNOC	Farley 1 & 2	6	ENSA	1999-2000
Constellation Nuclear	Calvert Cliffs 1 & 2	4	BWI	2000-2002
Entergy Nuc. Northeast	Indian Point 2	4	W	2000
Duke Power	Oconee	6	B&W	2003 +

⁽¹⁾The Watts Bar plant was the only one that performed electropolishing of the channel heads before start up; all the other plants electropolished the replacement SG channel heads

The data in Table 4-1 show that the channel heads in sixty steam generators have been electropolished in 19 plants. Data from the first two plants with electropolished channel heads were reported before. The dose rate buildup in Palisades after replacement did not exhibit any significant effect of electropolishing in that the dose rate trend after replacement continued to increase. This has been ascribed to the fact that Palisades was the first application of electropolishing and the technique was not completely developed. At Millstone 2, the results observed with the replacement steam generators confirmed an electropolishing effect. The average dose rate in the steam generators after replacement was about one-third of that before replacement after the approximate equivalent time of operation. However, it is noted that there were several other actions taken to reduce the dose rates, e. g., use of low cobalt SG tubing, changing from Inconel to Zircaloy fuel grids, and use of an improved coolant chemistry. Because of these factors it was difficult to quantify the electropolishing effect alone.

Data from an additional eleven Westinghouse designed plants with electropolished channel heads are available since that reported from the earlier two plants. Presentation and evaluation of these data are discussed below.

Evaluation Techniques

Multiple evaluation techniques were used to estimate the effect of electropolishing the channel heads. These include: (1) comparison of SG channel head center dose rates and the tube sheet to channel head dose rate ratio before and after steam generator replacement (SGR) with electropolished channel heads, and (2) comparison of the dose rates and distribution of dose rates in the Watts Bar plant to that in comparable plants that did not start up with electropolished channel heads.

The first evaluation technique is based on the fact that the steam generators represent about 85% of the corroding area in a plant. All other conditions being equal, when they are replaced the activity buildup trends would be expected to be similar to that in the original plant for the same time of operation. This trend was noted in the channel head center dose rate buildup in plants that replaced steam generators with normal cobalt tubing (4-1). However, the dose rate trends in plants that replaced steam generators with low cobalt tubing was different, as illustrated in Figure 1 depicting the dose rates in the Ringhals 2 plant before and after SGR (4-2). The trend after replacement is transposed to that before replacement to illustrate the difference.

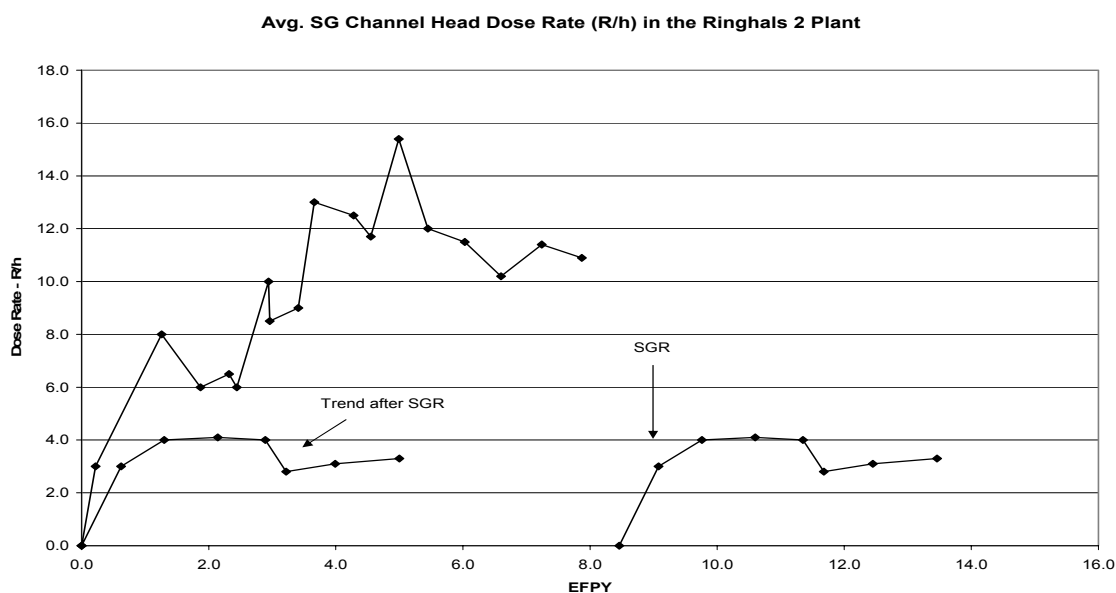


Figure 4-2
Average SG Channel Head Dose Rate in the Ringhals 2 Plant

As noted in the discussion of the Millstone 2 dose rates, evaluation of the trends after steam generator replacement is frequently confounded by implementation of other factors after replacement that are expected to influence dose rates. Thus, an estimate of the effect of these factors is needed to obtain a quantitative estimate of the electropolishing effect by itself. This is also applicable for Ringhals 2, since factors other than low cobalt tubing were applicable which would also be expected to result in lower dose rates. A quantitative effect of these factors in Westinghouse designed plants has been made (4-2), and will be used in this evaluation to normalize the dose rates so that the effect of electropolishing can be quantified.

Preconditioning Surfaces of Replacement Components

The technique also considers the distribution of the dose rates in the channel head by comparing the ratio of the dose rates at the channel head tubesheet to that at the channel head center before and after electropolishing. Based on the work done in reference 4-2, the percentage contributions of the following sources to the dose rate in the center of the SG channel head are: divider plate – 14%, bowl – 43%, tubes within the tubesheet – 20% and tubesheet and tube stub ends – 23%. Only the divider plate and the bowl are electropolished, thus if no activity were deposited on the electropolished surfaces the greatest reduction factor to be expected would be 0.43, or a factor of 2.3. Because of these contributions, the ratio of the dose rate at the tubesheet (a combination of that from the tubes within the tubesheet and the tubesheet itself) to the general area dose rate would be expected to change if the divider plate and bowl were electropolished.

The other evaluation technique compares the dose rate trend in the Watts bar plant, the only one that has started up with electropolished channel heads to that in comparable plants. Per reference 4-2, Watts Bar is considered one of twelve Group 7 plants. These plants would be expected to have lower dose rates because they had certain dose reduction factors, namely, use of Zircaloy fuel grids, avoided high cobalt contamination fuel grids and have operated with improved coolant chemistry.

Results of Evaluations**Plants that Replaced Steam Generators**

As shown in Figure 4-2, the dose rate trends in a plant that replaced SGs can be different after SGR compared to that before because of actions taken to reduce source terms. Thus, it is desirable to first “normalize” the data to account for these actions. There are two groups of Westinghouse designed plants that have replaced SGs with low cobalt tubing for which there are sufficient data available for evaluation. Four of them did not have the channel heads electropolished and ten of them did (Table 4-1).

The normalization technique involved taking into account the results of factors expected to reduce the dose rates as shown in Table 4-2. Based on the factors, the Westinghouse plants were assigned to seven Groups (noted in detail in ref. 4-2) depending upon when the fuel was made, when conversion to Zircaloy grids had occurred, and when improved chemistry control was initiated.

The after to before SGR ratio of dose rates was calculated by dividing the average of the channel head center dose rates after SGR to that before SGR up to the approximate equivalent time of operation. For example, in the case of Ringhals 2 (Figure 4-2), the plant had operated for 5.0 EFPY after replacement, thus the average of the dose rates to 4.99 EFPY since startup was used as the before SGR value. In calculating the average before SGR, dose rates prior to 0.5 EFPY were excluded, since the values would provide a low bias to the average. The tubesheet to channel head center dose rate ratios were calculated for the same equivalent time period.

Table 4-2
Approximate Effect of Various Source Reduction Techniques on Plant Dose Rates

Source Reduction Technique	Dose Rate Fraction of Reduction Technique
High vs. Low Cobalt Impurity Fuel Grid Nickel Braze	0.80
High vs. Low Cobalt Fuel Grids (Inconel vs Zircaloy)	0.72
High vs. Low Cobalt Impurity SG Tubing	0.70
Varying vs. Constant Coolant pH	0.86
Overall Reduction	0.35

Table 4-3
Summary of Certain SG Channel Head Center and Tubesheet Average Dose Rates (R/h) and Ratios in Plants Before and After SGR and a no-SGR Plant

Plant	No. of Cycles		Channel Head Center			Tubesheet		Tubesheet/ Ch. Hd.	
	Before SGR	After SGR	Before SGR	After SGR	After/ Before SGR	Before SGR	After SGR	Before SGR	After SGR
SGR Plants with Electropolished Channel Heads – Normal Coolant Chemistry									
Braidwood 1	4	3	5.45	2.54	0.47	7.33	4.07	1.33	1.63
Byron 1	4	3	6.97	3.62	0.52	8.66	6.35	1.25	1.75
Catawba 1	8	5	6.48	1.35	0.21	8.65	2.60	1.33	1.95
McGuire 1	4	3	8.16	1.11	0.14	12.53	1.90	1.53	1.72
McGuire 2	5	3	7.04	1.81	0.26	10.93	2.81	1.54	1.56
Harris	2	1	4.50	1.48	0.33	5.05	2.45	1.33	1.66
Summer	2	2	6.00	2.05	0.34	10.50	3.70	1.73	1.78
S. Texas 1	1	1	4.80	2.80	0.58	5.30	2.90	1.10	1.04
				Avg.	0.36			1.39	1.64
SGR Plants with Electropolished Channel Heads – Zinc Addition Coolant Chemistry									
Farley 1	2	1	13.3	0.62	0.05	19.4	1.32	1.41	2.14
Farley 2	1	1	8.50	0.34	0.04	11.6	1.19	1.36	3.29
				Avg.	0.045			1.39	2.72
SGR Plants with non-Electropolished Channel Heads – Normal Coolant Chemistry									
N. Anna 1	8	6	14.9	6.16	0.41	23.58	8.38	1.60	1.34
N. Anna 2	6	5	14.5	7.1	0.49	19.97	8.52	1.37	1.21
Ringhals 2	7	7	9.70	3.50	0.36	14.10	4.80	1.45	1.38
Ringhals 3	4	4	5.79	3.20	0.55	--	--		
				Avg.	0.45			1.47	1.31
Plants with Original SG Electropolished Channel Heads – Normal Coolant Chemistry									
Watts Bar 1	5	--	4.94			11.57			2.31

The results of the calculations are given in Table 4-3. Observations of the data include:

- The dose rates after SGR decreased significantly compared to those before SGR
- The average of the channel head center ratios after to before SGR in the electropolished plants with normal chemistry is lower than that of the non-electropolished plants indicating a

Preconditioning Surfaces of Replacement Components

beneficial effect of electropolishing, although the individual ratio values overlap between the two groups

- The very low after to before ratio in the zinc addition plants indicates a large effect of the combination of electropolishing and zinc addition on the dose rates
- The increase in the average tubesheet to channel head center ratio after compared to that before SGR in the plants that were electropolished indicates that a lesser amount of activity deposited on the divider plate and bowl surfaces compared to that before electropolishing. This indication is also evident in comparing the change in the ratio in the non-electropolished plants wherein the ratio has actually decreased slightly.

Although not a plant with SGR, the high tubesheet to channel head center ratio in the Watts Bar plant also reflects the change in the distribution of the dose rates after electropolishing.

To obtain a quantitative estimate of the effect of electropolishing, the data in Table 4-3 was normalized to account for the expected effects of other dose reduction techniques noted in Table 4-2. The elements of the normalization factors and the results are shown in Table 4-4.

Table 4-4
Normalized After/Before SGR Ratio to Estimate Electropolishing Effect

<i>Plant/Group⁽¹⁾</i>	<i>Elements of Normalization Factor</i>	<i>Normal. Factor</i>	<i>Ratio Before Norm.</i>	<i>Ratio after Norm.</i>
SGR Plants with Electropolished Channel Heads – Normal Coolant Chemistry				
Braidwood 1/7	Low cobalt Tubing (0.70)	0.70	0.47	0.67
Byron 1/7	Low cobalt Tubing (0.70)	0.70	0.52	0.74
Catawba 1/7	Low cobalt Tubing (0.70)	0.70	0.21	0.30
McGuire 1/2	Hi cobalt Impurity (0.80) and Low cobalt Tubing (0.70)	0.56	0.14	0.24
McGuire 2/2	Hi cobalt Impurity (0.80) and Low cobalt Tubing (0.70)	0.56	0.26	0.46
Harris/3	Like Group 7 since changed to Zirc. early, Low cobalt Tubing (0.70)	0.70	0.33	0.47
Summer/2	Hi cobalt Impurity (0.80) and Low cobalt Tubing (0.70)	0.56	0.34	0.61
So. Texas 1/3	Like Group 7 since changed to Zirc. early, Low cobalt Tubing (0.70)	0.70	0.58	0.83
		Avg.		0.54
SGR Plants with Electropolished Channel Heads – Zinc Addition Coolant Chemistry				
Farley 1/1	All factors in Table 2	0.35	0.05	0.14
Farley 2/3	Zirc. Grids (0.72) and Lo cobalt Tubing (0.70)	0.50	0.04	0.08
		Avg.		0.11
SGR Plants with non-Electropolished Channel Heads – Normal Coolant Chemistry				
No. Anna 1/1	All factors in Table 4-2	0.35	0.41	1.18
No. Anna 2/1	All factors in Table 4-2	0.35	0.49	1.40
Ringhals 2/1	All factors in Table 4-2	0.35	0.36	1.03
Ringhals 3/2	Hi cobalt Impurity (0.80) and Low cobalt Tubing (0.70)	0.56	0.55	0.99
		Avg.		1.15

⁽¹⁾Group designation as given in (4-2)

Observations from inspection of the data include:

- The average normalized ratio in the plants with electropolished channel heads and normal coolant chemistry is 0.54. This ratio is slightly greater than the “theoretical” limit of 0.43 noted above. These results thus indicate a beneficial effect of electropolishing, which on the average results in a dose rate about one-half of that if not electropolished. Inspection of the dose rate trends indicates that the long-term trend in plants with more than two data points after SGR appears to level off, thus suggesting a continuing benefit of electropolishing.
- The range of the reduction factors in the electropolished plants (0.24 to 0.83) indicate that for the low values all factors affecting the dose rates have not been taken into account and/or that the factors are variable depending upon the plant. One reason for the higher factors noted in Braidwood 1 and Byron 1 could be due to the greater EFPY after compared to that before SGR (about 1.1 EFPY before compared to 1.4 EFPY after). In South Texas 1, the higher factor could be due to the limited data after SGR.
- The low reduction factors in the zinc addition plants illustrate a significant effect of zinc addition on the channel head dose rates.
- The average value of 1.15 for the non-electropolished plants also indicates that not all the factors have been taken into account in the normalization factors. Inspection of the results shows that the reason for the greater than 1.0 average value is because of the North Anna data. In these plants, the channel head bowl and divider plates were mechanically polished. It was thought that this technique should result in lower activity deposition on the surfaces. However, the amount of ^{58}Co activity deposited on mechanically polished stainless steel strip clad specimens (presumably similar to that in the North Anna replacement SGs) exposed to a reactor coolant was several times that on as-received strip clad specimens. This effect may have occurred in the North Anna SGs, resulting in a higher dose rate and the greater than 1.0 ratio.
- The Ringhals results indicate that the factors accounting for dose rate variation have been taken into account.

Plants with Electropolished Channel Heads Since Startup

Watts Bar 1 is the only plant where the SG channel head bowl and divider plate was electropolished before plant startup. The effect on dose rates was evaluated by: (1) comparison to the channel head center trend to that of similar plants and (2) comparison of the tubesheet to channel head center dose rate ratio to that in a number of plants before and after electropolishing.

In terms of plant dose rate trends, Watts Bar 1 belongs to a group of plants (Group 7) that have exhibited relatively low dose rates due to several design and operational changes made in the time of their construction, e. g., avoided use of cobalt contaminate fuel grids, had Zircaloy grids since startup, and used improved coolant chemistry during operation.

The Watts Bar 1 dose rate is initially among the lowest observed in all of the plants, but the trend with time suggests that the electropolishing effect is diminishing because the dose rate is similar to Group 7 plants after about three cycles of operation. Nonetheless, it appears that

electropolishing has had the desired effect of providing lower channel head dose rates at least for several cycles of operation.

Electropolished Steam Generator Channel Heads - Summary and Conclusions

Results from activity deposition studies indicate that electropolishing of the steam generator channel head surfaces should result in lower channel head dose rates. The following sources contribute to the dose rate in the center of the SG channel head in the percentages indicated: divider plate – 14%, bowl – 43%, tubes within the tubesheet – 20% and tubesheet and tube stub ends – 23%. Only the divider plate and the bowl are electropolished, thus if no activity were deposited on the electropolished surfaces the greatest reduction factor to be expected would be 0.43, or a factor of 2.3. Because of these contributions, the ratio of the dose rate at the tubesheet (a combination of that from the tubes within the tubesheet and the tubesheet itself) to the general area dose rate would be expected to change if the divider plate and bowl were electropolished.

The dose rates in ten plants that have had their steam generator channel head bowl and divider plate electropolished after SGR were evaluated. The evaluation was performed by: (1) comparing the ratio of the average channel head center dose rate after to that before SGR, and (2) the change in the average tubesheet to channel head center dose rate ratio after to that before SGR. Factors that affect dose rate buildup were taken into account to normalize the data so that the effect of electropolishing could be quantified. The dose rate trend in one plant (Watts Bar 1) that had similar channel head components electropolished before startup was also evaluated by comparison to similar plants that did not have the channel head electropolished.

Observations and conclusions resulting from the evaluation include:

- The average normalized after to before dose rate ratio in the plants with electropolished channel heads is 0.54. This factor is slightly greater than the “theoretical” limit of 0.43 noted above. These results thus indicate a beneficial effect of electropolishing, which on the average results in a dose rate about one-half of that if not electropolished. Inspection of individual plant data indicate that the long-term dose rate trends appear to level off, thus suggesting a continuing benefit of electropolishing.
- The range of the reduction factors in the electropolished plants (0.24 to 0.83) indicate that for the low values all factors affecting the dose rates have not been taken into account and/or that the factors are variable depending upon the plant. Reasons for the higher factors noted in some plants could be due to the greater EFPY after compared to that before SGR or the limited data after SGR.
- The very low reduction factors in the zinc addition plants illustrate a significant effect of zinc addition on the channel head dose rates
- The average value of 1.15 for the non-electropolished plants also indicates that not all the factors have been taken into account in the normalization factors. The reason for the higher average value is due to the North Anna data. In these plants, the channel head bowl and divider plates were mechanically polished because it was thought that this technique should result in lower activity deposition on the surfaces. However, per reference 8, the amount of ⁵⁸Co activity deposited on mechanically polished specimens presumably similar to that in the North Anna replacement SGs exposed to a reactor coolant was several times that on as-

received specimens. Thus, this effect may have occurred in the North Anna SGs, resulting in a higher dose rate and the greater than 1.0 ratio.

- The channel head dose rate trend in Watts Bar 1 compared to that in similar plants shows that the dose rate is initially among the lowest observed in all of the plants. However, the trend with operational time indicates that the electropolishing effect is diminishing. Nonetheless, it appears that electropolishing has had the desired effect of providing lower channel head dose rates at least for several cycles of operation.

Electropolishing of Reactor Water Cleanup Pump (RWCU) for FENOC's Perry Plant

A spare RWCU pump was treated using the electropolish process. The complex geometries associated with a pump posed no difficulties to this process. However, as of this report publication date, that pump had not been installed for use and therefore no post-service performance data is available.

Evaluating Alternatives to Electropolishing

EPRI implemented a number of programs to evaluate alternative surface modification techniques to determine if other techniques could provide more substantial benefits than electropolishing. Measurements of the response of surface-modified specimens were performed at General Electric's Vallecitos Nuclear Center and at the X-2 loop of Atomic Energy of Canada's Chalk River Nuclear Laboratory. At both of these facilities the inside surface of narrow bore tubing was modified using coating techniques such as prefilming, chromium redistribution, and metallic coatings, in an attempt to lower recontamination rates. The treated specimens were exposed to simulated BWR and PWR coolant chemistry conditions, where cobalt-60 was added to the water, and the incorporation of this isotope into the growing films was measured with gamma spectroscopy as a function of time. Films that were formed in oxygenated air or water were most effective in reducing cobalt-60 pick-up from BWR coolant, while methods that resulted in a chromium-rich film were most effective in PWR coolant. An electroless layer of palladium (Pd) was the film most effective in reducing cobalt-60 pick-up in both types of coolant. The cobalt-60 pick-up by the Pd-coated specimens was about a factor of 20 less than that measured on control specimens without the coating.

However, subsequent exposure of small Pd-coated coupons in a commercial PWR showed evidence of substantial incorporation of radioisotopes indicative of fission products released from failed fuel rods. These results, and the high cost of Pd, rendered it less attractive as a coating to inhibit activity incorporation, so additional experiments were undertaken to identify other coatings with the desired attributes. These experiments were performed at the Doel Power Station in Belgium, a PWR, in fuel cycles 15 through 21. Results from these experiments led EPRI to focus on developing a chromium enhancement technique that was called the Stabilized Chromium Process (SCrP).

This section will discuss the initial evaluation and development of this process, its application to replacement components that have been placed in service in US LWRs, the recontamination measurements that have been performed to demonstrate the effectiveness of the technique, and

the further optimization and expansion of the technique to modify surfaces of more complex shapes. Lastly, we will identify other possible “non-traditional” applications of preconditioning techniques to improve the performance of nuclear plant components.

Doel Coupon Experiments

The Doel tests used small rectangular coupons (9.5 cm x 3.8 cm x 0.47 cm or 0.63 cm thick) made of Type 304L stainless steel and Inconel 600, which were first mechanically polished using 120 and 180 grit aluminum oxide. After polishing, the surface roughness ranged from 10 to 20 μin . Coupons were then electropolished in an electrolyte consisting of 3 wt% chromium trioxide dissolved in 85% orthophosphoric acid. After electropolishing, the surface roughness typically ranged from 9 to 24 μin . Various surface modification techniques were then applied to the electropolished coupons. Coupons with electropolished surfaces typically served as the standard against which other surface modification techniques were compared in each fuel cycle.

Coupons were bolted onto the manway seal plate in the steam generator channel head of the Doel-2 PWR. The seal plates were mounted on both the hot (314°C) and cold (284°C) leg sides of the steam generator channel heads. Thus, the coupons were exposed to the complete temperature and concentration ranges observed in the primary coolant throughout the operating cycle. Doel-2 operates on lithium/boron coordinated chemistry, with the calculated pH at 300°C ranging from 6.9 to 7.0. Doel 2 operates on 12-month fuel cycles and exposure times ranged from 5,500 hours to 7,900 hours.

The primary radionuclides contributing to activity buildup at Doel are ^{58}Co , ^{60}Co , and ^{54}Mn . Specimens were scanned each cycle for activity pickup after the reactor shutdown for refueling. Dose rates of the exposed coupons were measured using a Babyline 31, Type E433 ionization chamber and gamma spectroscopy. Measurements were made typically one week after the specimens were removed from the steam generator. Only dose rates from gamma radiation were measured. The amount of deposited activity was measured using a Li-drifted Ge detector.

The most effective surface modification technique identified from this work was subsequently designated the Stabilized Chromium Process (SCrP). SCrP involves electroplating a thin film of chromium (~3,000-10,000 Å thick) onto electropolished base metal and then preoxidizing the chromium film in hot moist air before exposure to primary coolant. Tests with different plating methods showed that chromium deposition from a hexavalent chromium-plating bath yielded far better results than other chromium plating techniques. Chromium thickness and application methodology were investigated over several fuel cycles to achieve the optimum conditions for application and practicality. Because chemistry conditions and exposure times varied somewhat from one operating cycle to another, dose rates were normalized to a reference surface exposed during that cycle.

Figure 4-3 shows the buildup reduction factor (a measure of the effectiveness of the film in reducing activity pickup) measured at Doel following exposure during both fuel cycles 19 and 20 for both stainless steel and Inconel coupons(4-4). The buildup reduction factor is the ratio of the total deposited activity measured on an electropolished reference coupon divided by that measured on a surface-modified coupon. Thinner Cr films (~3,000 Å) are more effective than thicker films (~43,000 Å). The dramatic reductions in activity deposition persisted over two fuel

cycles showing there is little degradation of the chromium coating, a result that is confirmed by the response of SCrP-treated components that have subsequently been placed in service in commercial LWRs. These data also show that better performance is achieved if the chromium-plating step is followed by the preoxidation step. (i.e., the preoxidation step provides additional benefits over “Cr only” surfaces).

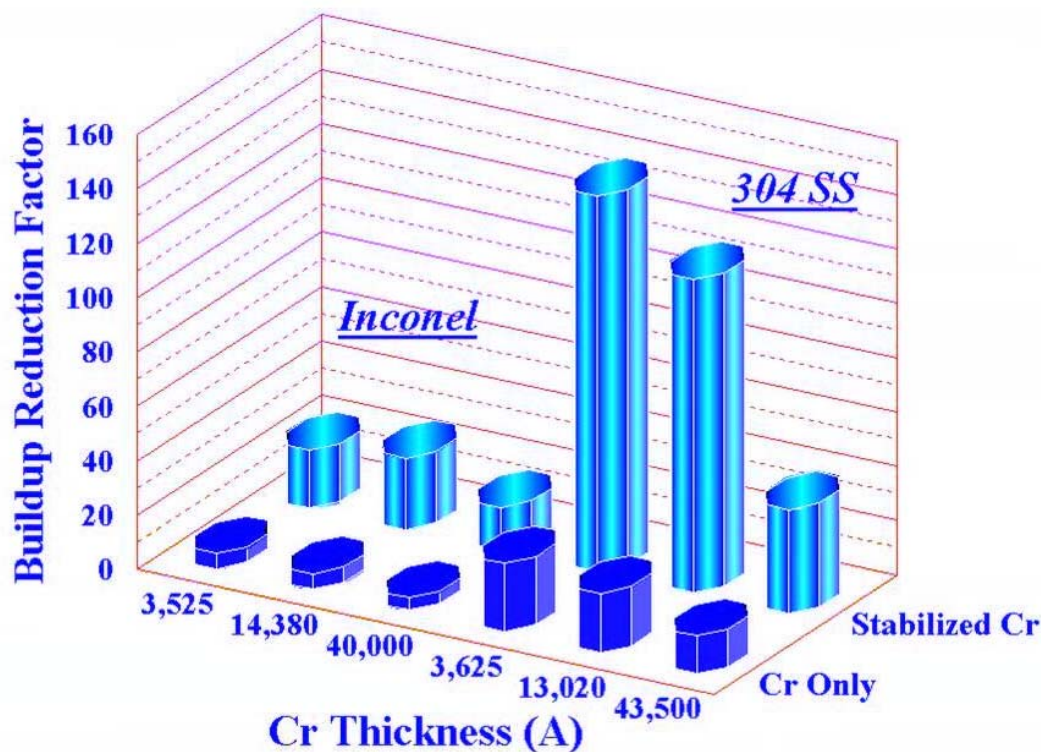


Figure 4-3
Buildup Reduction Factors for Chromium-Coated Coupons Exposed at the Doel 2 PWR

Other techniques for depositing thin chromium films were evaluated in Doel 2 during cycle 21, including coupons that were prepared by using; brush plated trivalent (Cr^{+3}) chromium, hexavalent (Cr^{+6}) chromium plating using an approach different from that used in SCrP, hypervelocity impaction of a chromium film, and a vacuum passivation process designed to enrich the outermost surface of the film with chromium. Subsequent measurements of the deposited activity showed that only the hexavalent chromium film resulted in activity reduction factors approaching those achieved with SCrP (4-4).

In the Doel experiments, deposition on Inconel 600 coupons was about a factor of ~3.5 lower than on similarly treated coupons of Type 304 stainless steel (Figure 4-3). This result is probably a consequence of the higher chromium content of the Inconel. A possible practical application of this observation will be presented in a later section.

After positive results with chromium coatings in the Doel experiments, subsequent laboratory studies identified the optimum parameters to be used for each of the steps that comprise the

Preconditioning Surfaces of Replacement Components

SCrP. The first step is mechanical and electrochemical polishing. The resulting average surface roughness should be between the 0.5 to 1.0 μm before chromium application, which is electroplated onto the electropolished surface by using a typical industrial plating process for hexavalent chromium. It is important that the chromium be applied to a freshly cleaned and prepared surface to minimize the amount of natural oxidation occurring between the electropolishing and chromium coating steps. After the chromium is applied, the component is then installed in a loop or chamber configured for controlled oxidation at typical reactor operating condition temperatures (between 290°C and 315°C) using cleaned moist air for about 100 hours. The moisture content of the hot air is maintained between 1 and 3 weight percent for the preoxidation step.

EPRI has optimized the technique for the stabilized chromium pretreatment process and has secured a patent. It has also encouraged nuclear utilities to implement use of the technology in replacement components and conducted investigations of the long-term performance of this surface modification technique. Field trials of SCrP-treated components have been conducted at eight PWRs and five BWRs. The preconditioned PWR components have been mostly steam generator manway diaphragms and the BWR components have been mainly reactor water cleanup system piping. The next section discusses recontamination results obtained from SCrP-treated components that have been placed in service in commercial LWRs.

Performance of SCrP-Treated Components in PWRs

Recontamination of Manway Seal Plates (Diaphragms)

A number of US utilities implemented field evaluations of SCrP-treated replacement components. Initially, manway seal plates, which provide access to the steam generator channel head for inspection and maintenance operations, were treated. In some cases, the entire surface of the plate was treated using SCrP, while in other cases, one half of the plate was treated with SCrP and the other half was electropolished. These plates are about 20" in diameter, and are made of 304L stainless steel or Inconel 600. The first seal plates that were treated with SCrP were placed into service in the Millstone 2 reactor. Seal plates treated with SCrP were placed in service at Catawba-1, McGuire-1 and -2, and Diablo Canyon-1. A total of 37 manway diaphragms were processed for Duke Power Company. Thirty of these were Inconel 690T and the other seven were 316 stainless steel. The first eight of these diaphragms were installed at Catawba Nuclear Station 1 after steam generator replacement in the fall of 1996. A second group of eight diaphragms were installed after steam generator replacement at McGuire-1 in the spring of 1997 and at McGuire-2 in the winter of 1997.

Table 4-5 summarizes manway seal plate SCrP experience to date.

Table 4-5
Plants Treating SG Manway Seal Plates Using SCrP

<i>Utility</i>	<i>Plant</i>	<i>Number of Seal Plates Treated</i>	<i>Year</i>
SCE&G	V. C. Summer	6	1994
Duke	McGuire	20	1996
Duke	Catawba	17	1996
RG&E	Ginna	12	1996
Exelon	Byron	8	1997
FP&L	St. Lucie	8	1997
PG&E	Diablo Canyon	8	1998
Northeast Utilities	Millstone-2	4	
Florida Power	Crystal River	4	1999
Entergy	Indian Point	8	2000
AEP	D. C. Cook	8	2000
Southern Nuclear	Vogtle	8	2001
Constellation	Calvert Cliffs	4	2001
Entergy	ANO	8	
Duke	Oconee	11	2002

Presented below are the results obtained from the dose rate measurements of the SCrP-treated diaphragms that were installed at Catawba-1 and then summarize the results obtained from other PWRs where treated diaphragms have been placed in service.

Catawba-1 Dose Rates

The dose rate data presented are the average dose rates of diaphragms from all four steam generators at Catawba-1 (cycle 12 data is the average of two steam generators). These dose rate measurements were made on the steam generator platforms using non-directional survey meters. Because of the high background dose rates on the steam generator platforms, the values reported for the diaphragms are influenced by the dose rate of the steam generators as well as other nearby sources. In fact, subsequent dose rate measurements in a low background area showed the actual diaphragm dose rates to be ten to twenty times lower than the dose rates measured on the steam generator platforms. However, earlier dose rate measurements of untreated diaphragms that were made on the generator platforms serve as the reference condition, therefore the current dose rate measurements of the diaphragms on the steam generator platforms are still used for evaluating the performance of the diaphragms with stabilized chromium pretreatment.

Preconditioning Surfaces of Replacement Components

Table 4-6 and Figure 4-4 show the historical dose rate results for the Catawba-1 manway diaphragms for cycles 7 through 13 (4-3). After exposure for three fuel cycles, the SCrP pretreatment provided dose rate reduction factors of 10.5 and 17.1 in the hot and cold legs of the steam generator, respectively. The dose rate reduction factor is defined as the ratio of the average dose rate for the two previous fuel cycles before application of the stabilized chromium pretreatment and the dose rate after application of the stabilized chromium pretreatment. As such, the dose rate reduction factor is analogous to the more-familiar decontamination factor.

At the end of cycle 9, diaphragms with the SCrP pretreatment were installed on the new steam generators. These diaphragms have shown excellent resistance to dose rate buildup. After the latest cycle for which data were obtained (EOC 12), the average dose rates of the hot leg diaphragms decreased by approximately 11% as compared to the end of the previous cycle (EOC 11). This slight reduction in the average dose rate of the hot leg diaphragms resulted in a small improvement of the dose rate reduction factor in that leg from 9.3 to 10.5.

The average dose rates of the cold leg diaphragms increased by 80 mR/hr (~21%) after cycle 12 as compared to the end of cycle 11. The increase in the average dose rate of the cold leg diaphragms reduced the dose rate reduction factor in that leg from 22.2 to 17.1. Although the slightly higher average dose rate of the cold leg diaphragms after cycle 12, it is still far lower than the average dose rate of the cold leg diaphragms before steam generator replacement, as show in Figure 4-4.

Table 4-6
Average Dose Rates of I-690T Manway Diaphragms at Catawba-1

<i>Unit/Cycle</i>	<i>Date</i>	<i>Average Dose Rate, mR/hr</i>	
		<i>Hot Leg</i>	<i>Cold Leg</i>
1C7	Nov. 1993	6,750	6,000
1C8	Feb. 1995	6,000	6,000
1C9	June 1996	SGRP	SGRP
1C10	Dec. 1997	250	275
1C11	May 1999	685	270
1C12	Oct. 2000	610	350
1C13	April 2002	NO S/G Work Performed	
EOC 10 Dose Rate Reduction Factors		25.5	21.8
EOC 11 Dose Rate Reduction Factors		9.3	22.2
EOC 12 Dose Rate Reduction Factors		10.5	17.1
EOC 13 Dose Rate Reduction Factors		NO S/G Work Performed	

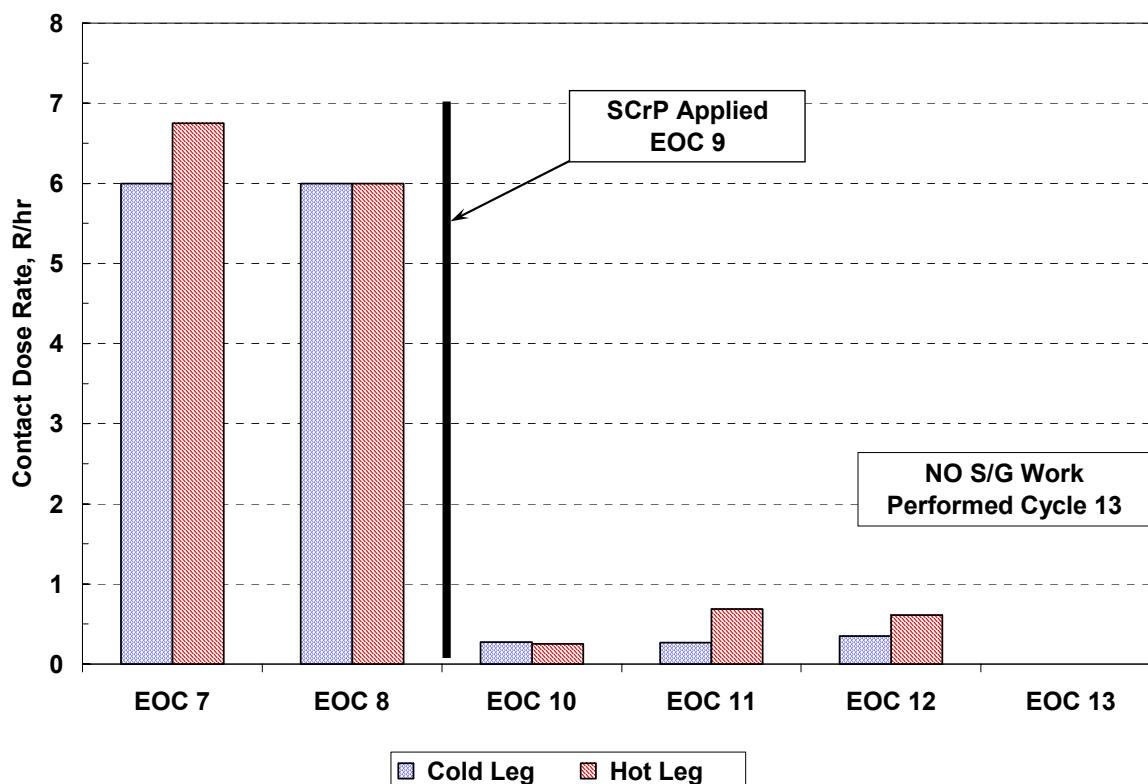


Figure 4-4
Dose Rate Comparison of Catawba-1 Diaphragms (I-690T) Before and After Stabilized Chromium Pretreatment

Catawba-1 Specific Activity Measurements

Specific activity measurements were made using a sodium iodide gamma detector in a low dose area. The quantitative activities were determined by normalizing with a reading using a carefully calibrated ion chamber. The estimated uncertainty in the activity values is approximately 20%, but the ratios of activities are somewhat more accurate.

Cobalt-58 is typically the most prevalent nuclide in PWRs. After the latest measurements following cycle 12, cobalt-58 was still the predominant nuclide on both the hot leg and cold leg diaphragms that had been treated with SCrP. Cobalt-58 represented 65% and 83% of the total activity in the hot leg and cold leg, respectively. Cobalt-60 was the next most abundant nuclide and represented 16-17% of the total activity in both legs.

These isotopic data were obtained from diaphragms that were installed in different steam generators, so it is not possible to trend changes in nuclide composition by cycle. As expected, plots of cobalt-58 dose rate and activity show good correlation (Figure 4-5).

Preconditioning Surfaces of Replacement Components

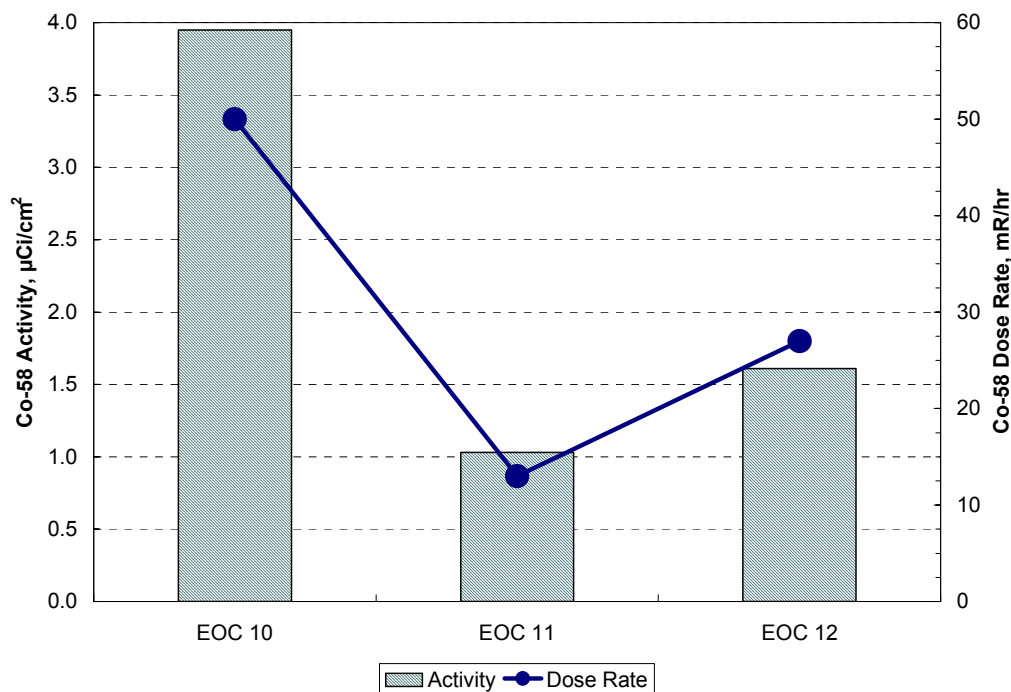


Figure 4-5
Co-58 Dose Rate and Activity, SG Cold Legs at Catawba-1

Electropolishing of Temporary Reactor Vessel Cover and Test Plates at TVA's Sequoyah

A temporary reactor vessel cover (TRVC) is a stainless steel dome that is ~ 30" high, 182" in diameter, and 1" thick. It is used to cover the reactor after the vessel head is removed for inspection and processing. The TRVC prevents foreign material from entering the reactor vessel and provides some shielding for workers. Both inside and outside surfaces are subject to contamination. TVA supported a project to electropolish a new TRVC that was to be used initially at Sequoyah but was later to be used at Watts Bar. Prior to shipment to Watts Bar, the TRVC was to be decontaminated to low levels, and it was believed that electropolishing would facilitate this decontamination.

Four test plates with various surface treatments (mechanical polishing, electropolished, electropolished and preoxidized, and SCrP) were also supplied to Tennessee Valley Authority's Sequoyah Nuclear Plant. These plates were then exposed to an environment similar to the TRVC. The plates were immersed in the refueling water cavity on 10/29/2001 and removed 11/11/2001, representing the duration that a TRVC would be immersed during a typical PWR refueling outage. Each plate was surveyed for beta and gamma dose and surface contamination. Surveys were performed both wet and dry in the as-received condition with no decontamination or rinsing, following rinsing, and following both wipedown and rinsing.

No gamma dose rates were measurable on any of the coupons. As a result, the contamination levels in dpm were used as the measure of the effectiveness of the surface treatment options.

The contamination levels measured for the mechanical polished, electropolished, electropolished and preoxidized, and SCrP-treated coupons are shown in Figure 4-6 through Figure 4-9, respectively (4-3). All of these figures have the same scale, allowing for direct comparison of the data.

As the surface finish is improved (lower Ra) by mechanical polishing, the surface area of the coupon is decreased. Lower surface area should lead to lower contamination levels. Electropolishing would reduce further the surface area of the coupon. Growing an oxide film on the coupons (preoxidation) has been shown to reduce the level of contaminants that are incorporated into the corrosion film. The lowest recontamination levels were measured on the SCrP-treated coupons.

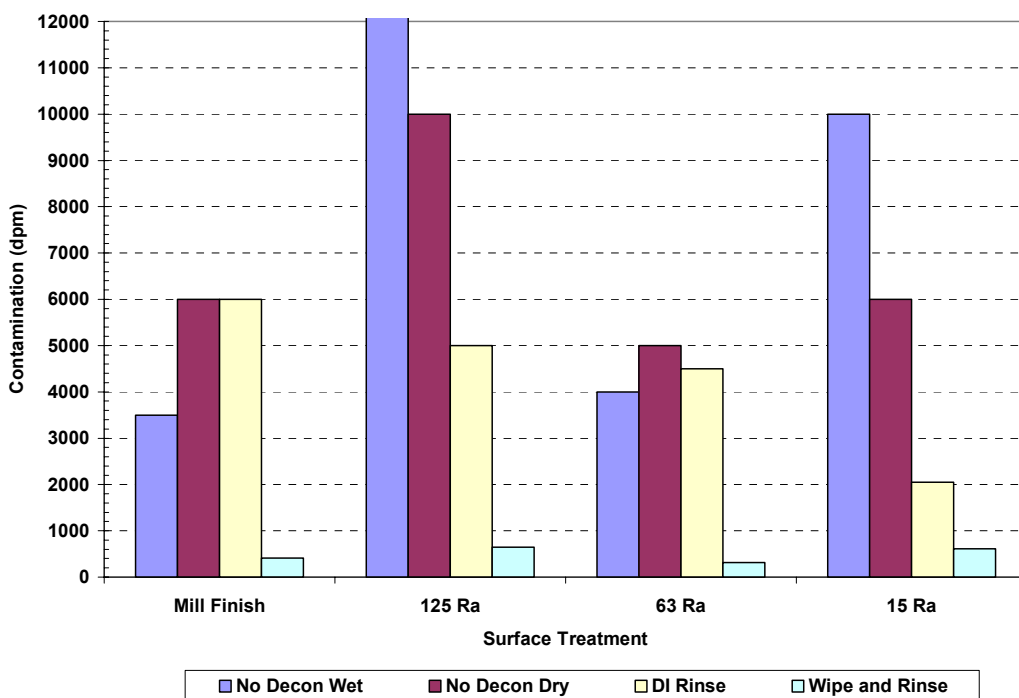


Figure 4-6
Coupon Contamination Levels – Mechanical Polish

Preconditioning Surfaces of Replacement Components

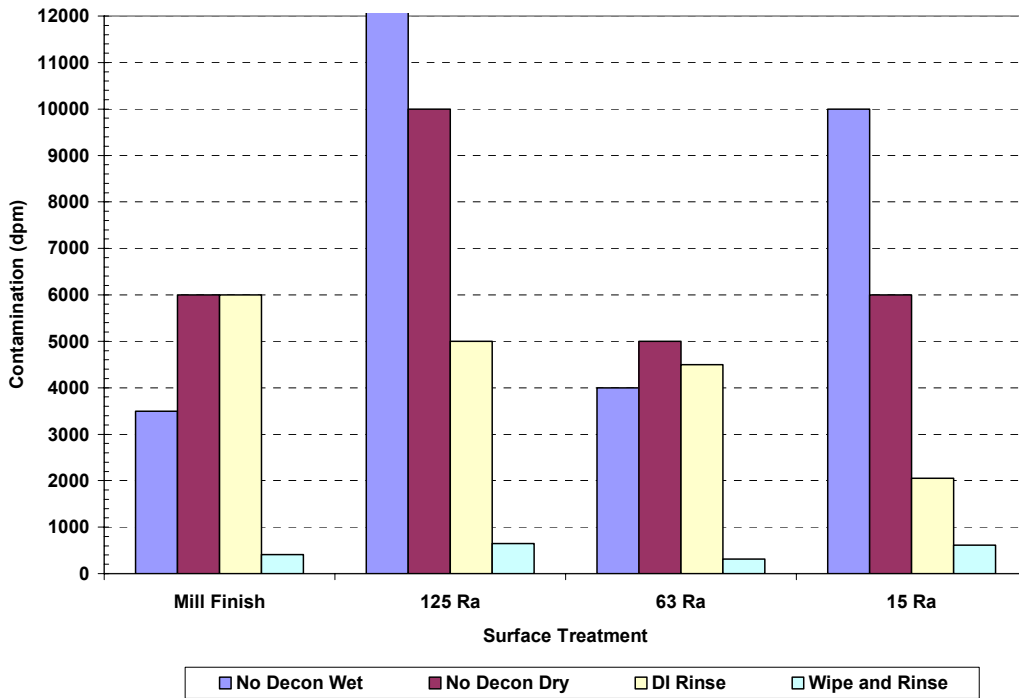


Figure 4-7
TRVC Coupon Contamination Levels – Electropolished

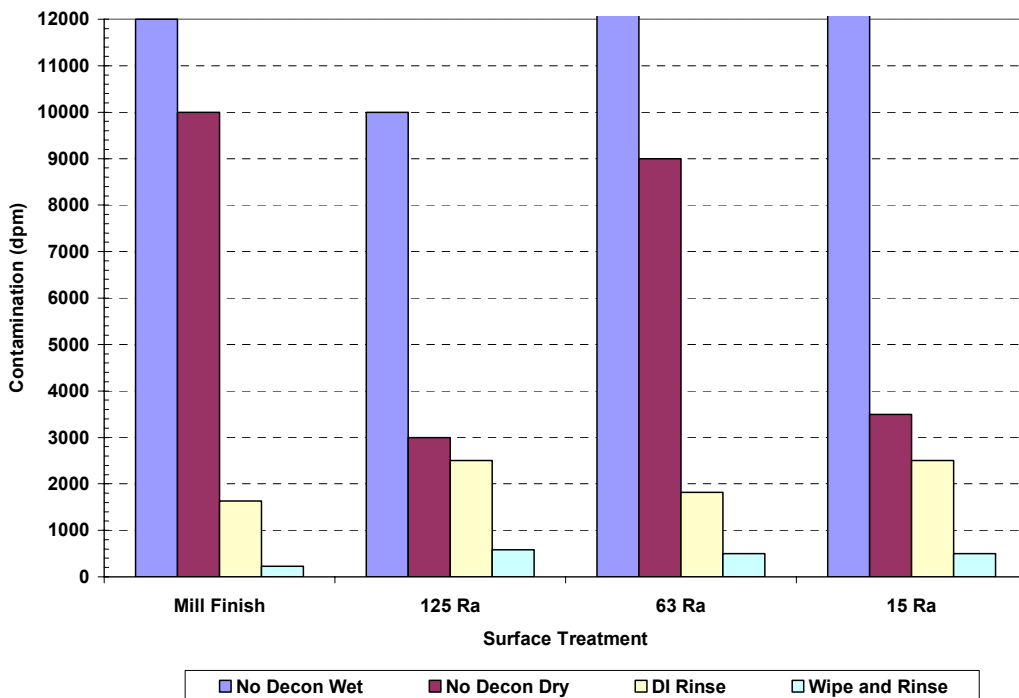


Figure 4-8
TRVC Coupon Contamination Levels – Electropolished and Preoxidized

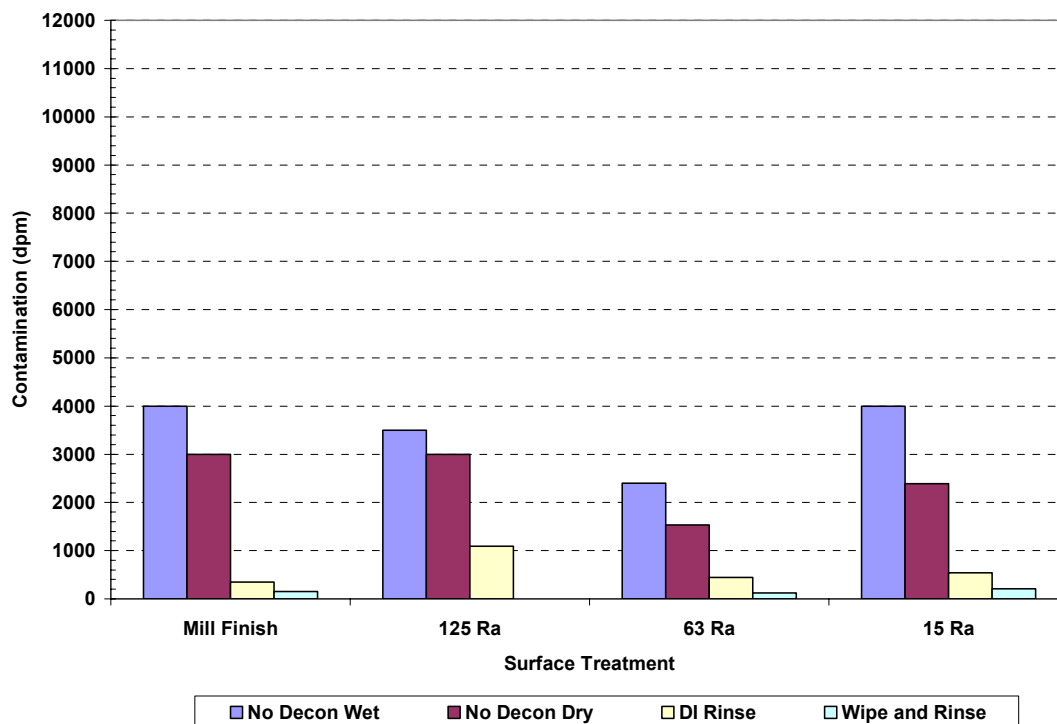


Figure 4-9
TRVC Coupon Contamination Levels – SCrP Treatment

Contamination measurements were also made directly on the electropolished TRVC. During U1C11 RFO, the TRVC was removed from the refueling canal and smearable contamination levels of 15 mrad/hour/100 cm² were measured. The only decontamination performed was low-pressure water spray. The TRVC was sprayed while suspended over the refueling cavity and allowed to drip-dry. The TRVC was not completely dry when moved, but it was no longer dripping. Contamination surveys at this point ranged from 60,000 dpm/100 cm² to 100,000 dpm/100 cm². The TRVC was wrapped, boxed and stored for future use. The TRVC was used again during the U2C11 outage. The same removal process was used for the U2C11 outage. TVA staff requested that a more thorough decontamination be performed because the TRVC was to be shipped to another site, but this decontamination was not performed. The decontamination method was again a low-pressure water spray. The survey documentation prior to decontamination indicates the TRVC contamination level was 25 mrad/hour/100 cm². The post-decontamination contamination levels at U2 were similar to those measured at U1C11, namely 60,000 to 100,000 dpm/100 cm². (TVA staff use a "rule of thumb" of 1 mrad/hour on a smear equates to about 200,000 dpm).

Dose Rate Measurements from Other SCrP-Treated Diaphragms

To date, manway diaphragms with the SCrP pretreatment have been installed at a total of seven PWRs for which recontamination rates have been measured. Dose rate and activity buildup data for these diaphragms have been reported previously (4-3) and are summarized in

Preconditioning Surfaces of Replacement Components

Table 4-7. Typically, dose rate reduction factors range from 3-10 for the hot leg and 10-20 for the cold leg. Diablo Canyon-1 (first exposure cycle) and McGuire-2 (third exposure cycle) appear to have realized less benefit from stabilized chromium pretreatment but these plants experienced significant particulate release before shutdown. It should also be noted that these data include diaphragms made from different base materials and different reference surfaces (untreated and electropolished).

The high particulate releases that occurred before shutdown of Diablo Canyon-1 (fuel cycle 9) and McGuire-2 (fuel cycle 13) reduced the benefit of the SCrP pretreatment because even most corrosion resistant surfaces will not prevent particulate deposition. Nevertheless, the manway diaphragms with SCrP pretreatment showed significant dose rate reductions when compared to the reference diaphragms. For McGuire-2, the dose rate reduction factors were 2 in the hot leg and 6 in the cold leg. These measurements were taken after the end of cycle 13, and it should be noted that loose particulate contamination was on the diaphragms. Cycle 14 data suggests that the particulate deposition was reversible, because the decreased dose rates cannot be explained by radioactive decay alone.

Based on the field performance data in Table 4-7, the SCrP pretreatment is generally more effective in reducing recontamination in the cold legs of the steam generators than in the hot legs. This may be attributed to different concentrations of soluble activation products in the hot and cold legs because of the retrograde solubility phenomenon of nickel ferrites. Other factors to consider include reaction kinetics and the diffusion rates of metal ions in the oxide films. However, reasons for the higher activity buildup in the hot leg have not yet been established.

Table 4-7
Performance of PWR Manway Diaphragms Following Application of SCrP

<i>Plant</i>	<i>Diaphragm Material</i>	<i>Exposure Cycle</i>	<i>Exposure Period</i>	<i>Reference Surface</i>	<i>Dose Rate Reduction Factor Hot /Cold Leg</i>	<i>Activity Reduction Factor Hot Leg/Cold Leg</i>
Diablo Canyon-1	304L SS	First	22 months	Electropolish	2.5* / 6.3*	1.1* / 2.8*
Millstone-2	Inconel 600	First	18 months	Electropolish	8-12 avg	15-20 average
		Second	6 months	Electropolish	5-9 avg	5-10 average
Catawba-1	Inconel 690T	First	18 months	Untreated	25.5 / 21.8	n/a
		Second	17 months	Untreated	9.3 / 22.2	n/a
		Third	17 months	Untreated	10.5 / 17.1	n/a
		Fourth	18 months	Untreated	No S/G Work Performed	n/a
McGuire-1	Inconel 690T	First	16 months	Untreated	3.0 / 9.7	n/a
		Second	16 months	Untreated	7.9 / 6.3	n/a
		Third	16 months	Untreated	7.7 / 8.3	n/a
McGuire-2	Inconel 690T	First	17 months	Untreated	4.1 / 17.1	n/a
		Second	18 months	Untreated	1.3* / 3.7*	n/a
		Third	17 months	Untreated	4.3 / 9.1	n/a
ANO	304L SS	First	18 months	Untreated	10/10	n/a
Calvert Cliffs-1	Inconel 690T	First		Untreated		

Performance Data from Other SCrP-Treated Components

Table 4-8 captures a summary of other applications of the SCrP process.

Preconditioning Surfaces of Replacement Components

Table 4-8
Other SCrP Applications

Application	Status
RWCU piping Monticello	5 years
RWCU piping Peach Bottom	Test pieces were in-service and then removed
RHR piping Diablo Canyon	In service
Barsebäck Tubing Tests	~ 4000 hours HWC chemistry ~ 2200 hours HWC and zinc injection
PRM housing Beaver Valley	In service
PRM housing VC Summer	In service
Temp Reactor Vessel Head Sequoyah	One time use to date
RWCU Pump Impeller	Demonstration Only
RWCU Pump Casing	Demonstration Only
Sample line tubing	Demonstration Only
Fuel Cask Rancho Seco	EP only – 21 uses with only rinse and wipe decontamination required

Diablo Canyon Residual Heat Removal (RHR) System Piping

Pacific Gas & Electric Co. replaced the RHR system piping at its Diablo Canyon Unit 2 during the plant's fifth refueling outage. The plant used this piping replacement project to evaluate various surface preconditioning treatments that were applied to four replacement piping spools. The treatments applied to the spools included electropolishing only, electropolishing plus preoxidation, electropolishing plus non-stabilized chromium (i.e., electroplated chromium), and SCrP. An "as-received" pipe spool also was included in this program to provide a reference surface.

After installation of the replacement RHR piping, the system was returned to service to permit reloading the reactor with fuel. This operation resulted in activity buildup on the replacement piping because of the existing inventory of activated corrosion products in the primary system and ongoing corrosion. The RHR system was removed from service after the plant was restarted. Shortly thereafter, a gamma spectroscopy analysis of the test spools was performed in May 1993 to determine the isotopic composition and the specific activity levels of the activated corrosion products in this system. The results of these measurements are shown in Table 4-9. Clearly, cobalt-58 is the predominant nuclide, and cobalt-60, Fe-59, and Mn-54 are present only in trace amounts. The activity detected is probably all from particulate deposition because the coolant temperature passing through the RHR system is quite low (<140°F) and the exposure time was about 36 days. These measurements served as a baseline case for comparison with later measurements. Only small differences were found for the various surface treatments, likely because of the short exposure period, but it is encouraging to note that the general trend of

activity buildup correlates with the different surface treatments. The SCrP-treated spool showed the lowest activity deposition, about a factor of two less than the electropolished-only spool.

Table 4-9
Activity Buildup on RHR System Test Spools at Diablo Canyon 2 (After Restart)

Pipe ID	Surface Treatment	Dose Rate (mR/hr)	Specific Activity ($\mu\text{Ci}/\text{cm}^2$)				
			Co-58	Co-60	Fe-59	Mn-54	Cr-51
RHR-8	SCrP	25 $\pm$ 5	1.18	1.6E-02	4.2E-03	1.9E-03	n/d
RHR-7	EP + Cr	20 $\pm$ 5	2.31	2.3E-02	4.6E-03	4.3E-03	n/d
RHR-10	EP + PV	25 $\pm$ 5	2.39	2.4E-02	5.1E-03	3.5E-03	n/d
RHR-9	EP only	20 $\pm$ 5	2.53	2.9E-02	6.4E-03	5.1E-03	n/d
RHR-AR	AR	35 $\pm$ 5	2.62	5.6E-02	5.6E-02	1.1E-02	n/d

Similar dose rate and activity deposition measurements were performed after the second exposure cycle in December 1994, and these results are shown in Table 4-10. As before, cobalt-58 is the predominant nuclide present. The deposited activity on the SCrP-treated spool was about a factor of two lower than any of the other pretreatments and about a factor of seven lower than the “as-received” spool section. The other surface pretreatments all showed cobalt-58 values of $\sim 0.5 \mu\text{Ci}/\text{cm}^2$.

Table 4-10
Activity Buildup on RHR System Test Spools at Diablo Canyon 2 (After Exposure for Two Fuel Cycles)

Pipe ID	Surface Treatment	Dose Rate (mR/hr)	Specific Activity ($\mu\text{Ci}/\text{cm}^2$)				
			Co-58	Co-60	Fe-59	Mn-54	Cr-51
RHR-8	EP + SCrP	4	0.24	1.4E-02	4.3E-03	3.0E-03	4.0E-02
RHR-7	EP + Cr	5	0.47	2.2E-02	8.4E-03	5.1E-03	1.2E-01
RHR-10	EP + PV	6	0.44	1.9E-02	4.8E-03	4.9E-03	3.6E-02
RHR-9	EP only	6	0.44	1.8E-02	2.3E-03	4.7E-03	3.3E-02
RHR-AR	AR	25	1.32	1.3E-01	1.0E-01	2.9E-02	7.7E-01

Dose rate and gamma spectroscopy measurements also were made after the third exposure cycle in June 1996, and the results are presented in Table 4-11 (4-4). The values are significantly higher than those measured after the second fuel cycle, but the relative amounts of activity deposition are similar to those measured in the earlier fuel cycles: the SCrP-treated spool is at

Preconditioning Surfaces of Replacement Components

least a factor of two less than all other surface treatments and a factor of four less than the “as-received” spool section. Reductions in activity deposition are not as large as seen previously on the SCrP-treated PWR diaphragms. It is possible that the difference arises because the RHR piping system operates at a low temperature and the system is in service for only a small fraction of each fuel cycle.

Table 4-11

Activity Buildup on RHR System Test Spools at Diablo Canyon 2 (After Exposure for Three Fuel Cycles)

<i>Pipe ID</i>	<i>Surface Treatment</i>	<i>Dose Rate (mR/hr)</i>	<i>Specific Activity ($\mu\text{Ci}/\text{cm}^2$)</i>				
			<i>Co-58</i>	<i>Co-60</i>	<i>Fe-59</i>	<i>Mn-54</i>	<i>Cr-51</i>
RHR-8	EP + SCrP	17	1.37	1.0E-02	2.7E-03	2.3E-03	n/d
RHR-7	EP + Cr	35	2.70	1.8E-02	2.5E-03	1.3E-03	n/d
RHR-10	EP + PV	50	2.82	1.9E-02	3.3E-03	2.1E-03	n/d
RHR-9	EP only	40	2.83	1.8E-02	2.4E-03	3.4E-03	n/d
RHR-AR	AR	70	2.68	3.0E-01	1.1E-01	9.5E-03	2.1E-01

VC Summer Radiation Monitor Housing

SCrP was applied to process radiation monitor housings at VC Summer. Prior to application of SCrP, the background count rate on the housings was 50,000 to 60,000 counts per minute (cpm). The post-SCrP background was maintained at 3,000 to 4,000 cpm for several years. The background has since increased but remains less than 15,000 cpm, which is still a factor of four reduction compared with the earlier background reading.

Performance of SCrP-Treated Components in BWRs***Monticello RWCU Test Piping***

Monticello Nuclear Plant identified a section of the RWCU system that was causing excessive radiation exposure to plant personnel because of high radiation buildup in the piping and implemented a project to replace a portion of the system with piping that was treated using SCrP. About 50 feet of 4-inch Schedule 80 pipe, seven 90 elbows, and two 45 elbows were replaced. The piping was cut into ten five-foot long sections to facilitate application of SCrP. The treated piping was installed at Monticello in March 1998.

After about 1-1/4 years of exposure to hydrogen water chemistry (HWC) conditions, the shutdown dose rate on the treated piping is only 80-100 mR/hr. This result is about 30 times lower than the value measured on the old carbon steel piping prior to its replacement. The dose rate trend for the SCrP piping is shown in Figure 4-10. Plant personnel have noted that a significant contributor to dose rates during plant operation stems from N-16, but this was not evident before pipe replacement because dose rates from the deposited corrosion products on the

old pipe overwhelmed the N-16 contribution. Dose rates on the pipe during operation are 500 – 600 mR/hr, which contrasts with the 80 – 100 mR/hr measured at shutdown after 1-1/4 years of operation.

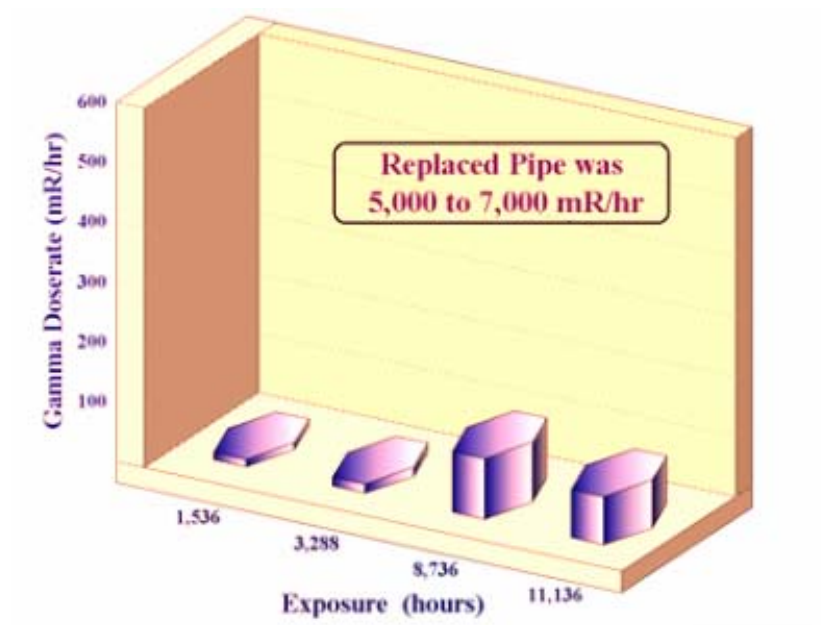


Figure 4-10
Dose Rate Buildup of Monticello RWCU Piping After Treatment with SCrP

Barsebäck Tubing Tests

Short sections of SCrP-treated piping 316 stainless steel piping were installed in the Barsebäck BWR (Sweden) in June 1998. After almost 4000 hours of exposure to HWC chemistry conditions (and 2200 hours to both HWC and zinc injection), the SCrP section of the tubing shows a dose reduction factor of 2.2 compared to a section that was only electropolished and a dose reduction factor of 6 when compared to the old piping. The dose rate buildup trends for the various treatments evaluated in these tests are shown in Figure 4-11. The somewhat low dose reduction factor found for the SCrP tubing is not surprising for two reasons: [1] the exposure period is only about 2/3 of a year and [2] the electropolished tubing has performed quite well. During this exposure period the dose rate of the old piping has doubled and the buildup trend is roughly linear. This contrasts with the response of the SCrP tubing, which appears to have leveled out at about 0.15 mSv/hr after reaching a value of 0.12 mSv/hr during the first 700 hours of exposure. This observation suggests that dose rates on the SCrP tubing will remain low, whereas dose rates from the other surface treatments, especially the untreated old piping, will continue to rise (4-5).

Preconditioning Surfaces of Replacement Components

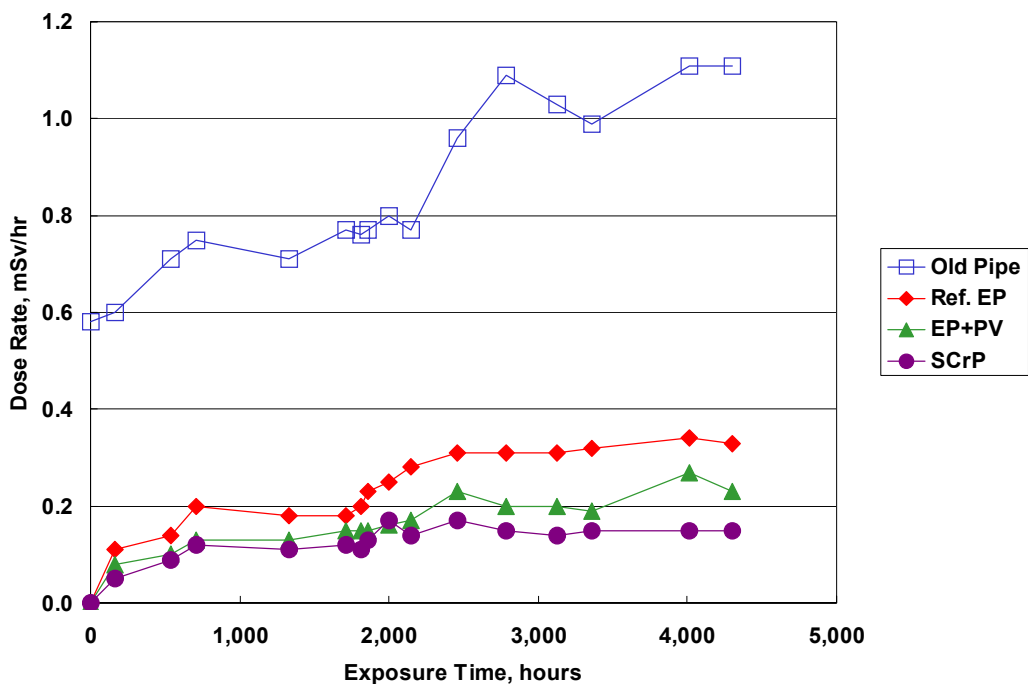


Figure 4-11
Dose Rate Buildup for Barsebäck Tubing Tests

Peach Bottom 2 and 3 RWCU Test Piping

SCrP-treated piping was also installed in the RWCU systems at Peach Bottom-2 and Peach Bottom-3 to assess the performance of SCrP under BWR normal water chemistry (NWC) conditions. These test pieces were installed in September 1993 when the Peach Bottom-3 RWCU system was changed from three pumps to two pumps. The spools at Peach Bottom-3 that were treated with SCrP showed activity reduction factors of approximately 1.5 to 2 relative to the electropolished plus passivated piping. The exposure time was approximately 20,400 hours for one fuel cycle. Stabilized chromium piping at Peach Bottom-2 has also shown lower radiation buildup than the reference electropolished plus passivated piping. However, after exposure for two fuel cycles, radiation buildup on the stabilized chromium test pipe is approaching that of the reference piping and is now only about 20% lower than the reference piping. Small reductions in RHR piping that was treated using SCrP were also found at Oskarshamn-1, a Swedish BWR that also operates, like Peach Bottom 2 and 3, under normal water (NWC) chemistry. It therefore appears that the stabilized chrome process is not as effective in BWRs operating with NWC as with plants using HWC, probably because oxidizing conditions remove the chromium as soluble chromate.

The more significant dose rate reduction seen with SCrP at Monticello and Barsebäck compared with those at Peach Bottom 2 and 3 and Oskarshamn 1 is probably a consequence of operation of the coated components under HWC conditions (4-5). HWC is a reducing environment and the chromium-rich film is stable under these conditions. This is not a significant restriction, because

all US BWRs are now operating under HWC. The high dose reduction factors also measured on components treated with SCrP that have been exposed in PWRs are consistent with this view.

Other Applications of SCrP

Although feasibility has been established in test programs, there is currently no plant experience for the following applications.

Valve internals

One key incentive to reduce activity pickup by valves is suggested by the observation that maintenance personnel often have to contend with high dose rates (15 – 20 R/hr) when repair or replacement of valves is required during plant outages. One factor that contributes to the high dose rates is that many valve internal surfaces are fabricated from castings. Castings are characterized by high surface porosity, a surface feature that serves as a sink for activated corrosion products. The first component with a complex shape where attempts were initiated to apply chromium coatings was two four-inch valve bodies. Efforts were implemented to plate the valve bodies using two processes: a proprietary chromium-plating bath developed by the Armoloy Corporation and the conventional EPRI SCrP. After plating, the valve bodies were cut lengthwise to facilitate inspection of the deposited chromium films. Both plating processes deposited a uniformly thick chromium layer. The measured chromium film thickness for the Armoloy process was found to be approximately 4.9 μm , and there was no evidence of film cracking based on optical and scanning electron microscopy measurements. The chromium thickness following application of SCrP was $\sim 1.7 \mu\text{m}$. This value is somewhat thicker than is normally obtained with this process. This is encouraging because this was the first attempt to plate a component with such a complex geometry using SCrP, and the earlier Doel coupon measurements show that chromium films of this thickness significantly lower activity deposition. Chromium-coated valve bodies have not been placed in service at any nuclear power plant. A valve body treated with SCrP is shown in Figure 4-12 (4-5).

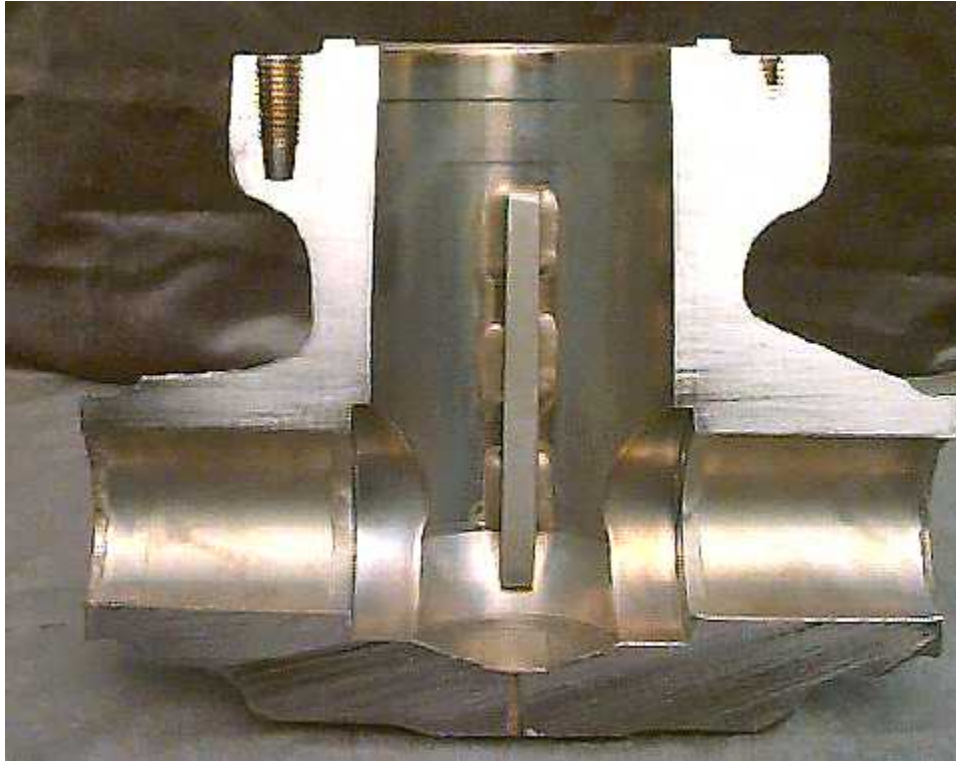
Preconditioning Surfaces of Replacement Components

Figure 4-12
Valve Body Following Application of SCrP

Pump elements

The incentives noted for valve internals are also applicable to cast surfaces in pump elements (impellers and casings) used in nuclear plants. The successful application of SCrP to cast and forged pump components has been demonstrated. Figure 4-13 shows a pump impeller to which SCrP was applied (4-3). The purpose of this application was to demonstrate the ability to apply SCrP to a component with a complex geometry. Although SCrP was successfully applied, this component has not been placed in service in an operating plant.

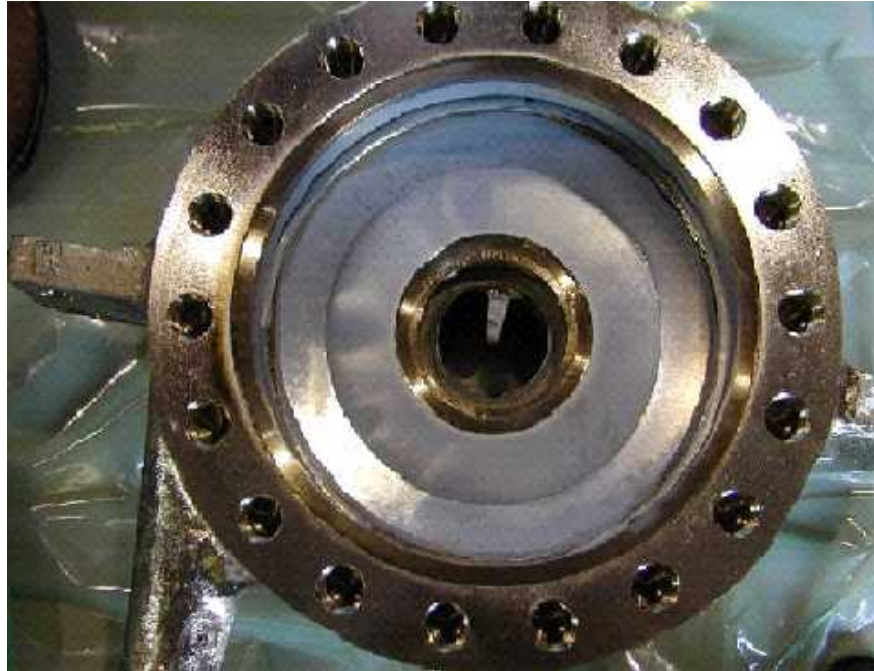


Figure 4-13
RWCU Pump Casing following Application of SCrP

Jet Pumps

Several BWR plants have reported evidence of jet pump fouling that have adversely affected power production at the end of fuel cycles. This prompted an investigation into the feasibility of applying surface pretreatments that may help reduce the fouling potential on these components. Southern Company's Plant Hatch provided a spare jet pump to EPRI to demonstrate the ability of applying SCrP to a very complex geometry. No difficulties were encountered during application of the three steps that comprise the SCrP to this component, although the chromium deposition and preoxidation (stabilization) steps were applied only to the throat region of the jet pump. A photograph of the jet pump following application of SCrP is shown in Figure 4-14 (4-3).



Figure 4-14
Jet Pump Following Application of SCrP

Other Surface Modification Opportunities

Electropolishing of Tubing Components - Zircaloy Fuel Rod Cladding and Alloy 690 SG Tubing

It is anticipated that application of electropolishing process to replacement SG tubing would lower corrosion product release rates because EP reduces the surface area. This may lower the crud inventory that deposits on the fuel, which could help mitigate the Axial Offset Anomaly (AOA). EDF has implemented a program to evaluate EP and other surface modification techniques for replacement Alloy 690 tubing. After processing tubing and small plate specimens were exposed to simulated PWR primary water chemistry ($T = 325^{\circ}\text{C}$ and $\text{pH} = 7.0$). The tubing was exposed for about 6 months, and EP and a gaseous oxidation process were found to be the two most promising treatments. Measured reductions in corrosion rates and metal releases were about a factor of five lower than measured on an untreated small plates and about a factor of three lower for tubing specimens. An evaluation of associated costs performed by EDF suggests that EP would add about 5% to the cost of a replacement SG. EDF continues to evaluate issues associated with introduction of this technology.

Key Considerations – Preconditioning Surfaces of Replacement Components

A synopsis of the most important aspects of this chapter.

1. Modification of the surfaces of replacement components that contact the primary coolant should be considered for reducing activity buildup on component and piping surfaces. Electropolishing and the SCrP are the two most widely used techniques in nuclear power plants. Chemical decontamination is not recommended after these processes because the passivated surface is lost.
2. Field measurements of recontamination in PWR SG channel heads that have been electropolished show this technique lowers dose rates by a factor of about four. An ALARA analysis of the benefits from electropolishing of replacement SG channel heads performed by Southern Company estimated the exposure savings associated with specific SG maintenance tasks would be lowered by ~13 rem per cycle for 11 fuel cycles.
3. The electropolished surfaces of a temporary reactor vessel cover (TRVC) facilitated subsequent decontamination of the cover using a low-pressure water spray.
4. SCrP has been applied most extensively to PWR steam generator diaphragms and BWR RWCU piping systems. Activity pickup is lowered by about a factor of 5 to 10.
5. The application of SCrP should be limited to components that operate under reducing coolant chemistry conditions (i.e., PWRs or BWRs under HWC). Lower activity savings associated with SCrP were seen in PWR applications that encountered significant levels of particulate deposition or in systems operating at low temperatures for short periods of time. However, in these applications SCrP performed better than other surface modification techniques.
6. The ability to apply SCrP to surfaces with more complex shapes has been demonstrated for the cases of valve bodies, pump elements (impellers and casings), and BWR jet pumps. These components have not been placed in service, so activity reduction data are not available.
7. If possible, utilities should avoid the use of replacement components in the primary systems that have cast surfaces. Castings contain significant amounts of porosity, which serve as sinks/traps for activity deposition.
8. It is important to consider that the activity that is not incorporated into components and systems will be transported to liquid processing filtration and ion exchange media. This will increase disposed waste activity levels, however this process is considered to be proactive management of that activity. It is equally important to recognize that in some instances the activity may be deposited in other locations such as low flow areas or similar crud traps.

References

- 4-1. Evaluation of PWR Radiation Fields: 1986 – 1990, EPRI, Palo Alto, CA, TR-100306, April 1992.
- 4-2. Bergmann, C. A., and Bencini, R. L., “Evaluation of PWR Radiation Fields: 1991 – 1996”, EPRI, Palo Alto, CA, TR-107566, February 1997.
- 4-3. Stabilized Chromium Process: Final Report, EPRI, Palo Alto, CA: 2002. 1003374.
- 4-4. An Assessment of to Reduce Radiation Buildup; 1996 Progress, EPRI, Palo Alto, CA: 1996. TR-107224.
- 4-5. Assessment of Chromium Coating Technology, EPRI, Palo Alto, CA: 1999. TR-112982.
- 4-6. Field Testing of Chromium Coating Technology, EPRI, Palo Alto, CA: 1998. TR-111666.

5

PWR PRIMARY COOLANT CHEMISTRY

This chapter is based on the 2003 edition of the PWR Primary Water Chemistry Guidelines, which should be consulted for further information. Note that this chapter focuses on radiation field issues, but materials and fuel issues must also be considered in determining water chemistry specifications.

The purpose of a PWR primary coolant chemistry program is:

- 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.

In certain instances, situations are encountered where chemistry conditions that are optimum for achieving one goal can lead to a decreased level of achievement relative to other goals. Unfortunately, this is the situation encountered in defining an optimum PWR primary coolant chemistry program. Specifically, operation at elevated pH can reduce out-of-core radiation fields but could lead to an increased likelihood of Alloy 600 cracking. (Recent evaluations indicate that this effect is relatively small.) In contrast, at a lower operating pH, the likelihood of Alloy 600 integrity problems may be slightly reduced but an increased buildup rate of radiation fields will result. The fuel cladding situation is even more complicated. Specifically, heavier crud deposits are expected on the cladding at low pH, possibly leading to increased cladding failure rates. Higher pH operation minimizes the rate of crud deposition. However, concerns continue to exist relative to the effect of operation at elevated lithium concentrations on fuel cladding corrosion.

As a result of considerations such as the above, the PWR Primary Chemistry Guidelines (5-1) define water chemistry parameters to achieve a balance among the three goals, recognizing that lower priority is assigned to radiation field control compared with that for materials and fuel integrity goals. Figure 5-1 illustrates the dilemma in defining an optimum RCS pH (lithium/boron concentration relation) to meet the conflicting requirements of pressure boundary integrity, fuels integrity, and radiation control. The figure illustrates how actions taken to improve one facet of plant operation often have an effect on one or more of the other considerations, and all considerations are directly affected by the primary coolant chemistry. Specifically, higher pHs reduce radiation buildup but can also affect materials and/or fuels performance.

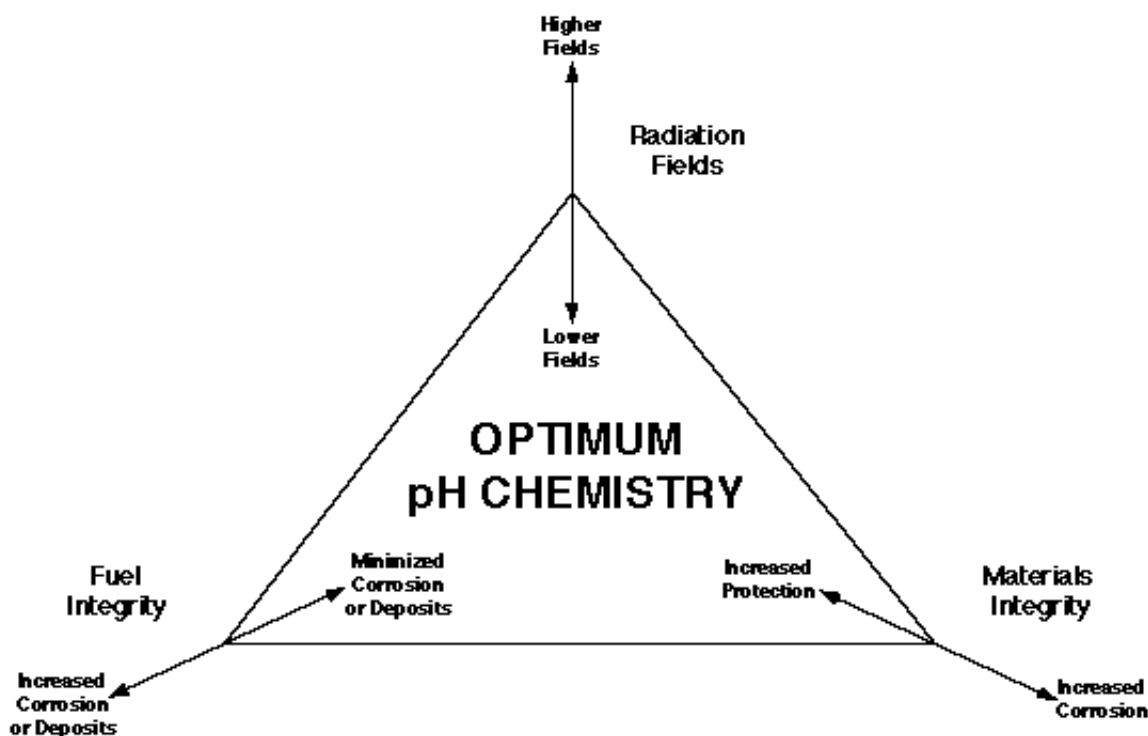


Figure 5-1
Schematic of the Problems with Optimizing RCS pH Control

Discussion of Chemistry Regimes

The following discussion of high temperature pH (pH_T) regimes is being provided to support the discussions of chemistry effects presented later in this section. Selection of an appropriate operating regime is part of chemistry optimization.

In the early 1980s, many plants began to employ **Coordinated Chemistry**, in which lithium is coordinated with boron to maintain a pH_T of 6.9. More recently, some plants have increased the coolant steady-state pH_T from 6.9 to 7.2-7.4 to minimize crud deposition on the core and reduce radiation fields in out-of-core regions. As discussed later, studies suggest that operating with $\text{pH}_{300^\circ\text{C}} = 7.4$ will minimize solubility-related nickel ferrite precipitation in the core.

In the late 1980s, several PWRs implemented a 3.5 ppm Li (max.)/ $\text{pH}_T = 7.4$ (**Elevated Lithium**) scheme to reduce out-of-core radiation fields. The Elevated Lithium chemistry programs were terminated due to concerns over the potential effects of prolonged exposure to 3.5 ppm lithium on primary water stress corrosion cracking (PWSCC) of Alloy 600 and Zircaloy cladding corrosion.

Instead, a **Modified Chemistry** regime with ~2.2 ppm lithium/ $\text{pH}_T = 7.2$ -7.4 was adopted by many plants. Maintaining lithium concentrations at a maximum of 2.2 ppm during startup, however, can result in a $\text{pH}_T < 6.9$ for plants operating with an initial boron concentration exceeding ~1200 ppm. Depending on the cycle length and fuel design, the startup boron concentration may exceed 2000 ppm, which will significantly lower the pH_T . Therefore in the

Modified Chemistry regime, the startup lithium and boron are coordinated to maintain $\text{pH}_T \sim 6.9$ until the required lithium concentration decreases to 2.2 ppm. At this point, the pH_T is permitted to increase with constant 2.2 ppm lithium, until it reaches 7.2-7.4. It is important to note that extended cycle chemistry may require significant concentrations of lithium for the early portion of the cycle.

Over the past few years, several PWR operators have experienced Axial Offset Anomaly (AOA) associated with a combination of high core power density, high operating temperatures, and high peaking factor core designs. The AOA problem, if not controlled, may require power reductions and/or plant shutdown. It appears that AOA is associated with the local concentration of boron in crud deposits on fuel rods with significant subcooled boiling. Crud deposits enhance the local concentration factor on the fuel and can lead to increased fuel surface cladding temperatures. For this reason, reducing the source term for crud (e.g., minimizing corrosion rates of system materials) is considered especially important for plants susceptible to AOA. Corrosion product release rates are reduced as the pH_T is increased from 6.9 to 7.4. The change in release rate becomes less dependent on pH_T as the pH_T approaches 7.4. This dependence is observed for both stainless steel and Alloy 600. This effect is more pronounced for Alloy 600, which is important because of the large surface area of SG tubing. Additionally, the corrosion and possibly the release rates are expected to be highest at the beginning of the cycle and decrease as protective oxides on system materials stabilize. On this basis, corrosion product generation and transport are expected to be greatest during the earliest parts of the fuel cycle when the pH is lowest under current practices.

To address this situation, several plants have started to use a **Coordinated Chemistry at Elevated pH** regime (see Figure 5-2) in which the pH_T is maintained as close to constant and as high as practical throughout the full cycle. In the example shown, the lithium concentration is limited to 3.5ppm at the start of the cycle, but many plants are now operating with higher lithium concentrations to maintain a constant pH for as much of the cycle as possible.

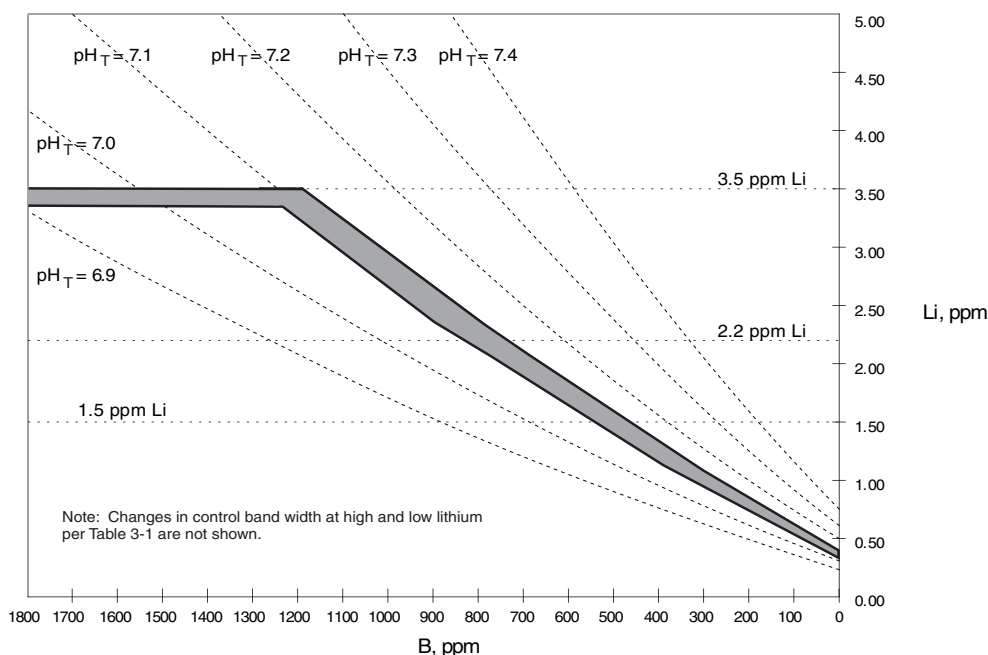


Figure 5-2
Schematic of Coordinated Chemistry at pH_T 7.1 Consistent with Lithium Below 3.5 ppm (at 300°C)

Effects of Chemistry Parameters

Accumulation of activated corrosion products on out-of-core surfaces is the main cause for buildup of radiation fields that persist after shutdown. There are three essential steps in this process. First, corrosion products are released to the coolant from out-of-core surfaces. Second, some of this material is deposited in the core region, where it is activated by exposure to a neutron flux. Third, some of the activated material is released from the core and incorporated in out-of-core oxides. Primary coolant chemistry influences each of these steps, and its variation during the fuel cycle has an important effect on the accumulated amount of out-of-core radioactivity.

Primary coolant pH is the key parameter in coolant chemistry. Corrosion rates of out-of-core materials, corrosion product release rates from these materials, solubility of corrosion products, the properties of corrosion product particles suspended in the coolant, the thermodynamics and kinetics of in-core deposition, and release and redeposition out-of-core are all a function of pH. The pH in the primary circuit is dependent on the local temperature and the existing water chemistry, primarily the concentrations of lithium and boron.

Corrosion products are carried by primary coolant in two forms: as solids (i.e., metal oxide particles) and as dissolved species such as metal ions and their complexes with hydroxyl ions. The principal ultimate source of primary-coolant corrosion products is the oxide film on the interior of steam generator tubing. These films have an inner layer of nickel-chromium-iron spinel and an outer layer of nickel ferrite. The chemical composition of nickel ferrites may differ

from place to place, since temperature and coolant chemistry conditions vary around the primary loop, determining which compositions are stable at any given location.

Corrosion products deposit on fuel as metal oxides, although metallic elements may also deposit under certain conditions. Deposits on fuel in moderate-duty cores contain mostly nickel ferrites (general formula, $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$). This general formula can be more accurately written as $\text{Co}_y\text{Ni}_x\text{Fe}_{3-x-y}\text{O}_4$ to account for the low (but dose-rate important) cobalt content. In this formulation, y is of course much smaller than x . Samples of fuel deposits from plants operating thermally uprated cores (in some cases with axial offset anomaly) contain relatively more nickel compared to the typical nickel ferrite based deposits of lower duty cores. Spectrographic examination of fuel deposits from Callaway cycle 6 (an AOA cycle) indicated a ferrite composition of $\text{Ni}_{0.3}\text{Fe}_{2.7}\text{O}_4$. Flakes of Callaway's Cycle 9 fuel deposits (the cycle with highest AOA) were composed of roughly equal fractions of NiO , ZrO_2 and a newly identified nickel-iron oxyborate Ni_2FeBO_5 (bonaccordite). Nickel ferrite comprised at most 10% of these high-duty deposits. These high-duty deposits are relatively insoluble, and behave differently under conventional shutdown chemistry practices.

Corrosion Product Release

Corrosion products containing iron, nickel and cobalt enter the primary coolant mainly as a result of general corrosion of out-of-core surfaces. This form of corrosion proceeds in primary coolant at such a low rate that it has no measurable effect on the integrity or performance of components, but it is of concern because of its consequences for activation and radioactivity redistribution and because it is the source of corrosion deposits on fuel cladding which can affect fuel performance (5-1).

It has long been recognized that general corrosion of carbon steel at temperatures corresponding to primary coolant conditions is at a minimum in otherwise pure water when the pH is raised by a strong base to around 10 to 11, measured at room temperature. This corresponds to pH_T from 7.4-8.4 at 300°C (572°F). General corrosion of stainless steels and Alloy 600 behaves similarly. Furthermore, laboratory tests indicate that corrosion product release rates for both Alloy 600 and stainless steel are low in coolant with $\text{pH}_{300^\circ\text{C}} = 7.0$ and even lower at $\text{pH}_{300^\circ\text{C}} = 7.4$.

Particulate Transport

Deposits on fuel and corrosion product particles in primary coolant and subsystems are visible evidence of corrosion product migration. Particulates in the coolant have received much attention, but quantitative treatment of the processes by which they are deposited on and released from in-core and out-of-core surfaces has been difficult. Nonetheless, the radiation management impact of uncontrolled particulate release from the core during a shutdown transient is demonstrated by separate experiences at two plants wherein high specific activity, highly nickel-rich deposits were discharged into the coolant during cooldown (5-3). Although no definitive root cause has been established, both plants had operated with thermally uprated cores and neither can exclude a combination of thermal hydraulic and chemistry disturbances as the cause for the releases.

Any attempt to understand the behavior in primary coolant of colloids, and larger particles as well, must consider the effects of the surface density of electrical charges that metal oxides acquire when immersed in aqueous solutions. Electrical charges affect the tendency of particles to deposit on another solid surface or to agglomerate with each other. The net charge on metal oxide surfaces is influenced strongly by pH.

Soluble Transport

Dissolved corrosion products can be transported, dissolved or deposited by the coolant based on solubility differences. The solubilities of nickel and iron depend on temperature, pH and redox potential, all of which vary with position around the non-isothermal loop. Also, the pH at each location changes with time as boron is removed during the fuel cycle, and redox potential may sometimes be altered if there is a change in dissolved hydrogen concentration. These differences cause deposits to grow by precipitation when concentrations of dissolved corrosion products exceed solubility limits and to dissolve when concentrations are lower. Correlating solubility as a function of temperature, pH and redox potential, allows one to examine the consequences of alternative strategies for control of lithium concentration as boron concentration is decreased. A key result from initial correlation of nickel ferrite solubility was that the temperature coefficient at 300°C (572°F) for solubility of iron (assuming constant concentration of lithium, boron and hydrogen) was predicted to change sign (from retrograde solubility to "normal" temperature dependence) at a $\text{pH}_{300^\circ\text{C}}$ of about 7.4,^{*} which was supported by later correlations.

Among other things, pH_T varies with hot leg and cold leg temperatures. By operating with $\text{pH}_{T_{\text{ave}}} = 7.4$, the solubility of iron in equilibrium with nickel ferrite should decrease slightly in the core inlet portion (slightly depositing) and increase slightly in the core outlet (slightly dissolving). One way to evaluate the effects of alternative lithium control strategies on radiation field buildup by solution transport processes is by computer simulation with plant-specific parameters. It is not likely that any single recommendation on pH will give best results for all or even most plants. However, there is no reason to doubt that the contribution of solution transport to out-of-pile radioactivity inventory can be minimized by coolant chemistries for which pH at 300°C (572°F) approaches 7.4 to 7.5 as early in the cycle as possible.

Several computer codes have been developed to address the radiation field buildup problem by simulation of processes in the primary system. Most of these embody a dozen or more mechanistic models of specific mass transfer processes, with empirical or estimated coefficients. A conceptually simple model that addresses corrosion product and activity transport resulting from precipitation/dissolution processes is CRUDSIM. This transport model only considers the driving force of solubility differences for nickel ferrites. Although CRUDSIM employs many simplifying assumptions, it has been somewhat successful in assessing the relative effects of various coolant chemistry conditions on radiation field buildup.

^{*} This is a distinctly more alkaline condition than the pH of 6.8 for zero temperature coefficient that is indicated by the correlation developed by Sweeton and Baes for their own data on magnetite solubility. The discrepancy is probably because their data did not provide an accurate estimate for the third hydrolysis constant of ferrous ion, which is important in alkaline water. Their measurements were mainly done with solutions on the acid side of neutral.

Several models have since been developed in the process of gaining an understanding of AOA. The more sophisticated of these consider the effect of local ionic concentration by the existing deposits, impacting the pH at the clad/crud interface, and in turn affecting the solubility of nickel and iron compounds as well as compounds containing lithium and boron. Applying these models to the high duty Callaway cores suggests that the principal corrosion product species on fuel should be NiO under boiling conditions, rather than nickel ferrite. The local chemistry conditions are such that dissolution and re-deposition of ZrO_2 is also possible, and as discussed above, formation of the highly insoluble Bonaccordite is also possible for deposits on high-duty fuel. It is expected that the transport of these intractable deposits will be different, and will affect ex-core radiation fields differently, than the nickel ferrite based deposits on conventional cores.

Verification Tests and Plant Experience

The preceding sections have discussed three important factors that affect radioactivity accumulation on out-of-core piping and components due to activation of deposits on the core: corrosion product release, particulate transport and solution transport. The discussions indicate that activity transport effects of all three factors should be reduced by coolant chemistry with high temperature pH_T between 7 and 7.4, with most effective mitigation at the higher end of the range. Uncontrolled releases of particulates from high reactivity regions of the core have occurred during changes in pH, temperature and thermal hydraulics at or near shutdown.

Extensive tests with pressurized in-pile loops at MIT have confirmed that ex-core radioactivity is minimized by increased coolant pH. The MIT loops were designed to model the primary circuit of a representative, non-boiling PWR plant. Seven one-month-long in-pile runs were carried out at lithium and boron concentrations selected to give $\text{pH}_{300^\circ\text{C}} = 6.5$ to 7.5. The results are summarized by, which shows the effect of pH on activity per unit area of the steam generator sections of the loops after the in-pile runs. Activities are normalized by megawatt-hours to allow results for two longer runs (indicated on the plot by A2 and B2) to be compared with the shorter runs. There is significant decrease of surface activity for both cobalt-60 and cobalt-58 as pH increases. Although this decrease may be caused by combined effects of pH on corrosion release and particulate and solution modes for corrosion product transport, the MIT team concluded that their results were consistent with the view that metal oxide solubility plays a dominant role.

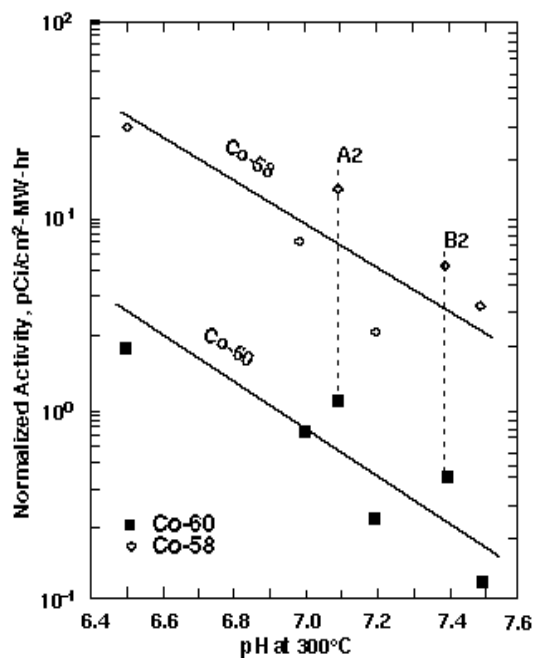


Figure 5-3
Variation with pH of Average Activities of Co-60 and Co-58 on Steam Generator Tubing at the End of MIT in-Pile Loop Tests

Plant Data

Because operation with various coolant chemistry regimes would be expected to influence plant radiation fields, a number of evaluations of plant dose rate data and special plant tests have been performed since 1980 in an attempt to define and/or corroborate the chemistry effect. However, other factors such as variations in cobalt input, component surface treatments, core thermal design and unusual releases of crud can also affect dose rates. The effects of these factors have been taken into account in the evaluations when information was available. This section summarizes the results of historical studies designed to evaluate the effects of the various coolant chemistry regimes on plant dose rates.

Uncoordinated Versus Coordinated Chemistry Operation

The first evaluations in 1984-1985 of the effects of pH on plant radiation fields indicated that operation with a lower pH as compared to a higher pH or coordinated pH 6.9 coolant chemistry resulted in generally higher dose rates (5-1). The evaluations used steam generator channel head dose rate data from about thirteen plants from the first one or two cycles of operation. The evaluations were based on a quality factor quantifying the degree of adherence of the operational chemistry relative to coordinated pH_T 6.9.

A later evaluation was based on data from about thirty-six plants and a number of cycles of operation and used two evaluation techniques (arithmetic average of all the data and a 1-year moving mean trend) and dose rate data representing the steam generator tubing and crossover

pipings in addition to the steam generator channel head. The evaluation concluded that operation with Coordinated Chemistry compared to uncoordinated chemistry resulted in a reduction in dose rates of about 18%.

EPRI now recommends that a utility consider operation at constant pH_T higher than 6.9, yet within the fuel and material integrity constraints (5-1). This strategy should reduce the release rate of soluble fuel deposit precursor species from the system surfaces. Evaluation of data from several plants indicates that operating with higher BOC (Beginning Of Cycle) pH lowers the median coolant activity by about 25 – 50%, depending on the nuclide. The chemistry and dose rate experience of plants that have utilized elevated pH in one form or another has been detailed in a series of recent EPRI reports. In general, significant reductions in dose rate were achieved following the first cycle with elevated pH, with lesser reductions on shutdown after the following cycle, suggesting stabilization of the corrosion product films under the new chemistry regime. One plant (Comanche Peak) has begun a program of elevated, constant pH to illustrate its impact on corrosion product transport. The BOC pH will be raised in two steps; to $\text{pH}_T = 7.3$ for the first cycle, and to 7.4 for the second cycle. Operation at constant $\text{pH}_T = 7.4$ requires a special review by the fuel vendor, because current lithium limits preclude BOC operation at pH_T 7.4, especially for high-duty, extended duration fuel cycles. The elevated, constant pH_T strategy is expected to be most attractive to plants concerned with total core crud deposit buildup, such as those with cores susceptible to anomalous axial flux depressions. Section 4 of the PWR Primary Water Chemistry Guidelines (5-1) provides a suggested procedure for making plant-specific decisions for optimizing the pH program.

Modified Versus Coordinated Chemistry Operation

The first evaluation of the effect of initial operation with Modified Chemistry operation was made in 1992. The evaluation was based on comparison of dose rates from four plants that operated since startup with Modified Chemistry and ten other plants with similar characteristics that started up with Coordinated Chemistry. Comparison of the dose rates following two cycles of operation between the two groups of plants at three locations indicated that initial operation with Modified Chemistry resulted in dose rates about 25% lower compared to operation with Coordinated Chemistry. The comparison was made by computing the average dose rate at the various locations at the average EFPY for the two groups of plants. No statistical evaluation of the data was made.

A second evaluation of Modified versus Coordinated Chemistry operation was made in 1994 (5-9). This evaluation was based on operation for two cycles and utilized data from the same four Modified Chemistry plants and three of the ten Coordinated Chemistry plants as used in the evaluation noted above. However, data from two other pH_T 6.9 plants not included in the above study were included. In addition, the coolant pH was calculated based on the plant chemistry data. (In the first evaluation, the coolant chemistry was assumed to follow the various regimes based on data provided or verbal discussion with plant personnel). The evaluation was made using two techniques: averaging the data after two cycles of operation, and comparison of the slopes of the linear regression of the dose rates versus cycle average pH values for one cycle and dose rate changes between one and two cycle operation as a function of changes in the average pH. The evaluation concluded that operation with Modified Chemistry yielded an average reduction in dose rates of about

15% relative to Coordinated Chemistry operation. The confidence level of the chemistry effect varied from about 70 - 98% depending upon the location.

Elevated Lithium Versus Coordinated Chemistry Operation

A number of plants (Ringhals 2, 3, and 4) have operated under Elevated Lithium control for several cycles and an Elevated Lithium test was run at Millstone 3 for two cycles following one cycle of Coordinated Chemistry. Evaluation of the results was performed by comparing the dose rate trends at three locations in the Elevated Lithium plants to a reference group of plants operating with Coordinated Chemistry and comparing the dose rate trends of the plants to that predicted by the CORA crud transport code. It was concluded that operation under an Elevated Lithium regime after one cycle of Coordinated Chemistry resulted in a reduction of dose rates of about 15% compared to operation with Coordinated Chemistry.

A second evaluation of the Elevated Lithium effect was performed by comparing cycle 1 and 2 dose rates trends at three locations in the five plants operating with Coordinated Chemistry noted above. The results showed an estimated dose rate benefit of about 25% (5-9).

Comparison of Radiation Field Trends as a Function of Coolant Chemistry

Figure 5-4 illustrates the overall trends in plants with Coordinated, Modified and Elevated Lithium chemistries using the steam generator channel head radiation fields as an index. The data are from a group of plants which have the same factors (other than coolant chemistry) that are expected to affect radiation fields. Using the three-year moving mean as an index, the radiation fields in the four plants that started up with Modified Chemistry are about 20% lower than those in the twelve plants that started up with Coordinated Chemistry. Note that the radiation field trends in the two plants that operated for two or more cycles with Elevated pH_T 7.4 operation (Millstone 3 and Ringhals 4) level off at a lower value after operation with the Elevated pH. In both plants, reverting to a lower pH resulted in an increase in the radiation fields for one or two cycles. The large increase in Millstone-3 is also partially attributed to increased crud deposition on the fuel due to subcooled boiling. The trend was reversed in Millstone-3 after using Modified Chemistry.

The trends in Figure 5-4 indicate the average radiation field benefit of Modified Chemistry operation, but operation under Elevated Lithium would provide a larger benefit. However, given the material corrosion concerns regarding operation above 3.5 ppm lithium for a significant amount of time, a plant-specific optimization program geared toward determination of the best overall pH program from among options consistent with the principles of Section 3 of the Primary Guidelines (5-1) should be undertaken. Operation with enriched boric acid (EBA) would alleviate the material corrosion concerns and provide an increased radiation field benefit.

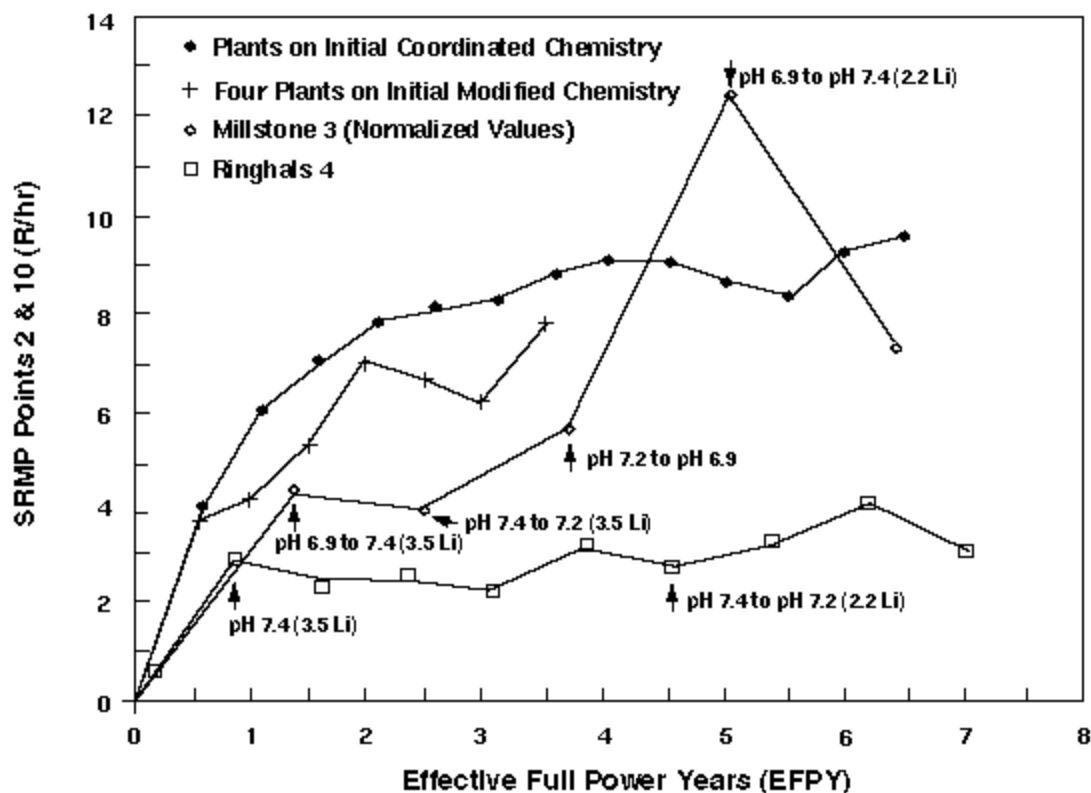


Figure 5-4
Steam Generator Channel Head Dose Rates (Comparison of Trends of Plants in Group 3 - Plant Startup after 1981) Data for Four Plants are Shown as Three-Year Moving Mean

Effects of Startup and Shutdown Chemistry

Optimized startup and shutdown chemistry controls can result in radiation field reductions. There are several critical issues that must be considered for shutdown or startup chemistry relative to activity release. These are:

- The crud inventory.
- The coordinated Operations and Chemistry plan impact on crud release in particulate form and subsequent deposition on plant surfaces.
- Boron concentration.
- Letdown purification flow rate and media capacity.
- Industry experience related to the release of soluble activity under shutdown conditions is not known to result in high radiation levels after the activity is cleaned up, unless precipitation occurs. That is, a driving force does not exist to incorporate soluble activity into corrosion films during shutdown conditions.

The primary objective of the refueling shutdown chemistry program is to prepare the reactor coolant system for safe head lift and refueling cavity flood up as quickly as is practical following breaker trip. Generally, a successful program will involve integration of efforts across

chemistry, radiation protection, fuels, materials engineering, low level waste, and operations teams. Volume 2 of the 2003 PWR Primary Water Chemistry Guidelines (5-1) is devoted exclusively to shutdown and start-up chemistry guidance; information and references on these topics can be located there. This section focuses on the impact of shutdown chemistry typical of the U.S. PWR fleet on radiation field control in the absence of fuel failures.

The most important goal of the shutdown chemistry program is to control where possible the release of activity from the core, in both soluble and particulate forms, and to provide for efficient clean up of such releases so that they do not adversely impact personnel dose and outage critical path beyond the expectation in the outage management plan. The overall strategy employed to achieve this goal is to induce controlled releases from the core in soluble form and to clean them up via ion exchange prior to opening the RCS. For example, a good rule of thumb for a typical domestic, 4-loop PWR is that the hard gamma emitter activity in the coolant (i.e., mostly radiocobalts) should be reduced to below 0.05 micro-Ci per ml prior to flood up in order to guarantee that the fields at the base of the refueling bridge will be tolerable to personnel working there. Generally, this strategy has been successful over nearly three decades of experience, although it does cost sometimes up to several days of outage critical path time since the letdown clean up system flow is only a small fraction of the total RCS (for example, 75-120 gpm).

Unfortunately, the same success cannot be claimed in general for particulate activity releases, especially in the recent ten years during which core power uprates, and the incidence of AOA (Crud Induced Power Shift), have altered fuel deposit chemistry and structure to the extent that it no longer is mostly nickel ferrite which can be reductively decomposed during Mode 4 of the shutdown (so-called ‘acid-reducing’ conditions) and deposits can now physically deteriorate during the initial cooldown. Such uncontrolled particulate releases are identified commonly as failures of shutdown chemistry programs even though extensive study of field experience has isolated few definitive chemistry causes for such releases.

In the event of a particulate release, the strategy for reaching the clean up endpoint prior to flood up remains the same as in the soluble release case. The clean up mechanism, however, can be costly both in terms of critical path time and personnel dose. In particular, hard gamma emitting particulates can settle out of suspension in low flow areas of RCS piping and sample points, creating unexpected “hot spots” that can adversely impact outage maintenance plans. Furthermore, letdown system filters, and at times reactor coolant pump (RCP) seal filters, need to be changed out far more frequently than planned, not because of particle loading but rather because of high dose rates.

The following paragraphs explore some of the fundamental aspects of the impact of refueling outage shutdown chemistry evolutions on activity release from the core and summarize critical features of successful programs for controlling them and cleaning them up. In addition, more recent concerns associated with higher thermal duty cores (which exhibit subcooled nucleate boiling) and shortened outage durations are discussed.

This section also discusses midcycle outages, whether planned or not, that lead to opening the RCS follow very similar shutdown chemistry programs as refueling outages. Additional complexity in midcycle outage chemistry arises when the plant management has the option to ascend back to power without forcing a controlled, soluble activity release (and cleaning it up).

These issues are reviewed in Volume 2 of the 2003 PWR Primary Water Chemistry Guidelines (5-1). Generally, the decision on whether to return to power without forcing soluble activity off of the core must recognize whether or not sufficient conditions were present to reductively decompose nickel ferrite fuel deposits to produce nickel metal. Plants suffering AOA may wish to avoid this circumstance. Plants near a refueling outage may wish to release and clean up this material prior to returning to power in order to avoid the uncertainty of a possible unplanned release during the upcoming outage. Other issues also arise in determining the manner in which the plant emerges from a midcycle outage, such as avoiding lithiated chemistry conditions in the secured residual heat removal (RHR) system. Some plants also treat for residual dissolved oxygen and for iron deposit in the RHR system following midcycle usage prior to a planned refueling outage.

Shutdown Chemistry Activity Releases

Following experience nearly three decades ago in which unplanned oxygen ingress during shutdown chemistry evolutions caused significant releases of fuel deposits to the ex-core of the RCS, a plan calling for forced oxidation of the RCS prior to flood up was devised and tested. This led ultimately to a very successful shutdown chemistry program for the controlled removal of nickel ferrite based fuel deposits. Until core uprates in the 1990's came along, the majority of the PWR fuel deposit was nickel ferrite (or, nickel metal and magnetite possibly during operation). With ^{58}Co being the (n,p) activation product of nickel, the majority of system dose rates coming from immediate release from the core upon cooldown were radiocobalt.

It should be noted that it has been determined via gamma scanning studies that the shutdown chemistry evolution in PWRs is nearly non-effective in removing dose from the system surface films, such as the steam generator bowl films. The dose rate obtained there is instead a result of incorporation of ^{60}Co (the activation product of trace ^{59}Co) and ^{58}Co into the films throughout the cycle, absent a sudden particulate release from the core. Reduction of film dose rates can be achieved by longer term addition of Zinc to the coolant (5-1). Shutdown chemistry studies involving ^{65}Zn dose at Diablo Canyon Power Plant are available (5-5).

Nickel ferrite deposits form on the core from deposition of trace metal impurities input into the RCS waters via general corrosion of the vast Inconel and stainless steel surface areas in the steam generators and reactor. Recall that the core is the ultimate getter of deposits such as these which exhibit retrograde solubility with temperature; that is, they are the least soluble under the hottest conditions. The thermodynamics of these deposits were extensively studied in the mid-1980's, and a series of reductive decomposition mechanisms were determined. Under appropriate conditions of dissolved hydrogen, pH, and temperature, the ferrites decompose to valence zero nickel (and by analogy, ^{58}Co) and magnetite. These conditions are generally achieved during Mode 4 of the shutdown, when the temperature is roughly 300 °F, the dissolved hydrogen is roughly 10-16 cc_{STP}/kg, and the pH is mildly acidic (below roughly 5.5). They are generally held for 12 to 24 hours. Also, under these "acid-reducing" conditions iron-containing species are just soluble. They precipitate out onto ex-core surfaces as temperature is lowered, which is usually not a dose rate problem unless they co-precipitate significant ^{60}Co . For this reason, some plants now flush their RHR system(s) of residual iron species prior to putting it in service at or just below Mode 4 temperatures.

The successful management of labile core deposits in the era prior to core uprates to subcooled boiling, therefore, involved reductive decomposition of nickel ferrite followed by forced oxidation of the RCS using hydrogen peroxide additions until a steady state of at least 2 ppm residual dissolved oxygen. The peroxidation caused a sharp spike in soluble ^{58}Co , typically on the order of 5 micro-Ci/ml, as the zero valence materials were oxidized to cations. Ion exchange in the letdown system successfully cleans up the soluble cations, using an H-OH mixed bed, thus allowing a safe head lift and flood up. Typically 2 to 5 kg of nickel might be removed this way, together with a couple thousand Curies of ^{58}Co . Experience since core uprates have become common still demonstrates that there is considerable nickel metal produced on the core during this acid-reducing shutdown sequence (or it already exists on the core during operation, as some recent data from hot-leg particulate samples might suggest). Thus, there have been considerable soluble cobalt spikes recorded following successful, forced peroxidation that still clean up by ion exchange even though they can be sometimes five times larger than seen prior to subcooled boiling on the core.

Unfortunately, core power uprates that demand subcooled nucleate boiling in the upper spans of the core guarantee that the core surfaces are the ultimate getter of particulates suspended in the RCS as well as soluble species that precipitate via retrograde solubility. The reason is that as the vapor generated on the hottest surface leaves that surface, the non-volatile materials convected to that hot surface with the supply water for that vapor remain as deposits. This has generally been the case since the mid-1990's, and is particularly troublesome as far as controlled shutdown release is concerned in plants exhibiting AOA. AOA plants form not only nickel ferrites on the fuel surface, but also nickel oxide, zirconium dioxide, and a nickel ferroboration particulate called Bonaccordite (5-2).

None of these new materials are sufficiently soluble, if at all, under acid-reducing chemistry to afford a soluble release and clean up strategy. Unfortunately, the majority of the radiation control problems seen during shutdown in the past ten years have been associated with uncontrolled release of particulates formed from these type of materials, especially nickel oxide, during the shutdown evolution. Typically these releases are occurring at higher temperatures than the acid-reducing conditions required for soluble release strategies, implying that their physical stability toward thermal hydraulic transients is at issue. Little of this is proven by independent laboratory or loop study, however. Nonetheless, over the last several years, analysis of anecdotal experiences in the industry allowed the 2003 Guidelines committee to formulate some general rules of thumb for placing a plant with an uprated core in the most optimistic state for avoiding a particulate release (5-2). They are:

- Achieve acidity as soon as possible in the cooldown sequence to the point that operations should consider delithiation in the last 24 hours of full power operation
- Borate through emergency boration pathway to achieve at least 1000 ppm boron within ten hours
- Maintain hydrogen during cooldown of at least 10 ccSTP/kg
- Avoid cycling RCPs in and out of service

If a particulate release occurs, it should be indicated via the letdown system filter dose rates. For plants planning on cleaning up the particulate release before opening the RCS, there has been a practice of using low micron rated filters (to 0.1 micron) with frequent change out while

maintaining as many RCPs in operation as allowed in order to attempt to keep the released material in suspension in the RCS. For other plants without available clean up time, it is prudent to assume that the particulates will settle to low flow areas and sample points in the RCS, and extra shielding may be required for work near these areas. Furthermore, opening the RCS and flooding up prior to achieve the 0.05 micro-Ci/ml hard gamma emitters still risks elevated radiation fields at the fuel handling bridge.

Finally, there is little doubt that some of the particulates suspended in the RCS are colloidal in nature. A colloid is little more than a solid of small enough size that Brownian motion keeps it in suspension even in the absence of bulk flow. For water at relevant temperatures, these materials can be roughly 10 to 100 nanometers in size. While they will likely not settle out of suspension and concentrate in low spots, they also will appear non-filterable in the laboratory and in the letdown system.

Recently, attempts have been made to capture these materials in the letdown system with limited success. Methods include the use of proprietary resin overlays in the letdown demineralizer that are advertised as having a strong affinity for these materials. Others have employed the use of macroporous resins in the demineralizer instead of gel-type media. The effects of these media have not been rigorously investigated. The larger surface pore geometry of these resins is more conducive to physically adsorbing colloidal materials as they pass through the demineralizer bed; it remains unlikely that the colloids are removed by a true ion exchange mechanism.

Source Term Control

Cores with upper span subcooled nucleate boiling required in order to meet the power generation demands, the likelihood is reasonably high of having some unplanned particulate release occur during shutdown evolution even if the soluble release is induced and cleaned up perfectly. Since there are few chemistry tools available to otherwise solubilize these materials, the concept of enacting stricter source terms control holds promise. In particular, many plants have changed their operating chemistry pH regime to the constant, elevated program currently recommended in the 2003 Guidelines. Studies of at least five plants found that raising the pH throughout the cycle resulted in lower cycle radiocobalts, and therefore presumably lower nickel release from ex-core surfaces (5-6). Recall that the ^{58}Co results from activation of nickel on the core. This result is explained by the fact that the release rate of nickel ion into the RCS water from Inconel is reduced as pH(T) increases. The effect is admittedly small, but still finite enough to be beneficial.

More beneficial, however, is to recognize that even in the hottest plants where nearly half of the fuel is discharged after only two cycles, there is still significant inventory of fuel deposit on the reload fuel. Given that the particulates can be released from the reload as well as from new deposits on new fuel, consideration should be given to evaluating the economic viability of removing those deposits before reloading the once burned fuel. EPRI technology is commercially available to safely ultrasonically clean reload fuel in fewer than six minutes per bundle, making it a viable off-critical path operation at some plants (5-7). Several domestic reactors have employed this process; it is discussed in detail in Chapter 8 of this document.

Recent Events

Following publication of the 2003 PWR Primary Water Chemistry Guidelines, there have been some recent industry experiences that may be related with that document's updated advice. These experiences also have occurred during a time when the economic pressure to shorten outages may have incubated conditions in the plant that were not yet considered by the 2003 Guidelines Committee. Root cause evaluations are at varying stages in each of these cases, delineated below. In addition, in June of 2004, EPRI held a Workshop on PWR Shutdown Chemistry experiences, and identified shortened outage demands as one main area in which to benchmark existing industry experience and to follow future outages for the possibility of developing specific interim guidance prior to the next revision of the Guidelines:

- In order to shorten cleanup time, some plants are implementing modifications to significantly increase design letdown flow limits. This may increase the cleanup filter(s) changeout frequency (in the event of a particulate burst).
- In order to shorten cleanup times, plants with loop stops are capable of draining to mid-loop and then adding peroxide using only RHR circulation. Without mid-loop stops, however, some plants still do forced peroxidation with all RCPs secured. Questions that have arisen include:
 - Is there sufficient flow to sweep loops of all hydrogen, especially in plants having replaced with larger surface area steam generators? Missing hydrogen in the loops will expose the core to reducing conditions on flood up, follow by oxygenation via air saturated refueling waters; this combination can cause a very undesirable particulate release from the core, possibly increasing refuel floor dose rates and degrading water clarity.
 - Is there either sufficient mixing, or representative enough sampling, to absolutely know when the RCS has achieved a uniform, steady state oxygen residual? As above, the potential consequence of under-oxygenating is a release upon flood up with air saturated refueling waters.
- If a small release occurs such that its only consequence is clarity of the cavity water, addition of peroxide directly into the cavity has been done to achieve clarity in the past, however there may still be an immediate negative impact on schedule driven refuel activities.

Plant Experience: One plant operating a high duty core recently observed a high activity, black deposit on the primary side of the steam generator tubes. Preliminary analysis suggests it is nickel metal, and the activity is mostly ^{58}Co . The early analysis of this event also notes a higher than expected concentration RCS particulate samples, and notes that the one loop that peroxidated with the RCP in service exhibited the least tube deposit.

Zinc Addition to the Primary Coolant

Zinc Addition History

Zinc in the PWR primary coolant can reduce out-of-core exposure rates and primary water stress corrosion cracking (PWSCC) of Alloy 600. This effect was demonstrated through a cooperative

program between EPRI and the Westinghouse Owners Group (WOG) to evaluate the effectiveness of zinc in mitigating radiation fields and also to determine the effects of zinc additions on Alloy 600 PWSCC and corrosion of fuel cladding. The program included pre- and post- zinc measurements of radiation dose rates at Farley 2 as well as chemistry and radiochemistry monitoring during Cycle 10. Zinc was added as natural zinc acetate after 190 days into Cycle 10. The coolant zinc concentration was maintained in the range of 35-45 ppb for approximately 9 months. At the end of Cycle 10, evaluations were made of radiation dose rates as well as fuel cladding oxide growth, crud scrapings, and PWSCC of steam generator tubes. Dose rate effects are discussed below, while effects on PWSCC and fuel are discussed in Sections 2.3 and 2.4 of the PWR Primary Chemistry Guidelines (5-1).

Since the initial Farley-2 work, zinc has been injected at eight other units in the U.S.; and four overseas PWRs. The incentives for these programs included radiation field (dose rate) reduction. The plants focusing only on dose rate reductions have generally injected zinc to an RCS concentration in the range of 5 to 7 ppb. Detailed reports of the domestic and international zinc addition programs have been published by EPRI, a summary of the zinc injection programs and their results (as of November 2003) is presented in (5-15). Table 5-1 summarizes the status of known plants, injection methods, and analysis techniques.

Measurements of dose rates after Cycle 10 at Farley 2 with zinc addition showed a reduction of 24% at steam generator channel heads of which 11% was attributed to zinc addition and shutdown chemistry practice. Zinc-65 was less than 10% of the radioisotopic mix and only a minor contributor to the radiation fields. A dose savings of 40 man-Rem per fuel cycle was estimated for Farley 2 after five cycles of natural zinc addition. No zinc was added during Cycle 11 at Farley-2. Dose rate measurements at the end of Cycle 11 showed that the downward trend in dose rates observed from non-zinc Cycle 9 to zinc Cycle 10 was reversed at end of Cycle 11 (5-15). Farley-2 resumed zinc addition in Cycle 12. However the period of zinc addition during Cycle 12 was too short (3 months) to assess its effect on either dose rates, fuel cladding corrosion, or PWSCC.

Diablo Canyon Unit 1 began adding natural zinc in June 1998. After the first application on Cycle 9, the levels of ^{58}Co in the reactor coolant increased significantly in both Unit 1 and Unit 2 (5-15). Only modest activity increases were observed following Cycle 10, the second with zinc injection. The data suggest that at least one cycle with zinc chemistry is required to stabilize the zinc-substituted corrosion product deposits. Zinc injection reduced shutdown dose rates for both Diablo Canyon units. After the second cycle with zinc chemistry, steam generator dose rates were approximately 42% lower than levels prior to zinc injection at Unit 1 and 59% lower at Unit 2, although other factors may have contributed to this improvement. The activity ratios of coolant particulates for the second cycle suggest that the corrosion product deposits were stabilized through the incorporation of zinc.

Nine USA PWRs were injecting zinc into the primary coolant as of November 2003. Levels ranged from 5 to 30 ppb, with the higher levels selected to mitigate PWSCC. The data from these plants indicates that zinc addition continues to lower shutdown dose rates, but the reduction is less for each succeeding fuel cycle. This trend is reasonable, since the corrosion films are becoming conditioned with respect to exchange of nickel and cobalt for zinc.

Zinc addition has also been implemented in Biblis, Unit B in Germany, which is operated by RWE Energie AG (5-14). The objective of the program was to reduce shutdown dose rates and postpone the need for full system decontamination. An in-plant surveillance program was

conducted which consisted of chemical and radiochemical analysis of coolant, dose rate and gamma activity measurements, fuel inspections, examination of reactor coolant pump seals and examination of oxide layers on steam generator manway cover seals. Depleted zinc acetate was added in Biblis Unit B during Cycle 17. Zinc addition was initiated in early September 1996 and zinc was detected in the coolant in mid-October 1996 after a dosage of approximately 1 kg of zinc. The zinc concentration was ~ 5 ppb and 3.5 kg of zinc was injected during the cycle. Dose rate measurements at the end of the cycle showed an average dose rate reduction of ~12%. There was no adverse effect of zinc on fuel cladding oxidation. The concentration of zinc in the fuel crud was very low. Zinc addition will be continued during the next cycle. In early 1998 two other German PWRs, Biblis A and Obrigheim, commenced zinc addition.

Table 5-1
Summary of Plants Implementation Parameters for PWR Plants Operating with Zinc Addition

<i>Plant</i>	<i>Start of Zinc Addition</i>	<i>Zn Conc</i>	<i>Zn Type</i>	<i>Injection Point</i>	<i>Analytical Technique</i>	<i>Gamma Spectrometry</i>
U. S. PLANTS						
Farley Unit 2	1993 (Cycle 10)	High	Natural ⁽¹⁾	VCT	Flameless AA	Yes
Farley Unit 1	1998 (Cycle 16)	High	Natural	VCT	Flameless AA	No
Diablo Canyon 1	1997 (Cycle 9)	High	Natural	Charging pump	Flameless AA	Yes
Diablo Canyon 2	1998 (Cycle 9)	High	Natural	Charging pump	Flameless AA	Yes
Palisades	1998 (Cycle 14)	Low	Depleted	Charging pump	SIMA	No
Sequoyah 1	2002 (Cycle 12)	Low	Depleted	(Not Known)	(Not Known)	(Not Known)
Sequoyah 2	2002 (Cycle 11)	Low	Depleted	(Not Known)	(Not Known)	(Not Known)
Beaver Valley 1	2002 (Cycle 15)	High	Natural	Charging pump	ICP	No
Callaway	2003 (Cycle 13)	Low	Depleted	VCT	AES	No
Non-U. S. PLANTS						
Biblis B	1996 (Cycle 17)	Low	Depleted	Charging pump	ICPMS	Yes
Biblis A	1997 (Cycle 19)	Low	Depleted	Charging pump	ICPMS	Yes
Obrigheim	1997 (Cycle 28)	Low	Depleted	RCS hot leg	Flameless AA	Yes
Angra	2000 (Cycle 1)	Low	Depleted	(Not Known)	Flameless AA	(Not Known)

Relationship of Dose Rate Reduction with Zinc Exposure

A relationship between zinc exposure and the degree of dose rate reduction was investigated. Zinc exposure is the integrated product of the average zinc concentration during the cycle and the time that this zinc concentration was maintained in the primary coolant. The dose rate reduction factor is determined primarily based on measurements at consistent physical locations in the plant; i.e., at EPRI standard radiation monitoring point (SRMP) locations.

This evaluation was based on data available at the time, which consisted primarily of data from the first cycle of zinc addition in operating plants. The relationship was further explored using additional second- and third-cycle data from the various plants as reported in Reference (5-15). The data in Table 5-2 summarizes the data accumulated since the original work and included in this report along with that from the Obrigheim and Biblis B plants reported in (5-15). Figure 5-5 is a plot of the data for the depleted zinc and natural zinc plants. Inspection of the data in the table and figure shows that the zinc addition effect appears to reach an “equilibrium” value after 3 to 4 cycles of operation for both the depleted and natural zinc plants. Because of the low zinc exposures for the depleted zinc plants this occurs at about 200 ppb-mos, where it occurs at about 800 ppb-mos for the natural zinc plants. The final dose rate reduction in the natural zinc plants is somewhat lower, about 50%, compared to the depleted zinc plants, at about 60%. The main benefit of using initially higher zinc concentrations (and thus higher zinc exposures) is to obtain a greater dose reduction in roughly the same operational time. The logarithmic fit to the data is also noted to be reasonably good as evidenced by the high correlation coefficient (R^2) values of 0.91 and 0.62.

These trends suggest that the corrosion films have become fully conditioned with respect to the exchange of zinc with nickel and cobalt after these zinc exposures. Additional cycles of operation are needed to define whether further dose rate reductions can occur in both the depleted and natural zinc plants.

PWR Primary Coolant Chemistry

Table 5-2
Zinc Exposure and Shutdown Dose Rate Reduction

<i>Plant/cycle</i>	<i>Cycle of Zn Add.</i>	<i>Type of Zn</i>	<i>Avg. Zn Conc., ppb</i>	<i>Zn Exposure ppb-months</i>	<i>Cycle Fraction Reduction</i>	<i>Cum. Fraction Reduction</i>	<i>% Piping Dose Rate Due to ⁶⁵Zn</i>
Biblis B,17	1	Depleted	4	42	0.80	0.80	0*
Biblis B,18	2	Depleted	4	52	0.83	0.66	0*
Biblis B,19	3	Depleted	4	60	0.92	0.61	0*
Obrigheim,28	1	Depleted	4	20	0.83	0.83	0*
Obrigheim,29	2	Depleted	5	53	0.89	0.74	0*
Obrigheim,30	3	Depleted	7	77	0.80	0.59	0*
Obrigheim,31	4	Depleted	8	88	1.02	0.60	0*
Beaver Valley 1,15	1	Natural	17	45	0.80	0.80	--**
Farley 1,16	1	Natural	29	350	0.72	0.72	--**
Farley 2,10	1	Natural	35	310	0.73	0.73	7.1
Farley 2,11	--	None	2	40	1.0	0.73	1.6
Farley 2,12	2	Depleted	9	140	0.85	0.62	0
Farley 2,13	3	1/2 Depl.	29	300	0.76	0.47	--**
Farley 2,14	4	Natural	29	370	0.94	0.44	--**
Diablo Canyon 1,9	1	Natural	31	235	0.71	0.71	6.5
Diablo Canyon 1,10	2	Natural	21	210	0.73	0.52	6
Diablo Canyon 1,11	3	Natural	15	225	1.04	0.54	4
Diablo Canyon 2,9	1	Natural	21	130	0.72	0.72	4
Diablo Canyon 2,10	2	Natural	16	230	0.94	0.68	8
Diablo Canyon 2,11	3	Natural	15	290	1.02	0.69	--**
Palisades,14	1	Depleted	5	30	0.80	0.80	0*
Palisades,15	2	Depleted	5	65	0.79	0.63	0*

*Assumed to be 0, since depleted zinc was used ** Gamma spectrometry not performed

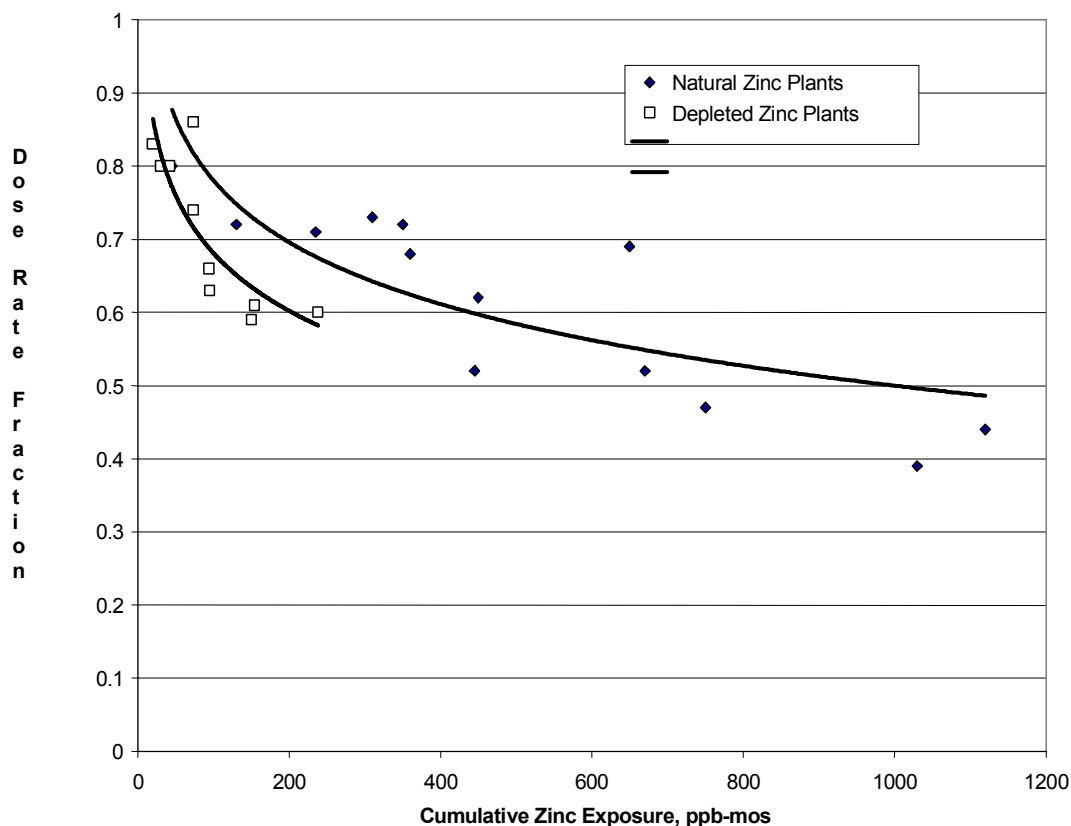


Figure 5-5
Relationship of Dose Rate Reduction and Cumulative Zinc Exposure

EPRI PRIMARY chemWORKS™ MODULES

In addition to laboratory studies and plant data evaluations, which improve the industry's understanding of the effects of primary water chemistry on radiation fields, EPRI has developed a series of chemistry tools. These chemWORKS™ modules are designed for improving chemistry control of the primary system and supporting plant efforts to reduce ex-core radiation fields and overall plant personnel exposure. These include:

- Primary System pH Calculator, Version 3.0 (EPRI ID #1007331, released 2002)
- Primary System Shutdown Chemistry Calculator, Version 2.1 (EPRI ID #1009063, released 2003)
- Primary-to-Secondary Leak Rate Calculator, Version 2.0 (EPRI ID #1000989, released 2000)

EPRI's SMART ChemWorks application, a real-time, online monitoring diagnostic system is also enabled to perform most of the functions of the Primary System pH Calculator and the Primary-to-Secondary Leak Rate Calculator. With real-time data from the plants, SMART ChemWorks conducts these calculations automatically, the results of which can then be viewed on a secure web site.

Primary System pH Calculator

The Primary pH Calculator calculates at-temperature pH, neutral pH, pH at 25°C, conductivity, boron, lithium, or ammonia for reactor coolant solutions. The user enters the system temperature and any three of the four parameter (boron, lithium, pH(t), or ammonia) values. The system determines the "missing" parameter and calculates a value for that parameter as well as neutral pH, pH at 25°C, and conductivity values.

A second function of the Primary pH Calculator is to calculate boron-lithium control bands for primary system pH control. The user enters the plant-specific information in a dialog box to describe the type of pH control regime to be used. From the user input, the pH calculator generates the boron-lithium control bands in both tabular and graphical forms. An example of the boron-lithium control band output and corresponding pH(t) is presented in Figure 5-6.

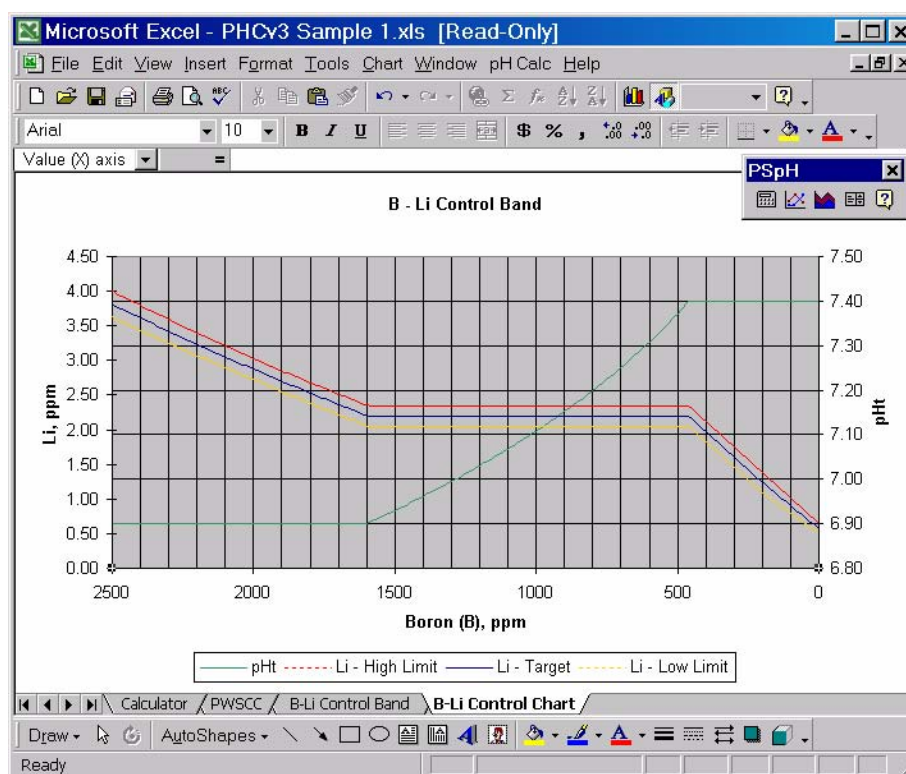


Figure 5-6
Boron-Lithium Control Band Chart

Figure 5-7 illustrates how SMART ChemWorks displays the boron-lithium control bands along with real-time data from the plant. Plant personnel can easily see when parameters are out of specification.

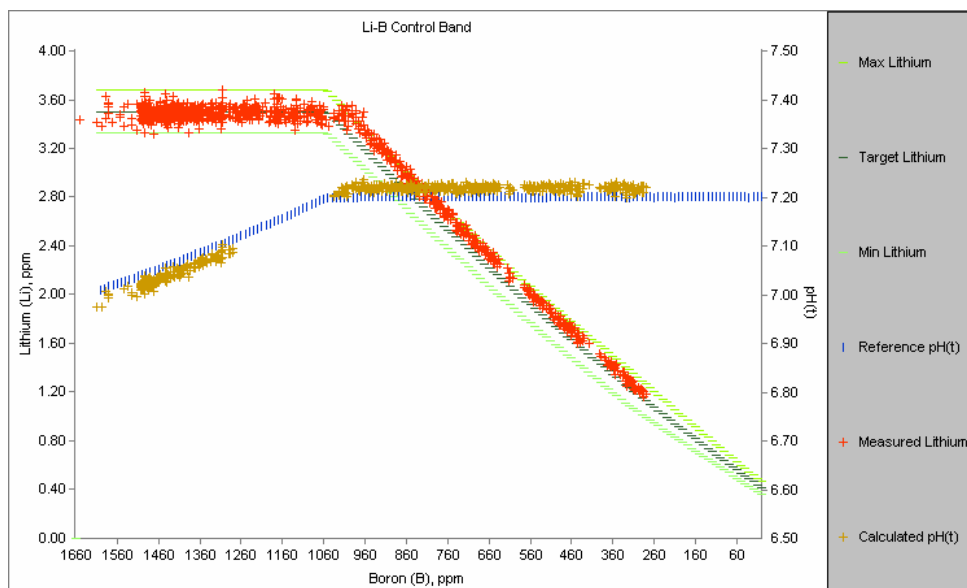


Figure 5-7
SMART ChemWorks Displays Real-Time Boron, Lithium, and pH(t) Data on Plant Specific Boron-Lithium Control Charts

Version 3.0 of the Primary pH Calculator has the added feature of a Primary Water Stress Corrosion Cracking (PWSCC) susceptibility calculation, which was based on a model of the effects of lithium, boron, and hydrogen on PWSCC initiation in Alloy 600 (MRP-68; EPRI ID #1006888). The PWSCC calculator will be updated when more data becomes available.

Primary System Shutdown Chemistry Calculator

The Primary System Shutdown Chemistry Calculator is a spreadsheet application for managing and interpreting the primary chemistry data from a plant shutdown. The input data sheet is used to enter plant parameters, RCS chemistry data, and radiochemistry data. The code calculates key shutdown chemistry parameters including:

- pH(t) , pH(n) , and pH(25°C)
- cobalt-58/Ni and cobalt-58/cobalt-60 ratios
- Cleanup efficiency, total curies released and removed, and cleanup half-life

The code also calculates release and removal rates and cumulative totals (curies or grams) for soluble, insoluble, and total fractions of key radiochemical species (Cr-51, Mn-54, cobalt-58, cobalt-60, etc.) as well as elemental species (Ni, Fe, and Co). An example of an output chart displaying cobalt, nickel and the cobalt-58/Ni specific activity ratio is shown in Figure 5-8.

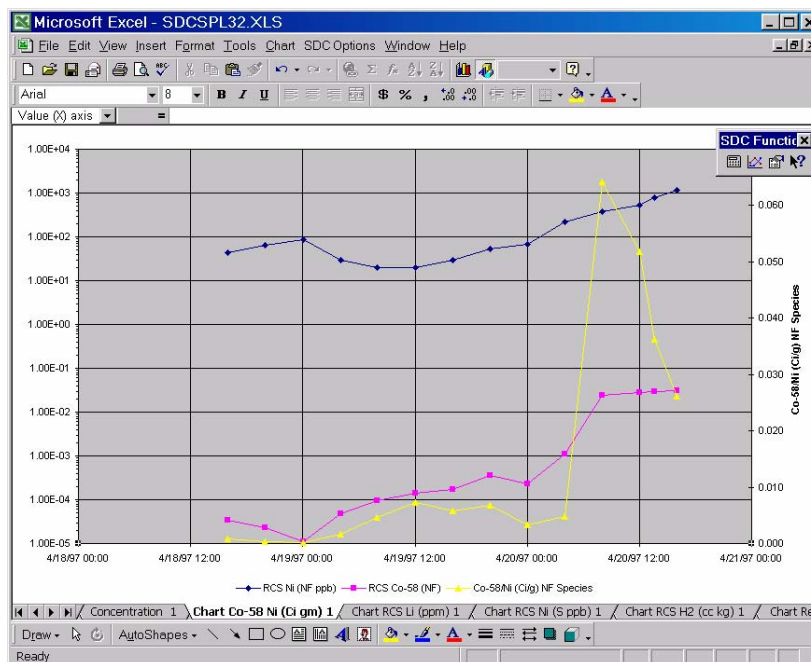


Figure 5-8
Example of an Output Chart from the Primary Shutdown Chemistry Calculator

Key Considerations – PWR Primary Coolant Chemistry

A synopsis of the most important principles for optimization of primary system chemistry.

1. Industry experience continues to identify new challenges and benefits related to primary chemistry program management. It is prudent to maintain an on-going, open dialogue with industry peers and organizations to ensure developments not addressed in existing industry documents are accurately assessed for applicability to individual stations.
2. Operate at or above $\text{pH}_{\text{Tave}} = 6.9$ to minimize crud deposition on fuel and crud-enhanced Zircaloy oxidation. If plant-specific considerations require operation below $\text{pH}_{\text{Tave}} = 6.9$, a fuel surveillance program should be considered. In some cases, fuel vendor concurrence may be required to comply with this principle, e.g., if operation above 3.5 ppm lithium is necessary.
3. Transition to operation with a target constant pH_{Tave} between 7.1 and 7.3. If necessary, develop a transition plan to move chemistry towards this goal. If a transition plan is needed, it should be consistent with the following:
 - a. Transition cycles should operate at or above $\text{pH}_{\text{Tave}} = 6.9$ to minimize crud deposition on fuel and crud-enhanced Zircaloy oxidation.
 - b. In order to decrease corrosion product deposition on the core, plants with recent AOA experience or with core designs susceptible to AOA should consider maintaining cycle pH_{Tave} constant and as high as possible consistent with fuel vendor limits on maximum lithium concentration and ppm-lithium days.

- c. For initial extended operation above 3.5 ppm lithium or the highest reviewed experience to achieve a $\text{pH}_{\text{Tave}} \geq 6.9$, a plant-specific fuel and materials review should be performed, and a fuel surveillance program should be considered.
 - d. Once beginning of cycle lithium has been established, lithium either can be controlled so as to continue operation with $\text{pH}_{\text{Tave}} = \text{constant}$ or it can be maintained constant, at or below a target of 3.5 ppm, until a specified pH_{Tave} between 7.1 and 7.3 has been reached.
 - e. The specified pH program goal at each step of the transition plan should be selected on the basis of plant-specific impacts on fuel and materials integrity, radiation field control, and in the case of AOA plants, core performance. $\text{pH}_{\text{Tave}} = 7.4$ should be considered an upper bound to the pH_{Tave} target.
4. For $[\text{Li}] > 3.0$ ppm, maintain lithium at the target value within $\pm 5\%$ of lithium concentration until lithium reaches 3.0 ppm, and then at ± 0.15 ppm until $[\text{Li}]$ decreases to 1.25 ppm. For $[\text{Li}] < 1.25$ ppm until the end of the operating cycle, maintain lithium at the target value within $\pm 12\%$ of lithium concentration. Lithium variations have a greater effect on pH at lower boron concentrations.
 5. Attempt to minimize pH_{T} fluctuations during power operation. During power level changes, some fluctuations in pH_{T} may be unavoidable due to the sensitivity of pH_{Tave} on temperature. As explained in Appendix A, Section 5, implementing the selected lithium/boron program using pH_{T} calculated at a fixed reference temperature (e.g., $\text{pH}_{300^\circ\text{C}}$) instead of at T_{ave} would eliminate the lithium addition and removal operations associated solely with fluctuations in the dissociation constant of water when evaluated at T_{ave} .
 6. Operation with lithium up to 3.5 ppm associated with 18 to 21 month fuel cycles is within the bounds of utility experience. Operating experience with lithium > 3.5 ppm now is fairly common for brief periods where xenon equilibrium is being established at the beginning of core life. Longer time periods with $[\text{Li}] > 3.5$ ppm should be considered developmental because there is no consensus on downside risk to fuel and materials integrity. This principle also applies to operation with greater lithium exposure for the purpose of further extending fuel cycles (e.g., to 24 months). It should be noted that most fuel cladding experience with $[\text{Li}]$ up to 3.5 ppm has been using Zircaloy-4 not ZIRLO or M5 and at a $\text{pH}_{\text{Tave}} 6.9$, and that the practice of operating with $\text{pH}_{\text{Tave}} 7.1$ to 7.3 will increase Li ppm-days exposure.
 7. If there is a fuel vendor concern with high lithium at the beginning of the cycle, Section 2.4 of the PWR primary water chemistry guidelines includes data on fuel issues that can be used to help support the use of higher lithium at the beginning of the cycle. The guidelines contain detailed information on methods of transitioning to higher pH regimes.
 8. The 2003 edition of the PWR Primary Water Chemistry Guidelines Contains the following recommendation on zinc injection: "Each PWR should consider adding zinc. The industry has observed dose rate reductions using 5 - 10 ppb in German and domestic plants. PWSCC benefits in laboratory tests have been observed at 20 - 120 ppb. Part of such consideration should be the impact of the zinc on consolidation of existing AOA deposits, and their impact on the resistance to shutdown chemistry removal of the deposits (e.g., bonaccordite, monoclinic zirconia, nickel oxide) that will be subjected to further sub-cooled nucleate boiling."

9. Startup and shutdown chemistry management can significantly impact cleanup filter generation rate and activity. This program aspect should be carefully evaluated and planned to ensure optimized particulate removal in conjunction with minimal personnel exposure.

References

- 5-1. “Pressurized Water Reactor Primary Water Chemistry Guidelines: Volume 1, Revision 5,” EPRI, Palo Alto, CA: 2003. 1002884.
- 5-2. “Fuel Integrity Monitoring and Failure Evaluation Handbook”, EPRI, Palo Alto, CA: 1998. TR-108779.
- 5-3. PWR Shutdown Chemistry Practices, EPRI, Palo Alto, CA: 1998. TR-109569.
- 5-4. S. G. Sawochka, Impact of PWR Primary Chemistry on Corrosion Product Deposition on Fuel Cladding Surfaces, EPRI, Palo Alto, CA: 1997. TR-108783.
- 5-5. Dose Rate and Coolant Chemistry Data at PWRs Operating with Alternative Primary Coolant Chemistry, EPRI, Palo Alto, CA: 2000. TR-1000153.
- 5-6. Evaluation of Cycle Length and Non-Standard Coolant Chemistries on PWR Plant Radiation Fields, EPRI, Palo Alto, CA: 2001. TR-1003123.
- 5-7. PWR Field Experience with Elevated, Constant pH, EPRI, Palo Alto, CA: 2001. TR-1003153.
- 5-8. A Survey of the Effect of Primary Coolant pH on Westinghouse PWR Plant Radiation Fields, EPRI, Palo Alto, CA: 1994. TR-104180.
- 5-9. PWR Primary System Chemistry: Experiences with Elevated pH at Millstone Point Unit 3, EPRI, Palo Alto, CA: 1992. TR-100960.
- 5-10. PWR Startup and Shutdown Field Experience: Operation with Zinc Injection at Diablo Canyon, EPRI, Palo Alto, CA: 2001. 10003154.
- 5-11. G. P. Sabol, et al., Rootcause Investigation of Axial Power Offset Anomaly, EPRI, Palo Alto, CA: 1997. TR-108320.
- 5-12. Assessment of Elevated pH Program for Comanche Peak Steam Electric Station, EPRI, Palo Alto, CA: 2001. 1006282.
- 5-13. Overview Report on Zinc Addition in PWRs, EPRI, Palo Alto, CA: 2001. 1001020.
- 5-14. Experience with Zinc Injection in European PWRs, EPRI, Palo Alto, CA, 2002. 1003378
- 5-15. PWR Operating Experience with Zinc Addition and the Impact on Plant Radiation Fields, EPRI, Palo Alto, CA: 2003. TR-1003389

6

BWR COOLANT CHEMISTRY

Introduction

This chapter is based on the 2004 edition of the BWR Water Chemistry Guidelines, which should be consulted for further information. Note that this chapter focuses on radiation field issues, but materials and fuel issues must also be considered in determining water chemistry specifications.

Radiation buildup in the BWR primary system occurs as the result of both soluble and particulate phase transport and the deposition of activated species. The primary activated species during shutdown is ^{60}Co , while ^{16}N is the activated species in the steam during power operation. The dominant transport phase varies with the location and operating conditions, therefore minimization of the dose rate build-up requires an understanding of which processes are likely to affect transport mechanisms. This understanding can help determine which of the actions that will be discussed in this chapter are likely to be most effective in dose rate reduction. The chapter is organized into three sections: description of the BWR coolant treatment options, effects of the treatment options, and control of feedwater iron. The chapter concludes with a discussion of the state of the current research as well as future work.

BWR Coolant Treatment Options

BWR plants employ a variety of treatments in the coolant system to optimize system performance. The treatment objectives are to minimize intergranular stress corrosion cracking (IGSCC) in the reactor and also minimize corrosion and activated species transport. Treatment options used currently in the industry are hydrogen water chemistry (HWC), depleted zinc oxide injection (DZO), and noble metals chemical application (NMCA).

Unfortunately, the solution of one treatment objective may aggravate another, e.g., hydrogen addition mitigates IGSCC but the reducing environment increases ^{60}Co and ^{16}N transport. These concerns lead to an engineering optimization with the final treatment strategy determined by the material and operational specifics of the plant. The following sections describe the treatment methods and their motivations and applications, while also demonstrating their effectiveness in BWR plants over time.

Hydrogen Water Chemistry

The oxidizing environment of the BWR coolant system under normal water chemistry (NWC) is a key factor for aggravating IGSCC. Implementing hydrogen water chemistry (HWC) was

shown to reduce the ECP (Electrochemical Corrosion Potential) of the reactor coolant and was successful in mitigating IGSCC of the reactor recirculation piping.

In a BWR, HWC converts most areas of the primary system from the normal oxidizing environment to a reducing environment. However, only a relatively small volume of the core region near the bottom of the fuel retains the reducing conditions. Above this small region, the fuel deposits remain in an oxidizing regime because of radiolysis. The hydrogen injection rate primarily determines the specific location of the interface between the reducing region and the oxidizing region.

In non-zinc plants under NWC, most (>95%) of the fuel deposits are α -Fe₂O₃. In zinc plants an appreciable fraction of the deposits exist as a zinc ferrite spinel. Under HWC, the fuel deposits in the reducing region at the bottom of the core, particularly the α -Fe₂O₃, are believed to restructure to form magnetite (Fe₃O₄) based spinels. During this process, the spinels release activated corrosion products to the reactor water in both soluble and insoluble form. The insoluble contaminants believed to be extremely fine particles that approach colloidal size. The reactor water then redistributes this activity throughout the primary system where it is deposited by various soluble incorporation and particulate deposition processes. Experience has indicated that the transition to HWC in zinc addition plants has less impact on crud transition and activity redistribution than in non-zinc plants because a significant fraction of the fuel deposits in zinc plants already exists in the spinel form.

The structural form of the protective corrosion films on the primary system piping and components under HWC is different than what is normally present under NWC. Under NWC, 304SS forms a protective corrosion film that has been observed to be approximately 70% α -Fe₂O₃ and 30% mixed metal spinel, while 316SS forms a film that is predominantly spinel (80% - 90%). Under HWC, both 304SS and 316SS form oxides that are predominantly mixed metal spinels (>90%). Spinel oxides have an inherently greater capacity than α -Fe₂O₃ for incorporation of soluble cobalt from the coolant. Variations in construction materials result in varying levels of coolant impurities such as zinc, nickel, and chromium. The composition of the oxides in different plants often varies significantly because these impurities are incorporated from the water into the indigenous corrosion films. A generic formula for the spinel may be $Zn_w Ni_x Fe_y Cr_z O_4$ with the subscripts being a function of the particular kind of stainless steel and the concentrations of the cation impurities in the coolant.

Natural and Depleted Zinc Oxide Addition

Both laboratory testing and plant experience have shown that the presence of trace amounts, (e.g., a few ppb) of soluble zinc in the reactor water reduces ⁶⁰Co buildup in the corrosion films on primary system piping and components. Early zinc addition experience used zinc oxide with the naturally occurring isotopic mixture of zinc. The natural zinc mixture contained 48% ⁶⁴Zn, which activates to ⁶⁵Zn when it is incorporated in the iron-based deposits on the fuel cladding surface. This caused ⁶⁵Zn to become a dominant isotope in the plant's radiochemistry and diminished the benefits of adding zinc. Since 1992, the primary source of zinc oxide used in BWRs has been depleted isotopically to less than 1% of the ⁶⁴Zn isotope. This DZO (Depleted Zinc Oxide) has eliminated ⁶⁵Zn as a concern and has maximized the benefit of zinc addition.

DZO is the recommended source material to be used with zinc addition under HWC. To date, all BWRs practicing zinc addition are injecting DZO.

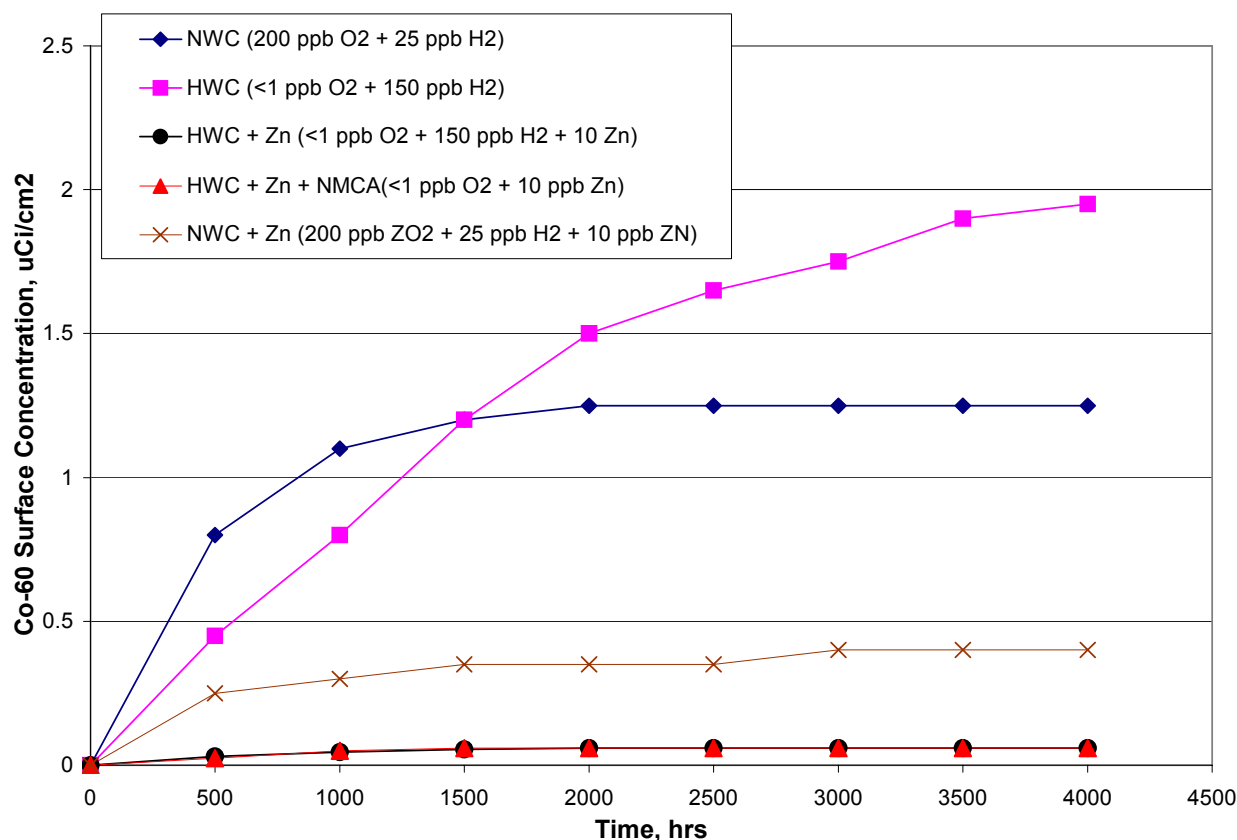


Figure 6-1
Laboratory Results Showing the Uptake of ^{60}Co by Type 304 Stainless Steel Under NWC, HWC, NWC + Zn, HWC + Zn and NMCA Treated Type 304 Under HWC + Zn Conditions (4-22)

The mechanism of the zinc ion effect was determined to be two fold. Measurements showed that aqueous zinc ion promotes the formation of a more protective spinel structured corrosion film on stainless steel, especially when reducing conditions are present. Secondly, both cobalt and zinc favor tetrahedral sites in the spinel structure, but the site preference energy favors zinc incorporation. Thus, available sites have a higher probability of being filled with a zinc ion than a cobalt ion (or ^{60}Co ion). All other factors being equal, the uptake of ^{60}Co into the film will be significantly less if zinc ion is present in the water.

The overall study concluded that the root cause of the shutdown drywell dose rate increase was two-fold. First, the conversion of the Fe_2O_3 type corrosion film oxide on the piping surfaces to the spinel type oxide compound (Fe_3O_4 type) resulted in an increase in the chemical cobalt (and ^{60}Co) concentration in the oxide due to the higher solid state solubility of transition metals in the spinel structure. The presence of a higher soluble reactor ^{60}Co concentration while this conversion was occurring only aggravated matters. The second contributor was the deposition of insoluble ^{60}Co particles released during the conversion process. The contribution from each

source was not established with certainty, but it was inferred that those plants with high feedwater iron input (high crud plants) had a larger contribution due to insoluble deposition of ^{60}Co containing particles.

Noble Metals Chemical Addition

Noble metal chemical addition (NMCA) was developed to overcome the operational deficiencies of HWC. Although HWC reduces the electrochemical corrosion potential (ECP) of the component to below $-0.230\text{V}(\text{SHE})$, only a few BWR owners were able to implement HWC for internals IGSCC protection because of the factor of 4 to 5 increase in operating dose rates that accompanies its use. The industry developed NMCA to address this shortcoming.

Very simply, noble metals such as platinum, palladium and rhodium catalyze the recombination of oxygen and hydrogen peroxide with hydrogen. When noble metals are deposited on a surface, and an excess amount of hydrogen (based on stoichiometry) is added to the coolant, their catalytic action removes all of the oxygen at the surface, thus allowing the protection of reactor internal components with lower levels of hydrogen injection.

The NMCA process is where platinum (Pt) and rhodium (Rh) chemicals are added to a shutdown BWR. After the solution is added, the reactor water temperature is maintained in the range of 120°C to 150°C for 48 hours. During that time, target concentrations of Pt and Rh are maintained in the reactor water. At the end of the 48-hour period the plant then either goes back to power or enters into a refueling outage.

The end result of the NMCA process is a uniform deposit of Pt and Rh metal at very low concentrations on the wetted surfaces of the reactor, with film concentrations on the order of 0.5 to $1.0\ \mu\text{g}/\text{cm}^2$. Consequently, hydrogen feed rates with NMCA will be substantially lower than with HWC. Very low ECPs, on the order of $-0.500\ \text{V}(\text{SHE})$, are developed on the wetted catalytic surfaces when less than $0.4\ \text{ppm}$ hydrogen is added to the feedwater during the next operation cycle. The low ECP mitigates the intergranular stress corrosion cracking (IGSCC) of the components, and there is little or no increase in operating dose rate because NMCA coupled with low feedwater hydrogen injection rates changes the surface chemistry and not the bulk reactor water chemistry. As of 2004, 26 plants have applied NMCA.

Radiation Field Buildup on Out Of Core Surfaces

The following subsections describe the various mechanisms for radiation fields buildup outside the core. The interactions of the buildup mechanisms with the various chemistry treatment options are also discussed.

HWC Effect on ^{16}N Radiation Increase in Main Steam Line

The ^{16}N ($t_{1/2} = 7.1\ \text{sec}$) activity is the primary source of radiation fields in the BWR coolant and steam systems during power operation. Because of its high-energy gamma rays, the radiation fields in the turbine building, plant environments and off site are dominated by the ^{16}N activity in

the BWR steam. Hydrogen addition to the coolant can significantly increase the operating dose rate by increasing the ^{16}N concentration in the steam.

The ^{16}N activity is produced in the reactor coolant by the $^{16}\text{O}(\text{n}, \text{p})^{16}\text{N}$ reaction in the core region. The production rate is approximately proportional to the reactor power level and cannot be changed by the chemistry environment. However, the chemical forms of ^{16}N and their volatilities change as the chemistry is changed. It is well documented that the ^{16}N concentration in the main steam line can be increased under HWC conditions. In an evaluation of HWC test results, it is suggested that as high as a factor of eight increase may be expected, depending on the level of hydrogen addition in the reactor coolant. Studies have been undertaken to understand the behavior of ^{13}N ($t_{1/2} = 10$ min.) in the BWR primary system and to obtain information that may shed some light on the potential to mitigate the main steam ^{16}N radiation field increase. These trends are illustrated in Figure 6-2.

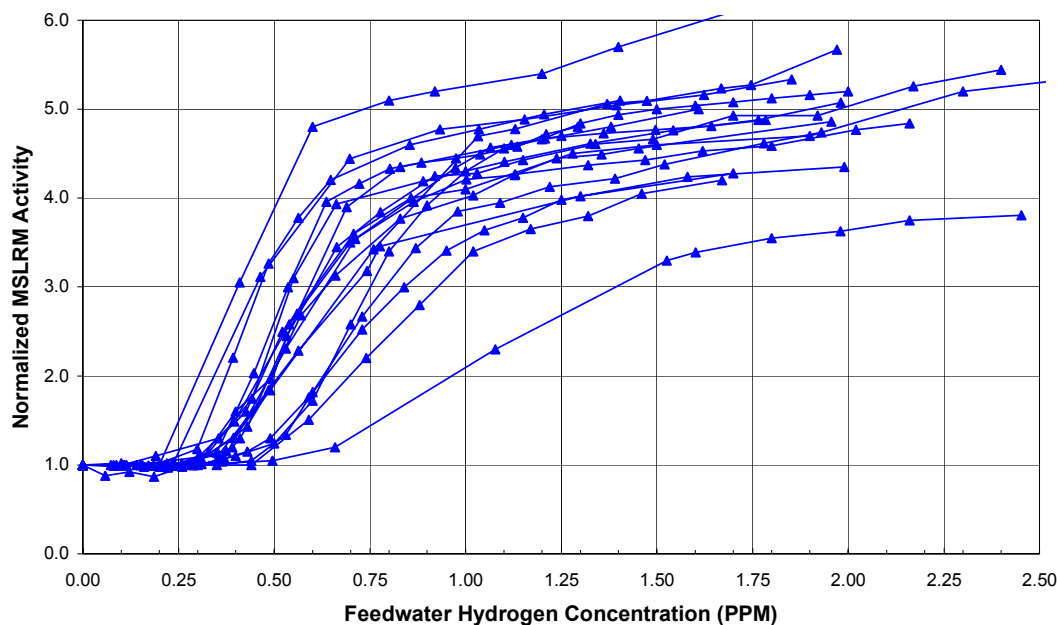


Figure 6-2
Main Steam Line Radiation Monitor Activity Increase as a Function of Feedwater Hydrogen Concentration

The increase in main steam line radiation (MSLR) level cannot be quantitatively predicted from the H_2 concentration in the feedwater. In an evaluation of hydrogen addition test results, the first sign of radiation increase occurred when the molar ratio of H_2/O_2 in the steam increased from just under 2 to approximately 2.5. Another radiation increase was observed at an H_2/O_2 molar ratio of approximately 20.

The increase in main steam line operating dose rate has affected plants differently. In some cases, only minor impacts were noted and they have been dealt with by administrative actions. In other plants, local shielding of turbine components has reduced the impact to acceptable levels. The projected impact of a 4-6-fold increase in main steam line operating dose rates has

curtailed plans for hydrogen injection at some BWRs and limited other BWRs to HWC-L. Recent work by several utilities has shown that the potential impact of the increase in main steam line dose rate can be reduced significantly by actions short of full turbine building shielding modifications. These actions are summarized as follows:

- Local shielding of sources
- Shielding affected people
- Moving people
- Reducing other man-made background sources, i.e., radwaste, etc.
- Redefining radiation control boundaries
- Personnel radiation training
- Administrative controls

The operational impact of increasing steam line fields should be considered during the assessment of the level of hydrogen injection on a plant-specific basis.

NMCA and the ^{16}N Radiation Increase in the Main Steam Line

Because of the impact of the increased operating dose rates associated by moderate HWC, many plants were unable to adopt this method of IGSCC mitigation. Noble Metal Chemical Addition (NMCA) was developed as a method of using feedwater hydrogen addition to establish the low potentials on reactor structural components without significantly affecting operating dose rates. As stated previously, the NMCA process deposits a nanolayer of Pt + Rh on the wetted surfaces of the reactor. These treated surfaces behave catalytically to the hydrogen redox reaction $2\text{H}_2 + \text{O}_2 \leftrightarrow 2\text{H}_2\text{O}$. When the addition of feedwater hydrogen increases the molar ratio of H_2 to O_2 to greater than 2, the ECP of the treated surfaces drops to the hydrogen/oxygen redox potential which is in the range of -450 to -500 mV(SHE). Figure 6-3 demonstrates that the MSLR response to hydrogen was not significantly affected by NMCA at Duane Arnold, and the same has been the case at other plants.

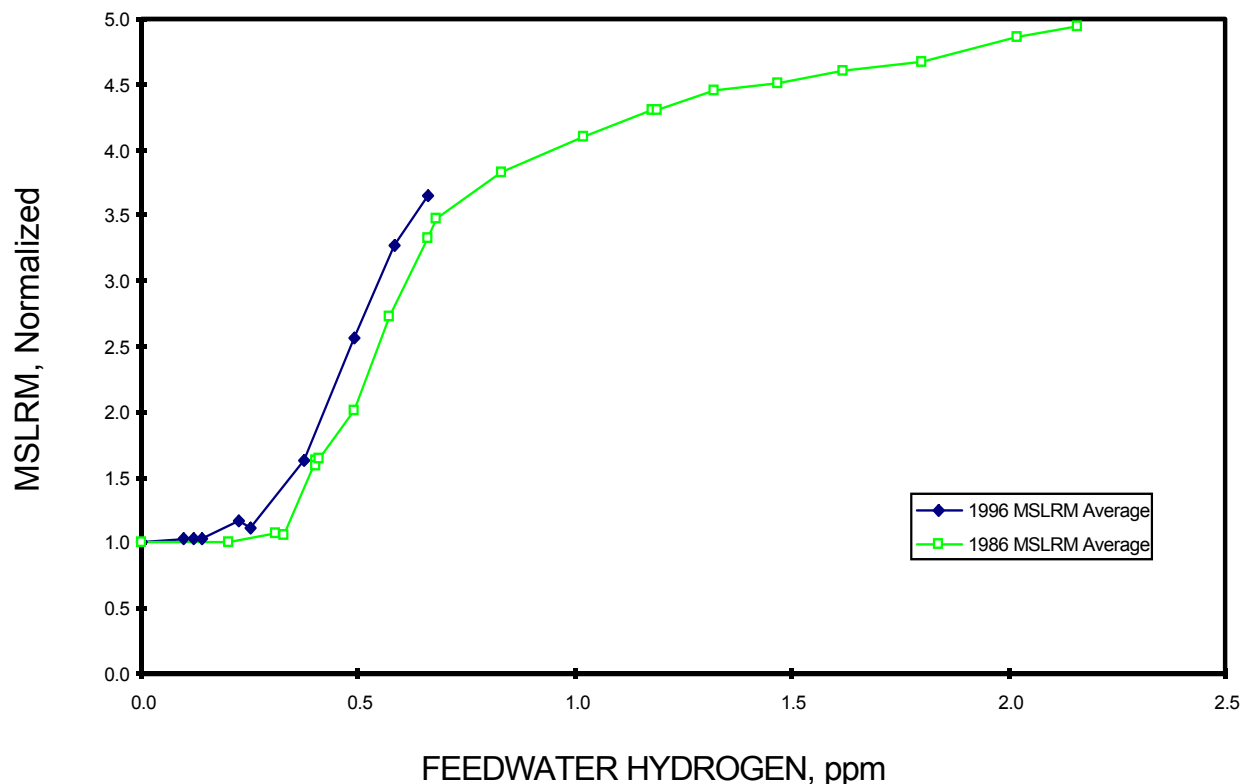


Figure 6-3
Main Steam Line Radiation Response at Duane Arnold Before and After NMCA

NMCA was developed to allow plants to operate at low potentials on reactor structural surfaces without the increase in main steam line radiation associated with moderate hydrogen.

Experience has shown that the technology has been successful in that regard. Figure 6-4 shows the hydrogen addition required to reach low potentials in several BWRs. In every case the target mitigation ECP is reached at a hydrogen injection level that causes at most a 20% increase compared to the 500% increase of moderate HWC.

Transient effects on the main steam line radiation levels have been observed at many BWRs on the initial startup after an NMCA application outage even before hydrogen injection has begun. An example of this behavior is shown in Figure 6-5. This effect is clearly a transient phenomenon, as the MSLRM values drop to normal pre-NMCA values after a few weeks to a month. When hydrogen injection is begun, the MSLRM values can increase again and then will decay to the normal (non-hydrogen) values over a period of a few weeks to several months. For comparison, a plant operating under moderate HWC will have a constant 500% increase in MSLRM readings during operation, a factor of 10 higher than the transient increase observed after NMCA application.

BWR Coolant Chemistry

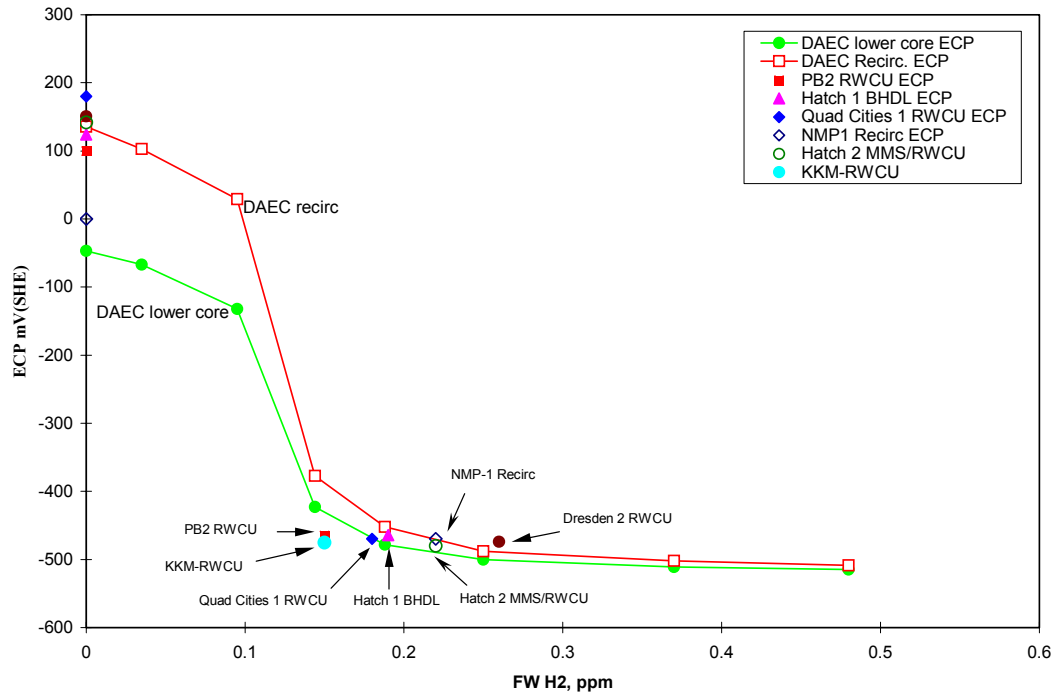


Figure 6-4
ECP Response of NMCA Treated Plants at Low Hydrogen Addition Levels

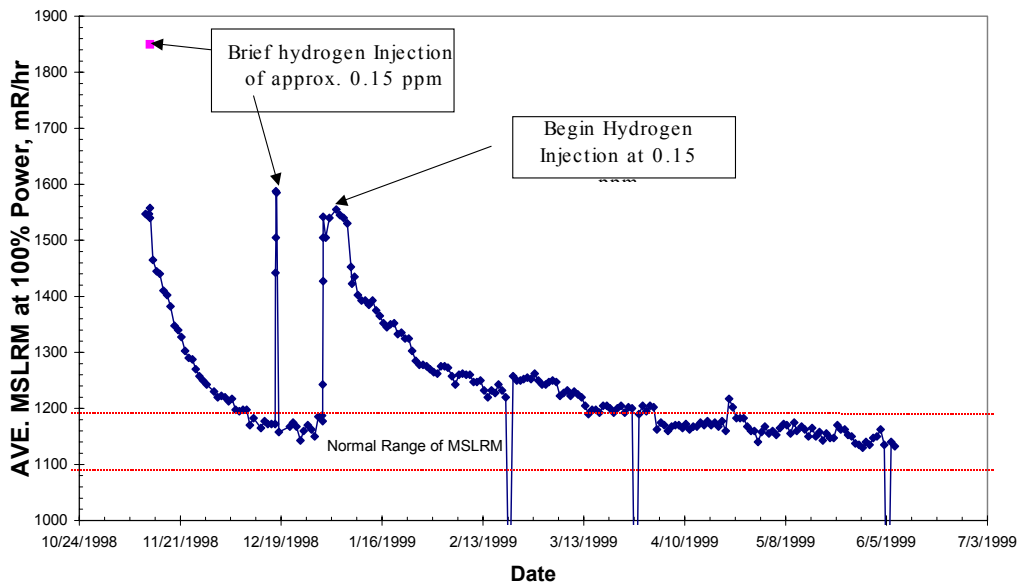


Figure 6-5
Main Steam Line Radiation Monitor Response at Peach Bottom 2 in First Post NMCA Fuel Cycle

⁶⁰Co Transport Processes in the BWR Primary System

Steam line fields are an important consideration; however, the major radiation source in the BWR for personnel exposure during shutdowns is activated corrosion products, mainly ⁶⁰Co ($t_{1/2} = 5.27$ years), deposited on primary systems surfaces. Exposures are generally accumulated at high radiation field locations where maintenance work is frequently needed. Although improvement of maintenance equipment and procedures, reduction of maintenance requirements, increased hot-spot shielding, and control of contamination dispersion have significantly reduced total exposure, further reduction of radiation fields is a major goal in programs for minimizing occupational radiation exposure. In several plants, hydrogen addition to the coolant has significantly increased shutdown dose rates by redistributing in-core activated corrosion products to out-of-core regions. A further goal is therefore to minimize the effects of HWC on shutdown radiation fields.

The primary source of radiation field buildup on out-of-core surfaces is ⁶⁰Co. The radiation fields commonly measured in a BWR at the straight vertical section of recirculation pipes are considered to be more representative for the purposes of radiation buildup trending and comparison with other plants and represent primarily the incorporation of soluble ⁶⁰Co on piping surfaces. However, radiation field buildup at other locations in the primary system may not occur by a similar mechanism or at the same rate. The deposition of particulate oxides that contain ⁶⁰Co and other activated species can also contribute significantly to out-of-core radiation levels in BWRs. This process is shown schematically in Figure 6-6. The particulate oxides, which vary in size, originate primarily from corrosion of the steam/condensate system.

The sole precursor of the gamma emitting ⁶⁰Co isotope is ⁵⁹Co. ⁵⁹Co is present as an impurity in structural alloys used in BWRs, (e.g., Type 304 stainless steel), and is the main constituent of wear-resistant alloys, (e.g., Stellite™), used as hardfacing in valve trim and other applications requiring outstanding wear resistance. Corrosion and wear lead to release of ⁵⁹Co into the coolant from these sources and is transported to the core and incorporated into the crud that deposits on the fuel rods. The ⁵⁹Co is activated to ⁶⁰Co by neutron activation, released back into the coolant, and incorporated as a minor constituent into the passive films that form on components that are inspected, repaired, and replaced by maintenance personnel. Components in the neutron flux, (e.g., the control blades), directly release ⁶⁰Co. Another gamma emitting isotope, ⁵⁸Co, is formed by the activation of nickel from stainless steel and nickel-based alloys. ⁵⁸Co has a shorter half-life and is not as major a contributor to radiation fields as ⁶⁰Co.

Plant data are widely scattered, and the activity transport process is complex and can be affected by many water chemistry parameters. A semi-empirical model has been developed by GE to describe and calculate corrosion product transport in the BWR primary system. The basic transport phenomena utilized in this model are presented in the block diagram shown as Figure 6-6. Some major transport processes in this model are summarized below:

- Metallic impurities in ionic, colloidal, and insoluble oxide forms (called crud) are released to the condensate and feedwater from metal surfaces and subsequently appear in the reactor coolant. In some plants forward-pumped heater drains contribute corrosion products and in all plants there is leakage through the condensate treatment system.
- Metal ions are also released to the coolant from corroding surfaces in the primary system. Colloidal particles of oxide or hydroxide are formed in the coolant when the saturation limit is exceeded.
- Some interactions between soluble ionic species and crud particles result in adsorption (scavenging) of ionic species on the crud particles suspended in the water.
- Crud and soluble species deposit on the fuel surface with different mechanisms. The nature of the crud plays an important role in the rate of soluble species deposition. Some of the loosely attached deposit in the outer layer may be transformed into a tenacious layer on the fuel surface.
- Neutrons activate the deposits on the fuel surface and the in-core structural materials. Radioactive species are released from in-core materials by dissolution, wear and from fuel surface deposits by erosion and spalling caused by hydraulic shear forces. There are other possible release mechanisms, e.g., ion exchange processes.
- The radioactive species redistribute themselves into “soluble” and “insoluble” species, depending on the solubility of the oxide and the concentration of iron crud that acts as a scavenger. Soluble and insoluble radioactive species deposit on out-of-core surfaces by different mechanisms. Incorporation into structural material corrosion films plays an important role in soluble radioactive species deposition, and slow ion-exchange reactions may also be involved. The insoluble species physically deposit in various locations with the kinetics of deposition being controlled by local hydraulic flow conditions, zeta potentials of both particles and substrates, and other variables.

Cobalt source removal is clearly important if radiation fields are to be minimized. Figure 6-7 shows the relationship between the soluble ^{60}Co concentration in the reactor water and recirculation pipe dose rates. Note that contact piping dose rate buildup is linear with soluble ^{60}Co concentration in the initial buildup phase, with dose rates at approximately 100 mR/h per 0.1 $\mu\text{Ci/kg}$. Hence, one of the first priorities for reducing radiation field is to remove the sources of cobalt.

Chemistry factors affecting the cobalt transport processes are briefly discussed in the following sections. All of these factors should be considered to achieve the goal of reducing the radiation field to a very low level.

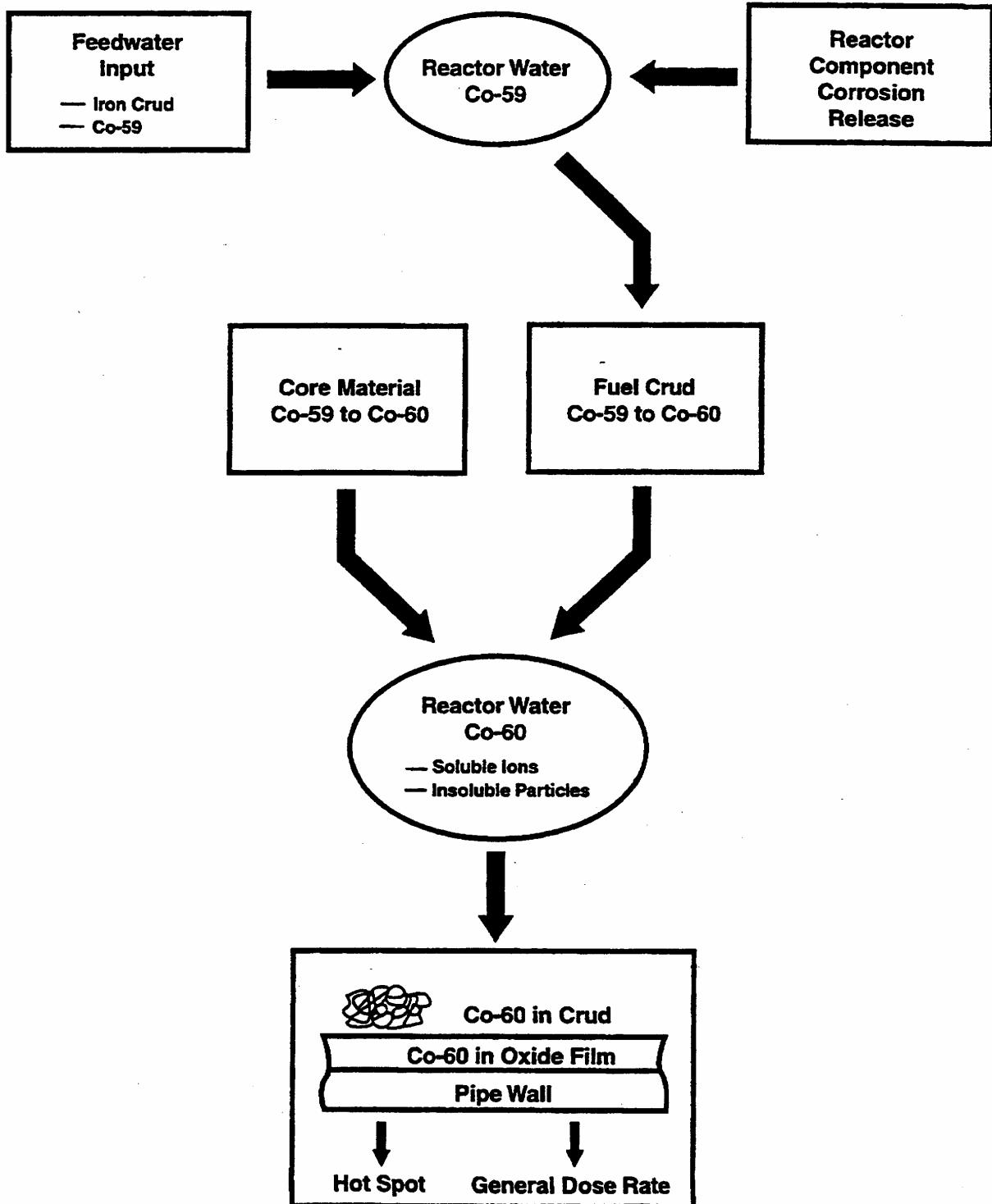


Figure 6-6
Schematic Diagram of ^{60}Co Isotope Creation, Transport and Deposition

Effects of HWC on ^{60}Co Transport

More than forty BWRs worldwide now operate under HWC, which leads to reactor coolant oxygen levels of <5 ppb with hydrogen levels ranging from 400 - 2000 ppb in the feedwater. As discussed earlier, one of the main adverse effects of using HWC has been a transient increase in shutdown dose rates. In some plants the increase on switching to HWC has been significant, but other plants have shown very minimal or no effect. The increase in radiation fields is greatest in the plants with the highest inventory or highest specific activity of ^{60}Co in the deposited corrosion products.

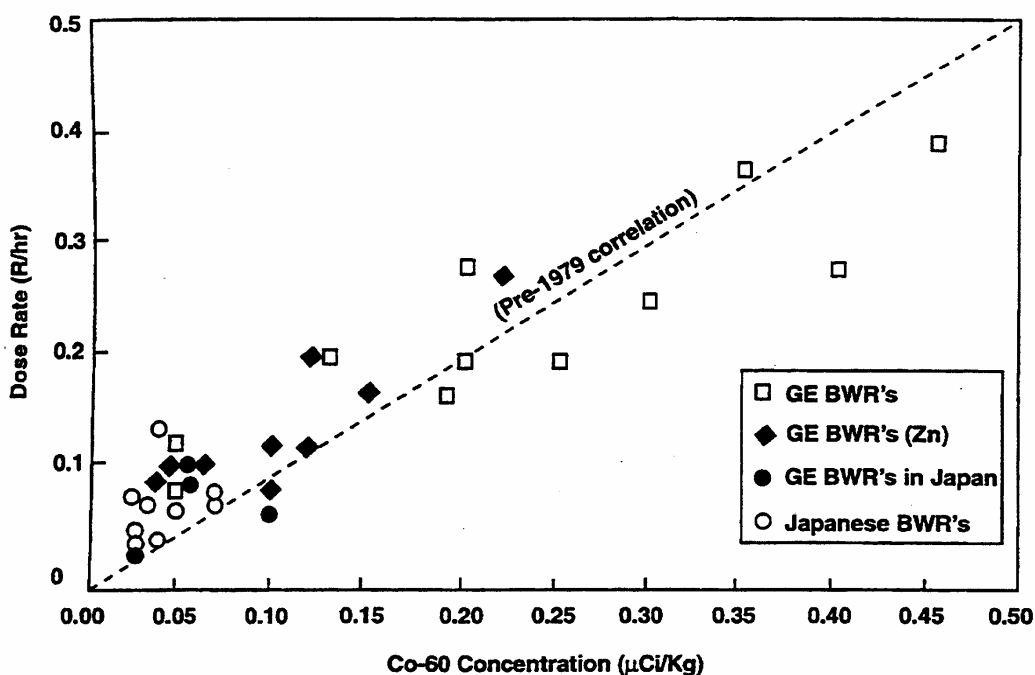


Figure 6-7
Correlation Between Soluble ^{60}Co Concentration in Reactor Water and Recirculation Pipe Dose Rates

When the chemical environment is changed by injecting hydrogen, the stable form of oxides present in the plant changes from the hematite structure to the spinel structure. As this transition occurs, some fraction of the oxides is released to the reactor water in various forms. Although soluble mechanisms can contribute, transport and deposition of insoluble isotopes are likely responsible for most of the increased dose rates, Figure 6-8.

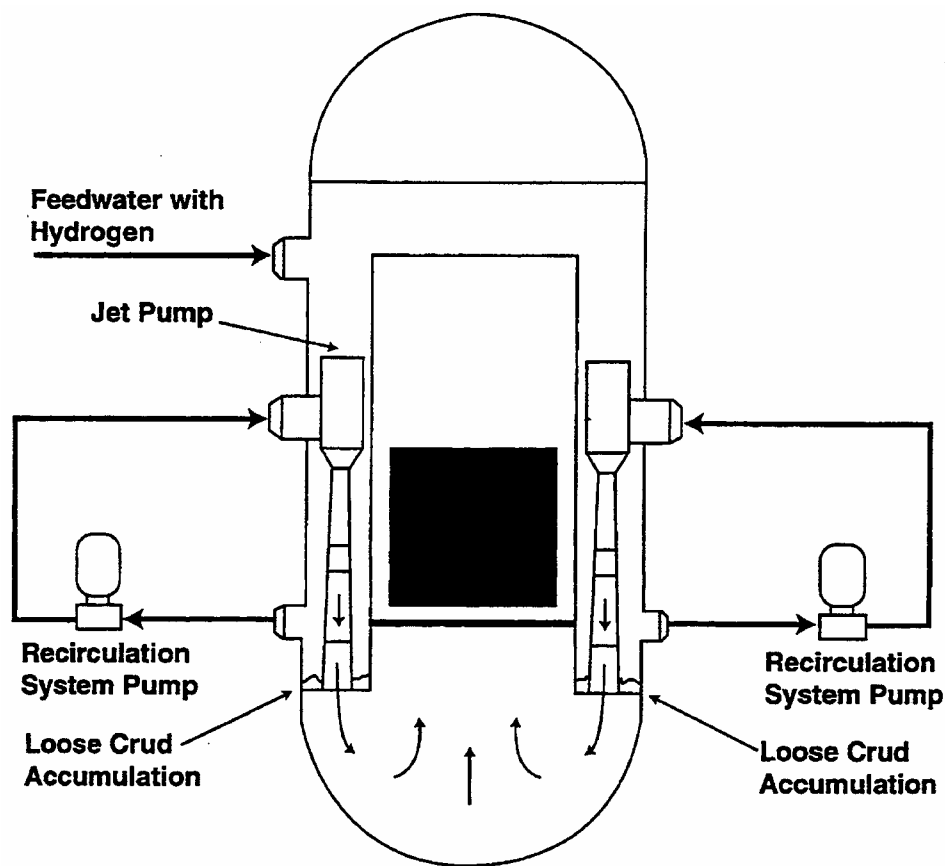
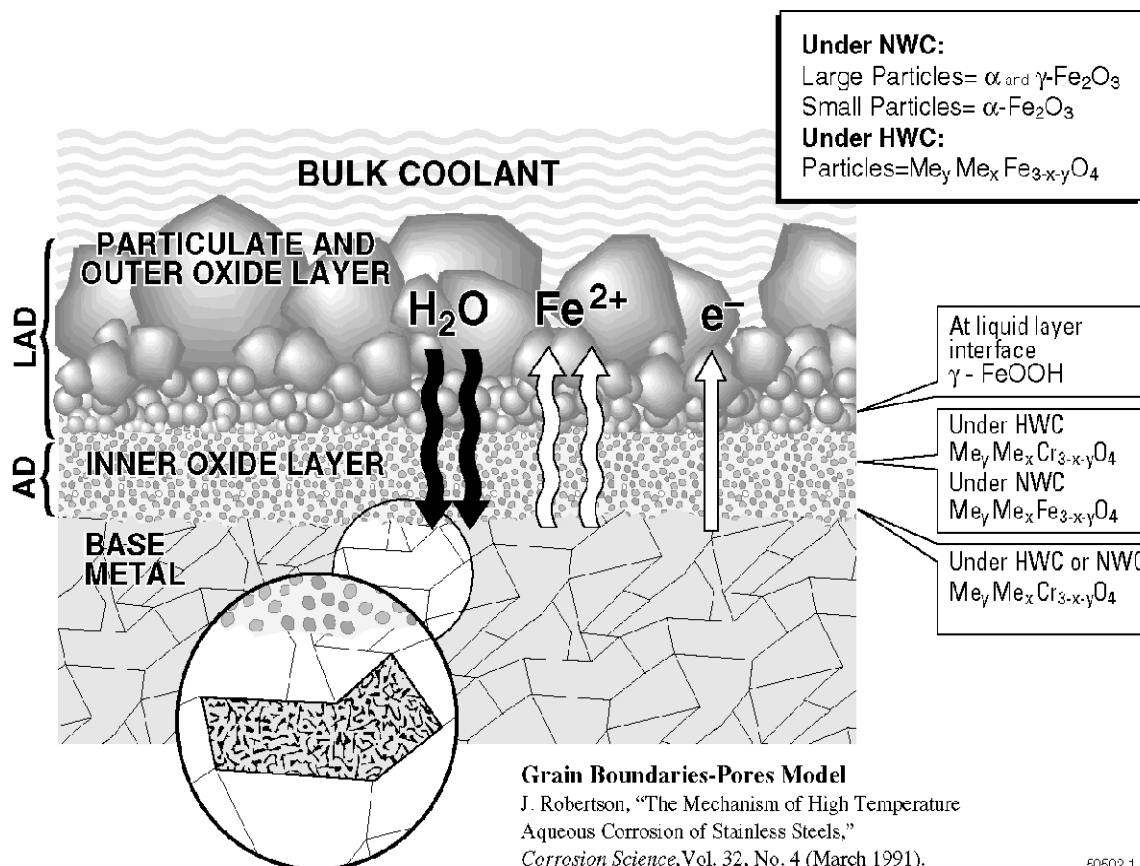


Figure 6-8
Potential Source of HWC-Related ^{60}Co

Loop experiments that measured deposited activity on austenitic stainless steel tubing specimens from soluble activation products injected under controlled conditions show that deposition rates of ^{60}Co are somewhat higher under HWC compared to NWC but increase dramatically when conditions are switched from NWC to HWC. These observations reflect the fact that HWC causes a change in the structure and chemistry of the films, as illustrated in Figure 6-9. The oxides that form under NWC and HWC consist of different structures. These consist of a fine-grained inner layer, a second layer with intermediate-size grains and particles, and an outermost layer that contains large particles. The inner layer under both NWC and HWC consists of $[\text{Fe}_x\text{Cr}_{1-x}]_3\text{O}_4$. Both the intermediate-size particles and the large-size particles in the outer layer consist of substituted Fe_3O_4 under HWC and $\alpha\text{-Fe}_2\text{O}_3$ under NWC. The oxide that forms under HWC is thinner, is more highly enriched in chromium, and can incorporate larger amounts of ^{60}Co , ^{65}Zn , and other transition metal isotopes. Also, the kinetics of film formation plays a role in these effects. The switch from NWC oxides to HWC oxides takes longer to reach equilibrium than the change from HWC oxides to NWC oxides.



50502.1

Figure 6-9

A schematic cross sectional view of the corrosion film growing on a stainless steel surface in BWR reactor water.

The activity buildup rate is greater under cyclic HWC/NWC conditions. In some plants, enhanced release of ^{60}Co activity has been observed and attributed to frequently changing HWC/NWC conditions. Data supporting this conclusion is shown in Figure 6-10.

These observations suggest some measures for reducing the impact of implementing HWC. When the HWC level required to mitigate IGSCC is identified, hydrogen injection should be implemented at this level, rather than approaching the target level in a step-wise manner. Inadvertent changes in reactor power level should be avoided to the extent possible, and operating strategies that lead to continuing power changes (e.g., load following), also should be avoided. Extended coastdowns at the end of a fuel cycle also should be avoided for similar reasons. While these proposals may not be implemented because they adversely affect fuel economics, if implemented they could prove effective in dealing with shutdown radiation fields.

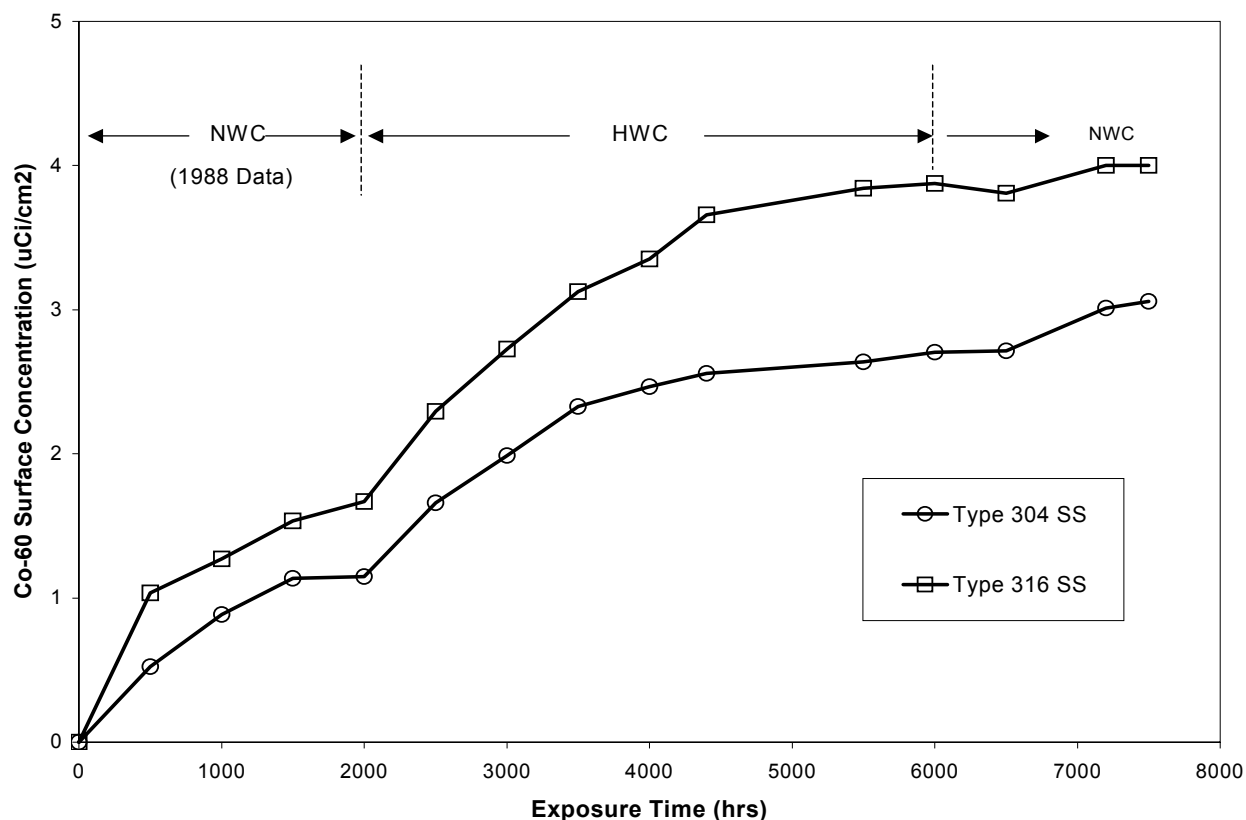


Figure 6-10

Laboratory Tests Showing the Effect of Switching from NWC Oxidizing Conditions (200 ppb O_2 + 25 ppm H_2) to HWC Reducing Conditions (<1 ppb O_2 + 150 ppm H_2) on the ^{60}Co Uptake on Type 304 and 316 Stainless Steel

With the above discussion in mind, we can simplify the film structure to show only the portions that incorporate cobalt and its associated ^{60}Co . Such a schematic is shown in Figure 6-11 for the case of a stainless steel component corroding under normal water chemistry conditions. The black dots represent ^{60}Co . In reality they represent all cobalt ions and the higher the specific activity of the water, the more ^{60}Co will be adsorbed. Also, the higher the cobalt concentration the more cobalt will be adsorbed and thus more of the accompanying ^{60}Co will be incorporated. (The specific activity is defined as the curies of an isotope per gram of the element.) Any increase in either specific activity or cobalt concentration increases the resulting ^{60}Co concentration in the film and the shut down dose rate. Note that the reactor water concentration of elemental cobalt indicated is 10^{-8} %, or only 100 parts per trillion. But also note that the concentration of cobalt in the corrosion film is on the order of 1%. This concentration factor of 10^8 of cobalt (and thus ^{60}Co) into the corrosion film from the reactor water is the root cause as to why significant shut down radiation fields occur. If stainless steel corrosion films didn't have this huge thermodynamic driving force to "getter" transition metal ions into their lattice, dry well shut down radiation fields would only be a minor irritant.

When enough hydrogen is added to the feedwater to establish reducing conditions in the vessel, the outer portion of the corrosion film will restructure and partially convert to the spinel form, to be in equilibrium with the lower ECP on the surface. The resulting steady state film is thinner

than the NWC case but has a greater solid-state solubility for the transition metal ions, such as cobalt. This is shown schematically in Figure 6-12. The net result is that there is considerably more ^{60}Co on the piping surface and the shut down dose rate increases significantly. This is the phenomenon seen by the earlier implementers of vessel protection levels of feedwater hydrogen such as Brunswick Unit 1 & 2 (and more recently by the two Susquehanna Units).

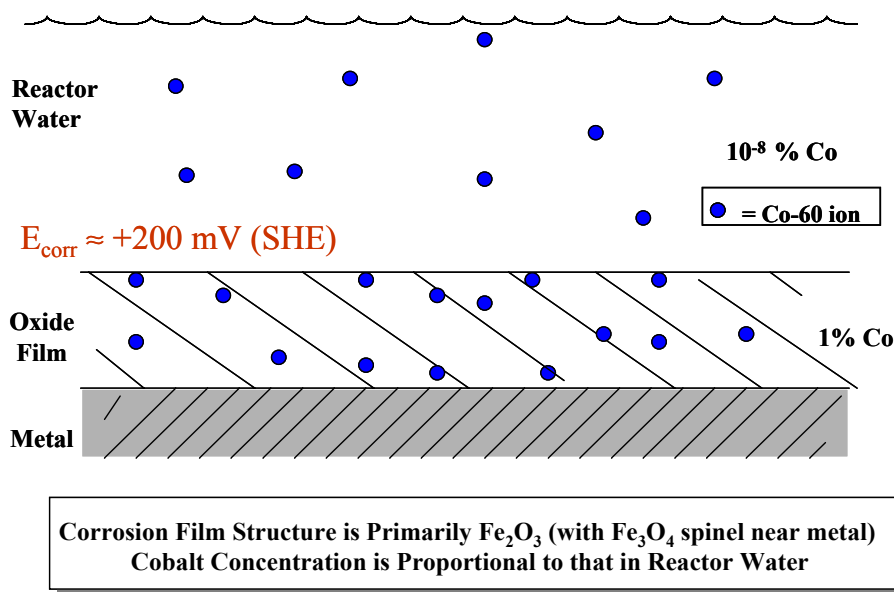


Figure 6-11
Schematic Representation of ^{60}Co Incorporation into Corrosion Film under NWC Conditions

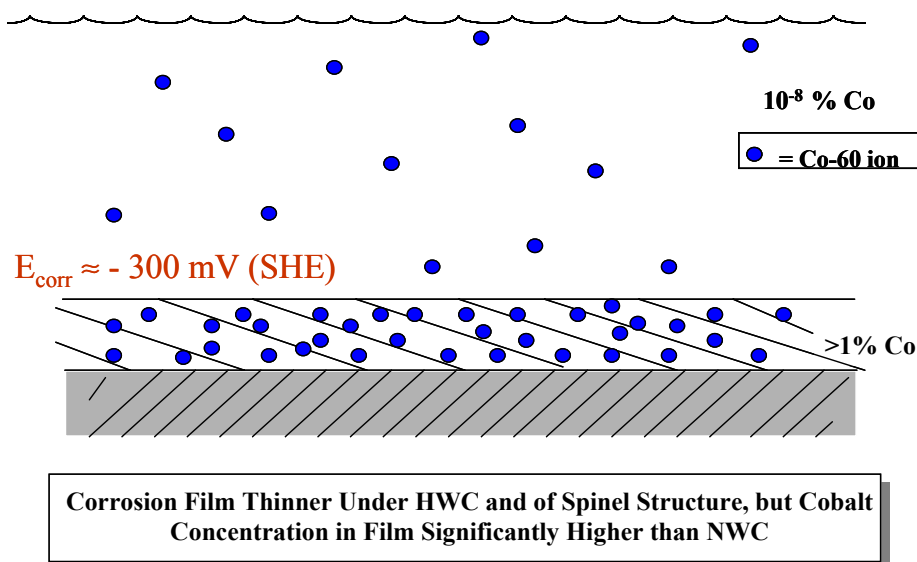


Figure 6-12
Schematic Representation of ^{60}Co Incorporation into Corrosion Film under HWC Conditions

When depleted zinc oxide is added to the feedwater, along with hydrogen, to establish a zinc ion concentration in the reactor water of 5 to 10 ppb, the resulting corrosion film structure is that shown schematically in Figure 6-13. In this case both the zinc and ^{60}Co ions are competing for the same types of sites in the spinel lattice. If the zinc concentration is high enough, the ^{60}Co concentration is reduced. However, there are a lot more preferable sites for the Zn and cobalt in the spinel structure. Laboratory and reactor measurement have shown that the resulting films are thinner when zinc is incorporated, but the reactor measurement show that the total amount of ^{60}Co curies in the film is not that much different than the normal water chemistry case. (This is signified by the fact that the number of ^{60}Co ions (dark circles) is the same in Figure 6-11 and Figure 6-13. Thus, dose rates are brought back to the normal water chemistry levels.

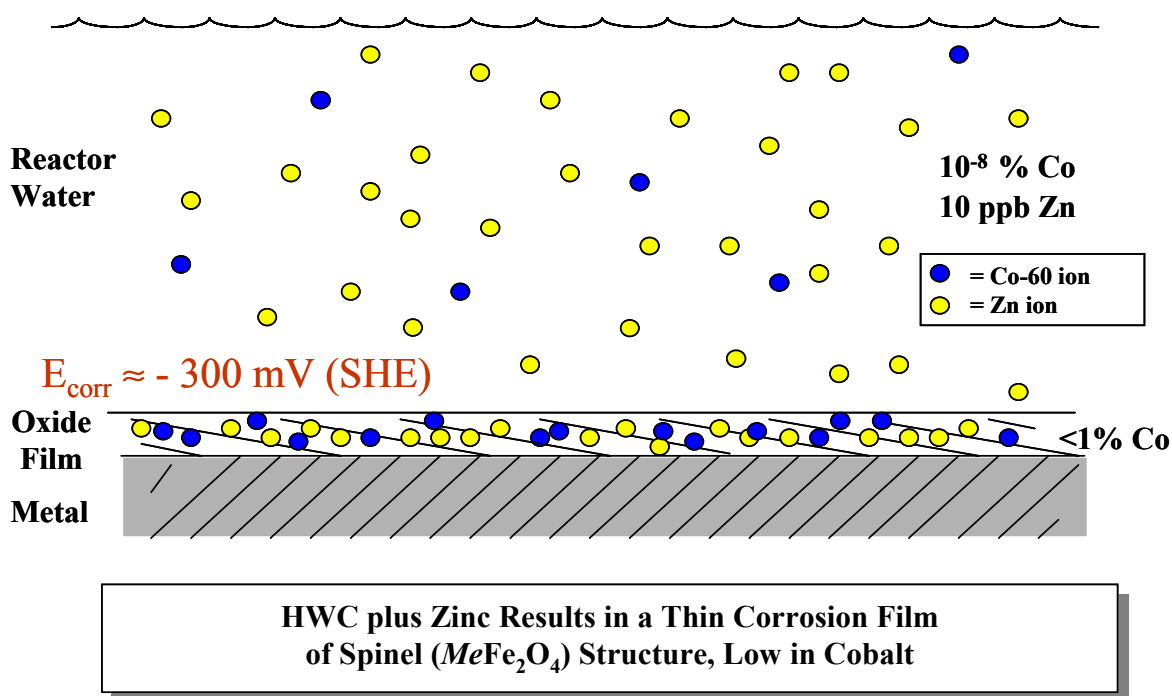


Figure 6-13
Schematic of ^{60}Co Incorporation in Corrosion Film Under HWC Plus Zinc Conditions

For the case of plants treated with NMCA and injecting hydrogen, the oxidant concentration on the surface of the stainless steel is zero (due to the Pt and Rh catalyzing the reaction of any oxidant with the surplus hydrogen). The net result is that the ECP is at or very near the hydrogen redox potential, typically about -490 mV (SHE) for neutral BWR water. The film thickness approaches the thin values seen on laboratory films under similar ECP and zinc conditions. This NMCA induced BWR film is shown schematically in Figure 6-15.

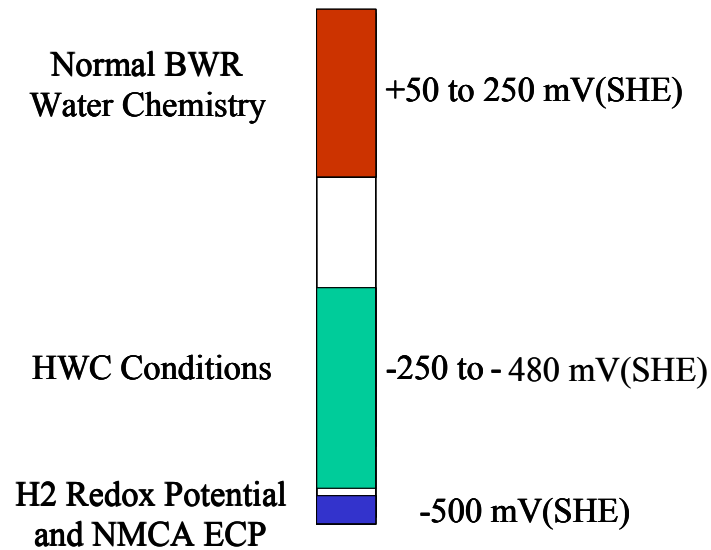


Figure 6-14
Summary of Range of Vessel ECP Measurement Made Under NWC, HWC and NMCA plus Low Hydrogen Conditions

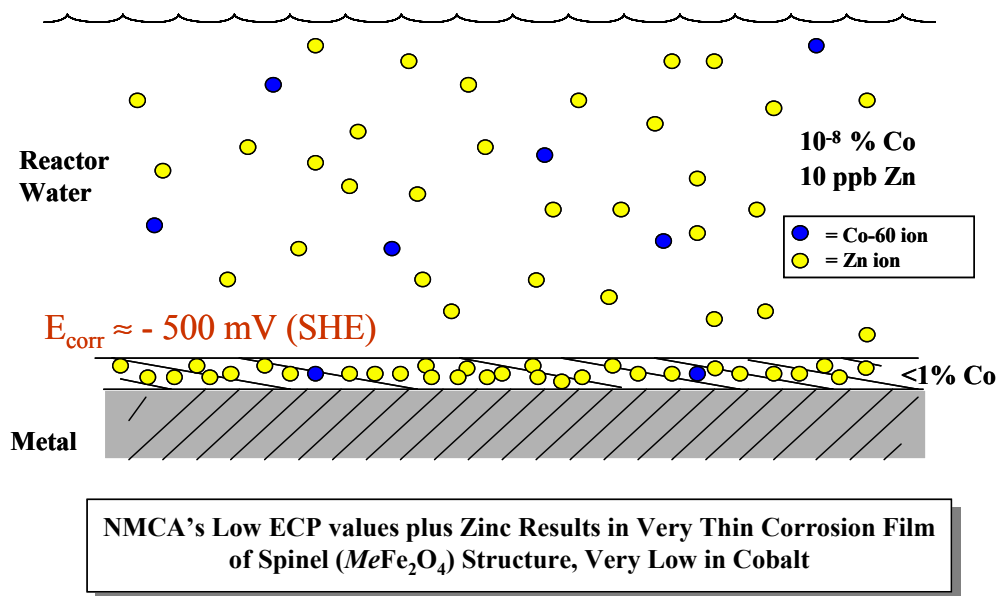


Figure 6-15
Schematic of ^{60}Co Incorporation into the Corrosion Film under NMCA plus Low Hydrogen plus Zinc Conditions

A summary of the range of ECPs observed in BWRs under normal water chemistry (NWC), moderate HWC (0.6 to 2.0 ppm feedwater hydrogen) and post NMCA plus low feedwater hydrogen is shown in Figure 6-14. What is remarkable is the tight and low ECP range for the NMCA plus hydrogen case. Whenever enough hydrogen is being injected to make the noble metal surface catalytic (usually greater than 0.15 ppm feedwater hydrogen) the ECP of the wetted BWR surfaces will be at hydrogen redox potential of -490 mV (SHE) and a 100% spinel film structure should be present. If there is enough zinc in the water, it will overwhelm the ^{60}Co in the race to be incorporated into the spinel lattice. However, if there is not enough zinc present, then the available lattice sites will fill with a much larger proportion of ^{60}Co atoms. In this case, the film will be thicker than the non-zinc case and the result is a marked increase in total ^{60}Co curies on the metal surface. Indeed this case occurred in practice at Nine Mile Point 1. After NMCA application and with only 0.5 ppb reactor water zinc the shutdown dose rates increased over 400% as the corrosion film restructured to the low ECP 100% spinel case and significantly increased its capacity for ^{60}Co .

To reduce cycling under HWC, a utility should first determine review historical data to determine the cause of HWC/NWC cycling. The review may provide insights that can lead to the identification of causal factors such as system components with high failure rates, scheduled maintenance activities, or routine testing that could be more effectively managed. Key plant organizations should work together to establish an agreed upon maintenance work schedule that minimizes the need for HWC cycling. Some plants have reduced scheduled HWC reductions to only once per month, using an established HWC reduction “ready backlog.” This is a schedule of non-routine work activities that must be completed during a HWC reduction or shutdown. Preparation (pre-staging) for these activities should be complete so that such activities can be initiated upon short notice in the event an unplanned/unscheduled shutdown of HWC occurs or a reduction is necessary. Once the factors responsible for cycling are determined and corrective actions are implemented, plant management should ensure that all personnel understand the true cost of cycling. NWC/HWC cycling should be viewed as a long-term, high-cost element that should be used as a last resort and not as a short-term solution for routine testing or maintenance.

One way to deal with the increased shutdown dose rates that accompany the switch from NWC to HWC is to perform a chemical decontamination at the outage after HWC is introduced. Nitric acid permanganate (NP) is an effective oxidation step that can solubilize the chromium-rich films that form under HWC. The use of NP is qualified for all ex-vessel applications (6-1). The use of the LOMI combination is generally the most effective solvent. High decontamination factors ranging from 10 to 52 have been obtained in recent decontaminations using NP/LOMI at Brunswick 2, Hatch 1, Pilgrim, and Ringhals 1 (6-3).

Another factor for reactors using HWC is that there is some frequency of cycling between HWC and NWC and unavoidable shifts between different hydrogen injection rates. This is caused by hydrogen addition system problems and/or the need to do maintenance in areas where steam line radiation from ^{16}N is a concern. Cycling affects the oxide films and causes restructuring processes to occur spontaneously as the ECP (Electrochemical Corrosion Potential) changes in the local environment. This restructuring offers an ongoing opportunity for additional incorporation of soluble activity from the coolant into the ex-reactor oxides. It also causes

additional restructuring in the fuel deposits at the bottom of the core. This cycling of the regime in the area of the fuel deposits can provide additional activity release to the reactor water for redistribution to the primary system. For these reasons, cycling frequency should be minimized and the target objective for cycling frequency should be no more than once per month.

The Effects of Depleted Zinc Oxide (DZO) Addition

Zinc addition has become an established tool for controlling shutdown dose rates in the BWR plants that are under either NWC or HWC. Zinc reduces the incorporation of ^{60}Co into the primary system films in the following ways:

- Zinc inhibits the corrosion of stainless steel surfaces in the primary system and thereby results in thinner films.
- Zinc competes with ^{60}Co for the same tetrahedral crystal sites in the spinel oxide film on the stainless steel surface.
- Zinc suppresses release of soluble ^{60}Co from the fuel deposits so that the reactor water concentration is decreased.

In some ways, ^{58}Co , with its shorter half-life is a better tracer of the dynamics of the reactor water. Any ^{58}Co found in the reactor water must have come from the core fairly recently, whereas ^{60}Co , with its 5.27 year half-life, can be contributed from any primary system surface.

Each of the three identified mechanisms is concentration dependent, with more zinc providing more benefit. To determine the optimum concentration to use with zinc addition, each utility must balance the increasing benefits of reduced dose rates/occupational exposure from adding more zinc, against the costs associated with using higher concentrations of DZO.

The cost of DZO is significant and is known to be an important factor for any utility using it. Each utility has different valuations for person-Rem savings, has different iron input rates (thus, different zinc consumption rates for the same target concentration), and evaluates the costs related to DZO addition differently. For these reasons, there can be no generic cost/benefit evaluation available for determining the best reactor water zinc target concentration. With NZO, the issues were not cost related, but rather the impact of ^{65}Zn on piping, refuel floor dose rates and in radwaste.

While it is believed that a reasonably optimized value is 5-10 ppb zinc in the reactor water so that the benefits can be maximized while still remaining comfortably within the historical experience band, each utility must perform their own cost/benefit evaluation to discern what concentration is optimum for them.

Experience has demonstrated that benefits are being achieved with reactor water zinc concentrations as low as 3.0 ppb and the technology shows that the higher the concentration that is maintained, the greater will be the benefit over the range of most plant experience. In KKL, where zinc was added within the recommended limits, an increase of ^{60}Co in the reactor water was observed. A similar increase in ^{60}Co was observed in the reactor water in Barsebäck 2. It is

recommended that each zinc addition plant conduct a test to determine the optimum zinc concentration for their specific plant. A suggested plan for this test is as follows:

- Operate for three months at a reactor water zinc concentration of 3 ppb, while closely monitoring the zinc consumption rate, as well as the reactor water soluble ^{60}Co and ^{58}Co .
- Then operate for three months at a reactor water zinc concentration of 6 ppb, again closely monitoring the zinc consumption rate, as well as the soluble ^{60}Co and ^{58}Co .
- Then operate for three months at a reactor water zinc concentration of 10 ppb, again closely monitoring the zinc consumption rate, as well as the soluble ^{60}Co and ^{58}Co . It is noted that ^{60}Co is expected to decrease only until zinc concentrations reach approximately 10 ppb. Above this concentration, no significant additional benefit is anticipated.

At the conclusion of the nine months, determine the zinc consumption rate, adjusted for changes in feedwater iron input, at each reactor zinc concentration and the related reduction in reactor water cobalt isotopes. Assume that the benefits for the other zinc mechanisms will parallel the cobalt isotope reduction, and perform a cost vs. benefit analysis on this basis. From the results of this study, set the reactor water target concentration for zinc addition.

An empirical equation that has been modified in light of recent field experience (6-4) was developed that relates zinc consumption to various plant design features and coolant chemistry parameters (6-5). Using representative values and assuming that the target reactor water zinc concentration is 10 ppb; calculations predict an annual zinc consumption of approximately 20 kg for a 1000 MWe plant.

NMCA and Shutdown Dose Rates

NMCA applications have had varied successes at United States BWR's. Initial applications at Duane Arnold, FitzPatrick, and Hatch-1 were very positive in the reduction of BRAC shut down dose rates, but the later applications at Peach Bottom-2, Quad Cities-1 and Nine Mile Point-1 had significant increases in the shut down dose rates. Naturally, the question arose about why the same chemical treatment caused different results, and substantial effort was invested to define a mechanism for the differences. The following sections address this issue.

In the first cycle after NMCA application, most plants have seen an increase in both soluble ^{60}Co (up to a 170% increase in cycle median) and insoluble ^{60}Co (up to 1500% increase in cycle median), resulting mainly from the release of material from fuel deposits during the post NMCA oxide restructuring. The ^{60}Co behavior at Duane Arnold for the cycle prior to NMCA and the four cycles after the initial NMCA application in October of 1996 is shown in Figure 6-16. This plot is interesting because it shows the initial increase in both soluble and insoluble ^{60}Co after the first post NMCA cycle (Cycle 15) with a lessening of the effect during the second cycle (Cycle 16). After the second NMCA application there is also an increase in both soluble and insoluble ^{60}Co but the magnitude is less than the first application (Cycle 17). During Cycle 18, the fourth cycle after the initial NMCA application, the soluble and insoluble ^{60}Co levels returned to the pre NMCA values and lower. This bodes well for plants entering their third post NMCA cycles as it indicates that with constant RW zinc levels (as is the case at Duane Arnold) that ^{60}Co levels eventually come down to (or below) their pre-NMCA values.

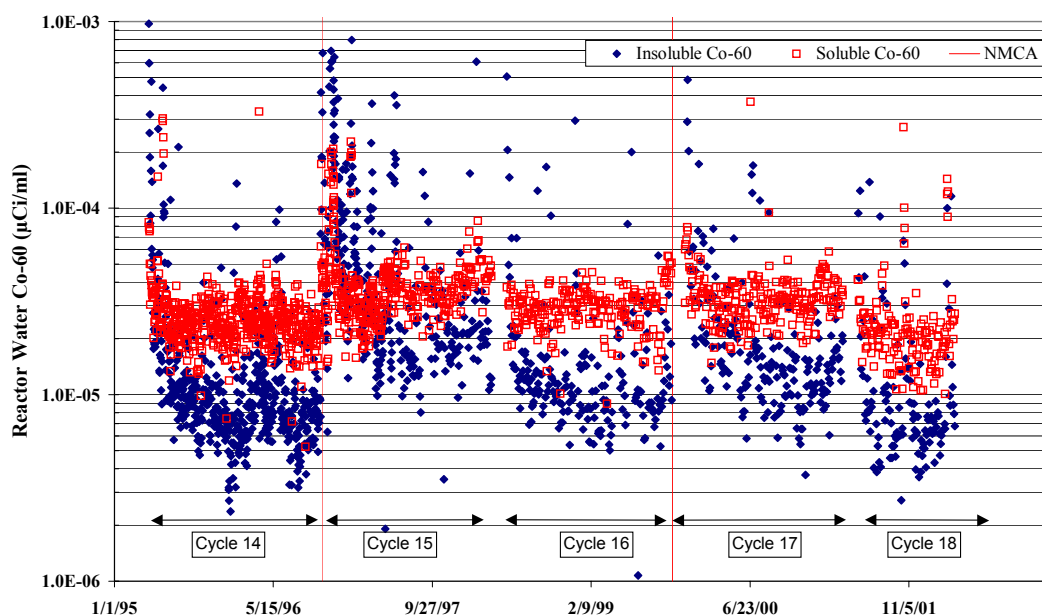


Figure 6-16
Pre and Post NMCA ^{60}Co Behavior at Duane Arnold (Note that there have been two NMCA applications at Duane Arnold)

Correlation of Shut Down Dose Rates with Reactor Water $^{60}\text{Co}(\text{s})/\text{Zn}(\text{s})$ Ratio

If the post NMCA shut down dose rate are determined by only the concentration of soluble ^{60}Co and zinc ions competing for sites in the growing spinel film, a plot of dose rates vs. the ratio of (soluble $^{60}\text{Co})/(\text{soluble Zn})$ should be a straight line. This behavior is shown to be generally the case when the data is plotted as shown in Figure 6-17. This treatment was first suggested by Malauskas (6-1). In this plot the BRAC shut down dose rates measured at the end of the first cycle after NMCA application is plotted against the cycle median value of $^{60}\text{Co}(\text{s})/\text{Zn}(\text{s})$. The fit is better than any others developed in correlating shut down dose rates and reactor water parameters such as total RW $^{60}\text{Co})/\text{Zn}(\text{s})$, RW $^{60}\text{Co}(\text{s})$ alone, RW insoluble ^{60}Co alone, total RW ^{60}Co , FW Zn, FW Fe/FW Zn, etc. The cycle median value is chosen over the mean value for determining the ratio because of the nature of ^{60}Co measurements. Usually there are many high and low “outliers” in the radioisotopic database. Using outlier values in a mean determination gives them undue weight to characterize a time period. The median value doesn’t weigh the “outliers” as heavily and the correlation is improved.

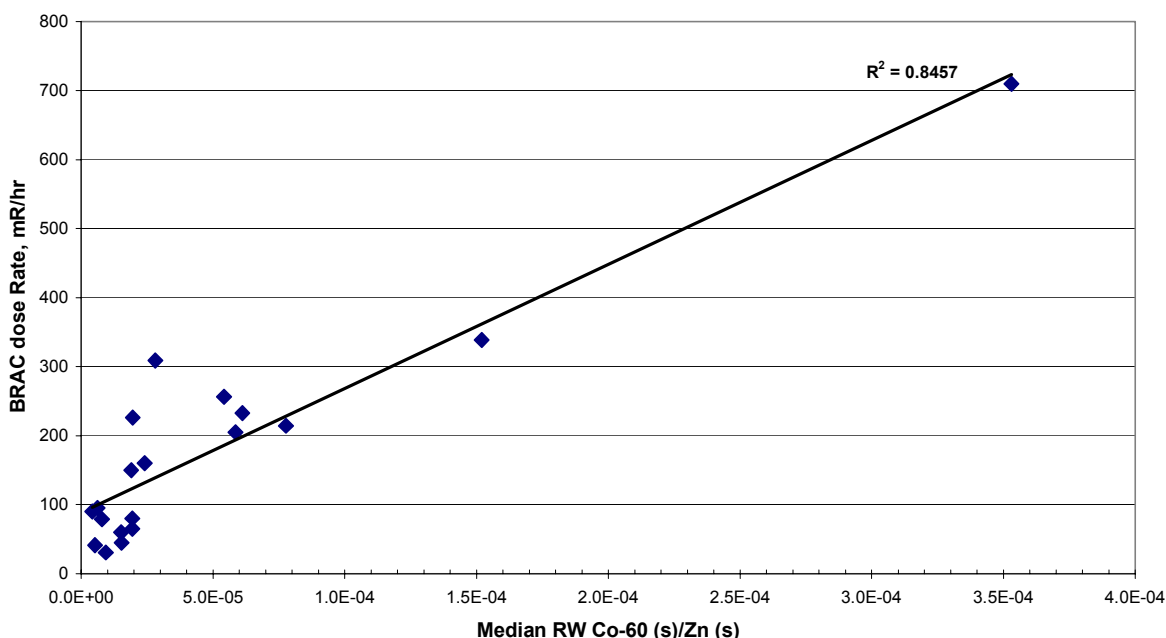


Figure 6-17

Comparison of measured BRAC dose rates versus cycle median ratio of RW ^{60}Co (s)/RW Zn(s) for 1st post NMCA cycle BWRs. (Data available as of April 30,2003)

The 10 plants in Figure 6-17 with a $^{60}\text{Co}(\text{s})/\text{Zn}(\text{s})$ ratio of less than the indicated 2×10^{-5} lines have dose rates less than 150 mR/hr and 9 of those are less than 100 mR/hr. This behavior is the basis for the operating recommendations at the end of the section.

Insoluble ^{60}Co Impact on Shut Down Dose Rates

The role of the insoluble ^{60}Co on post NMCA dose rates behavior is not as clear as the role of the soluble form. Even though the reactor water insoluble ^{60}Co concentration increases significantly in most plants through the post-NMCA cycle, the increase doesn't seem to be affecting shutdown dose rates significantly. At Hatch 1, the steady state insoluble ^{60}Co increased 400%, reaching a value of 1.0×10^{-4} , higher than the plant with the highest shutdown dose rate (NMP1), but Hatch 1 still observed greater than a 60% reduction in dose rate. Quad Cities 1 is one plant in which insoluble species do seem to be playing a significant role. This plant had been relying on decontaminations to control shutdown dose rates associated with high levels of feedwater hydrogen injection, but implemented the use of depleted zinc oxide (DZO), coupled with a decontamination, prior to NMCA. It appears that the zinc injection was having the desired effect as the shutdown dose rates observed during the NMCA outage had fallen from those measured after the decontamination to less than 150 mR/hr. However, at the beginning of the next outage six months later, the dose rates had increased to 780 mR/hr. But unlike other plants, a 50% reduction in dose rates was seen two weeks later in the outage. Reactor water measurements showed that the total ^{60}Co concentration peaked at $3.2 \times 10^{-1} \mu\text{Ci/ml}$ during the first part of the outage and fell by over two orders of magnitude in just seven additional outage days. It appears that the majority of the ^{60}Co activity was an insoluble form and its presence both in the reactor

water and as a loose deposit on piping surfaces accounted for the high initial dose rates. (Quad Cities 1 did have the highest post-NMCA reactor water insoluble ^{60}Co concentration during operation.) Continuous cleanup of the reactor water caused the removal of the insoluble ^{60}Co (and other isotopes such as ^{54}Mn , ^{58}Co , etc.) from the water and free surfaces, resulting in diminished dose rates. It is postulated that the reduction in feedwater zinc input during the post-NMCA operational period destabilized the fuel deposits and upon shutdown, a significant fraction of deposit restructured from the Fe_3O_4 form back to a Fe_2O_3 type structure, producing a significant particulate release during the process. With sufficient zinc concentration in the fuel deposits, the zinc modified Fe_3O_4 remains stable and less release occurs.

Summary of NMCA Shutdown Dose Rate Findings

A summary of the various findings regarding limiting post NMCA shutdown dose rates is listed below. Note that some of these findings may be contrary to limiting fuel operational risks.

- Both soluble and insoluble ^{60}Co will increase in most plants during the first post NMCA cycle
- Maintaining the reactor water $^{60}\text{Co}(\text{s})/\text{Zn}(\text{s})$ ratio to a value $< 2 \times 10^{-5} \mu\text{Ci}/\text{ml}/\text{ppb}$ will control post NMCA dose rates
- The above ratio should be established as soon as practical after NMCA application or recirculation system decontamination, to be most effective
- Plants that meet the above criteria have seen steady or decreased shutdown dose rates
- When the above condition are met, reactor water $\text{Zn}(\text{s})$ is usually in the range of 5 to 10 ppb, although plants with high ^{60}Co levels in the reactor water may not attain the desired ratio at this level of reactor water zinc
- For a given plant, the lower the feedwater Fe, the easier it is to maintain the reactor water $^{60}\text{Co}(\text{s})/\text{Zn}(\text{s})$ ratio within the desired range
- For a given plant, the lower the feedwater iron, the less DZO is required to establish the reactor water $^{60}\text{Co}(\text{s})/\text{Zn}(\text{s})$ ratio to a value $< 2 \times 10^{-5} \mu\text{Ci}/\text{ml}/\text{ppb}$
- It is preferred to operate at the lower end of the range of the feedwater hydrogen injection rate that assures a coolant molar ratio greater than 3 (as required for inspection relief per BWRVIP-62, see Chapter 7). For most plants this value is in the range of 0.15 to 0.25 ppm feedwater hydrogen.

Control of Iron Input

Iron-based corrosion products influence radiation buildup. By reducing feedwater iron, plants can suppress reactor water soluble ^{60}Co and insoluble ^{60}Co . Because ^{60}Co in the reactor coolant is the major contributor to radiation dose rates in BWRs, iron control also has an impact on suppressing dose rates. The most appropriate means of achieving the optimum amount of feedwater iron depends on plant-specific factors, such as the concentration of iron in the hotwell, feedwater drain path, and the type of condensate polishing. The actual impact of optimizing iron

control on radiation dose rates depends on operational chemistry factors (normal or hydrogen water chemistry, NMCA, and depleted zinc oxide injection).

The previous position on BWR iron control set the desirable range for feedwater iron between 0.5 and 3.0 ppb and kept the “Action Level 1” at 5 ppb (6-1). Experience has shown that operation at or below the Action Level 1 value avoids fuel performance concerns related to excessive iron loading on the fuel cladding. Recent experience at US BWRs indicates that all plants have consistently operated below Action Level 1. A summary of US plant experience for 2003 is shown in Figure 6-19. Most plants incorporating filtration in the condensate polishing system (pre-filters with pleated filter septa or plants using filter/demineralizers) have kept iron levels well below 3.0 ppb, the upper limit of the desirable range previously specified. Although deep-bed-only plants have a more difficult challenge to keep iron levels in the lower end of the desirable range, the use of advanced resin cleaning or URC optimization has allowed selected plants to approach the 1.5 ppb level.

In view of these experiences and additional iron monitoring studies, the 2004 BWR Water Chemistry Guidelines retain the value of 5 ppb for Action Level 1.

The BWR Chemistry Guidelines will also maintain the concept of a desirable range for feedwater iron; however, the extent of the range will change to:

Moderate HWC plus DZO: < 1.5 ppb FFW Fe

NMCA + HWC plus DZO: < 1.5 ppb FFW Fe

NWC: 0.5 to 1.5 ppb FFW Fe

The idea behind a “desirable range” is that according to industry data, feedwater iron in such a range is more likely to prevent excessive crud buildup on the fuel, to keep ⁶⁰Co transport and corresponding dose rates to acceptable levels, and to optimize the effect of zinc at levels that do not put fuel at risk of oxide spallation. Plants that are unable to achieve feedwater iron levels within the desirable range should analyze the cost of a required hardware retrofit (e.g., pre-filter installation), against the possible dose rate consequences of somewhat higher radiation levels on the out-of-core piping (BRAC values), the higher costs of depleted zinc oxide usage and the increased risk of fuel crud spallation.

The amount of feedwater iron crud entering the reactor is also a major factor in determining zinc demand in plants employing zinc addition, as most of the zinc incorporates into the iron based fuel deposit. The zinc concentration factor (ratio of reactor water zinc to feedwater zinc) increases as feedwater iron decreases below 1 ppb. This relationship is shown in Figure 6-18 for plants that have operated for several cycles on moderate HWC or HWC/NMCA and with zinc injection (or natural zinc) and had reached a steady state zinc demand. Plants with feedwater iron below 1 ppb show more efficient zinc addition and are able to reach higher levels of zinc in the reactor water with lower levels of zinc in the feedwater. Since all plants are trying to limit the mass of depleted zinc oxide (DZO) injected to limit costs, controlling feedwater iron input is one approach to limit the mass injected and still maintain desired reactor water levels of RW ⁶⁰Co(s)/RW Zn(s).

BWR Coolant Chemistry

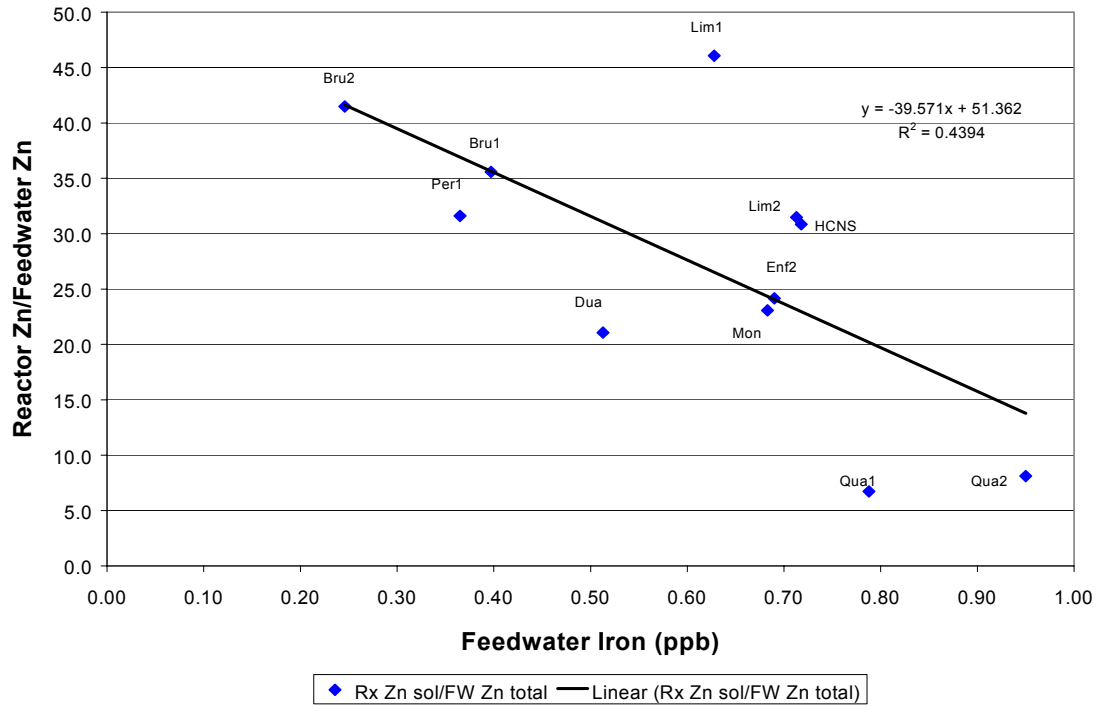


Figure 6-18
Reactor Water Zn/Feedwater Zn Ratio for Low Feedwater Iron Plants on HWC or HWC/NMCA with DZO Injection

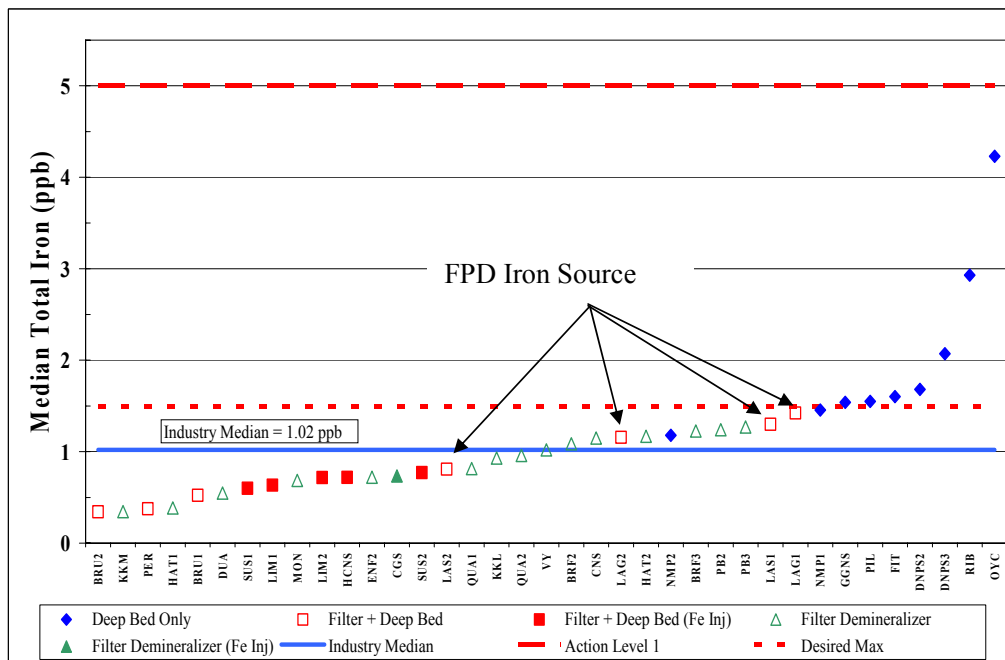


Figure 6-19
2003 Average Feedwater Total Iron

For plants with reducing conditions (moderate HWC or NMCA + HWC) and DZO injection, the desirable range for feedwater iron is set at 1.5 ppb and below. The 2004 BWR Guidelines gives a lower target recommendation for feedwater iron of 1.0 ppb; however, this target is meant to be a goal that plants should strive towards and it is recognized that for many plants the target will not be easily or inexpensively met. The value of the 1.0 ppb goal was determined by industry data shown in Figure 6-19. The figure plots the cycle average zinc values corresponding with cycle average feedwater iron values needed to achieve a $2\text{E-}5 \mu\text{Ci/ml/ppb Rx } ^{60}\text{Co/Zn}$ ratio. Plants with less than 1.0 ppb feedwater iron were able to achieve the desired Rx $^{60}\text{Co/Zn}$ ratio without exceeding the 0.4 ppb feedwater zinc value suggested to avoid fuel crud oxide spallation. Plants operating within the desirable range but above the target recommendation of 1.0 ppb may experience slightly higher dose rates and may incur higher zinc costs, compared to those operating at or below the target recommendation.

Regarding the lower end of the desirable range, there is limited plant experience at cycle average feedwater iron levels below 0.2 ppb. Nevertheless, plants should note that analysis of industry data suggests that under reducing conditions and DZO injection, lower feedwater iron values should result in lower ^{60}Co transport, lower drywell dose rates, and a decreased incidence of hot spots. There is currently no evidence to suggest otherwise. Plants with reducing conditions and DZO injection that are also injecting iron may want to consider gradually decreasing iron injection levels, with eventual elimination of iron injection.

However, for normal water chemistry plants with feedwater iron below 0.5 ppb there is still a lack of experience and adverse consequences have been reported from long term operation near 0.1 ppb in the US, Sweden and Japan; therefore, plants on NWC should continue to monitor both soluble and insoluble isotopics and trend shutdown dose rates.

Basis for Feedwater Iron Control – Activity Transport

Soluble Transport

Soluble ^{60}Co causes radiation fields due to incorporation into corrosion layers. ^{60}Co incorporation into recirculation system piping corrosion film, as manifested in the BRAC point dose rates and piping gamma scan measurements increases as soluble ^{60}Co in the reactor coolant increases under an established chemistry regime and at a constant reactor coolant zinc concentration. Under established NWC or HWC conditions, steady state plant operation and a constant level of reactor water soluble zinc, reactor water soluble ^{60}Co decreases as feedwater iron decreases.

Actual incorporation of ^{60}Co can be controlled by feeding DZO to control the reactor water $^{60}\text{Co/Zn}$ ratio, particularly for plants that have applied NMCA. Based on industry data, it appears that plants on HWC/NMCA with feedwater iron below 1.0 ppb are more easily able to control their Rx $^{60}\text{Co(s)}/\text{Rx Zn(s)}$ ratio at $2 \times 10^{-5} \mu\text{Ci/ml/ppb}$ or below, leading to lower BRAC point average dose rates (see Figure 6-20).

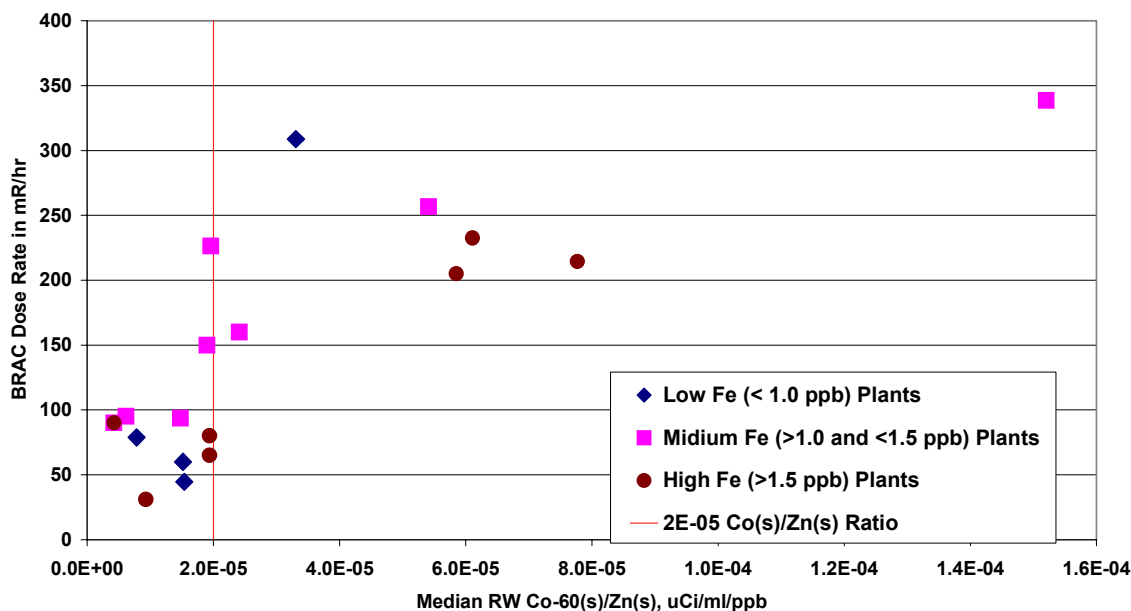


Figure 6-20

Data Excluding Highest Dose Rate Plant Showing Effect of Low FW Iron (<1 ppb) (Data Available as of 6/30/04)

Insoluble Transport

Activated insoluble crud particles rich in ^{60}Co tend to deposit on surfaces in low flow areas of the reactor vessel and associated piping, forming radiation “hot spots”. To evaluate the effect of feedwater iron on “hot spot” formation, reactor water insoluble ^{60}Co data and reactor vessel bottom head drain radiation surveys were collected.

Bottom head drain (BHD) dose rates reported are plotted as a function of insoluble ^{60}Co in Figure 6-21. In some cases, more than one data point is included from a single plant. The insoluble ^{60}Co values used are the average values for the cycle prior to the surveys. The results show an increasing trend in BHD dose rates as insoluble ^{60}Co increases. The available results show that the lowest BHD dose rates correspond to average insoluble ^{60}Co concentrations of less than $6\text{E-}5 \mu\text{Ci/ml}$. As insoluble ^{60}Co approaches and exceeds $1\text{E-}4 \mu\text{Ci/ml}$, for several plants BHD dose rates exceed 10 R/hr .



Figure 6-22 illustrates that at Brunswick 1, a plant that has been on HWC since 1990 and DZO injection since 1995, very low feedwater iron values are not correlated with high insoluble ^{60}Co values. From the time that zinc injection started, BRAC dose rates have been approximately 500 mR/hr or lower (Figure 6-23). Brunswick 2 shows similar behavior. BRAC dose rates at the Brunswick units are not the lowest in the industry; however, the point is that even with very low feedwater iron levels, BRAC dose rates have not increased with reducing chemistry and DZO injection. Current BRAC dose rates are a greater reflection of operation at reducing conditions without zinc addition (prior to 1995 and 1996), when corrosion films restructured to the spinel form, incorporating a greater concentration of ^{60}Co . At both units, insoluble ^{60}Co has been steadily decreasing over time after the start of DZO injection. In combination with the slow decay of ^{60}Co , BRAC dose rates should continue to decrease over the long term.

BWR Coolant Chemistry

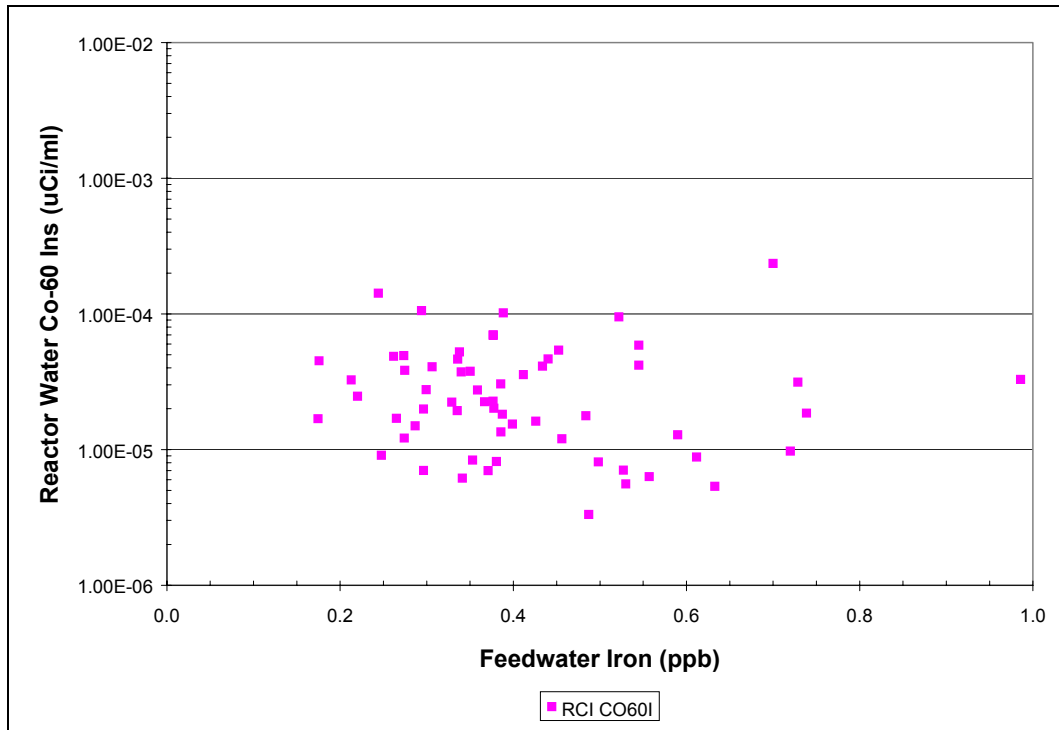


Figure 6-22
Brunswick 1 Reactor Water Insoluble ⁶⁰Co vs. Feedwater Iron

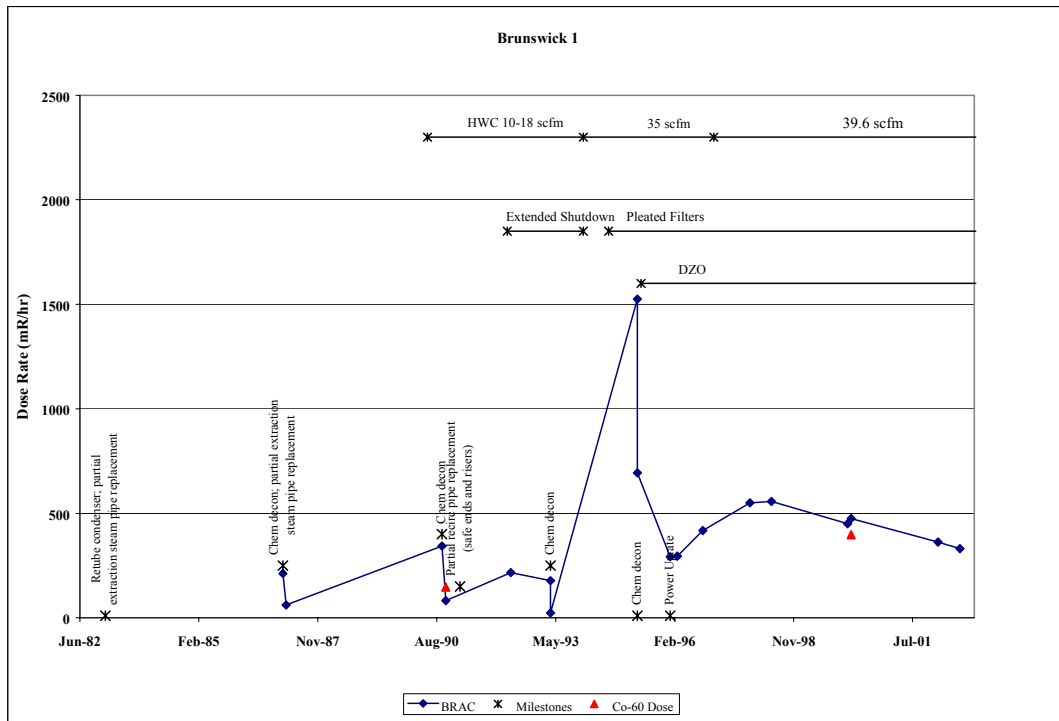


Figure 6-23
Brunswick 1 BRAC Results

Activity Transport Summary

Plants, regardless of chemistry regime, operating with average feedwater iron above 1.5 ppb should review plant parameters, (e.g., soluble/insoluble ^{60}Co , hot spots, costs, zinc usage, etc.), to determine if action should be taken. It is recognized that plants operating with a history of iron above 1.5 ppb, such as those using only deep beds condensate polishing, may have serious technical and economic difficulty in reducing iron. In their iron optimization, these plants should consider the costs of improved iron control means (filter system addition, resin cleaning improvements, alternative resins) against the increased difficulty and expense of maintaining a Rx $^{60}\text{Co}/\text{Zn}$ ratio below $2\text{E-}5 \mu\text{Ci}/\text{ml/ppb}$ to keep dose rates to a minimum.

At lower average feedwater iron levels (below 0.5 ppb), different chemistry regimes affect the behavior of ^{60}Co differently. Table 6-1 lists the different recommendations for plants with low feedwater iron on HWC/DZO or HWC/NMCA/DZO and NWC.

In summary, the industry experience with iron levels and radiation buildup suggests that iron control programs should be balanced with each plant's overall dose rate minimization efforts to provide cost-effective control over both soluble and insoluble ^{60}Co transport.

Table 6-1
General Principles for Iron Control at Low Levels (Below 0.5 ppb)

Plants with reducing conditions and DZO injection	Plants that are currently injecting iron may want to consider slowly reducing the amount of iron injected and eventually curtailing iron injection altogether. The current industry data suggests that the new HWC/DZO or HWC/NMCA/DZO chemistry regimes have altered the behavior of ^{60}Co transport, with lower feedwater iron leading to lower overall levels of Rx ^{60}Co and lower dose rates.
Plants on normal water chemistry	There is still a lack of industry experience with feedwater iron levels below 0.5 ppb. As a result of previous adverse plant experience, plants should consider an iron addition program to achieve a minimum average feedwater iron value of 0.5 ppb (See section 3.2.4.2) or should consider instituting a monitoring program for reactor water soluble/insoluble isotopics and for dose rate trends.

Corrosion and Corrosion Product Deposits

High Iron Levels

When ^{60}Co is in the insoluble form, it deposits at both low and high flow locations, causing local hot spots. Examples of hot-spot locations would be equipment drain lines, LPRM housings and the vessel bottom. In addition, following the transition to HWC, iron crud deposits can restructure and cause an increase in shutdown dose rates. Finally, the amount of feedwater iron crud entering the reactor is also a major factor in determining zinc demand in plants employing zinc addition, as most of the zinc incorporates into the iron based fuel deposit. This effect can greatly increase the cost of zinc addition. Thus, there is a large incentive to examine the potential benefits of decreasing feedwater iron input particularly for those plants with historically high levels.

*BWR Coolant Chemistry**Low Iron Levels**Moderate HWC or HWC/NMCA and DZO chemistry*

Advances in filtration technology have resulted in feedwater iron input levels of <0.1 ppb at some plants. Review of industry data collected since the last revision of the guidelines indicates that chemistry regimes play a large role in determining the behavior of ^{60}Co transport at low iron levels. The majority of the US BWR fleet is now on moderate HWC or HWC/NMCA and DZO chemistry. Data collected from these plants, as discussed in the previous section, do not show increased hot spots or reactor water activity increases with low iron levels. In fact, for these plants, low feedwater iron (<0.5 ppb) has a number of potential benefits:

For a given plant, the lower the sustained feedwater iron concentration, and thus the lower the iron oxide deposition on the fuel, the lower the zinc (DZO) demand to achieve the target ratio of reactor water $^{60}\text{Co}(\text{s})/\text{Zn}(\text{s}) < 2\text{E-}5 \mu\text{Ci/ml/ppb}$ for suppression of drywell shutdown radiation dose rates, particularly after NMCA is applied. One benefit of the lower zinc demand is the reduced operating cost of DZO injection.

The reduced zinc demand with low feedwater iron may help avoid conditions that contribute to fuel crud spallation, which has been related to high zinc feed rates. To minimize the fuel risk, BWRVIP-118 (6-7) recommends a cycle average feedwater zinc concentration of less than 0.4 ppb. With low feedwater iron, maintaining the reactor water $^{60}\text{Co}(\text{s})/\text{Zn}(\text{s}) < 2 \times 10^{-5} \mu\text{Ci/ml/ppb}$ to suppress drywell shutdown dose rates is achievable with <0.4 ppb feedwater zinc. At one station, the fuel supplier stated that operating at feedwater zinc levels above where industry experience has shown spallation to occur will result in an increase in fuel inspections, providing additional incentive to reduce feedwater iron to reduce zinc demand.

Avoiding high zinc input to the reactor limits the zinc inventory on the fuel, thus reducing the potential for high zinc release from the fuel under NMCA application and reapplication conditions (temperatures of 250 – 275 °F) and the consequent inhibition of noble metals deposition (6-7).

Normal Water Chemistry Plants

For plants on normal water chemistry with low iron, different recommendations apply. The following paragraphs discuss historical data pertinent to these plants. Plants on NWC with low iron levels have experienced unexpected phenomena such as increased hot spot and reactor water activity increase indicating that other methods of feedwater iron control (even by iron addition) may be necessary. Experience in Japan has explained the effect of corrosion product morphology on overall drywell dose rates. The newer plants, which are designed to greatly reduce the cobalt and iron source terms, have low dose rates and low person-Rem. In practice, these plants control feedwater iron in the 0.1 to 0.5 ppb range while on NWC and without zinc addition. However, the ^{58}Co level and ^{60}Co levels in the water and on out-of-core surfaces of the early "low crud plants" were much higher than anticipated. The higher levels resulted from a change in the form of the fuel deposit from predominantly Fe_2O_3 in the high crud plants to a NiO/CoO type deposit in plants with very low iron. The solubility of cobalt and nickel are high for this form of fuel deposit. The levels of ^{60}Co and ^{58}Co (activation products of cobalt and nickel, respectively) in the reactor water could be reduced by controlling the iron-to-nickel ratio

in the feedwater within the range of 3 to 5. This ratio results in a form of fuel deposit, $(\text{Fe,Ni,Co})_3\text{O}_4$, with a much lower solubility of transition metals.

When sufficient iron is present, BWR fuel deposits have a multi-layer structure. The +2 transition metal ions, Co^{+2} , Ni^{+2} , Zn^{+2} , etc., are enriched in the “inner” layer to form stable mixed metal ferrites (spinels), while the activated corrosion products, including ^{60}Co , appearing in the out-of-core deposits are mainly released from the loosely adherent, iron-rich “outer” layer. Minimizing the activity release from fuel deposits therefore requires total iron input from feedwater to be controlled within lower as well as upper bounds. Sufficient iron is thought to be needed on the fuel surface to transform the loosely adherent outer deposit layer into a tightly adherent inner layer.

Two Japanese plants that first operated in the 1990’s under iron/nickel control observed higher than expected soluble ^{60}Co . At one plant (with carbon-steel RWCU piping) the higher ^{60}Co levels caused increased out-of-core radiation levels. At the other plant, which has stainless steel RWCU piping, the out-of-core deposition rate was so low that the net result was still a decrease in out-of-core radiation. The cause of the high soluble ^{60}Co was mechanically polished, non-autoclaved surface preparation of the new Zircaloy fuel cladding. This material resists formation of a film that can stabilize cobalt. Chromium levels had become elevated at these plants, indicating destabilization of the adherent “inner” layer of the oxide film. This finding led to the concept called, “Ultra-Low-Crud/High Ni Control”. With this process cobalt deposition on piping surfaces can be reduced by maintaining very low feedwater iron (<0.1 ppb), while nickel in reactor water is allowed to increase to several ppb. Under these conditions, only a minimal fuel deposit is formed and most of the cobalt and nickel is removed by the reactor water cleanup system. Incorporation of ^{60}Co into the oxide film on the recirculation piping is suppressed by the high concentration of nickel, which has a similar “mass action” effect as zinc.

The general corrosion resistance of Alloy X-750 in the BWR environment is predominately controlled by prefilming of the Alloy X-750 during the precipitation hardening heat-treating process. In the late 1980s and early 1990s some Swedish BWRs identified very high Alloy X-750 spacer grid corrosion rate resulting in a significant increase in ^{58}Co in the reactor water. For example, the radiological situation was remedied at Forsmark 2 on an interim basis by injecting iron in the form of iron oxalate to increase the final feedwater iron concentration to 0.5 ppb from 0.05 ppb. After approximately half a year on iron injection, (not including the summer months when load following made it impossible to monitor the injection of iron), nickel concentrations dropped from 2.0 ppb to 0.5 ppb, ^{58}Co concentrations dropped by a factor of four, and ^{60}Co concentrations decreased by a factor of three. Dose rates and radiation exposure were greatly decreased (3-29). Corrosion resistance of the Alloy X-750 spacer grids has since been improved by optimization of the precipitation hardening heat treating process.

Plant Design Factors Impacting Iron Control

Two of the most important factors determining the feedwater iron input levels are (1) type of condensate treatment system and (2) design of the heater drain system *viz*: cascading all drains to the hotwell or pumping the high pressure heater drains (approximately 30% of the final feedwater flow) forward to conserve the heat value.

Historically, there have been three designs for condensate treatment systems utilized in BWRs. Some use only deep bed condensate demineralizers with bead ion exchange resins. This type of system has a high capacity for removing ionic impurities but is considerably less effective at the removal of particulate material such as iron crud. BWRs using this type of system are typically referred to as deep bed (DB) plants.

A second condensate treatment system design employs vertical, tubular filters installed in pressure vessels and pre-coated with ground ion exchange resins. This type of system serves as a combination filter/demineralizer. This design was demonstrated to be superior for the removal of particulates compared to the deep bed demineralizers, but has much less capacity to remove ionic impurities. BWRs using this type of system are typically referred to as filter/demineralizer (F/D) plants.

The third design is a combination of the DB and filter or F/D systems, and is referred to as a dual treatment (Dual) system. This type of condensate treatment system offers high efficiency removal of particulate impurities and high capacity for ionic impurities. Plants employing this type of system generally use non-pre-coated filters upstream of the deep beds, commonly referred to as "pre-filters."*

Variations on these three general condensate treatment types also exist. Table 6-2 lists the type of condensate polishing system for US and Swedish BWRs.

In recent years, filtration technology has progressed and new designs are being tested and applied at some BWRs. In Japan, hollow fiber filters (HFF) have been applied upstream of deep bed systems. These filters have provided extremely high efficiency iron particulate removal and are capable of producing final feedwater iron concentrations of <0.1 ppb. Similar filtration efficiencies are also being achieved at US plants utilizing pre-filters with pleated filter septa. These advances in condensate polishing have greatly reduced the iron levels in BWR feedwater.

Clearly, plants with filter/demineralizers and those with dual treatment (pre-filters + deep beds) have achieved the lowest FW iron levels. Some plants with combined filter and deep bed CD systems have operated below 0.5 ppb.

* The application of advanced membranes in condensate system filter/demineralizers, which allows the elements to operate with a minimum precoat or no precoat, can cause problems in liquid radwaste (LRW) processing. When using minimum or non-precoat elements, the waste slurry from the f/d's does not possess adequate spent media to promote efficient settling. Additionally, these elements have higher iron removal efficiency, and the F/D backwash contains a significantly higher percentage of small (< 1micron) iron particles. The population of very small and highly charged particles remains in suspension and takes on the characteristics of colloidal materials. Both of these factors contribute to poor settling characteristics and inefficient settling in the phase separator. TR-109442, titled, "Evaluation of Radwaste Processing Options for High Iron Liquids" contains information on different solutions and their economic aspects, including the use of polyelectrolyte pre-treatment in the phase separator(s) for particle agglomeration and the use of alternate filtration for pre-treating phase separator decant liquid.

Table 6-2
Types of Condensate Polishing Systems for US and Swedish BWRs

Deep Bed Only (6 BWRs)	Filter + Deep Bed (16 BWRs)	Filter Demineralizer (16 BWRs)
FitzPatrick	Full-Flow Pre-filters	Columbia
Grand Gulf (a)	Brunswick 1	Browns Ferry 2 (f) 100% pleated
Nine Mile 1 (c)	Brunswick 2	Browns Ferry 3 (f) 100% pleated
Nine Mile 2 (c)	Hope Creek (d)	Cooper (f)
Oyster Creek (b)	Laguna Verde 1 (d)	Duane Arnold (f)
Pilgrim	Laguna Verde 2 (d)	Fermi 2 (f)
	LaSalle 1 (d)	Hatch 1 (f)
	LaSalle 2 (d)	Hatch 2 (f)
	Limerick 1 (e)	KKM Leibstadt (f)
	Limerick 2 (e)	KKL (Mühleberg)
	Perry	Monticello (f) 100% pleated
	River Bend (d)	Peach Bottom 2 (f)
	Susquehanna 1 (d)	Peach Bottom 3 (f)
	Susquehanna 2 (d)	Quad Cities 1 (f) (g)
		Quad Cities 2 (f) (g)
	Partial-Flow Pre-filters	Vermont Yankee
	Clinton (g)	
	Dresden 2 (a) (d)	
	Dresden 3 (a) (d)	

Notes:

- EPRI-ARCS resin cleaner was added as retrofit
- JRCS resin cleaning method was added as retrofit
- Pre-Filter retrofits funded and in engineering design phase
- Pre-Filters were added as retrofit
- Deep beds were added as retrofit
- Precoated pleated septa use
- F/D vessel added for power uprate

The size of the reactor water cleanup system (RWCU) can also affect the reactor water iron concentration, but this factor is usually of minor importance. The majority of BWRs were designed with a RWCU flow capacity of 1% of the feedwater input. Given this arrangement, and the additional removal mechanism of metals plate-out on the fuel, the feedwater to reactor water concentration factor can be 5-20 for input species such as iron, nickel, zinc, cobalt, etc. There are eight GE-designed BWRs with RWCU capacity of 5-7% of the feedwater flow, although the majority of these plants typically run with 1-2% RWCU flow and save the added capacity for operation during water chemistry transients. Plants with higher RWCU flows may be able to put in low cross-linked resins or keep aged resins for improved iron control without a large impact on reactor water sulfate because the increased cleanup flow will keep sulfate low.

Summary on Control of Iron Input

Although the Action Level 1 value for feedwater iron in the BWR remains at 5 ppb, based largely upon dose rate experience, the desirable range is 1.5 ppb and below for plants with reducing conditions and zinc addition. If plants on moderate HWC or HWC/NMCA and DZO are injecting iron, they should consider slowly reducing iron injection and eventually curtailing injection altogether. However, plants on NWC with average feedwater iron levels below 0.5 ppb should continue to monitor reactor water activity (soluble and insoluble) and plant radiation buildup trends; and use these to evaluate the need for iron addition. For plants above 1.5 ppb average feedwater iron, regardless of chemistry regime, analysis of the tradeoff of installing pre-filtration equipment versus long term operation at somewhat higher out-of-core radiation levels and the increased expense of zinc and corresponding fuel issues should be conducted.

Key Considerations – Recommended Goals for BWR Water Chemistry Optimization

A synopsis of the most important, generic principles for optimization of BWR reactor water chemistry.

The 2004 edition of the BWR water chemistry guidelines provides “good practice” recommendations for targets that plants may strive towards in optimizing water chemistry while balancing the conflicting requirements of materials, fuel and radiation control. It is not considered mandatory, recognizing that significant time and expense may be required at some plants in order to achieve these targets. In such cases these goals should be considered in the context of the overall strategic plan for the plant.

The recommended goals for feedwater and reactor water chemistry are summarized in Table 6-1 and Table 6-2, respectively. The values in Table 6-1 and Table 6-2 are applicable to plant operation at greater than 10% power, and not necessarily intended for other modes of operation. The parameters of particular significance for radiation control are discussed below.

Final Feedwater Goals

Conductivity. The first requirement for all plants is to minimize coolant impurities, hence the feedwater conductivity target of $<0.060 \mu\text{S}/\text{cm}$, primarily for corrosion control, but radiation fields, and potentially fuel performance can also be adversely affected at high impurity levels of chloride, sulfate, etc.

Iron. High feedwater iron ingress results in increased crud formation on the fuel, which is undesirable, and also reduces the efficiency of zinc in controlling radiation fields. Hence more zinc is needed, and the challenge of meeting radiation control targets without potentially impacting the fuel is greater at plants with higher feedwater iron concentrations, particularly for NMCA plants (see below). The current upper target is <1.5 ppb, but the recommended long-term goal is <1 ppb. Reducing iron input below 1.0 ppb is more beneficial to fuel performance, relative to operation above this value. In addition, a lower feedwater iron concentration will reduce the amount of feedwater zinc needed to obtain a given zinc concentration in the reactor

water. It may take several fuel cycles of reduced feedwater iron to see the full benefit on reduced zinc input.

No detrimental effects have been observed from low iron levels in HWC plants, but there is relatively little data for HWC plants operating continuously below 0.1 ppb. Therefore the recommended lower limit is a cycle average of 0.1 ppb for feedwater iron, (Note: for plants not injecting hydrogen, the lower limit feedwater iron remains at 0.5 ppb).

Zinc. Depleted zinc oxide is required to control radiation fields when moderate HWC is used. While poolside surveillance data indicate spallation of tenacious crud from fuel surfaces in some NMCA plants with a cycle-average feedwater Zn concentration above 0.4 ppb, the surveillance data under HWC is not sufficient to provide a similar basis for these plants. However, careful consideration of fuel performance factors would be prudent for operation above 0.6 ppb zinc for these plants. For plants that have not received a noble metal application, operation with a feedwater zinc concentration above 0.6 ppb to achieve a reactor water zinc concentration in the 5-10 ppb range is an indication of excessive iron inputs, and places additional corrosion product burdens on fuel rod surfaces. The only exceptions would be the first three months of operation for initial startup of the zinc injection system, or, following a chemical decontamination of the recirculation system piping.

Table 6-3
Summary of Recommended Goals for Final Feedwater

<i>Feedwater Parameter</i>	<i>Moderate HWC Plants (HWC-M)</i>	<i>Plants using Noble Metals (NMCA)</i>
Conductivity ($\mu\text{S}/\text{cm}$)	≤ 0.060	≤ 0.060
Oxygen (ppb)	30-100	30-100
Copper (ppb)	< 0.05	< 0.05
Iron (ppb) (cycle average)	0.1-1.0	0.1-1.0
Zinc (ppb) (quarterly average)	< 0.6	< 0.4
Hydrogen (ppm)	Plant specific (≤ 2.0)	0.15-0.4
Hydrogen availability % (injection at target value, % of cycle)	$> 95\%$	$> 98\%$

Reactor Water Goals

Conductivity. Plants can be unduly penalized for innocuous reactor water conductivity contributions from non-detrimental species like soluble zinc during crack growth assessments. Because most BWRs are utilizing zinc injection, conductivity, should be corrected for the soluble zinc concentrations, during such assessments. Similar corrections to conductivity should be made for soluble ferrous iron during oxide restructuring periods following noble metal applications and resumption of hydrogen water chemistry. After these adjustments have been made, the residual conductivity should be less than $0.08 \mu\text{S}/\text{cm}$. Adjusted conductivity readings in excess of this value should be a trigger for complete cation and anion diagnostic evaluations to identify the constituents causing the increased conductivity.

Zinc. For plants that have not received a noble metal application, the recommended zinc concentration in reactor water is > 5 ppb. Concentrations significantly above 10 ppb may only provide diminishing returns with respect to decreasing the concentration of soluble ^{60}Co and reducing drywell dose rates. For NMCA plants, continuously maintaining the ratio of soluble $^{60}\text{Co}/\text{Zn}$ at a value of less than $2 \times 10^{-5} \mu\text{Ci/ml/ppb}$ is highly desirable. Maintaining the ratio below the indicated value throughout a fuel cycle may provide reasonable assurance of satisfactory dose rates.

Soluble ^{60}Co . Plants with routine soluble ^{60}Co concentrations below $5 \times 10^{-5} \mu\text{Ci/ml}$ and a well-managed zinc injection program historically have not had problematic drywell dose rate issues. For plants operating with NMCA, reducing the ^{60}Co concentration allows the achievement of the desired $^{60}\text{Co}/\text{Zn}$ ratio with a reduced reactor water zinc concentration, and reduced feedwater zinc input. Reducing the feedwater zinc input to the minimum quantity needed to obtain the $2 \times 10^{-5} \mu\text{Ci/ml/ppb } ^{60}\text{Co(s)}/\text{Zn(s)}$ ratio will minimize the tendency for crud spallation. All plants should continue with programs to reduce sources of Stellite™ and other high-cobalt alloys to reduce the production rates of ^{60}Co and its concentration in the reactor water.

Table 6-4
Summary of Recommended Goals for Reactor Water

<i>Reactor Water Parameter</i>	<i>Moderate HWC Plants (HWC-M)</i>	<i>Plants using Noble Metals (NMCA)</i>
Conductivity ($\mu\text{S/cm}$)	<0.08	<0.08
Sulfate (ppb)	<2	<2
Chloride (ppb)	<1	<1
Zinc (ppb)	>5	---
Copper (ppb)	<1	<1
Soluble $^{60}\text{Co}/\text{Zn}$ Ratio ($\mu\text{Ci/ml/ppb}$)	---	$<2.0 \times 10^{-5}$
Soluble ^{60}Co ($\mu\text{Ci/ml}$)	$<5.0 \times 10^{-5}$	$<5.0 \times 10^{-5}$
ECP (V_{SHE})	<-0.23	<-0.23
Hydrogen/Oxygen Molar Ratio	---	3:1
Noble Metal Input (normalized to fuel surface area) ($\mu\text{g/cm}^2$)	---	<30

Specific Recommendations for Plants Using NMCA (Developed from recommendations in 2003 NMCA Application Guidelines, BWRVIP-118)

1. Adjust feedwater zinc injection rate to achieve a reactor water zinc concentration of 5 to 10 ppb for at least six months prior to initial NMCA application. Note also that plants with higher feedwater iron or copper levels should carefully consider which levels of zinc are acceptable for use during that period. For three months immediately before NMCA, feedwater zinc should be limited to 0.4 ppb or less, to guard against excessive release of zinc while noble metals are being applied, which interferes with the application process.
2. If practical, initiate feedwater hydrogen injection at least six months prior to noble metal application and inject at the maximum rate possible, based on equipment capacity and main steam line radiation considerations. However, the injection rate should not exceed the maximum rate considered for moderate HWC (i.e., the final feedwater hydrogen concentration should not exceed 2 ppm). Maintain injection rate as constant as possible. Applying NMCA before initiating hydrogen injection is not recommended, as high radiation fields may result.
3. If the plant's history of feedwater iron input averages greater than 1.5 ppb, or a reactor water soluble ^{60}Co concentration greater than $1.0 \times 10^{-4} \mu\text{Ci/ml}$, applying NMCA during a mid-cycle outage presents a higher risk of increased shut down dose rates. For such plants, an end of cycle application is preferred for dose minimization.
4. All BWRs considering or using NMCA should consult with their fuel vendor(s) to determine whether a fuel surveillance program is needed at their plant. This is especially important for plants that have a history of relatively high feedwater iron input (averaging greater than 1.5 ppb) or significant feedwater copper (>0.1 ppb), because there is currently not sufficient surveillance data from such plants operating on NMCA. The surveillance program may need to include baseline fuel surveillance prior to operating with NMCA to confirm that existing amounts of crud and oxide on the fuel are low enough to avoid problems with the proposed water chemistry. Fuel surveillance after the first operating cycle with NMCA should also be considered to confirm that performance was as expected.
5. For the cycle immediately after application, higher feedwater zinc injection levels may be required to maintain a reactor water $^{60}\text{Co(s)}/\text{Zn(s)}$ ratio of less than $2 \times 10^{-5} \mu\text{Ci/ml/ppb}$. A secondary target of 5 ppb reactor water zinc has been successful at most plants, but the ratio value is of prime importance. Consult with the fuel vendor(s) to assess whether the amount of feedwater zinc to be added as a function of time is appropriate for their fuel and plant. In some cases the amount of zinc added to the feedwater may need to be limited due to fuel considerations. Operation with a quarterly-average feedwater zinc concentration above 0.4 ppb may increase the chances of crud spallation from the fuel. Fuel and chemistry operational experience and fuel surveillance data at a given plant should be evaluated as part of the justification for operating above 0.4 ppb feedwater zinc at that plant. Clearly, cobalt source term reduction programs have the beneficial effect of lowering the feedwater zinc injection rate required to maintain the desired ratio.
6. Monitor reactor water ^{60}Co during any end of cycle power coast down and be prepared to increase the zinc injection rate.

7. A passive injection system may require a larger loading of zinc pellets than normal. Monitor soluble and insoluble reactor water isotopes and feedwater and reactor water zinc at a frequency of three times per week and feedwater iron at a frequency of once a week until trends are established; and zinc once per week after trends are confirmed.
8. When initiating FW hydrogen injection or NMCA, be prepared for an increase in reactor water conductivity, and soluble and insoluble isotopic concentrations. Trend reactor water isotopics, especially ^{60}Co , and compare to past cycles. Also, compare behavior to other plants with NMCA experience.
9. NWC/HWC cycling should be viewed as a long-term, high-cost element that should be used as a last resort and not as a short-term solution for routine testing or maintenance. All efforts should be made to achieve an HWC system availability of greater than 98%. Any justification for “turning down” or “turning off” hydrogen for inspections should be reassessed, with the goal of eliminating as many hydrogen interruptions as possible. Because of “crack flanking” concerns, hydrogen availability should be greater than 95%, with a goal of 98%. In addition, any “turning down” or “turning off” hydrogen for inspections should be reassessed, with the goal of eliminating as many hydrogen interruptions as possible. The maximum time of any given hydrogen interruptions should be limited to < 4 hours. (See Section 7 on inspection relief and Section 2 on crack flanking). In addition, hydrogen injection should be begun as soon as practical after any startup and within a maximum of 12 hours.
10. Lower feedwater iron input will result in less fuel crud deposition and lower demand for depleted zinc. A target feedwater iron in the range of 0.1 to 1.0 ppb is believed to be optimum for dose reduction, and minimized potential for forming deposits that could accelerate fuel-clad corrosion.
11. Make contingency plans for possible increased shutdown dose rates at end of first post-NMCA cycle if there is a difficulty in maintaining a reactor water $^{60}\text{Co(s)}/\text{Zn(s)}$ ratio of less than $2 \times 10^{-5} \mu\text{Ci/ml/ppb}$.
12. Plan to operate RWCU at 100% capacity and maximum efficiency for as long as possible during the first post-NMCA refueling outage.
13. Limit the deposition of noble metal to $30 \mu\text{g}/\text{cm}^2$ on fuel surfaces and to once per bundle lifetime. Note that when noble metal is applied at the end of cycle N-1, the fresh fuel inserted for its first cycle of operation in Cycle N is considered to have been exposed to the application of NM because of the significant amount of redistribution that occurs after application. If greater than $30 \mu\text{g}/\text{cm}^2$ of noble metal is to be applied, e.g. a re-application is needed earlier than expected, this condition should be evaluated by the utility and fuel vendor for potential fuel impact. General Electric’s recommendation about reapplication of NMCA states: “The plant should prepare to reapply or should perform a more detailed evaluation of reapplication timing when the total noble metal deposition on the plant’s durability monitoring coupons is projected to decrease into the range of 0.10 to $0.15 \mu\text{g}/\text{cm}^2$.”

References

- 6-1. BWR Water Chemistry Guidelines- - 2004 Revision,. Palo Alto, CA: Electric Power Research Institute, December 2004. TR-103515-R3, 2004.
- 6-2. Qualification of the NP/LOMI Decontamination Process for BWRs under HWC, EPRI, Palo Alto, CA: 1998. Report TR-111667.
- 6-3. Decontamination Handbook, EPRI TR-112352, Palo Alto, CA,; July 1999., TR-112352
- 6-4. Experience with Depleted Zinc Oxide Injection in BWRs, 1999 Progress Report, EPRI TR-108741, Palo Alto, CA, June 1999.
- 6-5. Experience with Depleted Zinc Oxide Injection in BWRs, EPRI TR-107188, Palo Alto, CA, November 1996.
- 6-6. BWR Iron Control Monitoring: Interim Report, EPRI TR-108737, Palo Alto, CA, 1998.
- 6-7. BWRVIP-118: BWR Vessel and Internals Project, NMCA Experience Report and Application Guidelines, 1003193, EPRI, Palo Alto, CA, 2003.

7

SYSTEM AND COMPONENT DECONTAMINATION

Decontamination represents one of the more cost-effective methods for reducing out-of-core radiation fields. The most commonly used techniques include dilute chemical decontamination (DCD), which uses chemical solutions circulating through components or systems with the solution being purified by filtration and ion exchange media; hydrolasing internal large component or piping surfaces, and flushing high activity crud traps using high velocity and/or high pressure water jets. The use of these technologies has grown rapidly with process improvements.

The first “modern” DCD was of the reactor water cleanup system (RWCU) at Vermont Yankee in 1979. Over the next 10 years DCD grew rapidly into a mature, fully developed technology for component and sub-system decontaminations in both PWRs and BWRs. The technology has been reviewed thoroughly in the EPRI Decontamination Handbook published in 1999 (7-1). This chapter covers only decontamination of operating plants. For retired plants and components, more aggressive processes can be used as described in TR-112092 and TR-1003720.

In this chapter DCD technology is reviewed briefly, and developments since 1997 are discussed in more detail. In 1991, the LOMI process was qualified for full system decontamination (FSD) applications in BWRs, both with the fuel in and fuel removed, and there have been many applications since. The AP/LOMI and AP/CAN-DEREM processes were also qualified in 1991 for FSD applications in PWRs with the fuel removed. This work culminated in FSD at Indian Point 2 in February 1995. Work to qualify PWR FSD applications with the fuel in place is underway.

Although the FSD application at Indian Point 2 was the most significant achievement of DCD technology, component and subsystem decontaminations continue to be performed at a fairly steady rate. The number of U.S. plants performing chemical decontaminations since 1994 are shown in Table 7-1. These data do not include decontaminations performed by U.S. vendors in countries such as Canada, Korea, Mexico and Taiwan or those performed by vendors (principally Siemens/KWU) in Europe and Asia. Typically, U.S. plants, mostly BWR’s, perform about five decontaminations per year. Decontaminations are more cost effective in BWRs because outage maintenance workers tend to spend more time in radiation fields than do PWR workers, e.g., in the drywell, in RWCU heat exchanger rooms, etc. Most plants perform more than one decontamination during an outage so the total number of applications is higher than suggested by Table 7-1. For example, a BWR plant might use the LOMI process for the reactor recirculation system (RRS) piping and then a dilute organic acid process such as CAN-DEREM or CITROX for the reactor water cleanup system (RWCU). Either application might include an oxidizing step such as alkaline permanganate (AP) or nitric permanganate (NP). Reasons for employing an oxidizing step are discussed later in this chapter.

Table 7-1
US BWR plants under HWC using chemical decontamination since 1994

<i>Plant</i>	<i>Process</i>	<i>Results (DF)</i>
Brunswick '94	Citrox-AP	~ 1.5
Quad Cities '95	LOMI-AP	8.6
Brunswick '95	LOMI-NP	~ 20
Brunswick '96	LOMI-NP	50
Hatch '96	LOMI-NP	32
Pilgrim '97	LOMI-NP	43
Quad Cities '98	LOMI-AP	8
Laguna Verde '98	LOMI-NP	34
Susquehanna 2000	LOMI-NP	10
Susquehanna 2001	LOMI-NP	34
Browns Ferry 2001	LOMI-NP	59
Susquehanna 2002	LOMI-NP	21
Susquehanna 2003	LOMI-NP	28
Susquehanna 2004	LOMI-NP	Not available
Quad Cities	LOMI-NP	Not available

Plugs are used to isolate portions of the system from the decontamination solution. This method allows relatively positive control over the extent of decontamination and provides protection for fuel and components that could be negatively impacted by the decontamination solution. However, plugs have been known to leak, which results in chemical contamination of system liquids.

The most popular process was LOMI (almost all U.S. decontaminations), followed by CITROX and CAN-DEREM. Oxidizing steps such as AP and NP were employed in every PWR application and in some BWR applications depending upon factors such as:

- composition of the film (was it high in chromium?),
- was a high DF required (i.e. >10), or was the plant satisfied with a DF in the 5-10 range,
- allotted time, and
- amount of waste that could be tolerated.

Where an oxidizing step was required, AP was used in >90% of the applications and NP in <10%. The reasons for this choice are discussed in the following sections of this chapter.

With few exceptions, the non-regenerative, strongly reducing LOMI process was the process of choice for decontamination of large diameter primary system piping, while the regenerative, mildly reducing organic acid processes were favored for smaller subsystem, such as RHR heat exchangers, spent fuel pool cooling systems, letdown heat exchangers and pumps, etc. There are sound technical justifications for this division of the processes, which will also be discussed in

the following sections of this chapter. In Europe, the CORD process continues to be used on a regular basis for both subsystem and full system decontaminations. The various decontamination and oxidation processes are described in the next sections.

Decontamination Processes

CAN-DEREM

CAN-DEREM is a variant of CAN-DECON. The only difference between the two is that the CAN-DEREM reagent does not contain oxalic acid while the CAN-DECON reagent does. Under aggressive laboratory conditions, CAN-DECON may cause intergranular attack (IGA), which can lead to IGSCC on heavily sensitized SS 304. IGA/IGSCC has never been observed in field applications, but concerns of utilities dictated that the process be modified. CAN-DEREM does not cause IGA/IGSCC even under the most extreme conditions, nor is the effectiveness of the process on LWR oxide films significantly diminished by the elimination of oxalic acid. CAN-DEREM is based on a mixture of citric acid and EDTA. The CAN-DEREM concept is summarized in Table 7-2.

The chemicals circulate through the system dissolving the oxide deposits and releasing contaminants from the surfaces. Once in the liquid the contaminants are removed by purification. Dissolved metals and radionuclides are removed by ion exchange resins, while particulate material is removed by filtration. The decontamination is terminated by valving out the cation resin and placing on line a mixed bed of cationic and anionic resins. The anionic resins remove the chemical reagents, and the cationic resin removes any remaining dissolved metals.

Chemical decontamination involves the dissolution of metal oxides from the system surfaces. The principal non-chromium containing oxides found in LWRs (chromium oxides are discussed later) are magnetite (Fe_3O_4), nickel ferrite (NiFe_2O_4) and hematite (Fe_2O_3). When exposed to CAN-DEREM these dissolve by simple acidic dissolution. The EDTA and citric acid prevent redeposition of the metal ions by forming highly soluble chelate complexes. These chelate complexes breakdown when passed through strong acid cation resin (H:R). The resin breaks the chemical bond between the metal ion and the chelating anion, captures and retains the metal ion, and releases the chelating agent and a hydrogen ion. These are returned to the system to dissolve more deposits. Anion resin is used to remove the EDTA and citric acid.

Table 7-2
The CAN-DEREM Concept

<i>Feature</i>	<i>Advantages</i>
Low reagent concentration – typically 0.1 wt %	Minimizes corrosion Inhibitor only required when carbon steel present Permits cleanup with IX resins
Reagent added directly to water in system	Simplifies operation No tanks required for draining of system
Reagent is a soluble powder	Dissolves <i>in-situ</i> to form decon solution No need for large chemical mixing tanks
Reagent is a mixture of citric acid and EDTA	EDTA forms a very strong complex with ferric ions eliminating ferric ion corrosion
For full system application, reactor does not necessarily have to be defueled	Simplifies operation Fuel is decontaminated Reduces rate of recontamination
Regeneration of reagent by cationic resin	Continuous removal of dissolved contaminants so radiation fields remain low around equipment Reagent is, in effect, reused Effective concentration much higher than low initial concentration suggests
Removal of reagent by anionic resin	Solid wastes only (ion exchange resins)
Dissolves most metal oxides found in water-cooled reactors	Can be used in all types of water-cooled reactors but pretreatment required if chromium present
Decontamination factors of 5-20	Removal of 80-95% of the deposit and outer oxide film, but <u>does not</u> remove thin, inner protective film

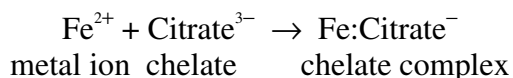
CITROX

CITROX is an acronym for citric plus oxalic acids. It is a decontamination reagent that was originally developed at Hanford by R.D. Weed for use in the plutonium recycle test reactor (PRTR). At that time it was described as “*the most effective procedure for removing corrosion product films from stainless steel.*” The original formula was 0.3 M (25,000 ppm) citric acid plus 0.2 M (58,000 ppm) oxalic acid representing a total reagent concentration of 8.3 wt%, plus inhibitors. In the early 1980s Pacific Nuclear Systems modified the process to produce a dilute version with a total reagent concentration of 0.2%. PNS CITROX A is applied without inhibitors while PNS CITROX B contains an inhibitor for use in carbon steel systems. Both versions are classified as dilute, regenerative, organic acid decontamination processes similar to CAN-DEREM. Although the reagent concentration is double that of CAN-DEREM, most of the features listed in Table 7-2 apply equally well to CITROX. The process tends to be a little more “aggressive” than CAN-DEREM due to the higher reagent concentration and the use of oxalic acid. Approximately double the amount of anion exchange resin is required for cleanup due to the higher reagent concentration. This process remains very popular and was second only to LOMI in the number of applications in the period 1990 to 1998. It is suitable for all LWR main systems, subsystems and components, but has not been qualified for FSD applications.

The most significant difference from CAN-DEREM is the absence of EDTA. This means that ferric ions that are released from the deposit are available to cause ferric ion corrosion since the citrate:ferric chelate is far less stable than the EDTA:ferric chelate. This effect is minimized by ensuring a large enough regeneration flow through cation resin to maintain the ferric ion concentration at less than 10 ppm. Experience has shown that corrosion is very low below this concentration.

The chemistry of deposit dissolution, chelate formation, reagent regeneration and reagent removal is almost identical to that previously described for CAN-DEREM. The major difference is that citrate ion rather than EDTA is the principal chelating agent.

Formation of Citrate Chelate Complex



LOMI

LOMI is an acronym for Low Oxidation state Metal Ion. It is fundamentally different from the regenerative organic acid processes, CAN-DEREM and CITROX. LOMI employs a strong reducing agent, vanadous picolinate, to reduce the cations (principally Fe^{3+}) in the oxide lattice by electron transfer from the low oxidation state metal ion, V^{2+} . This process destabilizes the oxide film and it rapidly dissolves in excess picolinic acid. This process is known as reductive dissolution. It is much faster than simple acidic dissolution and is usually complete within a matter of minutes. However, practical considerations involving reagent addition, transfer of the reagent to all parts of the system, and reagent removal, usually mean that it takes up to about six hours. This is still much faster than the organic acid processes which can take 12 or more hours.

The LOMI concept is summarized in Table 7-3. The reagent is formed in situ by the addition of sodium picolinate and vanadous formate. Although the process is non-regenerative, the total concentration of all chemicals is <1% (typically 0.6-0.7 % or 6,000-7,000 ppm as shown in Table 7.3) so it is still classified as a dilute process and is amenable to reagent removal by ion exchange resins. LOMI will dissolve all iron and nickel based deposits found in water-cooled reactors, but, like the organic acid processes, will not dissolve high-chromium deposits. This aspect is discussed in the Oxidation Processes section.

Table 7-3
The LOMI Concept

<i>Feature</i>	<i>Advantages</i>
Dissolves LWR deposits by reductive dissolution	Much faster than simple acidic dissolution Strong reducing conditions minimize corrosion Higher pH than organic acid processes thus lower corrosion
Reagent is a two-part concentrated liquid (vanadous formate and sodium picolinate) which is added directly to water in system	Simplifies operation No tanks required for draining of system No need for large chemical mixing tanks
Total reagent concentration is <1% so process is classified as dilute	Permits cleanup on IX resin Solid waste only
For full system application, reactor does not necessarily have to be defueled	Simplifies operation Fuel is decontaminated Reduces rate of recontamination
Radiation regenerates the reagent, thereby protecting the organic components from radiation damage	Makes the reagent particularly suitable for full system decontamination with the fuel in the reactor
No ion exchange columns on-line during deposit dissolution	Simplifies operation
Removal of dissolved deposits and spent reagent by cation and anion ion exchange resins in series	Solid wastes only (ion exchange resins)
Dissolves most metal oxides found in water-cooled reactors	Can be used in all types of water-cooled reactors but pretreatment required if chromium present
Decontamination factors of 5 – 20	Removal of 80 - 95% of the deposit but does not remove thin inner protective film

LOMI will dissolve deposits found in BWRs, CANDUs and the outer layer of PWRs. Like the organic acid processes, it is not effective with deposits which contain >10-15% chromium, i.e. most PWR deposits. A pretreatment step is required to remove the chromium. This technology is discussed later in this chapter.

Ion exchange resins are not used during the reductive dissolution phase (LOMI is not currently a regenerative process) but are used for cleanup at the end of the process. The absence of an ion exchange column during the actual deposit dissolution process simplifies operations but has the disadvantage that dissolved radionuclides continuously build up in solution. Thus radiation fields around the decontamination equipment and hoses tend to be much higher during LOMI than during a regenerative organic acid process.

When deposit dissolution is complete, a two-stage cleanup is required — cationic resin to break the chelate complex and capture the metal ions, followed by anionic resin to capture the picolinate and formate ions. The anion columns will contain very little activity compared to the cation columns. To obtain maximum shielding benefit and minimum radiation fields in the work area, the anion columns are placed in front and the cation columns behind them.

Typical process conditions for a LOMI decontamination are summarized in Table 7-4.

Table 7-4
Typical Process Conditions for LOMI Decontaminations

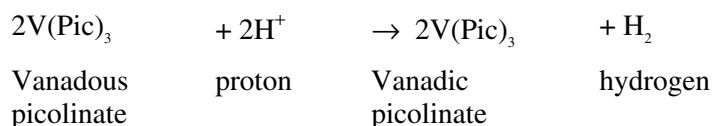
<i>Parameter</i>	<i>Concentration or Value</i>		
	(milli-Molar)	(wt %)	(ppm)
Vanadium (II) formate	8	0.08	800
Formic acid	16	0.07	700
Picolinic acid	36	0.44	4,400
Sodium hydroxide	12	0.05	500
Total - all chemicals	72	0.64	6,400
pH	4-5		
Temperature	180-200 (°F)		
Time	Up to 6 hours		

LOMI Compared to Regenerative Organic Acid Processes

LOMI is a non-regenerative process so the amount of deposit that can be dissolved is directly proportional to the amount of solvent. For systems that have a relatively small surface area to volume ratio (e.g., large diameter piping, steam generator channel heads), the total amount of chemicals required to dissolve the deposit can be added to the system in one step without exceeding the recommended upper limit of concentration (10 milliMolar V^{2+}). The LOMI process is very well suited for these types of systems. For systems that have a larger surface area to volume ratio (e.g., heat exchangers in an RWCU or letdown system, long lengths of small diameter piping, etc.), it may not be possible to add the required amount of reagent for the LOMI process without exceeding the recommended concentration limit. In addition, catalytic decomposition of the LOMI reagent (see reaction below) in these types of systems may be severe because of the large surface area and additional reagent equivalent to 100%, or more, of the theoretical amount may be required. The use of a regenerative organic acid process such as CAN-DEREM or CITROX that employs a fixed reagent concentration may be the best choice for these types of applications. The amount of deposit that these processes can remove is limited only by the amount of cation exchange resin available. It is usually not a problem to supply as much IX resin as necessary to complete the job.

Decomposition of Vanadous Picolinate

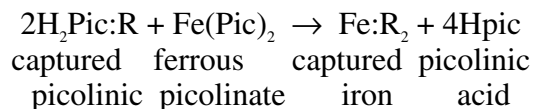
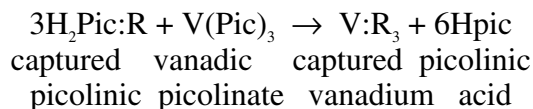
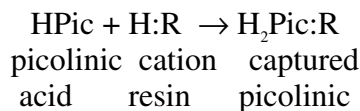
(Note: this reaction is catalyzed by metal surfaces)

**LOMI-2**

The traditional advantages of the LOMI process are its low corrosivity and its effectiveness on certain oxide types, specifically; the nickel ferrite films that occur in BWRs operating under HWC. Its chief disadvantages are that it is non-regenerative, which leads to more waste volume than other DCD processes, and LOMI is effectively limited to a concentration of 10 mM vanadium because of solubility restrictions. Thus, there is a limit as to how much oxide deposit can be dissolved in a given volume of decontamination solution. For many subsystem decontaminations this is not a problem. However, there has recently been interest in applying LOMI to the bottom of a BWR reactor vessel where the amount of corrosion product present might be in excess of the amount that can be dissolved in a standard LOMI application. LOMI is not usually chosen for decontamination applications where there is a high deposit loading, or a high surface area to volume ratio.

To circumvent this limitation, EPRI commissioned work to see if the picolinic acid could be recycled during the decontamination by using cation exchange resin. Vanadium (III) and dissolved metals would be continuously removed and the lost vanadium would be replaced by injection of fresh vanadous formate. Additional sodium hydroxide may also be required for pH control. Operation of the process in this way would remove the restriction of oxide dissolution capacity thus making LOMI effectively regenerative.

The researchers demonstrated that when cation resin is used continuously during the LOMI process, it initially becomes saturated with picolinic acid (in the form H_2Pic^+) but as the decontamination proceeds, the picolinic acid is displaced by metal ions, principally V^{3+} and Fe^{2+} . This process is shown in the following series of reactions where R symbolizes cation resin. Up to 90% of the picolinic acid can be recovered before significant metal leaks into the effluent.

Regeneration of Picolinic Acid During LOMI-2

The LOMI-2 process is different from the basic LOMI process in the following ways:

- sodium picolinate is injected initially and allowed to circulate;
- vanadous formate is injected slowly and continuously throughout the decontamination as opposed to a single addition at the start of the decontamination;
- cation exchange resin is placed on line when injection of vanadous formate commences;
- spent vanadium (V(III)) and other metal cations (Fe^{2+} , Co^{2+} , etc.) are continuously removed during the decontamination;
- picolinic acid is initially retained by the resin but then is released as metal ions take its place on the IX resin exchange sites;
- additional sodium hydroxide may have to be periodically injected for pH control;
- it is also possible to use anion exchange columns in an advantageous way to preferentially remove formate (which tends to build up in solution due to continuous injection of vanadous formate), but a detailed description of this procedure is beyond the scope of this report.

For the most part, these differences are procedural and require no significant changes in equipment or application conditions.

The advantages of LOMI-2 can be summarized as follows:

- removal of the reagent capacity restriction of LOMI;
- ability to decontaminate systems with a high deposit loading, or a high surface area to volume ratios, systems that were previously not amenable to the LOMI process;
- reduction in the amount of picolinic acid required, hence a corresponding reduction in the volume of radioactive waste ion exchange resin;
- reduction in the proportion of chelant in the waste (but does not eliminate chelant);
- continuous removal of radioactive species such as ^{60}Co results in lower general area radiation fields around the equipment and lower radiation exposure to personnel;

System and Component Decontamination

- longer time that V(II) is present in the system, thereby providing additional corrosion protect of carbon steels and low alloy steels.

There are also some disadvantages of LOMI-2:

- formate builds up in the system due to the continuous injection of vanadous formate, but this can be minimized through judicious use of anion columns, as referred to above;
- additional sodium hydroxide is required to maintain the proper pH;
- control of the process is not straightforward because the cation resin first binds then releases picolinic acid. The recycling scheme requires an initial injection into the system of a very dilute LOMI formulation followed by operation of a cluster of small cation exchange columns during the decontamination. Although stability of process conditions is best achieved by a large number of small columns, the technique can be applied with just two or three columns. For the most part, these differences are procedural and require no significant changes in equipment or application conditions.

To date, LOMI-2 has not been applied in a plant. Based on laboratory scale work, procedures have been developed for plant implementation. A U.S. patent has been obtained. LOMI-2 is now available for plant applications to decontamination vendors who are LOMI licensees.

CORD

CORD is an acronym for Chemical Oxidation Reduction Decontamination. CORD is a regenerative, DCD process that consists of four blended steps:

- (i) Oxidation with permanganic acid (HMnO_4 or more simply HP for analogy with AP and NP) at a concentration of 50-300 ppm and a temperature of 190°F. This step typically takes 3-6 hours. The permanganic acid can be produced in-situ by cation exchange of a solution of potassium permanganate, or it can be produced in a concentrated form in a separate ion exchange module prior to the start of the decontamination. Permanganic acid is produced from potassium permanganate by ion exchange.
- (ii) Addition of a stoichiometric amount of oxalic acid to reduce the remaining HMnO_4 to Mn^{2+} . If 300 ppm of HMnO_4 was used, approximately 550 ppm of oxalic acid would be required. There is no cleanup of the water at this point. Step (iii) follows directly.
- (iii) Addition of an excess of oxalic acid to perform the actual decontamination step. The chemical reaction for dissolution of magnetite in oxalic acid is shown below. Typically about 1,500 ppm is used. In practice, steps (ii) and (iii) are performed as one by the addition of 2,000 ppm of oxalic acid. Immediately after the addition of the oxalic acid, a cation exchange column is placed on line. This serves two functions. Firstly, it removes the Mn^{2+} ions produced by reduction of the HMnO_4 . Secondly, it removes cationic metal species such as Fe^{3+} , Fe^{2+} , Ni^{2+} , Co^{2+} , etc. which are formed as the oxalic acid dissolves the deposit. This regenerates the oxalic acid in an identical manner to that for EDTA under the description of the CAN-DEREM process.
- (iv) Removal of the oxalic acid on anion exchange resin or decomposition of the oxalic acid by hydrogen peroxide and UV light. The original CORD process used ion exchange resins for the cleanup step as do CAN-DEREM, CITROX and LOMI, but a recent innovation by

KWU/Siemens is the use of hydrogen peroxide and intense UV light to decompose the oxalic acid to carbon dioxide and water. The carbon dioxide is vented off, leaving only the metal cations to be removed by IX resin. A small amount of mixed bed resin is required for final polishing.

The process described above is a single CORD cycle. Most applications employ three to five such cycles. A typical CORD cycle takes 4-16 hours if IX cleanup is employed, and 10-36 hours if H₂O₂/UV decomposition is used. For the first CORD cycle, the oxidizing step with permanganic acid may be omitted if there is known to be an outer layer of deposit which contains very little chromium. This is typically the case in BWRs.

The CORD/UV concept is summarized in Table 7-5.

Table 7-5
The CORD/UV Concept

<i>Feature</i>	<i>Advantages</i>
Four blended steps: Oxidation (of Cr by HMnO ₄) Reduction (of HMnO ₄ by oxalic acid) Decontamination (with oxalic acid) Decomposition (of oxalic acid by H ₂ O ₂ /UV)	No need to cleanup or drain system between steps Simplifies operation Shorter time Less waste Oxidation step can be omitted for first cycle if low Cr. (Sometimes the case in BWRs)
Oxidation step uses permanganic acid	Faster and more efficient than AP Less waste since lower concentration and no additives such as NaOH or HNO ₃ . Also no K.
Reduction step performed in-situ with oxalic acid, the same chemical used for the decontamination step	Avoids contact of IX resin with permanganate ion Stoichiometric calculation unnecessary since large excess added so that decontamination step begins as soon as reduction of HMnO ₄ is complete
Decontamination step is regenerative using continuous flow through cationic IX resin	Mn ²⁺ ions from reduction step are removed Continuous removal of dissolved contaminants so radiation fields remain low around equipment Reagent is, in effect, reused. Effective concentration much higher than low initial concentration suggests
For full system application, reactor does not necessarily have to be defueled	Simplifies operation. Fuel is decontaminated Reduces rate of recontamination
Decomposition of oxalic acid by H ₂ O ₂ and UV light	Decomposition products are innocuous (CO ₂ and H ₂ O) No anion exchange resin required for reagent removal No chelates in waste
Dissolves most metal oxides found in water-cooled reactors	Can be used in all types of water-cooled reactors Separate pretreatment step not required - it is integral in the process
Each CORD cycle is independent	Number of cycles can be adjusted according to final dose rate or DF required
Decontamination factors range from 10 to >100, depending on number of cycles	Mildly contaminated components can be cleaned to free release limits

Oxidation Processes

CAN-DEREM, CITROX and LOMI work very efficiently with oxide deposits that contain predominantly iron and nickel. If the deposit contains a large amount of chromium (approximately 10%) in the form chromium oxide, Cr_2O_3 , or a mixed spinel such as iron chromite, FeCr_2O_4 , it will not dissolve in any of these processes. Chromium (III) oxides will not dissolve by simple acid dissolution in the mild acids employed in CAN-DEREM and CITROX, or by reductive dissolution in the LOMI process. At concentrations greater than about 10% (there are some reports that LOMI will tolerate up to 20% chromium), it stabilizes the oxide films to dissolution by these processes. Chromium (III) oxides are, however, readily oxidized to the highly soluble chromate, CrO_4^{2-} , or bichromate, HCrO_4^- , ions. Chromium-rich deposits dominate the contaminated oxide films found in PWRs and they are occasionally found in BWR films, especially those that have operated under hydrogen water chemistry for several cycles. To remove them a chemical oxidation step is required. Although many chemical oxidizing agents will work, those most commonly used in nuclear power plants are based on the permanganate ion, MnO_4^- . Three methods have evolved, alkaline permanganate, nitric permanganate and permanganic acid. Table 7-6 summarizes the operating conditions, advantages, and disadvantages of the three processes.

Alkaline Permanganate (AP)

AP consists of a dilute solution of potassium permanganate (1,000 ppm) and sodium hydroxide (100 ppm). It operates at a pH of 10-11. It is applied at a temperature of 200 °F for 6-12 hours. The high pH minimizes production of MnO_2 and also minimizes corrosion. It is the slowest acting of the three oxidation processes but it is also the most benign.

Nitric Permanganate (NP)

NP consists of a dilute solution of potassium permanganate (1,000 ppm) and nitric acid (200 ppm). Nitric acid was chosen because when combined with permanganate, the mixture passivates carbon steel. NP operates at a pH of 3-4, and is applied at a temperature of 200 °F for 4-6 hours. The low pH results in a more efficient oxidation since permanganate is a much stronger oxidizing agent at pH 2-3 than it is at pH 10-11. However, the low pH and the presence of nitric acid result in it being somewhat more corrosive than AP. The low pH also promotes decomposition of the permanganate; thus more MnO_2 is generated with NP than with AP.

The combination of NP and LOMI was found to be the most effective process for BWRs operating on hydrogen water chemistry with relatively high hydrogen concentrations to protect core internals. This is attributed to NP being very effective on high-Cr oxides on stainless steel, and LOMI being effective on nickel ferrite oxides.

Table 7-6
Summary of oxidation steps used for decontamination

<i>Parameter</i>	<i>Alkaline Permanganate (AP)</i>	<i>Nitric Permanganate (NP)</i>	<i>Permanganic Acid (HP)</i>
pH range	10.5 – 12.0	2.5 + 0.5	2.0 – 3.0
Optimum temperature	85-95 °C	85-95 °C	85-95 °C
Initial permanganate concentration	1.0 g/L	1.0 g/L (0.5 g/L)	0.3 – 2.0 g/L
Stability	Good	Poor	Fair
Optimal material for application	Inconel	Stainless steel, thick HWC oxide films	Stainless steel, thick HWC oxide films
Primary advantages	Stability useful for convoluted flow paths	Rapid reaction beneficial for HWC oxide films Well-tested in US BWR materials of construction Easier pH control	Rapid reaction beneficial for HWC oxide films Low pH
Primary disadvantages	Less reactive May not be effective for HWC films	Rapid production of MnO ₂ precipitate Training required for handling concentrated nitric acid	Limited US BWR history Unstable, must be produced on-site pH control more difficult

Permanganic Acid (HP)

HP consists solely of a dilute solution (50-300 ppm) of permanganic acid, HMnO₄. There are no other additives. It is employed at a temperature of 190-200 °F and a concentration of about 300 ppm although there are reports of it being effective at as low a concentration as 50 ppm. At a concentration of 300 ppm the pH is about 2.0. This low pH results in HP being an even stronger oxidizing agent than NP, thus allowing equivalent results with a lower concentration in a shorter time. The process is complete in 2-3 hours. The lower concentration and the absence of extraneous ions such as K⁺, Na⁺ and NO₃⁻, result in significantly lower waste quantities than for either AP or NP.

The oxidation reaction in HP is identical to that shown above for NP. Surprisingly, both decomposition and corrosion are much lower than with NP. This result is attributed to the absence of nitrate ions, NO₃⁻ which appears to promote corrosion and catalyze the decomposition reaction shown above. HP is an integral part of the CORD process previously described.

Cleanup Following Oxidation Step

Following the application of either AP or NP (HP is discussed separately below), cleanup of the residual permanganate and dissolution/removal of any deposited MnO_2 is required before the actual decontamination step (CAN-DEREM, CITROX or LOMI) can be applied. This can be accomplished by conversion of all residual MnO_4^- to Mn^{2+} with oxalic acid, as shown by the following reaction, followed by cleanup on ion exchange resin. Any deposited MnO_2 is dissolved at the same time. The chief advantage of this method is that it avoids contact of the IX resin with the strong oxidizer, KMnO_4 , and the possible introduction of resin degradation products into the reactor system. The disadvantages are several: it takes longer; it is more difficult to operate the decontamination equipment since much more gas (CO_2) is generated and almost continuous venting is required; more oxalic acid is required; more spent IX resin is generated.

Historically, some vendors have used direct ion exchange to clean up the permanganate; however, it has been discontinued for safety reasons. In addition to the potential for reaction with the resin, the resin may react later while in storage consideration, which may lead to pressure build up.

HP has only been used commercially as part of the CORD process. Conversion of the residual MnO_4^- to Mn^{2+} is an integral part of that process and a separate cleanup step is not required. Should HP ever be used prior to a CAN-DEREM, CITROX or LOMI application, then cleanup by one of the two methods described above would be necessary.

Decontamination Corrosion Issues

Corrosion issues and test programs relating to the three major decontamination processes employed in North America, CAN-DEREM, CITROX and LOMI, have been reviewed in previous editions of this manual and in the Decontamination Handbook. Therefore, information obtained prior to 1997 will only be discussed briefly as required for continuity. The emphasis of this section will be on tests performed in the period 1997 to 2004.

CAN-DEREM

CAN-DEREM was developed by AECL from the CAN-DECON process after some tests showed that under certain conditions CAN-DECON could cause IGA of highly sensitized material. The cause was established to be oxalic acid and removal of it from the formulation eliminated all concerns regarding IGA. The modified process was renamed CAN-DEREM.

The AP/CAN-DEREM process was one of two evaluated by Westinghouse for the full system decontamination at Indian Point 2. More than 50 different reactor coolant system materials were exposed to one five-step cycle and two four step cycles of AP/CAN-DEREM (equivalent to three FSDs) to obtain data on general corrosion, localized corrosion, stress corrosion cracking, and the influence of exposure on other material properties. A separate set of coupons was exposed to one five-step cycle of off-normal (i.e. "fault") conditions. The types of evaluations performed included weighing, dimensional measurements, visual examinations, sensitization etching,

hardness measurements, surface roughening measurements, and destructive examinations. Key observations from these tests include the following:

- maximum general corrosion metal loss of 50 mils (after three multi-step applications) on A-533 low alloy carbon steel (e.g., reactor pressure vessel and pressurizer);
- less than 1.1 mils general corrosion loss on all other metals, alloys and ceramics;
- slight etching of graphitar;
- color and weight change of Crane packing;
- less than 1 mil of surface roughening on 400 series stainless steels;
- deepest penetrations less than 1 mil on stressed specimens;
- no surface penetration on stressed Alloy X-750 springs;
- chromium plating microcracks opened and interfacial attack under the chromium plate on the Type 410 stainless steel;
- no stress corrosion cracking;
- no acceleration of stress corrosion cracking initiation kinetics on Alloy 600.

These evaluations demonstrated that full RCS chemical decontamination using the AP/CAN-DEREM process can be performed with a high degree of confidence, and that significant impacts on plant equipment will not occur.

Based on these positive findings, a full system decontamination was performed at Indian Point 2 in March, 1995. Examination of corrosion specimens and coupons that were exposed to FSD solvents at Indian Point 2 did not reveal any material compatibility issues that would have an impact on operation of the plant following the decontamination. Detailed assessments are available. Key observations were:

- General corrosion of 304 SS, 316 SS, mill annealed Alloy 600, and Stellite™ 6B was at least a factor of two lower than that observed in the qualification program. The first three materials had penetrations of <0.01 mils while Stellite 6B had approximately 0.02 mils.
- Corrosion of 410 SS was higher than expected from the qualification program (0.016 mils expected versus 0.04 mils observed). However the actual penetration was still very low and Westinghouse engineers had previously established that a metal loss of 0.15 mils would still be insignificant.
- There were no indications of crack initiation in the 410 SS bent beam, sensitized 304 SS U-bend, Alloy 600 mill annealed reverse U-bend, Alloy 600 thermally treated reverse U-bend, or Alloy 690 reverse U-bend specimens.
- The corrosion penetration of the cobalt-free hard facing alloy, Norem 02, was low (0.01 mils) and there were no indications of intergranular attack or surface roughening.
- The only materials that exhibited any significant corrosion during the decontamination were the Deloro 50 and Colmonoy 4 hardfacing alloys, which suffered corrosion losses of 0.14 and 0.20 mils, respectively. These losses were attributed, in part, to the welding procedure used to fabricate the test specimens.

CITROX

The only published references dealing with corrosion in dilute CITROX date back to the 1980s. IGA up to 75 μm (3 mils) was reported on stressed specimens and IGSCC was observed on CERT specimens that were subsequently exposed under BWR conditions. The vendor attributed these results to a combination of high ferric iron concentration and high sensitization. Based on work performed at AECL during development of the CAN-DEREM process, it seems more likely that these results were due to exposure to oxalic acid.

Ferric ion corrosion can be a problem with CITROX since there is not a strong chelant in the solvent to complex the ferric ions as there is with CAN-DEREM. This concern is minimized in field applications by ensuring that the total dissolved iron concentration is maintained at less than 20 ppm (less than 10 ppm preferred) through adequate online cleanup with ion exchange resin.

For these reasons CITROX is generally not employed for primary system decontaminations. It was not one of the processes selected by Westinghouse and EPRI for evaluation for full system applications. However, it is regularly employed for subsystem decontaminations, such as the RWCU, RHR and fuel pool cooling systems, because of its high degree of effectiveness and simplicity of application. Components in these subsystems can more easily be inspected and replaced if required, but in practice replacement has never been necessary. Results from a multitude of field applications have not confirmed the IGA observed in the laboratory testing. This is most likely because in field applications the base metal is protected from direct contact with the solvent for most of the decontamination. It is only for the last hour or two that the base metal is actually exposed. During laboratory testing there is no protective oxide and the base metal is exposed for the entire period of the test. Exposure time is certainly a relevant factor. In the lab testing, specimens exposed to a three-step process (CITROX/AP/CITROX) invariably showed much more IGA than those exposed to a single CITROX step. The difference cannot be attributed to the AP step, which is benign compared to CITROX.

LOMI

Extensive corrosion testing of the LOMI, AP/LOMI and NP/LOMI processes for subsystem applications was performed in the 1980s. In the 1990s, evaluations were performed for a full system application of the LOMI process in BWRs and of the AP/LOMI process in PWRs. The latter program was performed by Westinghouse and was very similar to that described above for the AP/CAN-DEREM qualification program. Results of all these programs can be summarized as follows:

- Corrosion of all 300 series stainless steels and nickel alloys such as Alloys 600 and X-750 showed very low corrosion rates ($<0.1 \mu\text{m/hr}$) during typical LOMI applications.
- Corrosion of the 400 series stainless steels was slightly higher at $0.5\text{--}1.0 \mu\text{m/hr}$.
- Carbon steels and low alloys steels exhibit corrosion rates in the range $1\text{--}2 \mu\text{m/hr}$.
- The above corrosion rates may increase by a factor of between 5 and 10 during exposure to spent and faulted LOMI conditions.

- LOMI does not cause IGA or IGSCC, nor does it exacerbate existing IGA or IGSCC. This conclusion applies to all materials found in BWRs and PWRs, including sensitized stainless steels and nickel alloys, and low alloy steels.
- IGA up to 15 μm (0.6 mils) was observed on furnace sensitized specimens of SS 304 and Alloy X-750 following exposure to six cycles of AP/LOMI under PWR conditions.
- The NP/LOMI process was shown to cause:
 - propagation of IGSCC and TGSCC from fatigue cracks in SA-302;
 - IGA of up to 10 μm in sensitized specimens of Alloy 600, SS 304 and SS 321;
 - enhanced crack growth rate (by a factor of 29) in WOL specimens of A-508;
 - enhanced general corrosion of low alloy steels relative to LOMI and AP/LOMI.

The final result of this testing was that the LOMI process was considered fully qualified for all BWR applications and the AP/LOMI process for all PWR applications. The AP/LOMI and NP/LOMI processes may be acceptable for some BWR applications subject to a case-by-case review and possible additional testing. The same conclusion applies to the NP/LOMI process for PWR applications.

In 1996, additional testing of the AP/LOMI process was performed to qualify it for a “loop-stop to loop-stop” decontamination at the Zion plant. Previous qualification testing results were reviewed and compared to the ZION RCS materials for applicability. Those materials that could not be reconciled were tested as part of this program. In addition, extensive testing on mill-annealed Alloy 600 was performed to determine the influence of decontamination solutions on samples with pre-existing flaws. Key observations from this program were:

- Based on measurements obtained on roll transition specimens, C-rings and reverse U-bends of Alloy 600, no appreciable differences in subsequent primary water SCC rates were observed.
- Coupons of SA-182, Grades F11 and F22, showed corrosion losses of 2.9 and 1.7 mils, respectively. There was no enhancement of these rates in crevice environments. Metallographic sections of the coupons showed some roughening of the surfaces on F11 and shallow pitting to a depth of approximately 2 mils on F22. Limited corrosion to this extent is not significant for valve stems and seats.
- Stressed bent beams of SA-182, Grades F11 and F22, above their yield strength gave no indication of stress corrosion cracking or localized attack.
- Low temperature (<200°F) crack extension was observed in both AP/LOMI and pure water reverse U-bend specimens of mill annealed Alloy 600. This result was unexpected. It was attributed to the prior precracking operation in high temperature steam plus hydrogen.
- Apart from the previous observation, the data generated in this program supports the conclusion that application of the AP/LOMI process will not contribute to steam generator tube degradation.

The assertion that the crack propagation observed in the reverse U-bend specimens of Alloy 600 was due to the pre-cracking operation in high temperature steam plus hydrogen could not be definitively proven. Since any risk of increasing the susceptibility of the Zion steam generators

System and Component Decontamination

to additional PWSCC was unacceptable, the decontamination process for Unit 1 in the 1995 fall outage was canceled. The reasons for performing a loop-stop to loop-stop chemical decontamination are still valid, therefore additional testing is warranted to determine the cause of the unexpected crack extension and to verify that the risk of affecting steam generator tube integrity is small enough to be inconsequential.

In the period 1995-1998 additional corrosion testing was performed with the NP/LOMI process. This testing was necessary since it had been found empirically that the oxide films formed in BWRs after prolonged exposure to HWC could only be effectively dissolved with this process. In summary, it was found that:

- The corrosion database for NP/LOMI has been significantly expanded and is now equivalent in both quantity and quality to any other decontamination process in use.
- Several materials qualification programs and in-plant applications provide strong support that the process can be used with minimal risk for RRS and subsystem decontaminations.

There are still some unresolved issues with respect to FSDs that include the RPV:

- general corrosion of carbon steels and low alloy steels under faulted LOMI conditions
- crack propagation in stainless steel-clad low alloy steels
- dendrite attack in Inconel 182

It remains for the plant owners to work with the NSSS and the decontamination vendors to determine, on a plant-specific basis, if the database is sufficient to support use of the NP/LOMI process. For RRS and subsystem decontaminations, the evidence appears overwhelmingly positive. For FSD applications, the extent of additional corrosion testing would need to be evaluated on a plant-specific basis.

CORD

Siemens/KWU personnel have been employing the use of the CORD process since 1983. A summary of the available CORD process information is presented in Table 7-7. This information was extracted from three references.

Attack of chromium-plated materials by CORD has been reported. This is similar to that reported for the AP step and is undoubtedly due to the HP oxidation step.

Siemens/KWU provided the following information: *“All materials in contact with the decontamination chemicals have been tested. No detrimental effects such as material loss or local corrosion have been observed.”*, and *“The material compatibility test data for CORD are sufficient to prove that no adverse effects are expected due to decontamination.”* Their current philosophy regarding process qualification can be summarized as follows: *“Due to the number of decontaminations performed, the material qualification tests are increasingly less important. Decontamination processes have been applied in many nuclear power plants for years with good results and without any problems. This practical field experience is better proof of material compatibility than would be possible on a laboratory scale with small coupons.”*

Table 7-7
Summary of Materials Compatibility Data for the CORD Process

Material	Corrosion in Typical Application		Visual Observations
	(mils)	(μm)	
SS 304	0.004-0.04	0.1-1.0	Surface roughening of <1 mil
SS 304 welds (bent beam specimen)	.		After decontamination, specimens exposed to BWR conditions. No IGA or IGSCC
SS 308L	0.03	0.8	Surface roughening of <1 mil
SS 321	0.008	0.2	
SS 347	0.02	0.5	
SS 410	0.22	5.6	Slight attack with grain boundaries accentuated
SA 508 Cl. 2 (clad crack specimen)			Pitting 2 mils deep
SA 533 Cl 1 (clad crack specimen)			Pitting 2 mils deep
Alloy 600	0.01-0.03	0.3-0.8	No localized corrosion
Alloy 800	0.015	0.4	
Zircaloy 4	0.0006	0.015	Unaffected. No attack.
DIN 1.4122	0.08	2	
DIN 1.4313	0.08	2	

BWR Decontamination

Effects of BWR Hydrogen Water Chemistry (HWC) and Zinc on Decontamination

Background

HWC was proposed by General Electric in 1977 to reduce oxygen levels in BWR primary coolant, which would in turn reduce the susceptibility of the primary system piping to stress corrosion cracking. It was first employed at Dresden-2 in June, 1983 and a summary of this regime's application is captured in Section 6 of this document.

It was recognized early in the program that the change in redox potential from oxidizing conditions (+0.3 V vs SHE) to less oxidizing (~0 V vs SHE), and eventually to reducing (−0.23

V vs SHE), would have some effect on the composition of the oxide film on system surfaces and might affect the effectiveness of decontamination processes. However, over the next 10 years very little effect was observed. Decontamination factors of 5-10 were routinely obtained with a single step application be it CAN-DEREM, CITROX or LOMI. Addition of an oxidizing step, generally AP, increased the DFs to greater than 10. But commencing with the decontamination at Monticello in February, 1993, some difficulties began to be encountered. A DF of only 2 was obtained in an RRS decontamination even though three steps (LOMI/AP/LOMI) were applied. Monticello had been on HWC for four years at this time. During earlier decontaminations in 1989 and 1991, DFs in the range of 10-30 were obtained.

Plant Experience

An experience similar to that at Monticello occurred at Brunswick. HWC was initiated in Unit 2 in 1989 and in Unit 1 in 1990. Three RRS decontaminations were performed in the period 1990 to 1993 with DFs in the range 5-10 being obtained. However, in 1994 a DF of only 1.5 was obtained following a decontamination of the Unit 2 RRS even though a three-step process was used (CITROX/AP/CITROX). Artifact testing prior to a similar decontamination of Unit 1 in 1995 showed a DF of only 2 with both a three-step AP/LOMI and a three-step AP/CITROX decontamination. Addition of two more steps increased the DF to about 4 in both cases. This was still well below the utility's goal of a DF >10. Substitution of NP for AP resulted in a DF of greater than 100. Based on this result a two-step process (NP/LOMI) was applied in the plant. The initial LOMI step was eliminated based on the artifact testing that indicated negligible activity removal. The application was highly successful with DFs of 11 and 54 being obtained on the RRS discharge and suction sides, respectively.

The reason for the failure of AP and the success of NP at Brunswick is because of changes in the oxide composition brought about by prolonged exposure to HWC at hydrogen concentrations of 1-2 ppm in the feedwater. When HWC was first initiated at Brunswick, the concentration of H₂ in the feedwater was <1 ppm. Over the next few years it was slowly increased to 1-2 ppm on the advice of General Electric when new data indicated that less than 1 ppm H₂ did not provide adequate protection against IGSCC to all vessel internals. Analysis of the oxide film in 1995 indicated a high proportion of chromium (39%) and some nickel (15%). The oxide film appears to become more tenacious and protective after prolonged exposure to HWC. "Low" HWC (i.e., less than 1 ppm H₂ in the feedwater) does not appear to have a significant effect on the film composition. This is the reason for the apparent lack of effect of HWC observed during the first 10 years of operation with HWC, as discussed above. "High" HWC (i.e., 1-2 ppm H₂ in the feedwater) appears to have a much more rapid effect on the formation of high chromium and high nickel films. Recent research has concluded that a film containing substituted chromites and nickel ferrite is most effectively removed through the use of the NP/LOMI process. AP does not result in adequate oxidation of the chromites formed under HWC. The poor result obtained with AP at Brunswick was not due to zinc. Monticello uses GEZIP while Brunswick does not and both experienced the same result.

Numerous scientific papers describe the reasons for the change in composition of the oxide film in BWRs under HWC and the effect HWC has had on radiation fields. A cross-section of these papers can be found in this chapter's references.

A decontamination at Plant Hatch also required use of the NP oxidation step for effective decontamination. This plant had been on HWC since 1987 and on GEZIP since 1991. As at Brunswick, it appears that a tenacious and recalcitrant deposit had formed. NP was used as the oxidation step during decontamination of the reactor recirculation and reactor water cleanup systems, while AP was used during decontamination of the fuel pool cooling system. The latter was not exposed to HWC and so had not developed the more intractable film. Good decontamination factors in the range 4 to 37 were obtained on the various systems.

Recent decontaminations of BWRs using HWC and zinc injection have applied the NP/LOMI system with good results.

Effects of BWR Noble Metal Chemical Addition

There are several implications for decontamination of plants using NMCA:

1. The much lower hydrogen concentration may slow down conversion of hematite to a spinel-type structure, making decontamination “easier”. The situation may revert to that of the first 10 years of HWC, i.e., no noticeable effect on decontamination. Once again, it may be possible to decontaminate BWRs with a single step process, or, if an oxidizing step is required, the less corrosive AP may suffice instead of resorting to NP.
2. On the other hand, the long-term effect of the very much lower ECP (–0.5 V vs SHE) on oxide film structure, composition and morphology is unknown. The technology is designed to lower the ECP of the coated stainless steel component and the theory behind this is well-documented. (S-7) However, there has been no discussion in the literature of possible effects on the overlying oxide film composition.
3. If the entire system behaves more like a PWR, which traditionally have lower radiation fields than BWRs, then NMCA may lower the rate of radiation field buildup, thus reducing the need for decontamination. Indeed, there is some preliminary evidence from Duane Arnold that this is the case.
4. The presence of small amounts of Pt and Rh in the oxide film is not expected to have any direct effect on the ability of DCD processes to dissolve the film. General Electric has determined their concentrations to be in the range 2-5 atomic %, or $\sim 0.2 \mu\text{g}/\text{cm}^2$. Using Cr as an analogy, it has no noticeable effect on decontamination until its concentration becomes greater than 10%.
5. Decontaminations of two plants using HWC/Zn/NMCA were successful using NP/LOMI. However, mitigation of IGSCC by NMCA may be lost for decontaminated surfaces, as the decontamination solvents remove the noble metals. At one plant, protection was restored by a low temperature reapplication of noble metals after the decontamination using the vendor's decontamination skid.

PWR Decontamination

Effects of Zinc Addition on Decontamination in PWR Plants

Because of the success of zinc injection in BWR plants for exposure reduction, programs were initiated to evaluate zinc injection for PWRs, with the potential benefits expected to be:

- thinner, denser and more protective oxide films;
- lower rate of incorporation of ^{60}Co into the oxide films hence lower radiation exposure;
- mitigation or inhibition of primary water stress corrosion cracking (PWSCC) on Alloy 600 steam generator tubes due to the presence of a more protective oxide

To date there has been no experience with decontamination of a PWR using zinc injection. One of the reasons there has not been a decontamination at Farley is that radiation fields have generally remained low, thus reducing the need for decontamination. There has also been very little laboratory work with zinc-rich films formed under PWR conditions. Zinc injection has recently been started at Diablo Canyon 2, and Palisades, and Beaver Valley, but as of this writing there are no data relevant to decontamination.

Based on experience from BWR plants, it seems that zinc injection will have little effect on the ability of current decontamination processes to perform effectively. However, prudence dictates that an artifact testing program be performed the first time such a decontamination is to be undertaken. If, for example, a zinc-rich outer layer has been formed (possibly zinc ferrite), it may be imperative to remove it by an initial reducing step, rather than applying an oxidizing step that would be totally ineffective. A cost-benefit assessment may have dictated that a four-step process be performed (i.e. start with an oxidizing step), but technical considerations could override it. At this time such a scenario is purely hypothetical but it serves to illustrate the type of situation that could arise with zinc injection. Until there is a significant database of experience with decontaminations of PWRs on zinc injection, an artifact testing program prior to a decontamination should be considered almost mandatory.

In addition to the references cited above, several papers on zinc addition to reactor circuits, principally PWRs, were presented in 1996. The reader is referred to these papers and additional EPRI technical reports for a more complete discussion of zinc addition to PWR primary circuits.

Decontamination Using Hydrolasing and Flushing

High pressure and/or high volume water jets for surface decontamination and localized high activity (hot spot) flushing has been used successfully for decades at the majority of U.S. plants. For some applications, the use of water at elevated temperatures improves the efficiency of both hydrolasing and flushing processes. Hot or warm water has demonstrated improved DFs compared to cold water at several stations. Similar to washing any surface, the hot or warm water may also result in breakdown of chemical impurities that trap crud on the surface.

Hydrolasing employs the use of a positive displacement pump to deliver a very high pressure water stream. The pressurized jet of water is typically applied via a hand held gun/wand with the wand tip in close proximity to the piping or component surface. For some applications the use of self traveling probes, custom wands, and fabricated supports are employed to improve the process efficiency through automatic rates of travel and optimized wand tip-to-surface proximity. A typical portable hydrolasing unit that delivers 8 GPM @ 10,000 psi is illustrated in Figure 7-1.



Figure 7-1
Typical Portable Hydrolasing Unit

Flushing hot spots can be accomplished using either hydrolaser units or high volume water jets. The water acts as an activity transport medium and requires capture and processing using either filtration or ion exchange or a combination of both technologies. Vibration or mechanical shock has proven to enhance this process in some applications.

Experience with Full System Decontaminations

Full system decontamination (FSD) refers to chemical decontamination of the entire primary system of the reactor, including the core. FSDs may be performed with or without the fuel in place. There are many benefits of FSD when compared to smaller subsystem decontaminations. Principal among these are general reduction in radiation fields all around the plant, with consequent saving in radiation exposure of all the workforce and not just those involved with maintenance on a particular system, reduced rate of recontamination since the major source of radionuclides (i.e. in-core deposits) will have been removed, and longer interval between subsequent decontaminations because of the lower rate of recontamination.

System and Component Decontamination

Commencing in 1991, KWU has performed five FSDs employing the CORD process. In the USA, work on qualification of the LOMI process for BWRs and the AP/LOMI and AP/CAN-DEREM process for PWRs commenced in 1987. All qualification work is now complete but to date there has been only one application; the Indian Point 2 FSD using the AP/CAN-DEREM process in March 1995.

Results of the application at Indian Point 2 have been reported. The systems decontaminated were: 1. reactor coolant system including the vessel and steam generators, 2. residual heat removal system, 3. most of the chemical and volume control system, and 4. portions of the primary sampling system.

The process consisted of the following steps:

1. initial CAN-DEREM step to remove outer iron-rich layer
2. AP step to oxidize exposed chromium
3. oxalic acid rinse to remove residual MnO₂
4. second CAN-DEREM step
5. second AP step
6. second oxalic acid rinse
7. third CAN-DEREM step
8. final cleanup of water to specifications for refueling

Some highlights are given below:

- fuel and control rod drive shafts removed,
- reactor head reinstalled with all of the studs torque,
- three of four main pumps operating to provide flow and heat,
- operations (i.e., pH 5-8, conductivity <10 μ S/cm and total
- organic carbon <5 ppm)
- each CAN-DEREM step lasted about 20 hours, each AP step about 14 hours and each oxalic acid rinse about 10 hours
- total gamma-emitting activity removed was 3,906 curies consisting of 46% ⁶⁰Co, 36% ⁵⁸Co, 8% ¹²⁴Sb, 7% ⁵¹Cr and 3% others (predicted 5,100 curies consisting of 56% ⁶⁰Co, 20% ⁵⁸Co and 24% others)
- 275 pounds of metals removed by FSD consisting of 37% Ni, 33% Cr and 30% Fe (predicted 630 pounds consisting of 26% Ni, 33% Cr and 40% Fe)
- average contact DF was 7.8 based on radiation measurements at 55 locations throughout the plant (goal >5)
- waste resin volume was 1,770 ft³ (goal <2,400 ft³)
- outage dose avoided 650 rem (goal >560 rem)

- estimated dose avoided over next five operating cycles (approximately 10 years) is 3,500 rem (goal >3,000 rem)
- corrosion of all 300 series stainless steels and Inconel 600 <0.01 mils (predicted 0.003 to 0.03 mils)
- corrosion of 410 stainless steel 0.04 mils (predicted 0.016 mils)

In general, most parameters were in reasonable agreement with the goals or predicted values as can be seen from the data presented above. The most notable exception is the amount of deposit removed. It had been estimated that 630 lb. of deposit (metals only) would be removed whereas only 275 lb. was actually removed. The estimate was based on 15 different plant samplings of both SG tubes and stainless steel surfaces. Obviously these samplings were not representative of the deposits found in IP-2.

Corrosion of 410 stainless steel was about 2.5 times that expected but the actual penetration of 0.04 mils was still very low. Westinghouse engineers had determined that a metal loss of 0.15 mils was still considered insignificant.

All waste IX resin was placed in high integrity containers (HIC), dewatered and shipped to Barnwell, SC for disposal. Prior to burial each HIC was placed inside a concrete overpack in accordance with the site licensing requirements.

Decontamination Wastes

Current Situation

The waste resulting from DCD applications consists almost entirely of spent ion exchange resin. All waste water is usually processed by the decontamination IX system to purity levels such that the plant will retain the water for internal use. If filters were employed during the application, the cartridges or bags are usually placed in the waste container along with the IX resin. More recently backwashable filters have been employed to eliminate handling of highly radioactive cartridges or bags and thus minimize radiation exposure of the DCD crew. These filters can be backwashed to either the plant's radwaste system or the DCD IX system.

The currently preferred method of disposal of spent IX resins is dewatering of resins, off-site volume reduction, and disposal of the residual waste volume in a high-integrity container (HIC). Studsvik, Inc. employs a pyrolysis technology for IX resin that is installed at a former nuclear fuel fabrication site in Tennessee. This proven technology was developed in Sweden and is now commercially available in the U.S. Their facility is currently processing a variety of wastes such as ion exchange resins, chelates, and non-metal filters. Studsvik does have activity and chemical characteristic limitations that should be evaluated during the planning phase of a chemical decontamination project.

As of this writing, the only resin waste form acceptable for direct disposal at Barnwell is dewatered in a HIC plus a concrete overpack for the HIC. The use of concrete overpacks was instituted by the State of South Carolina as part of more stringent licensing requirements for

continued operation of the Barnwell site beyond 1995. Barnwell has an upper limit of 8% chelates in the waste.

At Hanford there is no upper limit on the chelate content of the waste. However, the site does require that chelated wastes (>0.1 wt%) be stabilized and segregated from other wastes. In practice, this means the resin is dewatered in a HIC. If a high density polyethylene (HDPE) HIC is used, it is placed in an engineered barrier. This site only accepts waste from the northwest states and those belonging to the Rocky Mountain Compact.

The Envirocare site in Utah has been in operation since the 1970s accepting Class A wastes making anion and polishing resins from DCDs acceptable for burial if they meet license requirements.

Another option for nuclear power plants is long term storage of the IX wastes on the plant site. However, in some instance this is not allowed by law, and would only be used if no other alternative was available. The structural integrity of the waste resin relative to its long term storage exposure to both chemicals and high activity levels should be carefully assessed prior to implementing this option to ensure the media's physical characteristics will remain intact.

Mixed Waste Issues

Mixed wastes are defined as those which are both hazardous and radioactive. Such wastes cannot be directly buried at any of the licensed radioactive waste disposal sites. Process options are available for converting mixed wastes to a form acceptable for monitored, shallow land disposal, however, those processes are typically very costly and can significantly impact the cost effectiveness of related projects.

The one component of the waste that has the potential to create a mixed waste, particularly in wastes from PWR decontaminations, is chromium. The EPA limit for chromium for a non-hazardous waste is 5 ppm.(S-1) Since DCD resin wastes may contain as much as 1,500 ppm chromium, a special test must be performed to demonstrate that the leachate from the final resin form is <5 ppm. This test is referred to as the toxic characteristic leach procedure, TCLP. It involves leaching the sample with a solution of acetic acid adjusted to a pH of 4.5. Provided the chromium content of the leachate does not exceed 5 ppm the waste can be classified as non-hazardous. To date all DCD resin wastes have easily passed the TCLP requirements. However, the EPA has proposed a revised rule which would dramatically lower the allowable chromium concentration in the leachate.

Key Considerations – System And Component Decontamination

A synopsis of the most important decontamination program elements.

1. Decontaminations are more cost effective in BWRs due to the activity levels and most importantly, the number of person hours spent in radiation fields for plant operation and maintenance resulting from the inherent plant design and structural configuration.

2. LOMI-NP is the currently the most widely used chemical decontamination process, the combination of NP and LOMI was found to be the most effective process for BWRs operating on hydrogen water chemistry with relatively high hydrogen concentrations to protect core internals.
3. A full-system decontamination was performed at Indian Point 2 in March, 1995 using the AP/CAN-DEREM process. Examination of corrosion specimens and coupons that were exposed to the decontamination solutions did not reveal any material compatibility issues that would have an impact on subsequent plant operations.
4. “Low” HWC (i.e., less than 1 ppm H_2 in the feedwater) does not appear to have a significant effect on the film composition and subsequently the decontamination factors attained.
5. “High” HWC (i.e., 1-2 ppm H_2 in the feedwater) appears to have a much more rapid effect on the formation of high chromium and high nickel films. Recent research has concluded that a film containing substituted chromites and nickel ferrite is most effectively removed through the use of the NP/LOMI process. AP does not result in adequate oxidation of the chromites formed under HWC.
6. The HP/CORD UV process appears to be effective in dissolving the oxide film formed under HWC as evidenced by recent average decontamination factors of 40.7 at one unit.
7. Plants using HWC/Zn with or without NMCA have been successfully decontaminated by applying NP/LOMI, but the decontaminated surfaces lose the IGSCC mitigation benefits of noble metals.
8. The use of hydrolasing and high volume flushes may be adequate for some decontamination applications. The activity reduction results will generally be significantly lower than chemical decontamination processes.
9. Solid waste disposition for any decontamination process can be a critical cost and personnel exposure issue and should be carefully evaluated and incorporated into the process plan.

References

- 7-1. Decontamination Handbook, EPRI, Palo Alto, CA: July 1999, TR-112352
- 7-2. D. Bradbury, G.R. Elder and S.M. Scrivens, “EPRI LOMI-2 Decontamination Process”. EPRI Report TR-108740, May, 1998.
- 7-3. Code of Federal Regulations, Section 40, Chapter 1, Part 261, Identification and Listing of Hazardous Wastes. 7-1-89 Edition. Ibid. Appendix II - EP Toxicity Test Procedures.

8

ULTRASONIC FUEL CLEANING

History and Status

Ultrasonic fuel cleaning was originally developed for PWRs to enable them to operate with higher fuel duty and longer cycles. Under these conditions, sub-cooled nucleate boiling may occur in the upper fuel spans with resulting axially-asymmetric deposition of corrosion products. Boron can hide out in these deposits, causing a local flux depression called either axial offset anomaly (AOA), or more recently, crud induced power shift (CIPS). Ultrasonic fuel cleaning is an effective means for removing PWR fuel deposits, hence mitigating the AOA problem. When ultrasonic fuel cleaning was applied at PWRs for the mitigation of AOA, a reduction in ex-core dose rates, and consequently personnel exposure, was also observed. At the Callaway PWR, dose rate reductions on the order of 50% were observed for an outage following operation with cleaned reload fuel. Such reduced radiation fields can have a significant favorable impact on personnel dose, and these ALARA benefits can be advantageously achieved at BWRs as well. EPRI has sponsored modeling calculations by Westinghouse for PWRs and General Electric for BWRs to estimate the dose reductions to be expected through effective removal of corrosion products from reload fuel.

The EPRI ultrasonic fuel cleaning technique is ideally suited for fuel cleaning because it can remove deposits from an intact fuel assembly and the process does not produce any ancillary wastes other than the dislodged deposits. Earlier efforts at ultrasonic fuel cleaning were unsuccessful because the planar ultrasonic technology used for these earlier embodiments could not direct sufficient energy onto the inner fuel rods without simultaneously over-exciting the peripheral rods. The result was an unacceptable tradeoff of loss of fuel pellet integrity in the outer rods, or inadequate cleaning of the interior rods. The EPRI technique solved the problems of these earlier ultrasonic cleaning methods through use of an optimum arrangement of special transducers that create a radial energy field. The resulting ultrasonic energy field is able to “see around” the intervening fuel rods into the very center of the assembly, in effect producing an energy field of relatively uniform intensity throughout the fuel matrix. The interior rods of a fuel assembly are thus cleaned effectively, while limiting the energy intensity on peripheral rods to maintain pellet and cladding integrity.

That the process is benign toward fuel integrity was first inferred from results at the Callaway PWR, where no fuel failures attributable to the ultrasonic process have occurred; neither in the sixteen lead test assemblies, nor in two fuel cycles of fully cleaned reload fuel. In developing the technology for BWR use, hot cell studies were done of irradiated BWR fuel segments. These studies included microscopic examination of the fuel surfaces before and after ultrasonic excitation, as well as metallographic cross-sectioning, neutron radiography, and other tests to

confirm that ultrasonic excitation at the levels used for fuel cleaning did not harm the fuel cladding or fuel pellets.

Ultrasonic Fuel Cleaning for PWRs

Full reload fuel cleaning was first performed at the Callaway PWR, and the prototype fuel cleaner is still in use at this plant for cleaning fuel for successive outages. Fuel cleaning, perhaps in concert with other mitigation techniques, has rid this plant of its persistent history of AOA. For this reason, the utility considers the technique a success, and looks upon ex-core dose reduction as a secondary benefit.

South Texas Project instituted fuel cleaning as a means of safely achieving higher fuel duty, thus enabling rapid cost recovery of the cleaning system through more aggressive core designs using fewer feed-fuel assemblies. STP has implemented fuel cleaning at both units, and estimates a cost saving of four (4) feed-fuel assemblies per core. At the STP-2 outage in 2002, approximately 100 assemblies, all reload fuel, were cleaned. The work required a total of 46 mRem of dose and 286 hours of radiological work.

More recently, the Vogtle plant has implemented fuel cleaning. This plant intended to operate with zinc addition, and fuel cleaning was seen as a pro-active measure to reduce zinc demand and avoid potential fuel cladding problems.

Ultrasonic Fuel Cleaning for BWRs

As discussed above, the original incentive for developing fuel-cleaning methods was to mitigate AOA in PWRs. Although BWRs do not suffer from AOA, using ultrasonic fuel cleaning to remove crud from BWR fuel cladding surfaces will likely have several advantages:

- Mitigation of potential crud-related fuel problems, as discussed in Section 5, especially for plants with high iron levels.
- By removing the largest source of ^{60}Co , reactor water concentrations of this isotope will be reduced, which will in turn result in lower radiation fields and reduced demand for depleted zinc.
- Fuel cleaning after NMCA will remove high concentrations of noble metal from the fuel surfaces, allowing higher loading of noble metals on core internal surfaces during NMCA. This higher loading can offset the lack of redistribution of noble metal from fuel, which is believed to increase the durability of noble metals in providing NMCA mitigation.

The above points suggest that ultrasonic fuel cleaning can be of real benefit for BWRs, especially if cleaning occurs immediately following NMCA application. As noted in the NMCA Application Guidelines, the parameters for NMCA may need to be modified if NMCA is combined with fuel cleaning. The relatively high concentration of noble metals residing on the fuel after conventional NMCA application may serve as a source term for replacing the non-fuel noble metals as the latter are eroded or eluted from the plant components while in service. If such replacement redistribution from fuel to non-fuel surfaces is shown to be a significant mechanism, the presence of noble metals on fuel may increase the minimum interval between

reapplications of NMCA. Therefore, it may be necessary to use higher noble metal concentrations initially to avoid more frequent reapplication of NMCA if the fuel is cleaned immediately following NMCA.

The option of cleaning BWR fuel was first considered (but not used) at River Bend in 1999 as a means of recovering high-crud loaded, but low-exposure, fuel assemblies. Mockup and laboratory tests were conducted, forming the basis of a preliminary conclusion that ultrasonic fuel cleaning could be an effective method for BWRs.

BWR fuel cleaning was re-addressed by Exelon in 2003 as one factor in this Utility's comprehensive effort to reduce the comparatively high dose rates at Quad Cities. Design of a fuel cleaner adapted to BWR fuel was completed under a joint EPRI/Utility program with Exelon, TVA and Constellation as the utility participants. Construction of the BWR fuel cleaner was completed in January 2004, with demonstration tests in the Quad Cities fuel pool in January 2004, followed by cleaning 16 lead use assemblies (LUAs) that were reloaded following the Quad Cities 2 refueling outage in February/March 2004.

Crud Removal Characteristics

The crud on reactor fuel is generally characterized as either loose or tightly adherent. BWRs under normal water chemistry generally have mostly loose material. Under hydrogen chemistry, the relative amount of tightly adherent crud increases as a consequence of the more reducing conditions in the primary coolant. For the same reason, PWR crud tends to adhere more tightly to the fuel. The experimental work, both at Callaway for PWR fuel, at Vallecitos Nuclear Center for Duane Arnold BWR fuel segments, and at Quad Cities for the pilot and LUA cleaning, indicated that the loose deposits are effectively removed via ultrasonic cleaning. The more adherent deposits are removed to a lesser extent. This feature of the cleaning efficacy can be used to advantage, because the radioisotopes that redistribute from fuel to ex-core surfaces tend to be part of the loose crud layer. Thus the fuel crud that is most responsible for the shutdown dose rate will be preferentially removed, without unnecessarily adding to the rad-waste burden by transferring the tightly adherent crud from fuel to the filters. This strategy can also be of benefit when ultrasonic fuel cleaning is used at BWR plants using noble metal chemical application (NMCA) to control electrochemical potential of vessel-internal materials. NMCA is used for the purpose of IGSCC mitigation, however its application is limited by concern for the effect of the noble metal depositing on fuel. The noble metal tends to incorporate in the loose crud layer on fuel. However, if the fuel is cleaned following NMCA, most of the noble metal is removed, even after high levels of NMCA. The concern for fuel integrity is thereby reduced while allowing sufficiently high NMCA application to mitigate IGSCC.

General Description of Fuel Cleaning Equipment

The EPRI fuel cleaning system consists of one or multiple cleaning chamber(s), provision for pumping fuel-pool water through the cleaner, and a waste-collection module. The cleaner and waste collection modules are interconnected with flexible hose, so the installation can be adapted to the space available at the plant. The cleaning chamber consists of a rectangular channel that contains the fuel assembly to be cleaned, surrounded by the matrix of ultrasonic transducers, and

an external reflector-channel to reflect and focus the ultrasonic energy into the fuel assembly. The transducers are powered and controlled from an instrument console located on the pool deck. Pool water is drawn into the open top of the cleaning chamber, carrying away the dislodged corrosion products to the bottom, through the flexible hose, into the waste collection module, and back to the pool. A centrifugal pump has commonly provided water flow, although a recent version of the fuel cleaning system has used a jet pump for this purpose. Currently, waste collection has been through a bank of disposable cartridge filters, although alternate collection options have been explored as well. The spent cartridge filters are designed to encapsulate the collected corrosion products and can be stored in the pool or processed as radioactive waste at the option of the utility.

Current fuel cleaners commonly use a dual-chamber design. Having two chambers available to receive fuel allows one assembly to be cleaned while the spent fuel bridge is used to return the previously cleaned assembly to its storage location and fetch the next assembly from the racks. This arrangement speeds throughput and minimizes the impact of fuel cleaning on critical path. Since the fuel cleaning production rate is not limited by fuel cleaning itself, but by speed limitations of the fuel handling equipment, it is important to locate the fuel cleaner such that crane-travel time is minimized.

A schematic diagram of one possible configuration of the fuel cleaning system is shown in Figure 8-1. Figure 8-2 shows an artist's rendering of the fuel cleaning equipment as deployed in the spent fuel pool at the South Texas Project PWR, and Figure 8-3 shows the actual South Texas fuel-cleaning module being assembled and lowered into the spent fuel pool.

The PWR and BWR configurations of the ultrasonic fuel cleaning module are similar, with several important exceptions related to differences in design and performance of PWR vs. BWR fuel. For example, PWR fuel assemblies do not have an integral flow channel, thus the rectangular cleaner channel that receives the fuel assembly is solid and forms the flow path for the cleaning operation. Also, corrosion products tend to deposit primarily in the upper (boiling) regions of the fuel, thus the PWR cleaner has transducers only in the upper half of the cleaning module. On the other hand, BWR fuel has an integral channel, which is used as the actual flow path during cleaning. Thus the cleaner's fuel-receiving channel serves the purpose of alignment only, and can be of a minimal, perforated design. But since corrosion products tend to deposit along the entire length of BWR fuel, transducers are positioned along the entire length of the fuel-cleaning channel. In addition, a BWR channel is relatively rough, and contains some amount of corrosion product deposits, thus requiring higher transducer energy for the same degree of penetration into the fuel bundle. Finally, BWR fuel tends to have more massive deposits, and the activity is primarily the long-lived ^{60}Co isotope, compared to the principal ^{58}Co activity on PWR fuel. Thus, fuel cleaning a BWR generates more waste of higher, more persistent activity, and this fact needs to be considered in planning for storage or disposal of the waste.

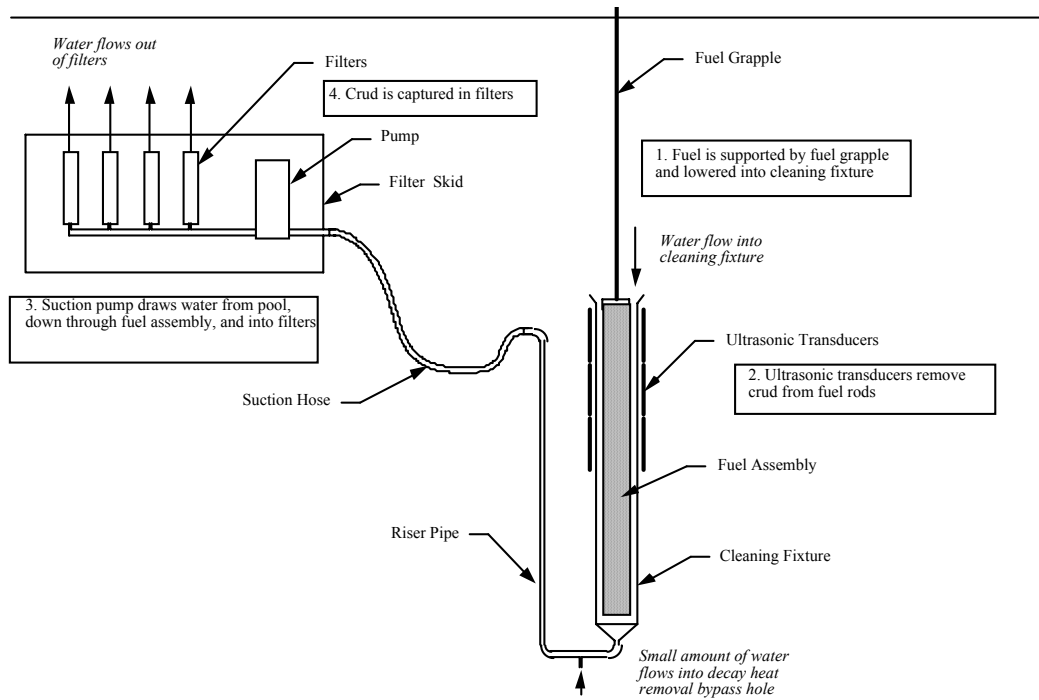


Figure 8-1
Schematic of EPRI's ultrasonic fuel cleaning system.

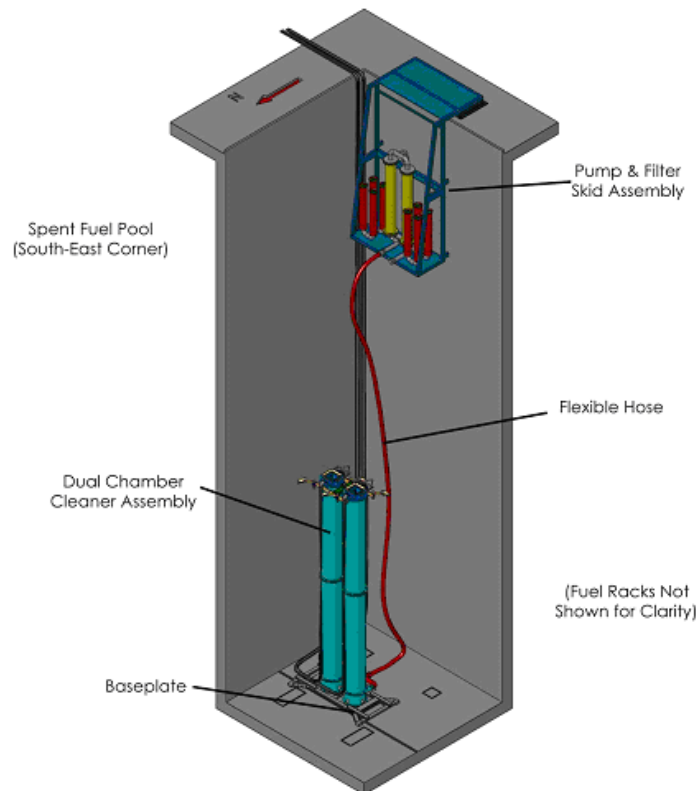


Figure 8-2
South Texas Ultrasonic Fuel Cleaning Equipment



Figure 8-3
STP Transducer Basket Insertion into Reflector Housing

Technical Issues

Mitigating AOA

As stated in the introduction, the original purpose of fuel cleaning was to mitigate AOA in high-duty PWR cores. This phenomenon is caused by driving the core hard enough to cause sub-cooled nucleate boiling in the upper reaches of the core. The boiling favors increased deposition of corrosion products, which incorporate boron. The shift in the neutron spectrum caused by the crud and increased neutron absorption by the hide-out boron depresses the power in the upper part of the core, retaining higher reactivity in this area than predicted by the core design calculations, and thus reducing shutdown margin late in the cycle. Fuel cleaning can mitigate AOA, or at least delay its onset later into the fuel cycle, by removing a significant fraction of crud from the reload fuel.

Shutdown Dose Reduction with Fuel Cleaning

The dose rate benefits from fuel cleaning for PWRs have been estimated from calculations using the Westinghouse CORA code (Ref: EPRI 1003125). The modeling was based on parameters and operating characteristics for the 4-loop Westinghouse PWRs, Diablo Canyon – 1 and Callaway. The CORA calculations suggest that ultimate shutdown dose rates at Diablo Canyon would be halved with regular, effective fuel cleaning, compared to the no-cleaning option. Likewise, CORA determined a roughly 30% reduction in Callaway's shutdown dose rate if full-reload cleaning is done every refueling outage.

At this writing, Diablo Canyon has never cleaned fuel. However, Callaway has cleaned its reload fuel for three cycles, thus the modeling estimates can be directly compared with plant data. Callaway has on-line radiation instrumentation at several plant locations, which makes it possible to trend radiation buildup as a function of time while the plant is at power. Dose rate data for the CVCS letdown heat exchanger inlet are shown for the most recent plant cycles in Figure 8-4, confirming a general decrease in dose rate for the post-cleaning fuel cycles; from Cycle 11 onward. The trend lines show that dose rates at this particular location are affected by other factors such as power reductions and unplanned shutdowns as well as fuel cleaning. In addition, zinc injection started in Cycle 13 may also impact future dose rate experience. However, the trend lines for cycles 11, 12, and 13, which are cycles that follow reload fuel cleaning, are consistently below those of earlier, pre-cleaning cycles. The plant staff estimates a dose rate reduction of as much as 50% attributable to fuel cleaning. This value compares favorably with the 30% estimated by the CORA code calculations.

The trend of Callaway's steam generator dose rates also confirms that the RCS source term is significantly reduced following fuel cleaning. For example, the channel head shutdown dose rate averages show a steadily decreasing trend for succeeding cycles with fuel cleaning, as illustrated in Figure 8-5. A comprehensive survey of the channel heads conducted during RFO 12 shows that dose rates at the bottom of the bowls are considerably lower than those measured during previous outages, suggesting less settling-out of particulates (Ref: EPRI 1007856).

CVCS Heat Exchanger Outlet Dose Rate Comparison

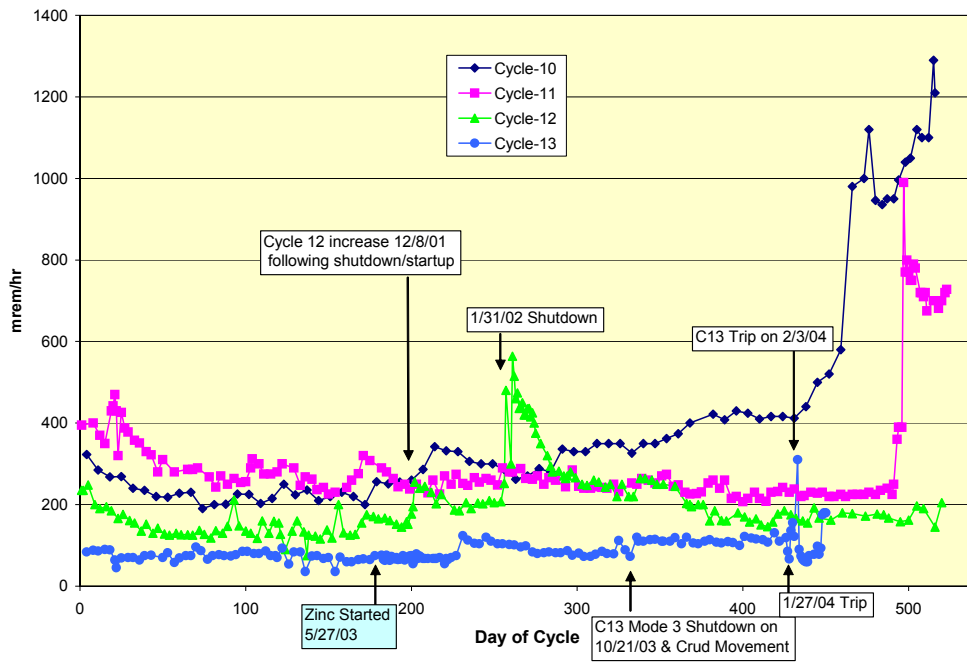


Figure 8-4
Callaway CVCS Heat Exchanger Pre- and Post-Cleaning Dose Rate Trends

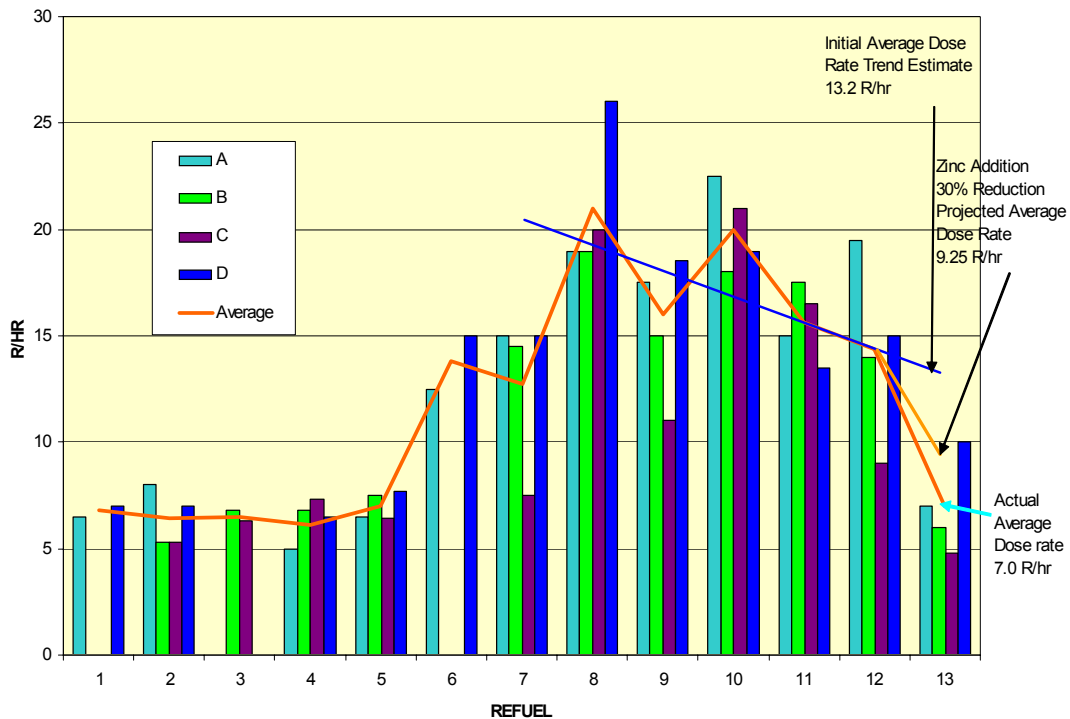


Figure 8-5
Callaway Steam Generator Channel Head Pre- and Post-Cleaning Dose Rates

The most telling ALARA data from the Callaway experience are the effect of fuel cleaning on personnel dose during refueling outages, as summarized in Table 8-1. The total outage man-Rem dose has decreased sharply for outages RFO 11 and 12, compared to the pre-fuel-cleaning outages RFO 9 and 10, even though the number of work hours in the RCA was roughly comparable for all four outages.

Table 8-1
Refueling Outage Worker Dose Trend, Callaway

	<i>RFO-9</i>	<i>RFO-10</i>	<i>RFO-11</i>	<i>RFO-12</i>
TOTAL RCA WORK-HOURS	80,914	98,381	93,191	83,708
TOTAL MAN-Rem DOSE	185.0	305.0	100.5	89.8
DOSE per RCA HOUR	0.0023	0.0031	0.0011	0.0011

Because BWR fuel cleaning is a more recent development, there are no plant data on impact of fuel cleaning on BWR shutdown dose rates. However, General Electric calculated an estimated shutdown dose effect for BWRs using the GENE Dose Rate Model (Ref: EPRI 1002818), in an analogous manner to Westinghouse's PWR calculations. Here too, the calculations suggested a valuable shutdown dose reduction effect from fuel cleaning.

Fuel Cleaning Efficiency

PWR Fuel Cleaning Efficiency

Tests on mock-ups and actual PWR fuel assemblies have shown removal of the simulated deposits to be rapid and uniform throughout the fuel assembly. Mock-up tests suggested that no more than ten minutes of cleaning time is required to remove most of the deposits from the fuel rods [See EPRI Report 1001052 *Pressurized Water Reactor Fuel Cleaning Using Advanced Ultrasonics*, EPRI, Palo Alto, CA, and AmerenUE, Fulton, MO: 2000]. In practice, the required cleaning time is even less, as illustrated for the 2002 STP-2 reload cleaning in Figure 8-6.

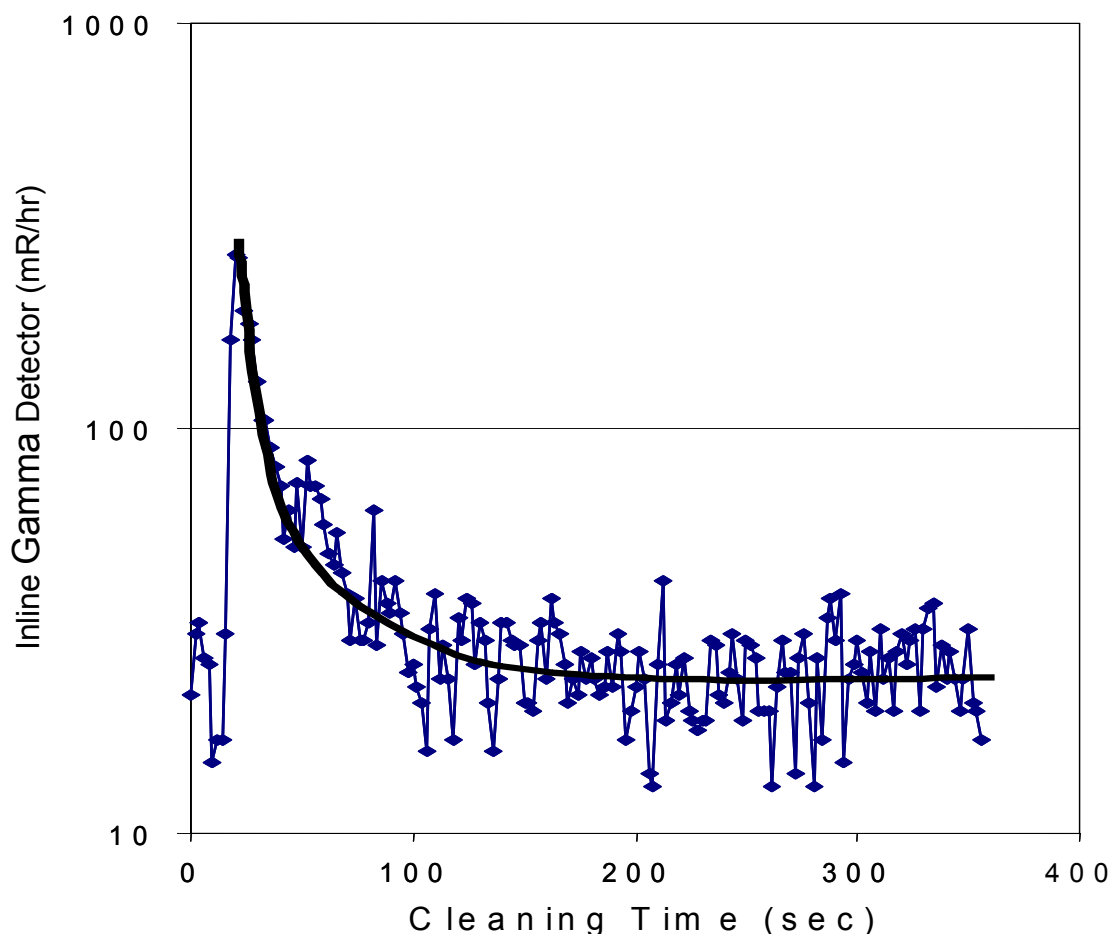


Figure 8-6
Time Required for Ultrasonic Fuel Cleaning STP2 Data

A sampling campaign was carried out with spent fuel in the Callaway fuel pool to establish the quantitative elemental and isotopic composition and removal efficiency that could be achieved with ultrasonic fuel cleaning (refer to EPRI 1003229). The fuel assemblies used for this study had been in stored in the fuel pool for an extended period; one assembly for approximately $\frac{1}{2}$ year, and the other for nearly two years. Hence the deposits were much sparser, and possibly of different composition and structure, compared to fuel deposits on freshly discharged assemblies. However, a review of this work still provides a useful indication of the nature of the deposits removed via fuel cleaning that must ultimately be handled as rad-waste.

Typical of PWR fuel crud, the elemental makeup of the samples was predominantly iron and nickel, with a large mixture of zirconium. Much of the zirconium in these samples is likely fuel clad oxide that was scraped off in the sampling process; however, a significant zirconia component that is truly a component of fuel crud has been reported earlier (refer to EPRI 1003129). The fuel crud activity from assembly M-74 is rich in ^{58}Co , typical of PWR fuel. This assembly had been in the fuel pool for nearly six months; sampling occurred October 2001, while the assembly was discharged from the core in April 2001. The activity of assembly L-80 is relatively higher in ^{60}Co because this assembly had been in the pool for nearly two years; being

discharged from the core in October 1999. The longer decay time had depleted the ^{58}Co relative to the longer-lived ^{60}Co .

The cleaning efficacy data are summarized in Figure 8-7 and Figure 8-8. The data confirm that fuel cleaning removes most of the crud from PWR fuel, although the removal is by no means complete. Interpretation of these sampling data is clouded because the distribution of crud remaining on the fuel was relatively non-uniform, thus it was difficult to sample “before” and “after” areas that were demonstrably identical in crud coverage. The low amount of crud on the fuel after its extended period of storage in the fuel pool added further imprecision to the measurements. However, the data summaries in the figures below illustrate that PWR crud removal via ultrasonic cleaning is typically in the range above 80-85%.

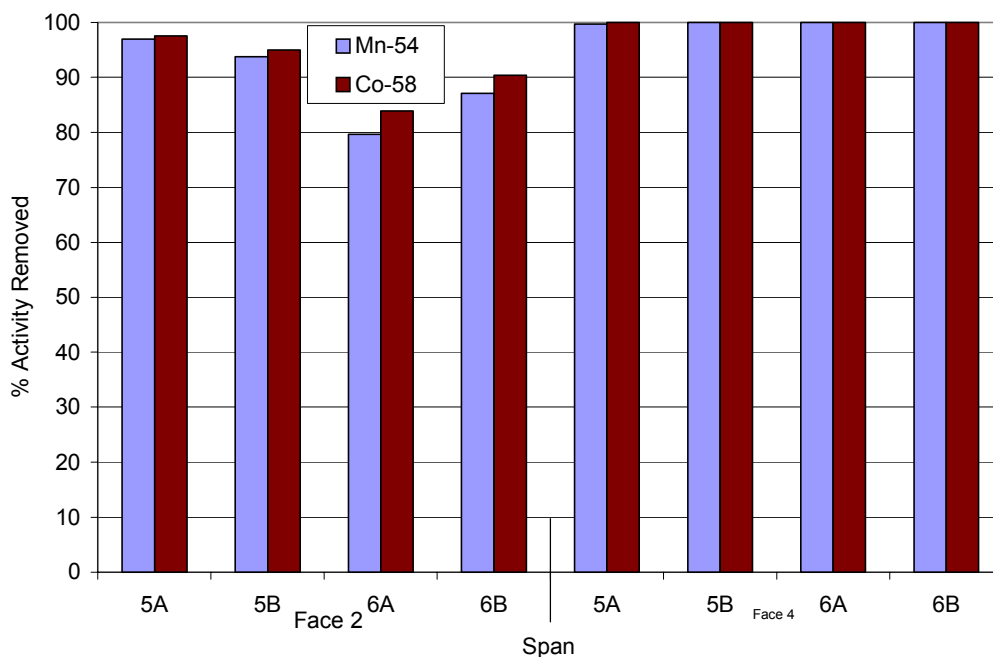


Figure 8-7
Callaway - Cleaning Efficiency Based on Isotopics

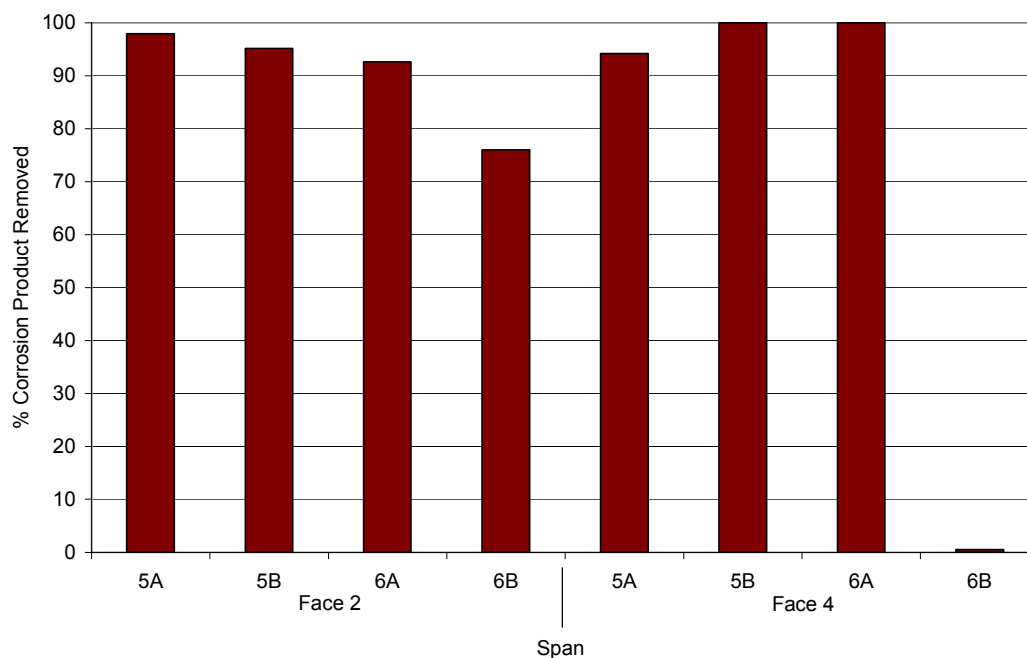
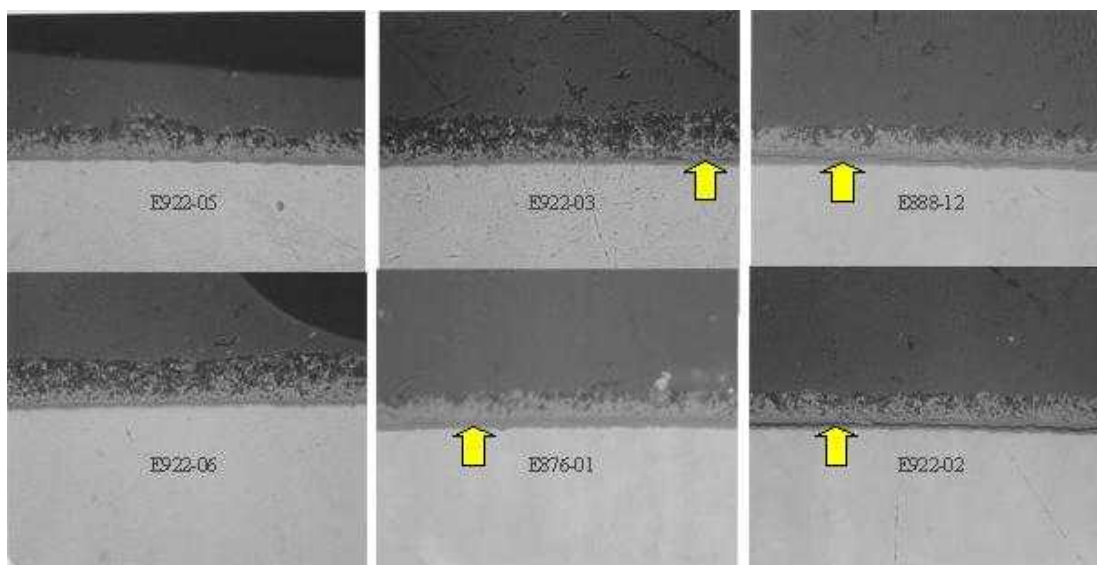


Figure 8-8
Callaway - Cleaning Efficiency Based on Mass Removal

BWR Fuel Cleaning Efficiency

As part of the final qualification process for the BWR fuel cleaner design, two sections of a fuel rod discharged from the Duane Arnold reactor (DAEC) were ultrasonically cleaned in the Vallecitos Nuclear Center hot-cells in June 2003. These tests consisted of applying ultrasonic energy to the fuel rod in a configuration and at an energy density comparable to that proposed for the full-scale cleaning apparatus. The dislodged particles of fuel deposit were collected through a grid plate perforated with ~ 0.3 mm holes, followed by cellulose acetate membranes of 0.45 μm pore size. The tests confirmed that the technique would remove essentially all of the loose deposits from BWR fuel, as well as a significant fraction of the more adherent deposits. The crud on fuel is subject to delamination because of the structure of the crud. These delamination areas are of concern because of possible steam entrapment and consequent “hot spots” on the fuel. Metallographic cross sections of the cleaned fuel rod sections indicated that the ultrasonic excitation in some instances completely removes flakes of the adherent crud layer from the fuel rod, reducing the “delamination” issue. But in other instances, the ultrasonic excitation caused further lifting of the crud, exacerbating the delamination issue. The delaminations represent only a small amount of the fuel rod surface area. Typical areas are shown in Figure 8-9. The net effect of fuel cleaning on delamination appears to be zero, however.



Similar oxide/crud delamination observed pre- and post-UT

Figure 8-9
DAEC Fuel Cross-Section Showing Crud and Areas of Delamination

The fuel rod sections were also examined via neutron radiography before and after cleaning. These radiographs, as well as the cross-sectioned fuel segments, showed no change in the condition of the fuel pellets, confirming that the ultrasonic excitation causes no unforeseen damage to the fuel pellets.

The prototype BWR fuel cleaner was deployed at Quad Cities early 2004, and used in January on four discharged assemblies as a pilot test to verify adequacy of the equipment and procedures; then used to clean sixteen lead use assemblies (LUAs) in March. The latter were returned to the core for another cycle of exposure after cleaning. Crud samples were obtained from some of the pilot assemblies for efficacy determination. Analysis of these samples is pending as of this writing, however visual examination of the pilot and LUA assemblies indicated that all or most of the loose corrosion product deposits were removed via the cleaning process. This result, illustrated in Figure 8-10, is confirmed by the gross dose readings from the filters used to capture the crud removed by cleaning. For the LUA cleaning, the crud was collected on a bank of four cartridge filters in parallel. At the conclusion of the LUA cleaning, the dose rate from the filters ranged from 400 to 800 R/hr, for a dose rate increase of 25-50 R/hr/assembly. Conversion of these gross dose rate measurements to an estimate of curies for the major isotopes is still underway.

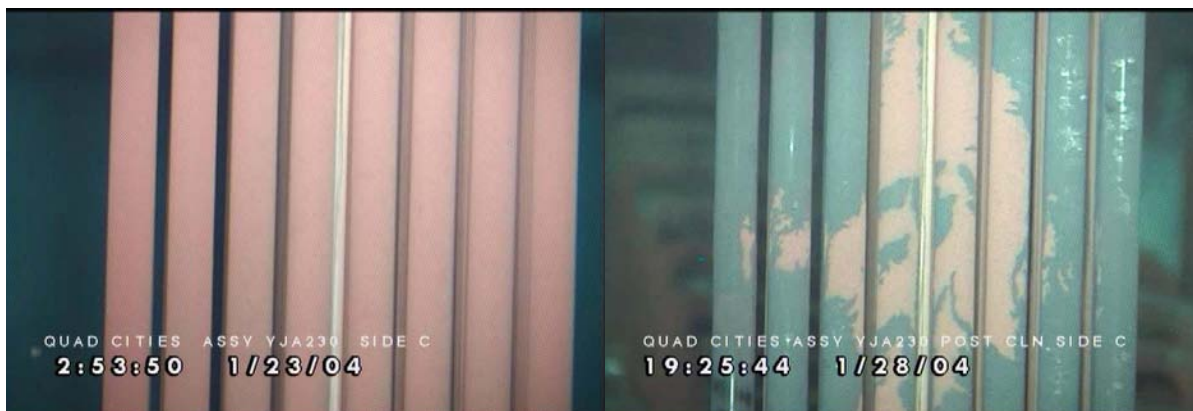


Figure 8-10
Quad Cities Assembly YJA 230, Before and After Ultrasonic Cleaning. Second Span, Between First and Second Spacers.

Waste Considerations

Crud Capture Media

To date, the corrosion product deposits released by ultrasonic fuel cleaning have been collected on discrete filter media. The cartridges for the Callaway and STP cleaning used organic membrane media because the intent was to dispose of the spent filters relatively soon after the cleaning campaign was completed. More recent filter designs have used sintered-metal media to provide more flexibility as to the length of time the spent cartridges could be stored in the fuel pool before disposal. The organic media tend to have a relatively brief useful life in the high radiation field of the crud captured on the filters.

An alternative crud collection method was proposed for full-scale Quad Cities BWR fuel cleaning. Here again, metal-media filter cartridges will be used, but they will be manifolded into a high integrity container (HIC) so that the crud from an entire fuel cleaning campaign can be shipped off-site without handling the individual spent filter cartridges.

A third method using sluice-able depth filtration media has also been proposed. Such media are best suited for capturing solubles (via ion exchange) or colloidal particles, and are not usually the best choice for collecting particulates. However, at sites where handling a large number of radioactive filter cartridges is of concern, sluice-able media may well provide an acceptable alternative crud collection strategy.

Crud Characteristics

The STP-2 cleaning consumed eight filter cartridges that were stored in the spent fuel pool for radioisotope decay until the next refueling outage approximately 18 months later. The cartridges were then to be packaged for off-site disposal.

Although no quantitative assessment was made of the crud collected from a given assembly, the filter dose rates were monitored. The activity build up on the filters from cleaning a single assembly is illustrated in Figure 8-11. As shown, the dose from the four parallel filter cartridges increased on the order of 5-8 R/hr for each assembly that was cleaned. The utility generally establishes a filter dose rate limit based on analysis of the radioisotopes and transportation and disposal criteria. For all fuel cleaning campaigns at PWRs to date, the dose rate limit was reached well before the pressure drop (P) limit mandated by the manufacturers of the filter cartridges.

The composition of the ultrasonically dislodged crud can be determined by side-stream sampling of the suspension in the line transferring crud from the cleaning module to the filter bank. Typical activities determined in this manner during the STP-2 fuel cleaning are shown in Table 8-2 and Table 8-3.

As discussed above, crud from BWR assemblies tends to be of greater magnitude, and greater activity than that from PWR fuel. In addition, the activity from BWRs is predominantly the long-lived ^{60}Co isotope, rather than the ^{58}Co predominating in PWR crud. Although full analysis of the crud removal at quad cities is still in progress, preliminary characterization of the Quad Cities filters has been discussed above, suggesting a dose increase of 25-50 R/hr on each of the four parallel filters for each assembly cleaned.

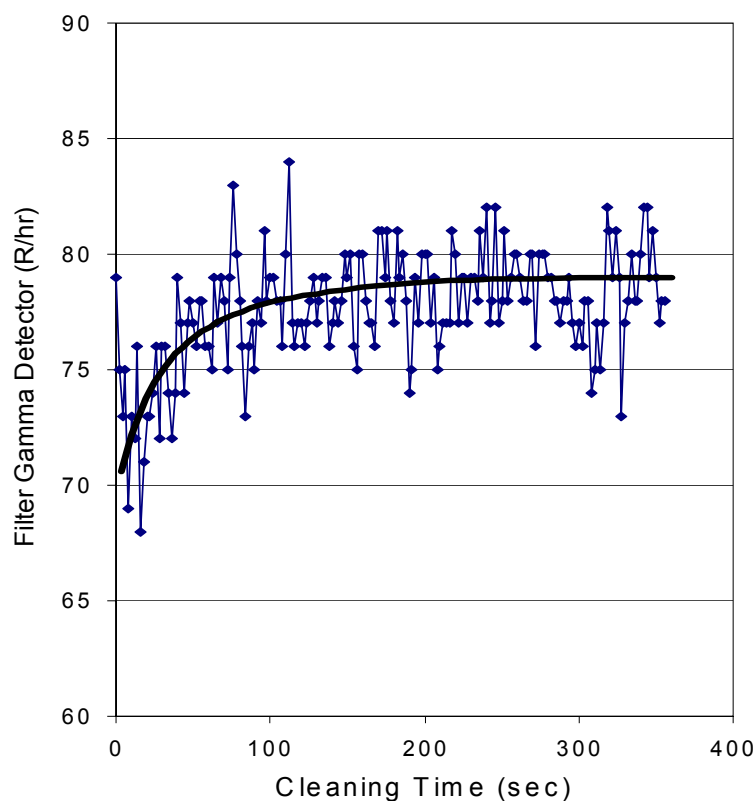


Figure 8-11
Activity increase on Fuel Cleaning Crud Capture Filters – STP2

Table 8-2
Measurements Required for Waste Characterization

Nuclide	Activity (Bq/Sample)
³ H	<1.11E+02
¹⁴ C	<1.41E+02
¹²⁹ I	<2.22E+02
¹³⁷ Cs	<5.18E+02
¹⁴⁴ Ce	<2.96E+03
²³⁸ Pu	9.21E-01
²³⁹ Pu	2.77E-01
²⁴⁰ Pu	2.75E-01
²⁴² Pu	7.81E-04
²⁴¹ Am	6.07E-02

Table 8-3
Most Prevalent Isotopic Composition of Fuel Crud, STP2

Nuclide	Activity (Bq/Sample)	Percent Activity
⁵⁴ Mn	2.10E+04	3%
⁵⁵ Fe	3.50E+05	56%
⁵⁸ Co	3.06E+04	5%
⁶⁰ Co	1.00E+05	16%
⁶³ Ni	1.20E+05	19%
Total	6.22E+05	100

Key Considerations – Ultrasonic Fuel Cleaning

A synopsis of the most important concepts related to ultrasonic fuel cleaning.

1. The EPRI ultrasonic fuel cleaning technique is ideally suited for fuel cleaning because it can remove deposits from an intact fuel assembly and the process does not produce any ancillary wastes other than the dislodged deposits.
2. Ultrasonic fuel cleaning is an effective means for removing PWR fuel deposits, hence mitigating the AOA problem, or at least delay its onset later into the fuel cycle by removing a significant fraction of crud from the reload fuel.
3. Ultrasonic fuel cleaning to remove crud from BWR fuel cladding surfaces will likely mitigate potential crud-related fuel problems, remove high concentrations of ⁶⁰Co in reactor water resulting in lower radiation fields and reduced demand for depleted zinc, and for

NMCA plants, remove high concentrations of noble metal from the fuel surfaces, allowing higher loading of noble metals on core internal surfaces during NMCA. This higher loading can offset the lack of redistribution of noble metal from fuel, which is believed to increase the durability of noble metals in providing NMCA mitigation.

4. Callaway's staff estimates a dose rate reduction of as much as 50% attributable to fuel cleaning. This value compares favorably with the 30% estimated by the CORA code calculations.
5. Crud capture media (filters) should be selected based on planned disposition of that waste stream. Organic based membranes can be used if "immediate" VR or disposition is the planned approach. Long term storage of that media in a high radiation field may result in premature structural breakdown in the fuel pool. The use of scintered-metal media provides storage duration flexibility prior to final packaging and disposal.
6. Waste classification, transport, and disposal criteria must be incorporated into fuel cleaning plans. BWR fuel cleanings involve greater magnitudes of crud and activity than that from PWR evolutions. In addition, the activity from BWRs is predominantly long-lived ^{60}Co , rather than the ^{58}Co predominating in PWR crud. Transuranics and other key isotopes should be carefully characterized to minimize the potential for generating Greater Than Class C waste.

A

EXELON COBALT REDUCTION PROGRAM SUMMARY

Evaluation and Estimation of Cobalt Introduction into the System by Valves

1. PURPOSE

- 1.1. The Source Term Reduction Program requires the estimation of cobalt release from hardfaced valve surfaces into plant systems. Stellite is a cobalt alloy commonly used for hardfacing valve surfaces that are subject to wear and could affect the valve's operability. The purpose of this T&RM is to provide methodology for the realistic estimation of cobalt released from stellite valve surfaces. This will provide information for the practical evaluation of valves as candidates for replacement or modification prioritized in RP-AA-551-1001.

2. TERMS AND DEFINITIONS

2.1. Abbreviations and Acronyms

- 2.1.1. **EPN** – Equipment Part Number
- 2.1.2. **EPRI** – Electric Power Research Institute
- 2.1.3. **INPO** – Institute of Nuclear Power Operation
- 2.1.4. **LLRT** – Local Leak Rate Test
- 2.1.5. **P&ID** – Piping & Instrument Diagram (a schematic system diagram)
- 2.1.6. **Abrasion** – Wear of contacting sliding surfaces when hard particles are present between them.
- 2.1.7. **Adhesion** – Wear due to bonding and material transfer that occurs when asperities on sliding material surfaces contact each other.
- 2.1.8. **Cavitation** – The phenomena when a liquid passes through a restriction and is transformed momentarily to the vapor state and back to the liquid state due to rapid compression of the vapor bubbles.
- 2.1.9. **Corrosion** – The act of chemically attacking a metallic surface by the media, and effectively resulting in a change in structure (e.g. steel rusting).
- 2.1.10. **Disc** – The moving portion of the valve assembly that contacts the mating surface of the valve body to effect shut-off.
- 2.1.11. **Erosion** – Wear caused by impingement of moving fluids or fluid-borne solid particles. The subdivisions of erosion are solid particle impingement, water droplet impingement, erosion by single-phase fluids, and cavitation erosion.
- 2.1.12. **Flashing** – The phenomena when a pressurized and heated liquid passes through a restriction to flow and is transformed to the vapor state.
- 2.1.13. **Galling** – Adhesive wear occurring as a result of high contact stresses.
- 2.1.14. **Hardfacing** – The application of a harder overlay material to the base material to enhance the wear characteristics and life expectancy of the assembly.

- 2.1.15. **Normally Closed** – A valve that is positioned to prevent system flow from passing through it during plant operation.
- 2.1.16. **Normally Open** – A valve that is positioned to allow system flow to pass through it during plant operation.
- 2.1.17. **Pitting** – Localized corrosion of a metal surface, confined to a point or small area, that takes the form of cavities.
- 2.1.18. **Seat** – The stationary portion of the valve body that is contacted by the mating surface of the disc to effect shut-off.
- 2.1.19. **Seat Test** – Measurement of the flow rate through a closed valve that is pressurized to determine the isolation capability. This includes “local leak rate testing” (LLRT).
- 2.1.20. **Engineering Judgment** – The method of applying engineering knowledge and power plant design experience to form an opinion or perform an evaluation by discerning and comparing that includes:
 - A conclusive statement based on quantitative comparison of input data between the case being evaluated and a previous case that was analyzed in detail; or
 - A qualitative, logical and conclusive discussion reflecting the general body of knowledge associated with preparing and reviewing a design analysis; or
 - Specific numerical results replaced by a “pass/fail” or “greater than/less than” level of accuracy. Engineering judgment shall be documented with a basis for the conclusion.
- 2.1.21. **Steam Cutting** – The erosive effect caused by small high velocity jets in closely spaced surfaces resulting from an unintentional gap causing localized damage (sometimes referred to as wire drawing).
- 2.1.22. **Stellite** – A trademarked name for hardfacing alloys made by the Deloro Company with high content of cobalt that are used in the valve manufacturing industry.
- 2.1.23. **Throttling** – The act of varying the flow through a valve by altering the position of the disc relative to the seat in response to system demands. The act of maintaining a constant flow through the valve by altering the disc position relative to the seat in response to upstream conditions.
- 2.1.24. **Velocity** – The speed at which the media passes over the metallic surface.

3. **MAIN BODY**

3.1. **Evaluation of Valves**

- 3.1.1. The basics of evaluating the release rates from the Stellite surfaces of valves may be characterized in the steps that follow: – Consider how the valve is used in the system (normally open, normally closed, seldom, intermittent, periodically, throttling, etc.). – Identify the surfaces that are effected by operation or use of the valve. – Determine, or estimate, the dimensions of the effected surfaces.

- Consider the media, and the operating conditions (air, steam, water, pressure, temperature, flow rate, velocity, etc.).

3.1.2. Using the guidance presented later in this document, and engineering judgment, calculate the estimated release rate of cobalt from each valve.

3.2. Valve List

3.2.1. 1993 Valve Lists

ComEd performed a comprehensive study that identified valves in the ComEd plants that contain Stellite. The valves identified were grouped into three priority groups, P1, P2, and P3. Similar studies were completed for the PECO and AmerGen plants. The S&L Priorities P2R1, P2R2, & P2R3 are identical to those in EPRI document TR-103296. Since P3 valves do not communicate with the reactor, they may be excluded from reviews utilizing this T&RM. The Priorities and Rankings utilized in the current program are detailed in RP-AA-551-1001.

3.3. Special Considerations Based on Valve Types, Installations, and Applications

3.4. Valves in use in the stations are subjected to varying operating conditions that result from the type of valve being used, the orientation of the valve, the configuration of the piping, the flowing media, etc. Each of these has an effect on how the release of Stellite is determined and quantified.

3.4.1. **Gate Valves:** These valves have four seating surfaces (two on the valve body and two on the disc) that may be hard faced. Normally, these valves are for isolation purposes only, and are either fully open, or closed. A valve that is fully open has the body seats exposed to flow, and a certain amount of turbulence, but the disc surfaces are protected in the valve bonnet, and are not expected to erode. These valves are not typically intended for throttling service, but may be used as such. In these cases, all four seating surfaces are exposed to the flow, and therefore the erosion. This will effectively reduce the minimum valve size to half of the size of a properly applied valve. Valves limited to occasional use in throttling service should be considered in their normal mode of operation only. Valves that are normally closed have **no** continuous flow, and should be evaluated only for the amount of time when fluid is passing through the valve. Disc guides and back seats are usually stellite, but are typically out of the flow stream, and **not** subject to corrosion. The guides will wear due to stroking of the valve, but will depend on how often and under what conditions.

3.4.2. **Check Valves:** These valves come on a variety of types. The most vulnerable to erosion are the swing and tilting disc types. Each has two surfaces (the seat and the disc) that may be hardfaced. Typically the body seat has a smaller hardfaced surface than that of the disc, but unless the actual dimensions are known, the same dimensions as estimated for gate valves will result in sufficiently conservative results. An error was identified in the EPRI calculations of cobalt release from check valves. EPRI has acknowledged this, and has corrected the mistake available in an errata sheet in their guidelines. Therefore, Exelon will adopt the use of corrected calculations for these valves. Lift type check valves (which

include in-line and nozzle checks) should be evaluated in the same manner as a standard globe valve.

If hinge pins and hinge pin bushings of swing or tilting disc type check valves are hardfaced, or made of high cobalt alloys, they must be evaluated separately from the valve seating surfaces. These components will not typically wear due to erosion, but rather due to mechanical wear if the flow is unstable or insufficient to hold the disc in a stable position. In these cases, the disc may flutter and be subjected to significant wear. This wear can result in cobalt release into the system of as much as triple the amount of erosion that may be credited to the seat. The Check Valve Program Engineer should be consulted regarding the stability of these types of valves.

- 3.4.3. **Globe Valves:** These valves typically have two seating surfaces (one on the disc, and one on the body seat), but there are often four seating surfaces depending on the valve design. Globe valves may also have flow in either direction (termed flow over the disc or flow under the disc), and are considered equal for the calculations of erosion and release of cobalt from the hardfaced surfaces.

Globe valves are also well suited to controlling flow, and therefore fluid velocity should also be considered when calculating erosion rates. Special versions of globe valves are used for regulating flow. These have double discs and cages, and are typically used in pairs, and are responsible for the greatest introduction of cobalt into the feedwater systems where they are used.

Caged globe valves with piston style discs must have the materials of the plug and the cage, and the areas exposed to erosion properly evaluated.

- 3.4.4. **Butterfly Valves:** Most of these valves have resilient seating elements made of rubber or Teflon type compounds. The mating surface of the seat or the disc is usually stainless steel or some other corrosion resistant alloy. These are typically not high cobalt content valves. Metal to metal seated butterfly valves should be evaluated in the same manner as a gate valve with one or two seating surfaces exposed to the flow if cobalt alloys have been used. Special consideration should also be given to velocity since butterfly valves are often throttling flow.
- 3.4.5. **Ball Valves:** Most of these valves are of small sizes, and should **not** be expected to have high release rates of cobalt.
- 3.4.6. **Pilot Operated Relief Valves:** These valves are subjected to wear resulting from seat leakage that results in wire drawing or steam cutting.
- 3.4.7. **Erosion:** EPRI assumes that erosion is one of the primary causes of cobalt release into plant systems. Fluid velocity and time in service are the most important considerations when evaluating erosive effects on Stellite surfaces. Low velocity flows, regardless of duration, and minimal usage, regardless of the velocity will **not** result in eroded surfaces. Aggressive flows for long periods of time are the applications that require the greatest attention. Valves that are throttled are most vulnerable to erosion due to the high velocity developed by the

partial open condition. Stellite disc edges and seat surfaces are also known to survive in aggressive flows in long-term continuous usage without degrading.

- 3.4.8. **Cavitation:** This is another significant source of Stellite degradation occurring in control valves. The explosive nature of a cavitating liquid causes surface defects that resemble deep pitting, or pock marking. This represents a heavy removal of material, and is dependent primarily on system pressure dropping below the vapor pressure, and recovering as it passes through the valve.
- 3.4.9. **Corrosion:** If the media can attack the Stellite chemically, a regular removal of material can result. Generally, the flow will erode the corrosion layer and expose raw metal that will corrode at a faster rate than a protected surface. All cobalt alloys possess excellent corrosion resistance at typical plant operating temperatures.
- 3.4.10. **Wear:** Mechanically moving two components against each other can result in wear of either or both surfaces, and introduce particles of metal into the system. This probably is the main cause of cobalt release, but performance history must be reviewed to assure that the seating surfaces are wearing rather than some other internal component.
- 3.4.11. **Local Leak Rate Testing:** Since erosion, corrosion, and mechanical wear are the primary mechanisms that result in release of cobalt into the systems, good leak rate performance should be considered favorably when evaluating cobalt release rates. Therefore, valves that are regularly subjected to LLRTs (either directly, or indirectly), and pass the test on a regular basis should not be considered high contributors of cobalt. The history of a valve should always be considered, and a cause of leak rate failure determined before making assumptions regarding cobalt release from seating surface degradation. The seating surfaces of failed valves should always be evaluated to determine if they are the cause of the leakage.

3.5. Calculation of Valve Size and Cobalt Release

- 3.5.1. Design Engineering at the stations shall be responsible for calculating the cobalt release rates, and providing Station Management with a valve list in order of cobalt introduction beginning with the highest contributor. The proposed table is provided in Attachment 1. This table provides information for the decision making process in RP-AA-551, RP-AA-551-1001, and RP-AA-551-1003.
- 3.5.2. Since many valves are ½ inch to 2-inch size, it is assumed that the cobalt contribution would be low. To confirm this assumption, Equation 1 uses information presented above and the information in Table 1 to permit the determination of the valve size that will introduce the threshold quantity of cobalt into a system (a Priority 3 Valve). Equation 2 is then used to determine the estimated cobalt release from valves exceeding that size. Each valve type and size should be evaluated individually. An example (Attachment 2) is for a normally open gate valve.
- 3.5.3. Valve drawings are **not** typically furnished with sufficient information to determine the dimensions of the seating surfaces of the body and disc. If the necessary information for the valves under consideration is **not** available **and**

Exelon Cobalt Reduction Program Summary

cannot be obtained, the list below provides generic dimensions that can be used to provide sufficient accuracy for the determinations that must be made.

- 2 inch through 4 inch valve = 0.375 inch wide seat surface – 6 inch through 10 inch valve = 0.500 inch wide seat surface – 12 inch through 16 inch valve = 0.750 inch wide seat surface – 18 inch through 24 inch valve = 1.000 inch wide seat surface – Greater than 24 inch = 1.500 inch to 1.875 inch wide seat surface

Table 1 MDV Values for Seating Surfaces from EPRI TR-103296

Valve Body Type	Max Degradation Value/Seat Area	Number of Seat Areas to Consider
Gate Valves	2.0 mg/dm ² /mo	2 or 4*
Check Valves	1.5 mg/dm ² /mo	2**
Globe Valves	0.5 mg/dm ² /mo	2***
FW Reg Valve	2080 mg/dm ² /mo	1****
2 Stage PORV	20 mg/dm ² /mo	1

* For normally open valves or throttled valves respectively

** For valves without Stellite hinge components

*** For typical globe valves (valve drawings should be reviewed) **** For pair of double disc globe valves (includes all surfaces) in BWRs

Equation 1 – Valve Sizing Calculation

$$\frac{P3}{mdv} \times \frac{100\text{cm}^2}{1\text{dm}^2} \times \frac{\text{in}^2}{6.45\text{cm}^2} = A_{\text{Total}}$$

Equation 2 – Estimated Cobalt Released Monthly

$$(\pi \cdot d \cdot w) \times \frac{6.45\text{cm}^2}{\text{in}^2} \times \frac{\text{dm}^2}{100\text{cm}^2} \times (mdv) \times s = \text{CoR}$$

Where: P3 = maximum cobalt release of a Priority 3 valve

d = valve size in inches

w = seat width in inches

mdv = max. degradation value in mg/dm²/mo equivalent (mg/dm²)/mo

s = number of seating surfaces considered

A_{total} = total area to be used in valve sizing

CoR = estimated amount of cobalt released in mg/mo

4. REFERENCES

- 4.1. EPRI NP-3444 – Wear Measurements of Nuclear Power Plant Components
- 4.2. EPRI TR-103296 – Cobalt Reduction Guidelines – Revision 1
- 4.3. INPO 91-014 – Guidelines for Radiological Protection at Nuclear Power Stations

- 4.4. RP-AA-551 – Cobalt Reduction Program
- 4.5. RP-AA-551-1001 – Identification, Ranking, and Prioritization of Cobalt Bearing Material
- 4.6. RP-AA-551-1003 – Cobalt Reduction Program Work Process
5. **ATTACHMENTS**
 - 5.1. Attachment 1, “Tabular Data Required”
 - 5.2. Attachment 2, “Example of Valve Calculations”

ATTACHMENT 1 Tabular Data

P/R	Co60 Input	Valve EPN	System	Valve Size	Valve Type	Valve Mfg.	Disc Facing	Seat Facing	Seat Insert

Explanation of Column Headings

- P/R – Priority and Ranking based on RP-AA-551-1001
- Co60 Input – Results of calculations using Equation 2.
- Valve EPN – The Equipment Number of the valve.
- System – The system the valve is installed in.
- Valve Size – The size of the valve in inches, or the size of the port for reduced port valves.
- Valve Type – Gate, Swing Check, Butterfly, Globe, etc.
- Valve Mfg. – The manufacturer of the valve
- Disc Facing – Stellite applied to disc face – Yes or No.
- Seat Facing – Stellite applied to seat face – Yes or No.
- Seat Insert – Solid Stellite seat insert – Yes or No.

ATTACHMENT 2 Example of Valve Calculations Page 1 of 1

To determine the maximum size of a normally open gate valve that would contribute less than 10 mgm/dm²/mo (the smallest gate valve size that must be considered), the following values were used for the variables in Equation 1.

Where: P3 -10.0 mg/mo²
mdv -2.0 mg/dm²/mo
Valve Surface Area πdw (assume 0.750 inch width)
Seat Areas Considered 2

The minimum valve size is therefore calculated using Equation 1:

$$A_{\text{Total}} = \frac{10 \text{ mg/mo}}{2 \text{ mg/dm}^2/\text{mo}} \times \frac{100 \text{ cm}^2}{\text{dm}^2} \times \frac{1 \text{ in}^2}{6.45 \text{ cm}^2} = 77.52 \text{ in}^2$$

$$2 \text{ seat areas} \rightarrow A = \frac{1}{2} \times (77.52 \text{ in}^2) = 38.76 \text{ in}^2$$

$$0.750 \text{ inch wide seat} \rightarrow d = \frac{38.76 \text{ in}^2}{\pi(0.75 \text{ in})} = 16.45 \text{ in valve}$$

Therefore, the smallest gate valve that should be considered is a 16-inch size if it is normally open, and only two seating surfaces are exposed to the erosive action of the fluid.

NOTE: For a gate valve with all four seating surfaces exposed to the erosive media, it can be shown that the smallest valve size to be considered should be 10 inch due to the smaller seating width of 0.500 inch.

It is now possible to estimate how much cobalt might be released (CoR) into a system for larger valves using Equation 2.

$$\text{CoR} = (\pi \cdot 24 \text{ in} \cdot 1.0 \text{ in}) \times \frac{6.45 \text{ cm}^2}{\text{in}^2} \times \frac{\text{dm}^2}{100 \text{ cm}^2} \times (2.0 \text{ mg/dm}^2/\text{mo}) \times 2 = 19.47 \text{ mg/mo}$$

Therefore, it is estimated that a 24 in. normally open gate valve would release 19.47 mg/mo

Identification, Ranking, and Prioritization of Cobalt Bearing Material

1. **PURPOSE**

- 1.1. This document describes the process of identifying, ranking, and prioritizing equipment or materials that can become activated as Cobalt 60 within plant primary systems due to the operation of the nuclear reactors.

2. **TERMS AND DEFINITIONS** - None

3. **RESPONSIBILITIES**

- 3.1. Site Engineering is responsible to identify components that contribute cobalt to the reactor and to quantify the amount of cobalt contributed to the reactor. Engineering is also responsible to rank and prioritize candidate components.
- 3.2. Radiological Engineering is responsible to track the station's cobalt inventory and to identify candidate components for replacement.
- 3.3. Chemistry is responsible to evaluate filter efficiencies in association with cobalt removal.

4. **MAIN BODY**

- 4.1. Identification of Cobalt Bearing Equipment and Components:
 - 4.1.1. The Site Engineering Department shall evaluate plant systems to identify valves that should be targeted as candidates for replacement parts in the Cobalt Reduction Program.
 - 4.1.2. **IDENTIFY** those systems that can communicate with the reactor coolant system (or primary system) and reactor core under any potential conditions.
 - 4.1.3. **IDENTIFY** all components within the identified systems that could contribute cobalt to the core inventory as a result of corrosion, wear erosion, or maintenance. Any component with cobalt-based hardfacing in a system that eventually communicates with the core should be ranked and considered a candidate for eventual replacement.
 1. **USE** engineering drawings, specifications, purchase orders, historical work documents, and technical manuals to determine which components have high cobalt alloy hardfacing.

4.2. Prioritization and Ranking of Cobalt Bearing Equipment:

4.2.1. The Site Engineering Department shall prioritize and rank components to determine best candidates for replacement

1. Prioritization of components determination:

- A. Site Engineering shall estimate the release rate of cobalt from components considering corrosion, wear erosion and maintenance using EPRI Report TR 103296.
- B. If a component such as a filter or ion exchanger is in the system and is located between the valve and the coolant system (or primary system), Chemistry should provide an evaluation of the efficiency of the filters or ion exchanger to remove dissolved and particulate cobalt.
- C. Other considerations concerning cobalt contribution may include, but are **not** limited to, component use, system configuration, and process parameters.
- D. Prioritization will be of a numerical value range from 1 to 3.
 1. Priority 1 (P1) is components with cobalt input into the reactor > 0.1 gm/mo (>100 mgm/mo).
 2. Priority 2 (P2) is components with cobalt input into the reactor > 0.01 gm/mo but less than 0.1 gm/mo (>10 mgm/mo).

NOTE: Priority 3 components do **not** need to be quantified if it can be pre-determined the cobalt input to the reactor from that component is < 0.01 gm/mo (<10 mgm/mo). However, it is recommended to quantify these components as total cobalt input to the reactor can be estimated.

3. Priority 3 (P3) is components with cobalt input into the reactor
 < 0.01 gm/mo (<10 mgm/mo).

2. Ranking of components is to be determined based on:

- A. Ranking will be of a numerical value range from 1 to 3
 1. Rank 1 (R1) is components located downstream of filters or ion exchangers for water or steam systems that operate during normal plant operation and are located in the main flow path leading to the reactor core.
 2. Rank 2 (R2) is components directly wetted by the reactor water but are **not** located in the main flow path leading to the reactor core. This includes branch lines off of the main flow path up to the first isolation point (e.g. safety injection check valve, etc.)
 3. Rank 3 (R3) is components located upstream of filters or ion exchangers which are in the main flow path to the

Exelon Cobalt Reduction Program Summary

reactor core and operate during normal plant operation
(e.g. main steam isolation valves, etc.).

- 4.2.2. Engineering shall identify and download information associated with component cobalt contribution to the reactor into either PIMS (e.g. component records list) or Passport (e.g. TIMD034 panel) in order to facilitate identification of candidate components during future work activities. Records are to be updated when stellite parts are removed from components.

5. **DOCUMENTATION** -None

6. **REFERENCES**

- 6.1. TR-103296, EPRI Report, Cobalt Reduction Guidelines
- 6.2. TR-107991, EPRI Report, Radiation Field Control Manual

B

BROWN'S FERRY UNIT 1 RESTART SOURCE TERM REDUCTION INITIATIVES

Introduction

This Appendix is the summary of a presentation given by John Underwood of the Brown's Ferry Unit 1 Restart team. At the time of this document, Brown's Ferry Unit 1, a BWR, had the unique opportunity to restart the plant after several years of inactive status. Considerable effort was given to removing potential source terms in the plant with the goal of having the lowest radiation fields possible. The following describes some of the actions taken.

Overview

- Review of unit 1 restart valve replacements, showed that cobalt reduction was not being actively pursued.
- A level B PER was initiated and a HIT was formed to improve the process on Unit 1.
- Units 2 and 3 also have a standing PER for increase of source term.
- EPRI and INPO were contacted to provide Industry experience in cobalt reduction.
- Hatch, Fermi, Quad Cities, Grand Gulf, Duane Arnold, River Bend were identified as industry leaders in Cobalt reduction efforts.
- Plant Hatch cobalt reduction project manager provided a presentation to the HIT on their successful effort in the 1990's.
- Using industry benchmarking, an overall cobalt reduction plan was developed and is being implemented.
- EPRI critique indicates that BFN1 plan is comprehensive and aggressive.

Cobalt in Perspective

- ^{60}Co is the principal contributor to out-of-core radiation fields in boiling water reactors. A hard facing alloy trade name Stellite®, which has high ^{59}Co content, is identified as the primary source of ^{60}Co in reactors. Cobalt is released through erosion, corrosion, friction, and through debris left from work on components containing Stellite®. When cobalt is released it travels through the vessel and is activated. After the ^{59}Co is activated it becomes ^{60}Co and plates out in plant piping. ^{60}Co is a high energy gamma emitter with a 5.3 year half life. This contaminant produces long term high radiation areas in the plant.

Brown's Ferry Unit 1 Restart Source Term Reduction Initiatives

- 1 gram of ^{60}Co is equal to 1,132 Curies of radioactivity and as a point source (a metal sphere 6 mm in diameter) emits a radiation field of 1,500 R/hr at 1 meter.
- The majority of this is deposited on the fuel and vessel components. However, a portion is deposited on associated piping in the drywell and reactor building.
- Based on EPRI research, 70% of the dose accrued on BFN operating units is due to ^{60}Co . This is equal to 330 man-rem for FY 04.
- For each gram of cobalt introduced into the reactor, \$1000/yr of depleted zinc (DZO) injection into the feed water is required to suppress the deposition on plant piping systems.
- Less than 1/10th of a gram of ^{60}Co is removed during chemical decon of the drywell recirculation piping at a cost of \$2 million.

What is Cobalt?

- Cobalt is an element of Stellite® used for its hardness throughout the plant.
- Typically 2 types of Stellite® are used namely, Stellite® 6 and Stellite® 21.
- Both Stellite® 6 and 21 contain approximately 60% Cobalt.
- Stellite® 6 is harder and more brittle than Stellite® 21.
- Stellite® 21 is more desirable of plant in-situ repair by welding.
- Historical industry data indicates Stellite® 6 will release more Cobalt particles over time than Stellite® 21.

Replacements for Stellite®?

- Yes, there are alloys that can be used other than Stellite® in some cases.
- 400 series Stainless Steel
- Deloro 50®
- NOREM®
- In some cases such as GL89-10 MOVs Stellite® maybe the only acceptable material with a successful industry experience base at this time.

Where is the Cobalt?

- Vessel Internal Components
- Turbine Components
- Components in the flow path to the Reactor
- Valves
- Plant Piping Components and Heat Exchangers

- Pump impellers
- Data obtained from benchmarking and current BFN lab analysis indicates
 - 30% is from vessel internals
 - 40% is from the Turbine side
 - 20% is from debris left in the system after maintenance/modification work activities.
 - 10% is from valve erosion or corrosion

How Do We Reduce Cobalt?

- Replace key components with Stellite® free materials i.e., <0.5% cobalt by content.
- Improve Maintenance/Modification FME Practices in cleanup after valve work.
- Electro-polish and pre-oxidize the wetted surfaces of plant piping, valves, pumps, and heat exchangers.
- Use DZO injection in feed water to suppress cobalt plate out on reactor building piping.
- Revise procedures to eliminate or reduce introduction of cobalt into reactor coolant.

Action Plan Status

- New Control Rod Blade material, pins and rollers are cobalt free. In addition the HIT was able to get vendor agreement to further reduce cobalt content of blade material from <0.05% to <0.02 %.
- Jet Pump inner mixer wedges have been approved for replacement with x-750 alloy.
- Low Pressure Turbine Stellite® hardened blades are being replaced with flame hardened blades. This is chrome moly material with a ceramic coating.
- Replacing candidate valves that have the best “Payback” potential for reduced maintenance and dose. (29) valves approved thus far.
- Condenser tube replacement material is 0.124 % cobalt.
- Self Assessment of Unit 1 FME completed. Plan in implementation phase.
- Purchasing Equipment to prevent introduction of Stellite® debris during maintenance and to enhance cleanup after maintenance.
- Change the culture to allow dose for cleanup in order to save future long term dose.
- Electro-polish and Pre-oxidize piping to reduce cobalt plate out.
- Use analysis of Unit 2 and 3 systems to “fingerprint” cobalt inputs.
- Purchase equipment to allow rapid empirical analysis of elemental cobalt for maintenance cleanliness.

Brown's Ferry Unit 1 Restart Source Term Reduction Initiatives

- Revise Procedures: ALARA, Design, Engineering, Procurement, Purchasing, Planning, Scheduling, Radcon, Maintenance, FME, Refueling, and Chemistry to ensure awareness and legacy of cobalt reduction.
- Survey Industry and suppliers for best cobalt removal resins for optimum cobalt reduction.
- An in-depth plan for flushing and cleanup of debris prior to flood up and reassembly.
- An in-depth plan for vessel cleanup and piping FME inspections/flushing.
- Ensure training on FME issues and cobalt prevention with employees to show that what used to be acceptable is now unacceptable.

Summary

⁶⁰Co is the primary dose contributor at BFN. Implementation of the Unit 1 restart cobalt reduction plan will be a critical component in the plan to return Unit 1 to service as a top decile performer in terms of collective radiation exposure.

C

SOUTHERN NUCLEAR HWC DIAL DOWN DECISION TOOL

NOTE:	ONLY the HP Superintendent (or higher) may authorize deviation from these guidelines.
--------------	--

STEP	IF	AND	THEN
1	The work activity is NOT in the vicinity of a nuclear steam system or component (see Note 1)		DO NOT reduce injection rate
2	The work activity IS in the vicinity of nuclear steam system or component (see Note 2)	There is NO immediate need to enter the area	Reschedule activity for power reduction
		There IS an immediate need to enter the area (see Note 3)	Proceed to step 3
3	Reactor power is	$\geq 75\%$	Do NOT reduce injection rate
		$\geq 50\%$	$< 75\%$ *Have Operations reduce injection rate to 4 SCFM
		$\geq 30\%$	$< 50\%$ *Have Operations reduce injection rate to 2 SCFM
		$< 30\%$	Hydrogen injection has a design trip below 30% reactor power and should thus NOT be in operation

* HP personnel will verify that hydrogen injection is at the correct flow rate prior to allowing personnel entry into the affected area(s).

NOTES:

Note 1: Examples- RWCU Pump Rooms, RWCU Heat Exchanger, FPC Heat Exchanger

Note 2: Examples- Main Steam Lines, Steam Chase, Condenser Bay, Turbine Enclosure, SJAE

Note 3: Examples- Required surveillances, events which could lead to taking unit off line, as determined by SOS or Scheduling, as determined by HP/Chem

D

SUMMARY OF REFERENCES

Chapter 2: Radiation Fields: Origins, Regulations, and Countermeasures

C. A. Bergmann and R. L. Bencini. Evaluation of PWR Radiation Fields: 1991-1996. Palo Alto, CA: Electric Power Research Institute, February 1997. TR-107566.

BWR Water Chemistry Guidelines - 2004 Revision. Palo Alto, CA: Electric Power Research Institute, December 2004. TR-103515-R3

Development of a Successful Reactor Cavity Decontamination Plan, 1009576

Chapter 3: Cobalt Source Term Reduction

Compilation and Evaluation of NOREM Test Results: Implications for Valve Applications: Generic Background Information for 10 CFR 50.59 Evaluations: EPRI, Palo Alto, CA: 1999. TR-109343.

Performance of NOREM™ Hardfacing Alloys, EPRI, Palo Alto, CA: 1999. TR-112993.

BWR Water Chemistry Guidelines - 2004 Revision. Palo Alto, CA: Electric Power Research Institute, December 1996. TR-103515-R3.

Perock, J. D. and Bergmann, C. A., “Evaluation of PWR Radiation Fields: 1986-1990”, EPRI TR-100306, April 1992.

Bergmann, C. A., and Bencini, R. L., “Evaluation of PWR Radiation Fields: 1991-1996”, EPRI TR-107566, February 1997.

ANSI N45.2.1, Cleaning of Fluid Systems and Associated Components During Construction Phase of Nuclear Power Plants

Chapter 4: Preconditioning Surfaces of Replacement Components

Evaluation of PWR Radiation Fields: 1986 – 1990, EPRI, Palo Alto, CA, TR-100306, April 1992.

Summary of References

Bergmann, C. A., and Bencini, R. L., “Evaluation of PWR Radiation Fields: 1991 – 1996”, EPRI, Palo Alto, CA, TR-107566, February 1997.

Stabilized Chromium Process: Final Report, EPRI, Palo Alto, CA: 2002. 1003374.

An Assessment of to Reduce Radiation Buildup; 1996 Progress, EPRI, Palo Alto, CA: 1996. TR-107224.

Assessment of Chromium Coating Technology, EPRI, Palo Alto, CA: 1999. TR-112982.

Field Testing of Chromium Coating Technology, EPRI, Palo Alto, CA: 1998. TR-111666.

Chapter 5: PWR Primary Coolant Chemistry

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

“Fuel Integrity Monitoring and Failure Evaluation Handbook”, EPRI, Palo Alto, CA: 1998. TR-108779.

PWR Shutdown Chemistry Practices, EPRI, Palo Alto, CA: 1998. TR-109569.

S. G. Sawochka, Impact of PWR Primary Chemistry on Corrosion Product Deposition on Fuel Cladding Surfaces, EPRI, Palo Alto, CA: 1997. TR-108783.

Dose Rate and Coolant Chemistry Data at PWRs Operating with Alternative Primary Coolant Chemistry, EPRI, Palo Alto, CA: 2000. TR-1000153.

Evaluation of Cycle Length and Non-Standard Coolant Chemistries on PWR Plant Radiation Fields, EPRI, Palo Alto, CA: 2001. TR-1003123.

PWR Field Experience with Elevated, Constant pH, EPRI, Palo Alto, CA: 2001. TR-1003153.

A Survey of the Effect of Primary Coolant pH on Westinghouse PWR Plant Radiation Fields, EPRI, Palo Alto, CA: 1994. TR-104180.

PWR Primary System Chemistry: Experiences with Elevated pH at Millstone Point Unit 3, EPRI, Palo Alto, CA: 1992. TR-100960.

PWR Startup and Shutdown Field Experience: Operation with Zinc Injection at Diablo Canyon, EPRI, Palo Alto, CA: 2001. 10003154.

G. P. Sabol, et al., Rootcause Investigation of Axial Power Offset Anomaly, EPRI, Palo Alto, CA: 1997. TR-108320.

Assessment of Elevated pH Program for Comanche Peak Steam Electric Station, EPRI, Palo Alto, CA: 2001. 1006282.

Overview Report on Zinc Addition in PWRs, EPRI, Palo Alto, CA: 2001. 1001020.

Experience with Zinc Injection in European PWRs, EPRI, Palo Alto, CA, 2002. 1003378

PWR Operating Experience with Zinc Addition and the Impact on Plant Radiation Fields, EPRI, Palo Alto, CA: 2003. TR-1003389

Chapter 6: BWR Coolant Chemistry

BWR Water Chemistry Guidelines- - 2004 Revision,. Palo Alto, CA: Electric Power Research Institute, December 2004. TR-103515-R3, 2004.

Qualification of the NP/LOMI Decontamination Process for BWRs under HWC, EPRI, Palo Alto, CA: 1998. Report TR-111667.

Decontamination Handbook, EPRI TR-112352, Palo Alto, CA,; July 1999., TR-112352

Experience with Depleted Zinc Oxide Injection in BWRs, 1999 Progress Report, EPRI TR-108741, Palo Alto, CA, June 1999.

Experience with Depleted Zinc Oxide Injection in BWRs, EPRI TR-107188, Palo Alto, CA, November 1996.

Post-NMCA Duane Arnold Fuel Surveillance Program, EPRI TR-1128868, Palo Alto, CA, to be published.

BWR Iron Control Monitoring: Interim Report, EPRI TR-108737, Palo Alto, CA, 1998.

BWRVIP-118: BWR Vessel and Internals Project, NMCA Experience Report and Application Guidelines, 1003193, EPRI, Palo Alto, CA, 2003.

Chapter 7: System and Component Chemical Decontamination

Decontamination Handbook, EPRI, Palo Alto, CA: July 1999, TR-112352

D. Bradbury, G.R. Elder and S.M. Scrivens,” EPRI LOMI-2 Decontamination Process”. EPRI Report TR-108740, May, 1998.

Code of Federal Regulations, Section 40, Chapter 1, Part 261, Identification and Listing of Hazardous Wastes. 7-1-89 Edition. Ibid. Appendix II - EP Toxicity Test Procedures.

Export Control Restrictions

Access to and use of EPRI Intellectual Property is granted with the specific understanding and requirement that responsibility for ensuring full compliance with all applicable U.S. and foreign export laws and regulations is being undertaken by you and your company. This includes an obligation to ensure that any individual receiving access hereunder who is not a U.S. citizen or permanent U.S. resident is permitted access under applicable U.S. and foreign export laws and regulations. In the event you are uncertain whether you or your company may lawfully obtain access to this EPRI Intellectual Property, you acknowledge that it is your obligation to consult with your company's legal counsel to determine whether this access is lawful. Although EPRI may make available on a case by case basis an informal assessment of the applicable U.S. export classification for specific EPRI Intellectual Property, you and your company acknowledge that this assessment is solely for informational purposes and not for reliance purposes. You and your company acknowledge that it is still the obligation of you and your company to make your own assessment of the applicable U.S. export classification and ensure compliance accordingly. You and your company understand and acknowledge your obligations to make a prompt report to EPRI and the appropriate authorities regarding any access to or use of EPRI Intellectual Property hereunder that may be in violation of applicable U.S. or foreign export laws or regulations.

About EPRI

EPRI creates science and technology solutions for the global energy and energy services industry. U.S. electric utilities established the Electric Power Research Institute in 1973 as a nonprofit research consortium for the benefit of utility members, their customers, and society. Now known simply as EPRI, the company provides a wide range of innovative products and services to more than 1000 energy-related organizations in 40 countries. EPRI's multidisciplinary team of scientists and engineers draws on a worldwide network of technical and business expertise to help solve today's toughest energy and environmental problems.

EPRI. Electrify the World

SINGLE USER LICENSE AGREEMENT

THIS IS A LEGALLY BINDING AGREEMENT BETWEEN YOU AND THE ELECTRIC POWER RESEARCH INSTITUTE, INC. (EPRI). PLEASE READ IT CAREFULLY BEFORE REMOVING THE WRAPPING MATERIAL.

BY OPENING THIS SEALED PACKAGE YOU ARE AGREEING TO THE TERMS OF THIS AGREEMENT. IF YOU DO NOT AGREE TO THE TERMS OF THIS AGREEMENT, PROMPTLY RETURN THE UNOPENED PACKAGE TO EPRI AND THE PURCHASE PRICE WILL BE REFUNDED.

1. GRANT OF LICENSE

EPRI grants you the nonexclusive and nontransferable right during the term of this agreement to use this package only for your own benefit and the benefit of your organization. This means that the following may use this package: (I) your company (at any site owned or operated by your company); (II) its subsidiaries or other related entities; and (III) a consultant to your company or related entities, if the consultant has entered into a contract agreeing not to disclose the package outside of its organization or to use the package for its own benefit or the benefit of any party other than your company.

This shrink-wrap license agreement is subordinate to the terms of the Master Utility License Agreement between most U.S. EPRI member utilities and EPRI. Any EPRI member utility that does not have a Master Utility License Agreement may get one on request.

2. COPYRIGHT

This package, including the information contained in it, is either licensed to EPRI or owned by EPRI and is protected by United States and international copyright laws. You may not, without the prior written permission of EPRI, reproduce, translate or modify this package, in any form, in whole or in part, or prepare any derivative work based on this package.

3. RESTRICTIONS

You may not rent, lease, license, disclose or give this package to any person or organization, or use the information contained in this package, for the benefit of any third party or for any purpose other than as specified above unless such use is with the prior written permission of EPRI. You agree to take all reasonable steps to prevent unauthorized disclosure or use of this package. Except as specified above, this agreement does not grant you any right to patents, copyrights, trade secrets, trade names, trademarks or any other intellectual property, rights or licenses in respect of this package.

4. TERM AND TERMINATION

This license and this agreement are effective until terminated. You may terminate them at any time by destroying this package. EPRI has the right to terminate the license and this agreement immediately if you fail to comply with any term or condition of this agreement. Upon any termination you may destroy this package, but all obligations of nondisclosure will remain in effect.

5. DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

NEITHER EPRI, ANY MEMBER OF EPRI, ANY COSPONSOR, NOR ANY PERSON OR ORGANIZATION ACTING ON BEHALF OF ANY OF THEM:

- (A) MAKES ANY WARRANTY OR REPRESENTATION WHATSOEVER, EXPRESS OR IMPLIED, (I) WITH RESPECT TO THE USE OF ANY INFORMATION, APPARATUS, METHOD, PROCESS OR SIMILAR ITEM DISCLOSED IN THIS PACKAGE, INCLUDING MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, OR (II) THAT SUCH USE DOES NOT INFRINGE ON OR INTERFERE WITH PRIVATELY OWNED RIGHTS, INCLUDING ANY PARTY'S INTELLECTUAL PROPERTY, OR (III) THAT THIS PACKAGE IS SUITABLE TO ANY PARTICULAR USER'S CIRCUMSTANCE; OR
- (B) ASSUMES RESPONSIBILITY FOR ANY DAMAGES OR OTHER LIABILITY WHATSOEVER (INCLUDING ANY CONSEQUENTIAL DAMAGES, EVEN IF EPRI OR ANY EPRI REPRESENTATIVE HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES) RESULTING FROM YOUR SELECTION OR USE OF THIS PACKAGE OR ANY INFORMATION, APPARATUS, METHOD, PROCESS OR SIMILAR ITEM DISCLOSED IN THIS PACKAGE.

6. EXPORT

The laws and regulations of the United States restrict the export and re-export of any portion of this package, and you agree not to export or re-export this package or any related technical data in any form without the appropriate United States and foreign government approvals.

7. CHOICE OF LAW

This agreement will be governed by the laws of the State of California as applied to transactions taking place entirely in California between California residents.

8. INTEGRATION

You have read and understand this agreement, and acknowledge that it is the final, complete and exclusive agreement between you and EPRI concerning its subject matter, superseding any prior related understanding or agreement. No waiver, variation or different terms of this agreement will be enforceable against EPRI unless EPRI gives its prior written consent, signed by an officer of EPRI.

Program:

1003390

Nuclear Power

© 2004 Electric Power Research Institute (EPRI), Inc. All rights reserved. Electric Power Research Institute and EPRI are registered service marks of the Electric Power Research Institute, Inc. EPRI. ELECTRIFY THE WORLD is a service mark of the Electric Power Research Institute, Inc.

 Printed on recycled paper in the United States of America