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Pressurized Water Reactor Secondary Water Chemistry Guidelines—Revision 7

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REPORT SUMMARY

State-of-the-art water chemistry programs reduce equipment corrosion and enhance steam generator reliability. A committee of industry experts prepared these revised *PWR Secondary Water Chemistry Guidelines* to incorporate the latest field and laboratory data on secondary system corrosion and performance issues. Pressurized water reactor (PWR) operators can use these guidelines to update their secondary water chemistry programs.

Background

EPRI updates industry water chemistry guidelines periodically as new information becomes available. Previous versions of these *PWR Secondary Water Chemistry Guidelines* identified a detailed water chemistry program deemed consistent with the then-current understanding of research and field information. Each revision discussed the impact of these guidelines on plant operation, noting that utilities may wish to revise the guidelines' program following a plant-specific evaluation for implementation. Utility feedback since publication of Revision 6 in December 2004 revealed additional areas requiring evaluation and potential *Guidelines* revision.

Objectives

To update the *PWR Secondary Water Chemistry Guidelines—Revision 6*.

Approach

A committee of industry experts, including utility specialists, nuclear steam supply system vendor representatives, Institute of Nuclear Power Operations representatives, consultants, and EPRI staff, collaborated to review available data on secondary water chemistry and secondary cycle corrosion. From these data, the committee generated water chemistry guidelines that utilities can adopt at all PWR nuclear plants. Recognizing that each nuclear plant owner has a unique set of design, operating, and corporate concerns, the guidelines committee developed a methodology for plant-specific optimization. The document then underwent a rigorous review and adoption process via the Steam Generator Management Program (SGMP).

Results

Revision 7 of the *PWR Secondary Water Chemistry Guidelines* provides guidance for PWR secondary system chemistry of all manufacture and design, and includes the following chapters:

- Chapter 1 contains a list of management responsibilities and addresses secondary water chemistry program requirements for compliance with Nuclear Energy Institute (NEI) 97-06 and NEI 03-08.
- Chapter 2 presents a compilation of corrosion data for steam generator tubing and balance-of-plant materials. This information serves as the technical bases for the specific parameters and programs detailed in the document.

- Chapter 3 discusses the role of the concentration processes in local regions of the steam generator and the chemistry "tools" available for modifying the resulting chemistry within these concentrating regions. It briefly identifies the supporting aspects of and the considerations for adopting these chemistry regimes. It refers readers to more detailed documents for application of the chemistry strategies.
- Chapter 4 presents a detailed methodology for determining an optimized plant-specific chemistry program.
- Chapters 5 and 6 present water chemistry programs for the recirculating steam generator (RSG) and once-through steam generator (OTSG), respectively. These are the chapters most frequently referred to by chemistry personnel. The tables in these chapters provide boundaries for plant-specific optimization procedures described in Chapter 4.
- Chapter 7 provides information on data collection, evaluation, and management. This chapter describes methods of using EPRI ChemWorks ™ modules for evaluating plant data and predicting high-temperature chemistry environments throughout the cycle.
- Chapter 8 captures all specific elements contained within these *Guidelines* that are identified as mandatory, shall or recommended, consistent with NEI 03-08 and NEI 97-06.
- Appendix A provides examples of methodologies for implementing integrated exposure programs.
- Appendix B provides an assessment of PWR steam chemistry considerations.

EPRI Perspective

This seventh revision of the *PWR Secondary Water Chemistry Guidelines* is endorsed by the utility executives of the EPRI Steam Generator Management Program. The document represents another step in maintaining proactive chemistry programs to limit or control secondary system degradation, with consideration given to corporate resources and plant-specific design/operating concerns. Each utility is to examine its plant-specific situation to determine how this guidance is best implemented.

Keywords

PWR
Water chemistry
Corrosion protection
Nuclear steam generators
Secondary coolant circuits

EPRI FOREWORD

Industry water chemistry guidelines are updated periodically as new information becomes available. Previous revisions of these guidelines have identified a detailed water chemistry program that was deemed to be consistent with the then current understanding of research and field information. Each revision, however, has recognized the impact of these *Guidelines* on plant operation and has noted that utilities should optimize their program based on a plant-specific evaluation prior to implementation. To assist in such plant-specific evaluations, Chapters 3 and 4 provide additional details regarding water chemistry control strategies and how to implement them into an optimized plant-specific water chemistry control program, respectively. The chapters of Revision 7 cover the following:

- Chapter 1 contains a list of management responsibilities and addresses secondary water chemistry program requirements for compliance with NEI 97-06 and NEI 03-08.
- Chapter 2 presents a compilation of corrosion data for steam generator tubing and balance-of-plant materials. This information serves as the technical bases for the specific parameters and programs detailed in the document.
- Chapter 3 discusses the role of the concentration processes in the various locations of the steam generator and the chemistry "tools" available for modifying the resulting chemistry within these concentrating regions. It briefly identifies the supporting aspects of and the considerations for adopting these chemistry regimes. It refers the reader to more detailed documents for application of the chemistry strategies.
- Chapter 4 presents a detailed methodology for determining an optimal plant-specific chemistry program.
- Chapters 5 and 6 present water chemistry programs for the recirculating steam generator (RSG) and once-through steam generator (OTSG), respectively. These are the chapters most frequently referred to by chemistry personnel. The tables contained within these chapters provide the boundaries for the plant-specific optimization procedures described in Chapter 4.
- Chapter 7 provides information on data collection, evaluation, and management. This chapter describes methods of using EPRI ChemWorks™ modules for evaluating plant data and predicting high-temperature chemistry environments throughout the cycle.
- Chapter 8 captures all of the specific elements contained within these Guidelines that are identified as mandatory, shall or recommended, consistent with NEI 03-08 and NEI 97-06.
- Appendix A provides detailed guidance with regard to use of the integrated exposure concept.
- Appendix B provides an assessment of PWR steam chemistry considerations.

These *Guidelines* were drafted by the Revision 7 Committee with support from an industry Technical Review Team and the technical committees of the Steam Generator Management Program, and the PMMP Executive Committee. Key technical changes in this revision include:

- All of the chapters were reviewed and revised to reflect experience gained and information learned since issuance of Revision 6.
- Guidance was revised in Chapters 1, 5, and 6 to clearly indicate the elements of the *Guidelines* that are mandatory and shall requirements and those that are recommendations, consistent with NEI 03-08 and NEI 97-06.
- Chapter 2 was revised to reflect recent research results regarding specific impurity effects on IGA/SCC including a summary discussion of the improvement factors of 600TT, 690TT and 800NG relative to 600MA steam generator tubing for different chemistry environments, the effect of the hydrazine/oxygen ratio on the ECP of steam generator tubes under startup conditions, an assessment of steam generator wet layup conditions on steam generator materials corrosion, updated information on the effects of hydrazine on flow accelerated corrosion, an evaluation of chemistry effects on turbine corrosion, and new information on dispersant application for mitigation of steam generator fouling.
- The treatment of deposit control practices was updated in Chapter 3 to reflect current practices and currently available methods. The section on the effects of interruptions in hydrazine addition was updated, along with the addition of new information on the effect of the hydrazine/oxygen ratio on steam generator tubing ECP. Dispersant application was added as a viable, safe option for mitigation of steam generator fouling. Discussions of plant experience (e.g., with BAT, titanium) were updated.
- The main discussion of integrated exposure was relocated from Chapters 4 and 7 to Appendix A.
- Chapter 4 was reorganized and revised to reflect lessons learned from its use since Revision 6 and from the development of similar programs (e.g., BWRVIP 2005-215).
- Chapter 5 was substantially revised to incorporate additional guidance regarding application of material improvement factors, added flexibility during startup, improved guidance relative to the effect of the hydrazine/oxygen ratio on steam generator tubing ECP, and improved guidance for steam generator wet layup. The control tables for RSGs in Chapter 5 were thoroughly reviewed and edited. Some of the more significant changes are:

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Content deleted - EPRI Proprietary Information

- Chapter 6 was also updated to incorporate the revised guidance regarding control of steam generator wet layup. In addition, the operating conditions were categorized relative to plant conditions (i.e., temperature, reactor critical / not critical, power), and the table headings were revised accordingly. Some of the main changes are:

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- Chapter 7 was revised to incorporate updated guidance on corrosion product sampling (see Section 7.3.2.1). Guidance was added on the alternative to continuous blowdown sampling for sodium for OTSGs during startup (see Section 7.3.6). The section on EPRI ChemWorks™ software was updated (see Section 7.4.2). The section on hideout return evaluations was updated based on recent work completed in EPRI's Steam Generator Management Program (see Section 7.4.4.4).

- A new Chapter 8 was added that captures all of the specific elements contained within these *Guidelines* that are identified as mandatory, shall or recommended, consistent with NEI 03-08 and NEI 97-06.

- Appendices A and B were reviewed and updated as appropriate.

This revision of the *Guidelines* continues the approach of helping utilities maintain a proactive chemistry program to mitigate steam generator degradation while taking into consideration limits on corporate resources and plant-specific design/operating concerns.

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INTRODUCTION AND MANAGEMENT RESPONSIBILITIES

1.1 Introduction and Objectives

Water chemistry programs have been established for operating pressurized water reactors (PWRs) to minimize corrosion concerns. It is recognized that there is no single water chemistry program that provides acceptable corrosion risks and satisfies corporate business objectives. The objective of this document is to provide guidance on determining and implementing a set of plant-specific water chemistry requirements for the secondary cycle of PWRs. Accordingly, this document presents the corrosion data that provide the technical bases for water chemistry control (Chapter 2), the various water chemistry control strategies that are available (Chapter 3), a recommended methodology for plant-specific optimization (Chapter 4), generic water chemistry guidelines for RSGs and OTSGs (Chapters 5 and 6, respectively), suggested data collection, evaluation, and management techniques (Chapter 7), and summary of mandatory, shall and recommended elements (Chapter 8).

The U.S. nuclear power industry established a framework for increasing the reliability of steam generators by adopting NEI 97-06, *Steam Generator Program Guidelines* [1, 2, 3]. This initiative references EPRI's Water Chemistry Guidelines, including this document, as the basis for an industry consensus approach to chemistry programs. Specifically, the initiative requires that U.S. utilities meet the intent of the *EPRI PWR Secondary Water Chemistry Guidelines*. The focus of the NEI initiative is steam generator integrity. These *Guidelines* include control parameters and monitoring requirements which must be incorporated into a plant's water chemistry program in order to meet the intent of these *Guidelines*.

The U.S. nuclear power industry has more recently produced a policy that commits each nuclear utility to adopt the responsibilities and processes on the management of materials aging issues described in NEI 03-08, *Guideline for the Management of Materials Issues*. NEI 03-08 was established in May 2003 [4], and the addenda to NEI 03-08, *Materials Initiative Guidance*, were most recently issued in April 2007 x[5]. Revision 1 of NEI 03-08 was issued in April 2007 [6]. The scope of NEI 03-08 extends to:

- "PWR and BWR reactor pressure vessel, reactor internals and primary pressure boundary components",
- "PWR steam generators (SG)",
- "Non Destructive Examination (NDE) and chemistry/corrosion control programs that provide support to the focused programs above", and

- "Other materials related items as may be directed by the Materials Executive Oversight Group (MEOG)."

In addition, NEI 03-08 states, "as deliverables or guidelines are developed, actions should be classified as to relative level of importance: 'mandatory'—to be implemented at all plants where applicable; 'needed'—should be implemented whenever possible but alternative approaches are acceptable, and 'good practice'—implementation is expected to provide significant operational and reliability benefits, but the extent of use is at the discretion of the individual plant/utility."

The Steam Generator Management Program (SGMP) has issued formal guidance [7] that is to be followed by guideline revision committees with regard to specifying which portions of guidelines are mandatory, "shall" requirements (equivalent to "needed" per NEI 03-08), and recommendations (equivalent to "good practice" per NEI 03-08) in accordance with NEI 03-08 [4, 5, 6]. The following descriptions of these categories are quoted from [7]:

1. Guideline elements designated as "mandatory" are important to steam generator tube integrity and should not be deviated from by any utility. Steam generator tube integrity is defined as meeting the performance criteria as specified in NEI 97-06. Each utility is ultimately responsible for the operation of their plant(s) and actions taken at those plants, but must realize that it is highly unlikely that any deviations from mandatory elements would be supported by the industry.
2. Guideline elements designated as "shall" are important to long-term steam generator reliability but could be subject to legitimate deviations due to plant differences and special situations.
3. Guideline elements designated as "recommendations" are good or best practices that utilities should try to implement when practical.

The *PWR Secondary Water Chemistry Guidelines* in accordance with NEI 97-06, NEI 03-08 and the SGMP guidance adopted this framework, starting with Revision 6, to indicate the mandatory requirement, shall requirement, and recommendation portions. In addition to consideration of the steam generators (per the three items listed above), the other major components / subsystems of the secondary system are also considered in determining the mandatory, shall and recommended elements, per the guidance in NEI 03-08. The mandatory, shall, and recommended elements are specifically identified in Chapter 8 of these *Guidelines*. All other parts of these *Guidelines* are to be considered informational only.

Two significant considerations that were deliberated during the Revision 7 process, the results of which informed the committee regarding classification of items as mandatory, shall or recommended, were:

- the relationship between chemistry and steam generator tube structural integrity (as defined by the SGMP), and
- the recognition that NEI 03-08 specifically recognizes that "reliable and efficient operation" is part of the "management of materials issues", and thus "performance" includes, for example, the generation of steam (e.g., thermal performance) and not just corrosion mitigation.

It is the opinion of the Revision 7 committee that the action level values and action level responses create an infrastructure such that chemistry will not impact the structural integrity of the steam generator tubes. Thus, the action level values and action level responses do not rise to the level of a mandatory element. However, the development and maintenance of the Strategic Water Chemisty Plan is a mandatory element (see Chapter 4). Also, the recognition that "reliable and efficient operation" is part of the "management of materials issues" per NEI 03-08 requires that elements addressing maintenance of steam generator thermal performance, for example, be considered as shall elements.

Deviations to mandatory and shall requirements shall be handled in accordance with the guidance in the current revision of the Steam Generator Management Program (SGMP) Administrative Procedures. Additionally, these Guidelines recommend that any exception to a recommended element (see Chapter 8) be documented in the Strategic Water Chemistry Plan (see Section 4.1.1).

A temporary non-compliance to a shall monitoring frequency requirement, such as a temporary inability to take continuous samples, should not be treated as a deviation per the SGMP Administrative Procedures as long as it occurs as a result of normal maintenance activities (such as calibration or preventive maintenance) or as long as all of the following conditions are met:

- Compliance to the required monitoring frequency is restored as soon as reasonably practical.
- The reasons for the temporary non-compliance, together with the actions taken, are documented in accordance with the station's corrective action program.
- The actions include a sampling and analysis program that quantifies the parameter at a frequency defined as reasonable in plant specific documentation.

1.2 Water Chemistry Management Philosophy

Nuclear station management is charged with generating safe, reliable, and low-cost electric power. Management is periodically faced with a choice of either keeping a unit available to produce power to meet short-term system demands or maintaining good control of chemistry to help assure the long-term integrity of the steam generators, balance-of-plant (BOP), and turbines. To effectively deal with these concerns, it is important that all levels of utility management understand that a successful chemistry program must ensure compliance with regulatory commitments and with established industry guidelines for system/materials integrity, while meeting the economic demands of power generation. Management must understand that operation with off-normal chemistry may result in loss of availability of that unit and that this long-term loss of availability can be minimized by limiting the magnitude and duration of off-normal chemistry. Utility management must support the chemistry guidelines both in principle and in detail at *all* levels to ensure their effectiveness. The goal should be to extend the operating life of the steam generators, BOP components, and turbines, while providing an acceptable level of unit availability.

The information presented in this chapter is based on observations that operating and maintenance philosophies with regard to chemistry can significantly affect major component life span. The philosophy and policies discussed reflect the desire to operate in a proactive rather than a reactive mode. The cost associated with maintaining secondary water chemistry within these industry guidelines is less than those associated with the repair or replacement of steam generators or large turbine rotors and the outages associated with those efforts.

While it is recognized that variety among individual utility organizations exists, there are basic goals and functions common to all. This chapter addresses key management considerations but makes no attempt to specify how they should be integrated into a specific organizational structure. Additional organizational and administrative guidelines are presented in the *INPO Guidelines for the Conduct of Chemistry at Nuclear Power Stations* (INPO 06-007)[8]. Utility personnel are encouraged to combine the recommendations in this chapter with the INPO recommendations when developing/revising their site-specific programs.

This version of the *Guidelines* addresses research results and operational experiences that have developed since publication of Revision 6. Incorporated by reference are several EPRI application guidelines that are used to help implement some of the chemistry control strategies discussed in the chapters.

1.3 Generic Management Considerations

This section lists and discusses the considerations which are common to most utilities, including the elements of organizations which are needed to carry out the water chemistry program effectively. Actions are identified without specifying responsibility for completing them. Utility-specific implementation policies and procedures should assign the responsibilities to specific positions within the organization. One major element of these *Guidelines* is the need for every level of management to understand the importance of the mandatory, shall and recommended elements identified in Chapter 8 and their potential impact on, and benefits to, the utility company. In addition, there is a need for management to support a data collection, evaluation, and management system similar to the approach discussed in Chapter 7.

1.3.1 Policies

An important ingredient of a successful management plan for secondary water chemistry control is a set of specific written policies which implement these operating *Guidelines*. Each policy should:

- State the need for the policy
- State the corporate goal regarding secondary water chemistry and station operation
- Highlight corporate management support for the policy/procedure
- Assign responsibility for:
  - Preparation and approval of procedures to implement the policy
  - Assessment of the effectiveness of chemistry control in minimizing steam generator and other balance-of-plant degradation
  - Monitoring, analysis, and data evaluation for the chemistry program

  - Surveillance and review functions
  - Corrective actions
- Establish the authority to:
  - Carry out procedures
  - Implement corrective actions
  - Resolve disagreements

Procedures implementing these policies normally are separate documents but should, when taken together, contain the level of detail necessary for personnel at all levels to understand and carry out their responsibilities. For plants under construction these procedures should cover both design and operation of the power plant.

The potential for control of operating chemistry is determined during the design phase of a nuclear power plant. The EPRI utility requirements document (URD) [9] provides guidance in support of the next generation of nuclear plants. It provides information about the standards, limits, and expectations of each design element to allow for the flexible implementation of proven technologies. The design recommendations related to water chemistry control are found in Volume III (Passive Plants): Chapters 1 (Overall Requirement), Chapter 2 (Power Generation Systems), Chapter 3 (Reactor Coolant System and Reactor Non-Safety Auxiliary System), and Chapter 4 (Reactor Systems). The water chemistry design recommendations include:

- Available and proven chemical control options for corrosion control, fuel performance and reliability, and source term control
- Up-to-date materials specifications for source term control and corrosion control
- Operational chemistry protocols and techniques
- References to the latest Water Chemistry Guidelines, including these *Guidelines*, for the most up to date water chemistry guidance

The latest water chemistry revisions to the URD will be incorporated into the document by the end of 2008. The key revisions and rationale of these water chemistry revisions can be found in in Appendix A, Section 3 of [10].

As construction of the plant proceeds, the operating procedure options may be limited. Preoperational modifications or equipment additions may be identified as necessary to meet state-of-the-art technology. Post-operational modifications to improve chemistry control should also be considered, when judged to be cost effective.

Utility personnel responsible for plant design in chemistry related areas should:

- Understand steam generator design, secondary system materials of construction, and the operational chemistry relationship.
- Ensure that the system design is reviewed by experienced plant operating personnel, vendors, and/or consultants, as appropriate.

During the operating phase, the steam generators and turbines are particularly sensitive to water and steam chemistry/purity. Operating procedures should address:

- Chemistry control limits and corrective action requirements.
- A plant-specific chemistry monitoring/surveillance program to assure that chemistry excursions are quickly identified.
- Detailed chemistry procedures containing action levels, specific responses to each action level, and corrective action notification and responsibilities.
- Plant approved analytical procedures to ensure accurate laboratory results.
- Provisions for data review to assure program implementation.

1.4 Training and Qualification

A program for periodic (continuing) training of all personnel involved with secondary water chemistry control should be established. This program should incorporate the latest information available from EPRI, other utilities, and the steam generator/turbine vendors. Some indoctrination in the basics of the program should be considered for all employees who, by virtue of their job responsibilities, can affect water chemistry.

The training programs should be designed for the level and qualifications of personnel being trained. The following elements should be included:

- A clear statement of the corporate policy regarding secondary water chemistry control, including clarification of the impact of this policy upon the various areas of responsibility.
- Identification of the impact of poor chemistry control on major component performance, unit availability, and corporate economic performance should be emphasized.
- Techniques for recognizing unusual conditions and negative trends should be addressed, particularly for the station chemists and laboratory technicians. Potential corrective actions and their consequences should be thoroughly discussed.
- The interaction of system operations and chemistry.

1.5 Summary

It is recognized that a specific program applicable to all plants cannot be defined due to differences in design, experience, management structure, and operating philosophy. However, the goal is to maximize the availability and operating life of major components such as the steam generator and the turbine. To meet this goal, an effective corporate policy and water chemistry control program are essential and should be based upon the following:

- A recognition of the long-term benefits of, and need for, avoiding or minimizing corrosion degradation of major components.
- Clear and unequivocal management support for operating procedures designed to avoid this degradation.

- Adequate resources of staff, equipment, funds, and organization to implement an effective chemistry control policy.
- An evaluation of the basis for each chemistry parameter, action level and specification, as well as those of similar guidelines.
- Management agreement at all levels, prior to implementing the program, on the actions to be taken in response to off-normal water chemistry and the methods for resolution of conflicts, and unusual conditions not covered by the guidelines.
- Continuing review of plant and industry experience and research and revisions to the program, as appropriate.
- A recognition that alternate water chemistry regimes, if used, should not be a substitute for continued vigilance in adherence to the guidelines.

1.6 References

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2
TECHNICAL BASIS FOR WATER CHEMISTRY CONTROL

2.1 Summary

Corrosion of steam generator tubes has been the major issue affecting selection of secondary water chemistry parameters. However, corrosion and flow-accelerated corrosion (FAC) of steam generator internals and other secondary system components are also important concerns. The objective of this chapter is to review the causes of this corrosion and FAC and to provide the technical bases for measures to control these concerns.

Corrosion of steam generator tube materials is mainly affected by the following water chemistry related factors, in addition to non-water chemistry factors such as material susceptibility, temperature and stress:

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2.2 Introduction

This chapter of the secondary water chemistry guidelines discusses corrosion issues affecting PWR steam generators and balance of plant components, with the objective of providing bases for selecting secondary water chemistry parameters that minimize problems due to corrosion.

The objective of secondary side water chemistry control is to minimize corrosion damage and performance losses for all secondary system components and to thereby maximize the reliability and economic performance of the secondary system. To achieve this objective, the water chemistry has to be compatible with all parts of the system including steam generators, turbines, condensers, feedwater heaters, moisture separator reheaters (MSRs), and piping. The variety of materials used in the many components in typical secondary systems, and the range of temperatures, pressures, phases, and velocities place constraints on the selection of water chemistries for secondary systems.

In this chapter, corrosion and chemistry issues affecting the steam generators are discussed first and in considerable detail, since these issues have been the main factors influencing secondary water chemistry guidelines. The remainder of this chapter deals with BOP components. The discussion of BOP issues is limited in depth and is general in nature since corrosion issues for the BOP are not the main factors controlling the secondary water chemistry guidelines. In this regard, secondary system impurity limits are generally not controlled by BOP corrosion issues, but pH agent selection and concentrations, and thus feedwater pH, take into account the full BOP circuit.

2.3 Corrosion of Steam Generator Tubing Alloys—Scientific Aspects

This section is a technical review of the causes and mechanisms of corrosion of steam generator tube materials.

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2.3.1 Role of Protective Oxide Films

The main constituents of Alloys 600, 690 and 800 are nickel, chromium and iron. At typical secondary side conditions, nickel, chromium and iron are more stable as oxides than as metals. The reason that these tube alloys can be used, despite the reactivity of their constituents, is that a thin protective oxide film (typically less than 1 μm thick) forms on the metal surface that reduces reaction rates of the base metal with the environment to low levels. A drawback of using a material that relies on thin films for protection is that it makes the material susceptible to modes of corrosion that involve disruption of the integrity of the films. If wholesale instability of the film occurs, general corrosion or wastage results (also known as thinning). If localized breakdown of the film occurs, pitting can occur at that location. In the presence of stress, stress corrosion cracking (SCC) can occur.

2.3.2 Potential—pH (Pourbaix) Diagrams

The regions of thermodynamic stability of metals and oxides are typically evaluated using potential - pH (Pourbaix) diagrams of the type illustrated in Figure 2-1, which shows the stable phases for the nickel - water system [5]. The abscissa is the conventional at-temperature pH of the solution in contact with the metal. The ordinate is the electrochemical potential (ECP), which is often referred to as the potential. Potential only has meaning when measured relative to some standard; by convention, the potential is normally shown relative to the potential of a standard hydrogen electrode (SHE). The stability region for water lies between the H_2O - H_2 ("hydrogen") line, indicated as line (a) on the figure, and the O_2 - H_2O ("oxygen") line, indicated as line (b) on the figure. Note that the hydrogen line goes through the zero - zero point, i.e., has a zero potential at zero pH. Conditions for wetted tube surfaces are normally between these two lines. The specific locations of the lines vary somewhat depending on the partial pressures of the oxygen and hydrogen. By convention, the lines are shown for one atmosphere partial pressures.

The potential at the metal surface (i.e., the vertical position on the diagram) is determined by the concentrations of oxygen and hydrogen and other oxidizing or reducing species (such as copper oxides, hydrazine, etc.). For fully deaerated conditions with no other oxidants such as copper oxides present, the potential will be close to the hydrogen line at the system pH.

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Figure 2-1
Potential—pH (Pourbaix) Diagram for Nickel-Water System at 288°C (Dissolved Species Activities of 10^{-3}) [5]

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The potential - pH diagrams for the other two main alloying elements in tubing alloys, chromium and iron, are shown in Figure 2-2 and Figure 2-3 and are similar to that illustrated in Figure 2-1 [5]. All of the metals dissolve or form soluble compounds at high or low pH, are resistant to dissolution type corrosion at low potential where the metal state is stable, and are protected by oxide films in the middle of the pH range when the potential is in the mildly reducing range (i.e., slightly above the hydrogen line). In the low potential region where the metal will not corrode in the sense of dissolving, it can still be damaged by chemistry-related processes such as hydrogen embrittlement. The diagrams for the tube alloys are believed to have the same general features as the diagrams shown in Figure 2-1 through Figure 2-3 for pure metals, but the specific fields of stability will vary somewhat depending on the alloy composition [7].

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Figure 2-2
Potential—pH (Pourbaix) Diagram for Chromium-Water System at 288°C (Dissolved Species Activities of 10^{-3}) [5]

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Figure 2-3
Potential—pH (Pourbaix) Diagram for Iron-Water System at 288°C (Dissolved Species Activities of 10^{-3}) [5]

Potential - pH conditions in crevice areas of steam generators are not well known. As impurities accumulate and concentrate in crevices, the pH can either increase or decrease, depending on the balance between cations and anions that are not removed by volatilization, precipitation or reaction. As long as conditions are fully deaerated, the potential will tend to remain close to the hydrogen line, i.e., increase or decrease at the same rate as the hydrogen line (-110 mV per unit increase in pH at 288°C). **Content deleted - EPRI Proprietary Information**

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2.3.3 Effects of Potential on Corrosion, and Protectiveness of Oxide Films

An important factor not shown on potential - pH plots is whether the oxide film, in regions where it is stable and the underlying metal can oxidize, will protect the metal despite its tendency to oxidize. This question can be explored via a polarization plot. A typical polarization plot is shown on Figure 2-4.

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Figure 2-4
Schematic Diagram of an Anodic Polarization Curve of an Active/Passive Alloy (Adapted from Figure 10-16 in [9])

Experiments show that different forms of corrosion typically occur in different regions of the polarization plot. These forms vary depending on the alloy, pH and specific chemical species involved. Using a polarization plot for 600MA in caustic as an example, Figure 2-5, the following points can be noted:

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Figure 2-5
Polarization Curve for Alloy 600 in Caustic at 300°C (Adapted from [10])

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A polarization plot for Alloy 600MA in a highly acidic chloride - sulfate solution is shown in Figure 2-6.

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Figure 2-6
Polarization Curve for 600MA and 600SR in Complex Acid Environment [10]

Another polarization curve of interest is that for 800NG in chloride containing AVT water, shown in Figure 2-7, part a) [11].

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Figure 2-7
Polarization and Pitting Behavior of Alloy 800NG in Acid Chlorides [11]

A final polarization curve of interest is one for near neutral concentrated sodium chloride, shown in Figure 2-8.

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Figure 2-8
Polarization Curve for Alloy 600MA in Near Neutral Concentrated Sodium Chloride [10]

The main point of interest to chemists with regard to polarization is that localized corrosion (such as SCC and pitting) of passive alloys generally worsens as the potential becomes more oxidizing. For this reason it is desirable to minimize the possibility of oxidizing conditions developing at locations where corrosion could be a concern, such as crevices in steam generators.

Another factor that needs to be kept in mind when evaluating effects of potential and protectiveness of oxide films is that the thickness and protectiveness of the oxide film depends on the past history of the metal surface. It is generally believed that the protectiveness of the film increases as it grows thicker during exposure to benign high temperature conditions. Conversely, tubing alloys have increased susceptibility to corrosion if the protective film is removed and the tubing is exposed to aggressive conditions without an opportunity to regrow the protective film. Evaluations of chemical cleaning methods and post cleaning startup procedures should consider the possible effects of these operations on the protective films.

2.3.4 Effects of Specific Species

Chemical species in solutions contacting metal surfaces affect corrosion behavior in several different ways. The first ways are by affecting the potential and pH, thereby causing modes and rates of corrosion to vary. For example, dissolved oxygen and oxidizing corrosion products or ions raise the potential, and can accelerate many forms of corrosion. Acid and alkaline species shift the pH and thereby affect the rate and mode of corrosion. In addition to these "global" effects, certain species appear to affect corrosion by modifying the protectiveness of the oxide films that are the barrier against corrosion. The main species that are known or suspected of strongly affecting steam generator tube alloys are briefly discussed below. More information is covered for some of them in the later discussion of engineering aspects.

2.3.4.1 Known Deleterious Species

- *Caustics.* Numerous tests have shown that concentrated caustics lead to IGA and SCC of all of the tubing alloys [13]. In these environments the rate of attack can be very rapid if oxidizing deposits are also present.

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- *Lead, Other Low Melting Point Metals, and Arsenic.* The current state of knowledge regarding lead accelerated stress corrosion cracking has recently been summarized in an EPRI sourcebook [14].

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- *Sulfur.* Sulfur in the form of sulfate (i.e., fully oxidized) appears to affect IGA/SCC of tubing alloys only by its effect on pH, i.e., not as a specific species (see next paragraph relative to wastage). However, if the sulfur is present at a lower (reduced) oxidation state, the sulfur appears to have species-specific and more detrimental effects. Possible sources of reduced sulfur species in the SGs include ingress of cation resin beads and fines and reduction of sulfate in the SG by the reducing environment associated with the presence of hydrazine. Reduced sulfur species appear to interfere with formation of passive films on nickel surfaces and to assist in the breakdown of these films.

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Figure 2-9
Cracking Time in Sodium Tetrathionate for Alloy 600 C-Rings with Two Different Heat Treatments [19]

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- *Chlorides.* All of the tubing alloys are susceptible to chloride pitting under acid oxidizing conditions [25]. In addition, chlorides cause SCC of austenitic stainless steels, which have about 18% chromium and 8% nickel. Alloys 600MA, 600TT and 690TT are believed to be essentially immune to this type of specific ion attack, though SCC can occur in these alloys in acid chlorides, apparently due to the low pH.

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- *Fluorides.* The effect of fluorides on tubing alloys is similar to the effect of chlorides, except that the strength of the effect in liquid environments is generally less for the same molar concentrations [27, 28]. Fluorides are more volatile than chlorides, and thus are less likely to accumulate in liquid filled crevice areas.

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- *Copper*. Copper when present as copper oxide has been shown by tests in AVT water and in caustic to accelerate SCC of 600MA

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2.3.4.2 Possibly Deleterious Species

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2.3.4.3 Possibly Beneficial Species

- *Boric acid.* Tests indicate that boric acid in the secondary water inhibits denting corrosion and SCC due to concentrated caustics [47]. Effects of boric acid on denting corrosion are discussed in Section 2.4.6.

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- *Titanium and zinc.* Tests indicate that titanium and zinc become incorporated in films on 600MA and thereby increase resistance to SCC in high temperature caustic solutions [50]. Zinc is reported as having a similar effect regarding inhibiting against SCC in primary water [51]. Plant data regarding effects of inhibitors are discussed later in the discussion of engineering aspects.
- *Silica.* Comparisons of plant IGA/SCC data with blowdown silica levels indicated that lower rates of IGA/SCC have been experienced at plants with silica levels above about 40 ppb in the blowdown [52, 53].

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2.3.5 Modes of Corrosion Affecting Alloys 600, 800 and 690

A useful way of illustrating the corrosion behavior of materials is to show the regions of passivity and the regions where different modes of corrosion occur on potential - pH plots. This type of plot is called a "mode diagram." A mode diagram for 600MA based on the work of Staehle is shown on Figure 2-10 [57].

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Figure 2-10
Alloy 600 Corrosion Mode Diagram (T~300°C) (Adapted from Staehle, [57])

The following features in Figure 2-10 are of note:

- The potential - pH region that results in the least corrosion is the one marked "Passive Region" which is the region where passive oxide films make the material resistant to corrosion. This region spans pH 5 to 9, and has potentials about 50 mV and higher above the one atmosphere hydrogen line.

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- Submodes I_{IGA} and I_{SCC} are the alkaline modes of IGA/SCC that occur at high pH with potentials close to or above the hydrogen line.

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- Submode II_{SCC} is for SCC that occurs under mildly acidic conditions, e.g., for pH about 4.

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- Submode III_{SCC} is for SCC in a low potential region which spans a large range of pH. This is the mode that includes pure and primary water stress corrosion cracking (PWSCC).

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- Submode IV_{SCC} is for SCC that occurs under strongly oxidizing acidic conditions. It is unlikely to develop in steam generators, unless extreme oxidizing conditions exist.

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As can be seen from Figure 2-10, there are several environments that can cause IGA/SCC of 600MA. If lead is present, it is difficult to avoid operating in areas where IGA/SCC occurs with typical steam generator temperatures and tube stresses. Nevertheless, the region of lowest susceptibility is believed to be in the pH 5 to 9 range, with potentials slightly above the 1 atmosphere hydrogen line.

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Figure 2-11 is similar to Figure 2-10, and compares the behavior of 600MA, 600TT, and 690TT [65]..

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Figure 2-11
Corrosion Mode Diagram for Alloys 600MA, 600TT and 690TT (Based on CERT Tests at 300°C) (from [65])

2.3.6 SCC and IGA Growth Rates

The growth rates of cracks and IGA for 600MA have been found to be affected by at least the following variables:

- Metallurgical structure (result of composition and fabrication and heat treatment history)
- Presence of cold work
- Stress and stress intensity
- Temperature
- pH
- Potential
- Specific chemical species (e.g., lead)

Trend-line type curves for IGA growth rate and SCC growth rate in 600MA have been developed from experimental data and are shown in Figure 2-12 and Figure 2-13 [74]. The data on which these curves are based have been normalized for temperature and, in the case of SCC growth rate, also for stress or stress intensity. The SCC figure shows growth rates only for relatively severe stress/stress intensity conditions. The SCC figure also shows the effects of having lead present in the environment. Variations for metallurgical structure - heat treatment history are not explicitly addressed, but it is believed that the curves represent 600MA material that is relatively highly susceptible. Some points to note about these curves and the underlying data:

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Figure 2-12
IGA Growth Rate vs. pH at 315°C for 600MA (Adapted from [74])

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Figure 2-13
SCC Growth Rate vs. pH at 315°C for 600MA (Adapted from [74])

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2.4 Corrosion of Tubing Alloys—Engineering Aspects

The previous discussion covered scientific aspects regarding corrosion of tubing alloys. This portion of Chapter 2 discusses engineering aspects. It is focused on IGA/SCC of 600MA since this is the corrosion mode - alloy combination that historically has been of most concern to the industry. However, other corrosion modes and alloys are covered where appropriate.

Significant amounts of IGA/SCC of 600MA developed in many PWR steam generators, with corrosion occurring at many areas of the tube bundle. The main factors that appear to be involved in this IGA/SCC are reviewed below.

2.4.1 Susceptibility in a Variety of Possible Environments

As discussed above, at the temperatures present in PWR steam generators, 600MA is susceptible to IGA/SCC in a range of environments. This increases the chances that an environment that can cause IGA/SCC will develop at some time and location in a steam generator. An additional consideration is that it appears that cracks, once initiated, can continue to grow in environments that are not sufficiently severe to initiate cracks.

Model boiler tests have been used to explore the effects of the environments that can develop under heat transfer conditions.

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In summary with regard to model boiler tests with 600MA tubes, they indicate that:

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2.4.2 Effects of Material Condition and Type on Susceptibility to Corrosion

Plant experience indicates that there is a range of susceptibility of 600MA tubing to secondary side IGA/SCC.

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Table 2-1
Relative Corrosion Behavior* of Alloys 600, 690 and 800 [77]

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Figure 2-14
Laboratory Test Based Improvement Factors for Alloy 600TT versus Alloy 600MA From Data Reviewed in Reference [94]

Test data indicate that the susceptibility of Alloy 690TT to caustic can be highly variable among product forms, apparently as a result of differences in microstructure introduced by the fabrication route [96]. However, other tests show that use of a high enough mill anneal temperature results in satisfactory resistance, regardless of fabrication route [97], and a review with suppliers indicated that all Alloy 690 tubing supplied to US utilities had been mill annealed at sufficiently high temperatures to provide good resistance [98].

Several evaluations of the relative resistance to degradation of various tubing alloys have been performed.[94, 95, 99, 100, 101, 102, 103]

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Figure 2-15
Laboratory Test Based Improvement Factors for 690TT versus Alloy 600MA From Data Reviewed in Reference [99]

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Figure 2-16
Laboratory Test Based Improvement Factors for Alloy 800NG versus Alloy 600MA From Data Reviewed in Reference [102]

In summary with regard to effects of material and microstructure, laboratory tests indicate that

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2.4.3 Elevated (Anodic or Oxidizing) Electrochemical Potentials

Elevated potentials can be caused by ingress of oxygen or reducible corrosion products such as hematite, goethite, lepidocrocite, and copper oxide (these oxidized corrosion products are also known as reducible metal oxides or RMOs). This has been demonstrated by measurements for metal surfaces exposed to oxidants in caustic and near neutral environments [105].

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Figure 2-17
Maximum Crack Depth vs. Specimen Potential for 600MA and 600TT Exposed to 10% NaOH at 315°C (Adapted from 108)

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A loss of hydrazine addition can also result in elevated potentials. This scenario is discussed in Section 3.5.2.

2.4.4 Depressed (Cathodic) Electrochemical Potentials

Laboratory tests [111] and plant experience have clearly shown that high stress - high cold-work areas of 600MA are susceptible to pure or primary water stress corrosion cracking (PWSCC) at reducing conditions. For this reason, this type of cracking is sometimes called low potential stress corrosion cracking or LPSCC. This subject is thoroughly reviewed in two 2007 reports regarding possible changes to primary side hydrogen concentrations to ameliorate PWSCC [112, 113].

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Hydrazine is known to depress the potential in a manner similar to hydrogen (Figure 2-18).

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Thus, sufficient hydrazine could increase the possibility for LPSCC to occur at cold worked high stress areas on the secondary side.

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Figure 2-18
Corrosion Potentials of Type 304 Stainless Steel as a Function of Hydrazine Concentration at 100, 200, 250 and 288°C in High Purity Water [115]

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Figure 2-19
Effect of Hydrazine-to-Oxygen Ratio on Alloy 690 ECP (pH_T Corrected) [114]

2.4.5 High Temperature, High Stress, and Local Cold Work

Temperature, stress, and local cold work (surface damage) are not factors under the control of plant chemists. Nevertheless, chemists should be aware that increases in any of these three factors increase susceptibility to SCC.

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2.4.6 Denting

Denting is the process by which a corroding component deforms a SG tube due to the volumetric expansion that occurs during corrosion when the oxide occupies more volume than the metal from which it formed. Stresses and strains due to denting can aggravate IGA/SCC and can also cause PWSCC.

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Laboratory tests indicate that boric acid reduces the rate of denting. Evaluation of plant data suggests that use of on-line boric acid additions and boric acid soaks during plant startup tend to reduce the rate of denting.

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Figure 2-20
The Influence of pH and Electrode Potential on the Radius Change of Carbon Steel and Type 405 Stainless Steel at 280°C [118]

2.4.7 Effects of Lead

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2.4.8 Pitting

Pitting severely affected the original steam generators at three seawater or brackish water cooled plants with 600MA tubing:

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2.4.9 Contaminated Steam and Internal Oxidation

Attack in steam contaminated with small amounts of impurities has been hypothesized as a possible cause of IGA/SCC on the secondary side [8]. The hypothesis is that the IGA/SCC occurs in a steam environment contaminated with small amounts of moisture and impurities. Support for this hypothesis includes:

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A related hypothesis is that the cracking occurs as the result of an internal oxidation mechanism [127]. The internal oxidation theory involves oxygen diffusion down grain boundaries that embrittles them.

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2.4.10 Fouling Issues

The principal fouling issues that have affected PWRs that are related to secondary side water chemistry are feedwater venturi fouling, degradation of steam generator thermal performance, and problems caused by changes in flow patterns.

Feedwater Venturi Fouling. The main cause of feedwater venturi fouling is corrosion product deposition in high velocity regions of the venturi. This type of buildup is relatively reproducible and rapid, typically occurring during the first few months after cleaning of the nozzle.

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Steam Generator Thermal Performance Degradation. A review of PWR experience indicates that, at many plants, steam pressure at 100% reactor power initially increases and then decreases steadily as the plant ages (Figure 2-21) [136]. Figure 2-22 from this same review indicates that tube scale thickness increases steadily as plants age. In some cases, reduction of steam pressure is due to decreases in the secondary heat-transfer coefficient as a result of insulating tube scale.

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Figure 2-21
Steam Pressure Deviation from Design at Several Japanese Plants [136]

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Figure 2-22
Scale Thickness as a Function of Operating Time [136]

The main driving factor leading to buildup of tube scales is the fact that boiling is occurring with high heat fluxes, which tends to result in deposition of particulates and dissolved solids from the water onto the heat transfer surfaces.

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As noted earlier, in addition to the thickness of the tube scale, the morphology of the scale has a strong influence on heat transfer performance. For example, porous scales with wicks and chimneys for fluid flow can promote the boiling process and improve heat transfer relative to clean tube surfaces. On the other hand, solid scales without through-thickness channels for fluid flow retard heat transfer. The factors controlling the morphology are complex and are similar to those controlling the thickness [139].

One of the leading theories for deposit formation on tube surfaces involves the zeta potential, which is a strong function of the pH (the zeta potential is developed by surface charges) [139].

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Deposit formation is also affected by the iron oxidation state.

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Steam Generator Tube Support Fouling. Another factor affecting steam generator thermal performance is increases in pressure drops across tube support plates caused by deposit buildup at flow passages.

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Potential Impact of Iron Form in Determining Tube Scale Heat Transfer Properties. There is a general tendency for thinner steam generator tube scale to be neutral or even beneficial with regard to heat transfer while thicker scale layers tend to be insulating. However, recent investigations [147, 148] have suggested a correlation between the form of the depositing impurities and the heat transfer properties of the resultant tube scale, regardless of the scale thickness.

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Experiences at several PWR steam generators tend to support this hypothesis [147], as very thin tube scale has been shown in some cases to contribute to thermal performance decreases, even though many plants have experienced the opposite trend with thin scale (no effect or a performance benefit)..

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Investigations of the impact of particulate and soluble species on fouling rates and boiling heat transfer were carried out by AECL as part of an EPRI funded project [142]..

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The potential benefits of this finding are significant for those plants that operate with little available margin for tolerating heat-transfer decreases. (Factors which can affect steam generator thermal performance margin are discussed in Reference [149]).

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Problems Induced by Flow Pattern Changes.

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2.4.11 Considerations Regarding Use of Inhibitors

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Boric Acid.

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A limited amount of testing of the effects of boric acid in non-caustic environments has been performed.

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Phosphates. Phosphates have been used for many years as a water treatment additive in fossil plants. The phosphates serve to combine with hardness forming chemicals and thus minimize development of hard scales on heat transfer surfaces. The phosphates also control the pH and buffer against development of acidic or caustic conditions [162]. Phosphates were widely used in PWR steam generators in the early days of nuclear power.

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Titanium Compounds. Laboratory tests using C-rings and constant extension rate specimens have shown that titanium inhibits SCC in caustic environments [50, 166]. Titanium appears to provide this benefit by being incorporated into and enhancing the protectiveness of the oxide film.

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2.4.12 Considerations Regarding Wet Layup of Steam Generators

During shutdown periods steam generators are often put into wet layup. The objectives of wet layup are as follows:

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Figure 2-23
Corrosion Rates of Unfilmed 1010 Carbon Steel, Data from References [173, 185]

There are a number of plant-specific factors which could make lower hydrazine concentrations acceptable, including the following:

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Test data for carbohydrazide and diethyl hydroxylamine (DEHA) [173] indicate that assessing the effectiveness of these oxygen scavengers based on a hydrazine equivalent (1.4 ppm of carbohydrazide or 1.2 ppm of DEHA being equivalent

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Although there is some indication that higher pH values result in less corrosion in the range 9.0 to 10.0, the benefit of higher bulk pH is expected to be small in deaerated solutions. When considering a layup pH specification, the following calculated values of solution $pH_{25°C}$ are useful:

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An additional aspect of maintaining effective layup conditions is the cover gas. Sections 5.6.1 and 6.5.2 of these *Guidelines* recommend a nitrogen cover gas.

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2.4.13 Dispersant Application for Mitigation of Steam Generator Fouling

Dispersants have been used to inhibit corrosion product fouling in fossil boilers for several decades. However, only in recent years has a dispersant of sufficient purity become available for nuclear application for the purpose of reducing steam generator (SG) deposit fouling rates.

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Based on the extensive qualification efforts and the two plant trials completed at ANO-2 and McGuire 2, utilities can anticipate achieving the following goals with PWR dispersant injection, based on a typical dispersant feedwater concentration of about

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Figure 2-24
Iron Removal Efficiencies During ANO-2 and McGuire 2 Dispersant Trials [150]

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Based on the extensive qualification work and the two plant trials, sufficient information to support safe and effective long-term use (LTU) of dispersant for reducing SG deposit fouling rates has been developed. The dispersant application sourcebook [150] provides summary discussion of all the technical bases as well as detailed guidance to utilities to apply dispersant at one or more of their stations.

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This element is captured in Table 5-7.

2.5 Balance of Plant Considerations

With regard to the secondary system, the main objectives have been to minimize corrosion of the components in the systems so as to maximize their reliability and to minimize the transport of corrosion products from the secondary system to the steam generators. These objectives have mainly been addressed by control of pH around the system, by minimizing or controlling the concentration of oxidants in the system, and by minimizing impurity concentrations. Technical information related to these approaches is reviewed below.

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2.5.1 General Corrosion and Flow-Accelerated Corrosion (FAC) of Piping and Components, Including Steam Generators

The two main objectives for controlling general corrosion and flow-accelerated corrosion (FAC) in the secondary system are to reduce the rate of metal loss in secondary cycle components and to reduce the transport of corrosion products, including reducible metal oxides (RMOs), to the steam generators. Achieving these goals will minimize thermal performance losses in the steam generators due to deposit buildup, minimize development of aggressive crevice conditions due to deposit buildup, and reduce the likelihood of increasing the ECP in crevice areas and thereby aggravating corrosion. Methods used to address these objectives are discussed below.

2.5.1.1 Effect of Secondary System pH on General Corrosion and FAC

Feedwater pH has generally been selected to minimize corrosion of all of the materials in the system.

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Figure 2-25
Equilibrium Corrosion Product Release Rate from Alloy 706 (90/10 Copper Nickel) for an Oxygen Concentration of 20 ppb [195]

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Figure 2-26
Effect of pH on Iron Concentration at the Economizer Inlet—Crane Station [201]

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2.5.1.2 Selection of Secondary System pH_T Control Approach

The primary chemistry factors that control the rates of general corrosion and FAC are the local at-temperature pH, i.e., the pH_T, and the oxygen concentration or electrochemical potential (ECP).

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2.5.1.3 FAC Considerations

EPRI TR-106611-R1 provides a thorough review of water chemistry effects on FAC [207]. Additional work has been performed to evaluate the effects of redox conditions on FAC [208]. The effects of pH, oxygen, hydrazine, and electrochemical or oxidation/reduction potential are discussed below separately, but it should be noted that the variables interact and must be considered in an integrated manner.

2.5.1.3.1 Effects of pH_T on FAC

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2.5.1.3.2 Effects of Oxygen Concentration on FAC

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2.5.1.3.3 Effects of Hydrazine on FAC

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Figure 2-27
Relative FAC Rate (Ratio to FAC Rate without Hydrazine and Oxygen) Measured in a Single-Phase Flow at 180°C and 235°C Using Ammonia ($pH_{25°C}$=9.0) with Different Amounts of Hydrazine and Oxygen [208]

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Figure 2-28
FAC Rates of Carbon Steel as a Function of Hydrazine Concentration (17-131 ppb) in Water Conditioned with NH_3, $pH_{25°C}$ of 9, Test Temperature of 235°C [224]

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Figure 2-29
Relative FAC Rate (Ratio to FAC Rate without Hydrazine and Oxygen) versus Hydrazine Concentration for Tubular Carbon Steel Specimens (0.009% Cr) Exposed to a Single-Phase Flow at 180°C Using Ammonia ($pH_{25°C}$=9.0) and With Oxygen Maintained Less Than or Equal to 0.5 ppb [208]

In summary, FAC is affected by several chemistry variables, especially pH_T, oxygen concentration, and electrochemical potential. In parts of the system where oxygen is very low (e.g., steam drains), the potential is low and control of the pH_T is generally the only practical chemistry approach for controlling FAC. (However, note that oxygen injection was used at Philippsburg as discussed above.) In the condensate-feedwater system, control of oxygen content and thus potential is a possible strategy for the reduction of general corrosion and FAC. However, this objective must be balanced against the objective of ensuring that fully reduced conditions are maintained in the steam generators. This balance is covered in Chapters 3 and 4.

2.5.1.4 Effect of Amines on Steam Generator Fouling Rates

As discussed above, the selected amine and its concentration strongly influence general corrosion and FAC rates in the secondary system, and thus the concentration of corrosion products being transported to the steam generators.

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2.5.2 BOP Layup Considerations

The Steam Generator Owners Group (SGOG) and EPRI have sponsored a number of surveys and assessments of layup practices and their effects on corrosion of secondary system components.

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2.5.3 Startup and Cleanup Considerations

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2.5.4 Turbines

2.5.4.1 Turbine Corrosion Considerations

Considerations regarding the effects of water chemistry on steam chemistry and PWR turbines are covered in Appendix B, which should be consulted for more details.

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2.5.4.2 Effects of Turbine Hideout Return in OTSG Systems

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2.5.5 Secondary System Heat Exchangers

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2.6 Once-Through Steam Generators (OTSGs)

Once-through steam generators (OTSGs) are used in PWRs originally supplied by Babcock & Wilcox. The thermal hydraulics and water chemistry behavior of OTSGs differ in some respects from those of the more numerous recirculating steam generators (RSGs). For this reason, this subsection has been prepared to highlight some OTSG-specific information.

OTSGs are straight tube heat exchangers in which the feedwater is preheated to saturation and then enters at the bottom of the tube bundle and exits at the top as superheated steam. A two phase mixture is present in the lower portion of the bundle, and superheated steam is present in about the top one third [235]. The design basis of the OTSG was that it would be provided with high purity AVT feedwater and that the small amounts of ionic impurities that entered the tube bundle would be carried out with the steam.

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More than half of the original OTSGs had been replaced by 2007. The remaining units are scheduled for replacement between 2009 and 2015. The replacement units are all tubed with Alloy 690TT and have various other design changes.

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2.7 References

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3
WATER CHEMISTRY CONTROL STRATEGIES

3.1 Introduction

Chapter 2 discussed the corrosion mechanisms that can lead to degradation of steam generator tubing, with specific emphasis on the corrosion of Alloy 600MA. Chapter 2 also noted that Alloys 600SR, 600TT, 800NG, and 690TT are subject to the same corrosion mechanisms as Alloy 600MA, although they are somewhat more resistant. This chapter presents a variety of chemistry control strategies that can be used to adjust those parameters that were shown to accelerate corrosion of steam generator tubing materials. Included in this chapter are:

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Before discussing these options, this chapter will first discuss the role of the localized concentration processes. It is believed that the localized concentration factors achieved in flow-occluded regions are responsible for development of localized chemistry environments that are quite different from bulk water chemistry.

3.2 Role of Concentration Processes

Chemistry is controlled outside the steam generator to limit transport of impurities into the steam generator. Most impurities are at or near their minimum detectable concentrations by traditional analytical techniques. When the impurities increase above preset concentrations, actions are taken by station personnel that may include reduced power operation or plant shutdown. These Action Levels and associated concentrations are described in detail in Chapters 4, 5 and 6. In general, the chemistry parameters controlled during normal operation are based on room-temperature analyses of cooled samples of condensate, feedwater, or steam generator blowdown. Despite the various sample locations to which Action Levels are applied, all species are controlled based on their impact on the various steam generator, BOP, and turbine corrosion processes (discussed in Chapter 2).

It is understood by most that the concentrating effects of the steam generators are generally necessary to produce localized environments that are aggressive to steam generator tubing materials. Previous versions of these *Guidelines* have emphasized the role of liquids produced by the concentration factors achieved in various regions of the generator. This section will discuss the role of these concentration processes.

3.2.1 Concentration on Clean Tube Surfaces and Shallow Tube Scales

Steam generator bulk water impurities can be concentrated due to localized boiling processes on clean tube surfaces and within shallow oxide deposits on the tubes. Stable concentration factors (CF) on clean tube surfaces are thought to be less than 20 [1]. Figure 3-1 gives the data of Picone et al (1963) as cited in Reference [2] along with an extrapolation to typical PWR hot and cold leg heat fluxes. The data suggest that concentration factors of approximately 50 to 100 can be achieved within a shallow (1 mil) deposit on cold leg and hot leg surfaces, respectively. Experimental data using actual steam generator deposits of ~0.4 mil thickness suggest higher CFs of 13,000 can be reached [3]. In general, it is believed that the concentration process is governed by the physical geometry (e.g., deposit porosity) of the boiling region, since the ability of bulk water to replenish the concentrating solution is controlled by the communication between it and the deposit. Such a concentration process is deemed to be kinetically limited as is described by Figure 3-2 [4].

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Figure 3-1
Concentration Factors vs. Heat Flux for 1 mil Deposit [2]

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Figure 3-2
Schematic of a Kinetically-Limited Concentration Process, adapted from Reference [4]

Figure 3-3 shows the solution pH_T predicted for various chemistry inputs by MULTEQ for concentration factors from 1E0 to 1E6. The chemistry inputs are shown in Table 3 1. It should be noted that this curve is shown as an example, since a slight variation in input chemistry will result in different output.

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Figure 3-3
Crevice pH as a Function of Concentration Factor (MULTEQ Version 4.0, Database Version 5.0, Options: Temperature = 270°C, Static, Precipitates Retained, Vapor Removed)

Table 3-1
Chemistry Input for Determining Effects of Localized Concentration

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3.2.2 Concentration in Flow-Occluded Regions of RSGs

In portions of RSG steam generators that are flow occluded, where communication between the bulk water and the localized area is very poor, steam blanketed conditions can exist. This can occur, for example, in top of tubesheet crevices and sludge piles, in tube-to-tube support intersections, and in thick dense tube deposits.

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Figure 3-4
Crevice pH as a Function of Concentration Factor and Boiling Point Elevation for Na=3XCl (MULTEQ 4.0, Database 5.0, Options: T=270°C, Static, Precipitates Retained)

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Figure 3-5
Crevice pH as a Function of Concentration Factor and Boiling Point Elevation for Na=Cl (MULTEQ 4.0, Database 5.0, Options: T=270°C, Static, Precipitates Retained)

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Figure 3-6
Crevice pH as a Function of Concentration Factor and Boiling Point Elevation for Cl=3XNa (MULTEQ 4.0, Database 5.0, Options: T=270°C, Static, Precipitates Retained)

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Figure 3-7
Crevice pH as a Function of Concentration Factor and Boiling Point Elevation for Sulfate Solutions (MULTEQ 4.0, Database 5.0, Options: T=270°C, Static, Precipitates Retained, Vapor Removed)

In a thermodynamically limited crevice, similar chemistries will be produced if the ratios of impurities remain the same, even if bulk water concentrations vary. Therefore, driving bulk water impurity concentrations extremely low (e.g., to below detection limits) will not necessarily result in improved crevice chemistry, since similar chemistries will result even when concentrations are increased by a factor of 10. However, the mass of crevice solution will be lower, so that the surface exposed to potentially aggressive environments is lower. This discussion shows why proactive measures (e.g., corrosion product transport reduction, chemical cleaning, etc.) should be considered before concentrations in localized regions become thermodynamically limited.

It is generally well accepted that the mass of concentrated solution formed within a crevice is a function of the crevice evaporation rate and the concentrations of species in steam generator bulk water [5]. Given the presence of flow-occluded regions and the unknown characteristics of the crevices, the crevice evaporation rate is uncertain and beyond the control of the chemistry personnel. Bulk water chemistry is within the control of chemistry personnel. These guidelines, as well as previous revisions, continue to recommend the practice of maintaining impurities as low as reasonably achievable (commonly termed ALARA chemistry) to minimize the mass of crevice solution formed during operation. Note that ALARA chemistry does not mean that all parameters must be maintained below their analytical detection limits. It simply refers to the fact that lower bulk water concentrations will result in a lower mass of crevice solution.

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3.2.3 Conclusions

The chemistry program must be designed to provide local chemistry environments that are compatible with tubing materials, as identified in Chapter 2. However, such control cannot be accomplished without consideration of the concentration factors that are inherent in most steam generators. Steam generator tubing degradation experience within the industry suggests that ALARA chemistry alone has not been adequate to prevent corrosion initiation and propagation of Alloy 600.

The water chemistry control strategies available today are based on one or more of the following philosophies:

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3.3 pH and ECP Optimization to Minimize Iron Transport

The principal methods of controlling steady state corrosion product transport in the secondary system of PWRs are through pH control around the secondary system and electrochemical potential (ECP) control in the condensate-feedwater system. Feedwater corrosion products enter the steam generator and deposit on tube surfaces or deposit on tube supports and the tubesheet. The latter can form the flow-occluded regions described in Section 3.2. It has been emphasized that minimizing corrosion product transport to the steam generators can decrease the likelihood of formation of flow-occluded regions, limit the ingress of lead and oxidants, minimize loss of thermal performance, reduce tube support plate fouling, and extend the life of balance-of-plant (BOP) components.

3.3.1 pH Control

Secondary cycle pH optimization is an accepted practice in the all-volatile treatment (AVT) secondary chemistry control program. Such a practice involves consideration of BOP materials of construction and design, environmental concerns and costs.

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A plant-specific pH additive(s) should be selected based on a variety of factors, such as the following:

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3.3.1.1 Supporting Aspects of Alternate Amine Treatment

- The accumulation rate of corrosion product deposits in the steam generators and possibly the consolidation of those deposits can be reduced without risk of increased copper transport due to increased ammonia concentrations. Reduced deposit accumulation and consolidation can have a positive impact on steam generator corrosion, thermal performance, and operating costs.
- Secondary cycle chemistry control can be optimized using various amines or amine combinations. Corrosion of components subject to FAC can be reduced.

3.3.1.2 Considerations for Advanced Amine Treatment

- When implementing advanced amine treatment, a site-specific materials compatibility review will be necessary to ensure that components, particularly elastomers, are compatible with the amine.
- When implementing advanced amine treatment, additional tanks and pumps and/or various plant modifications and procedure modifications will be required.
- Training of personnel should be conducted for effective implementation.
- Amine treatment has a major impact on condensate polisher performance, including run times, regeneration frequencies/separation techniques, and sodium slippage. In some cases, resin fouling has also been observed. Some plants have found benefit in operating some of their beds in the amine form.
- Amine treatment impacts blowdown demineralizer run lengths and performance. Many plants have successfully operated the blowdown demineralizer; (a) past the amine break (i.e.,

using resin initially in the HOH form), or (b) in the amine form (i.e., using resin initially in the amine form).

- Additional chemical analyses are required.
- Decomposition products will elevate cation conductivity.
- The amine may have an impact on plant discharges, particularly via resin regenerations.
- Matrix effects on analytical procedures may be encountered.

3.3.2 Targeted pH Control by Tailored Injection of Amines

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3.3.3 ECP Control

Control of the electrochemical potential (ECP) to minimize FAC and iron corrosion product pickup in the condensate-feedwater system has been receiving increasing attention in the industry.

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3.4 Controlling or Adjusting Water Chemistry or Power Level to Minimize the Formation of Aggressive Water Chemistry Environments in Flow-Occluded Regions

3.4.1 ALARA Chemistry

Over the past 20 years or so, average blowdown impurity concentrations in U.S. steam generators have been reduced from several ppb to the sub-ppb range. Many PWRs today have steam generator blowdown concentrations near or below the analytical detection limit.

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ALARA chemistry is the most acceptable approach for minimizing the rate of impurity accumulation in steam generator crevices. The approach recommended in these and previous guidelines is to maintain ALARA chemistry.

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Some of the other water chemistry control regimes noted in this chapter are slight deviations from the "pure water chemistry" described by the ALARA concept. In other words, some of the regimes involve adding species to the bulk water rather than working to maintain all species at their lowest concentrations. For example, molar ratio control can involve the addition of chloride ions to "balance" the cations that cannot be reduced via source term reduction programs. Boric acid treatment (BAT) involves the addition of boric acid to feedwater. Dispersant application involves the addition of the dispersant to the feedwater. Such approaches are worthy of consideration based on plant-specific degradation mechanisms, operational considerations, and interactions. A discussion of this site-specific evaluation process is presented in Chapter 4.

3.4.2 Molar Ratio Control (For Recirculating Steam Generators)

As noted, industry wide application of ALARA chemistry in RSGs has not been able to preclude continued steam generator tube degradation where aggressive localized chemistries were thought to have been a factor. In most plants, pursuit of ALARA chemistry has resulted in sodium-rich feedwater and blowdown chemistry simply due to reliance on ion exchange as the key water purification mechanism. Molar ratio control (MRC) describes a control strategy that adjusts the bulk water chemistry, generally sodium and chloride, such that the solution that is developed in the flow-occluded region is targeted to be near neutral. Such an approach involves a variety of unknowns (e.g., hideout fractions) that must be estimated from previously analyzed data, like hideout return. There are limited data that suggest MRC may have some effectiveness, though most of the recently generated data are not conclusive. An additional consideration is that, if the sodium and chloride ratio is not too extreme, it is expected that the other impurities that are normally present such as calcium, magnesium, and silica will buffer the crevice solution to prevent extreme pH's. Nevertheless, because of concerns that the pH could become aggressive despite this buffering effect, MRC is considered to be a useful protective measure.

Implementation of MRC requires an iterative process in which the steam generator bulk water ratio of cations to anions is adjusted to provide a near neutral pH in steam generator crevices on the basis of hideout return. Field test data confirm MULTEQ analyses that suggest sodium often concentrates in the crevices more efficiently than chlorides [10, 11, 12, 13]. Reference [4] suggests that a low molar ratio index (MRI =0.5) in steam generator blowdown is most likely necessary to prevent alkaline crevice chemistry, though the actual value is steam generator specific [4].

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A major obstacle in implementing molar ratio control is to determine which species and their amounts in the hideout return came from crevices relative to the hideout return from other areas in the steam generator. The hideout return data are used to modify the bulk chemistry control during subsequent operation. Detailed assistance for evaluating hideout return data is presented in the EPRI PWR Hideout Return Sourcebook [16]. The preferred approach is to reduce the concentration of the dominant strong anion or cation. When this approach is exhausted or no longer cost effective, the remedy for excess cations over anions in some cases is to add chloride. The remedy for excess anions over cations is to reduce the anions. This is particularly difficult if the excess anion is sulfate, since the behavior of sulfate is different than that of monovalent anions such as chloride.

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3.4.2.1 Supporting Aspects of Molar Ratio Control

- The theory of molar ratio control is sound.
- Application of MRC has limited downside risks.
- MRC, once implemented, is not manpower intensive.
- MRC can be responsive to minor chemistry upsets.

3.4.2.2 Considerations for Implementing Molar Ratio Control

- The effectiveness of MRC is not yet proven.
- The behavior of sulfate is not completely understood. This may be a potential concern if sulfate levels are excessive in the hideout return and if sulfate dominates crevice chemistry. The specific issue is the extent to which the sulfate is associated with the crevice liquid or is adsorbed on oxides.
- When the presence of excess sulfate in the crevices is inferred, the recommended action is to reduce the sulfate concentration. As many plants are already working to reduce sulfate concentrations to the practical minimum, such a reduction may be quite manpower intensive or costly.
- Various plant modifications and procedure modifications may be required to permit the injection of (ammonium) chloride or to vary polisher regeneration approaches.
- Significant costs or manpower may be required to reduce sources of sodium.

3.4.3 Low Power Soaks

Low power soaks provide a method for removing some of the impurities that have collected in flow-occluded areas. The equilibrium concentration of impurities in flow-occluded areas is controlled by the available superheat, which is directly related to the heat flux or power level. As a result, a reduction in power level results in a reduction in the equilibrium concentration of the liquids in the flow-occluded areas. The effects of a power reduction on removal of the concentrated liquids are expected to differ depending on the characteristics of the flow-occluded area:

- *Shallow Flow-occluded Areas.* Such areas include free span surface deposits and line contact crevices with little deposit buildup. This type of shallow flow-occluded area has a low available superheat and is likely to have been filled with concentrated impurities at a relatively low equilibrium concentration. If a liquid diffusion path is established between the crevice solution and the bulk water as a result of the power reduction, return of impurities to the bulk water can occur.
- *Crevices.* It is expected that crevices with high available superheat do not fill with concentrated impurities during a fuel cycle and remain mostly steam blanketed. This is because of the small volume of concentrated liquid produced during a fuel cycle due to the low bulk concentration and the high concentration factor. The effects of a reduction in power level are not obvious in this situation since establishment of a liquid diffusion path when the power level is reduced does not necessarily occur. Nevertheless, return of some of the impurities may occur when power is reduced.

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In summary, reductions in power are expected to effectively remove impurities from shallow flow-occluded areas such as surface deposits, but are less likely to be effective for deep crevices. The effectiveness of power reductions at causing hideout return is expected to increase as the power level decreases. This effect is observed at plants, with increasing amounts of hideout return occurring as power is reduced.

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3.4.3.1 Supporting Aspects of Low Power Soaks

- Experience indicates that power reductions and low power soaks can promote hideout return at some plants.
- Radiotracer tests using plant TSP crevice samples indicate that sodium is effectively removed from deep crevices by soaks at zero power.
- Theoretical considerations indicate that low power soaks should be effective at removing impurities from relatively shallow flow-occluded areas such as surface deposits and line contact crevices.

3.4.3.2 Considerations for Implementing Low Power Soaks

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3.5 Controlling the ECP in Localized Regions of the Steam Generator

3.5.1 Elevated Hydrazine Operation

The operation of PWR steam generators with elevated hydrazine levels is thought to decrease the likelihood and severity of IGA/SCC and pitting of the steam generator tubing. The initiation and growth of IGA and SCC have been directly related to elevated corrosion potentials in caustic, acid, and neutral environments. Laboratory data indicate that the potential for steam generator corrosion can be reduced by maintaining the ECP of the tubing near the hydrogen reduction line (see Chapter 2).

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Additional ECP and iron species data from tests in France, Sweden and the USA [18, 19, 20, 21, 22, 23] confirm that high hydrazine results in low oxygen levels and low ECP in the final feedwater.

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Figure 3-8
Feedwater and Steam Generator ECP Measurements at St. Lucie 2 as a Function of FW Hydrazine (ppb)/CPD O_2 (ppb) [24]

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Figure 3-9
Percent of Iron as Magnetite in Steam Generator Blowdown as a Function of FW Hydrazine (ppb)/CPD O_2 (ppb) [25]

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Figure 3-10
Percent of Iron as Magnetite in Steam Generator Blowdown as a Function of FW Hydrazine (ppb)/CPD O_2 (ppb) [26]

Recent laboratory testing investigating the relationship between hydrazine and oxygen concentrations on the ECP of Alloy 600, Alloy 690, 304SS, 316SS and carbon steel demonstrates that it is the hydrazine-to-oxygen ratio that controls the ECP of these materials [27] (see Section 2.4.4).

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3.5.1.1 Supporting Aspects of Elevated Hydrazine

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3.5.1.2 Considerations for Implementing Elevated Hydrazine Chemistry

- Hydrazine is a suspected carcinogen and is controlled in plant discharges. Hydrazine use and discharge have historically been sensitive issues.
- Hydrazine thermally decomposes into ammonia, hydrogen, and nitrogen. The increased ammonia production from high hydrazine treatment can have a negative impact on the condensate polisher (decreased run times and increased sodium throw with operation past the ammonia break).
- Increased ammonia production from hydrazine decomposition may impact plant discharges.
- Some laboratory tests indicate that increasing hydrazine concentrations may increase the extent to which sulfate is converted to reduced sulfur species. However, other experimental evidence indicates that this increase is not significant in the range of interest (e.g., 10 to 1000 ppb hydrazine). Furthermore, as also discussed in Chapter 4, there is extensive plant experience indicating that use of higher hydrazine concentrations has not aggravated IGA/SCC.
- The higher pH from ammonia production may increase copper transport to the steam generators at plants with copper alloys.
- Low Potential Stress Corrosion Cracking (LPSCC) is not considered to be a significant concern based on
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3.5.2 Effects of Interruptions in Hydrazine Addition

As discussed in Chapter 2 and in Section 3.5.1, maintaining a low ECP in the steam generators is important to minimizing corrosion of steam generator tubing. A main method of achieving low ECP is maintaining sufficiently high concentrations of hydrazine in the feedwater and steam generators. The conclusion that it is important to maintain high concentrations of hydrazine leads to the following question: How rapidly is it necessary to re-establish hydrazine if it is lost?
The balance of this section addresses this question.

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Figure 3-11
Crack Growth Rate Changes with ECP, 20% Cold Worked Alloy 600 [29]

3.5.3 Startup Oxidant Control

Because of possible exposure of the secondary system and steam generators to oxidizing conditions during shutdown, layup, and startup periods it is especially important to control the ECP in crevice areas and under sludge deposits during initial power operation immediately following shutdown periods. This can be done by limiting oxygen concentrations and ensuring adequate levels of hydrazine during the startup and early power operation periods. Recent investigations sponsored by EPRI [30, 31] provide test data and a calculational methodology that can be used to assist in evaluating control of ECP (by controlling the development and reduction of copper oxides) during this period.

3.6 Minimizing Other Corrosion Accelerants

3.6.1 Lead

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3.6.1.1 Supporting Aspects of Lead Minimization

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3.6.1.2 Considerations for Lead Minimization

- Lead is present at very low concentrations in feedwater during operation.
- The concentrations of lead required to accelerate cracking rates are estimated from laboratory work but are not quantitatively verified by field data. Most steam generator deposits contain some lead.

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3.6.2 Copper

Copper oxide has long been considered a potential oxidant in steam generator deposits. Copper surfaces can be oxidized during shutdown and layup modes and be easily reduced during operation. Such a process can lead to elevated localized ECP and accelerated corrosion of Alloy 600. Minimizing copper in feedwater corrosion products is accomplished by removal of copper alloys from the system and controlling secondary cycle pH. Additionally, control of the oxidation state of copper present in steam generator deposits should be considered, as discussed in Section 3.5.3.

3.6.2.1 Supporting Aspects of Copper Minimization

- Minimizing the presence of copper in steam generator deposits is expected to reduce its impact on corrosion and steam generator performance.
- If copper is eliminated in the BOP, alternate secondary cycle chemistries can more readily be adopted to minimize feedwater iron concentrations.

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3.6.2.2 Considerations for Copper Minimization

- Copper removal can be an expensive process requiring significant outage efforts and possible loss of thermal efficiency as a result of the lower thermal conductivity of non-copper alloy heat exchanger tubes.
- Copper residuals in condensate and feedwater piping and other components can continue to release copper long after copper alloys are removed.
- While traditional methods of copper removal from steam generators are either costly (chemical cleaning) or only partially effective (sludge lancing), scale conditioning agent technology has been shown to be effective in removal of copper from existing steam generator deposits [33].

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3.6.3 Reduced Sulfur Species Combined with Oxidizing Conditions

Partially reduced sulfur species such as thionates and thiosulfates are aggressive against sensitized materials, and can lead to rapid IGA/SCC of these materials at low temperatures if oxidizing conditions are present.

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3.6.3.1 Supporting Aspects of Minimizing Reduced Sulfur Species Combined with Oxidizing Conditions

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- Minimizing the combination of reduced sulfur species and oxidizing conditions is expected to reduce risks of low temperature IGA/SCC of sensitized tubing in plants with such tubing.
- Minimization of oxidizing conditions has been shown to be practical and to greatly reduce risks and rates of low temperature attack.

3.6.3.2 Considerations for Minimizing Reduced Sulfur Species Combined with Oxidizing Conditions

- Sulfates are present at only low concentrations in feedwater and steam generator bulk water during operation.
- The concentrations of sulfate in the bulk water required to result in the accumulation of sufficient amounts of reduced sulfur species in crevices to raise risks of attack of sensitized materials are not known.

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3.7 Adding Chemicals to Inhibit Corrosion

3.7.1 Boric Acid Treatment

Boric acid treatment (BAT) is considered an accepted remedial action for both denting and IGA/SCC in recirculating steam generators [41]. The recommended implementation of boric acid includes a multi-step procedure in which consideration is given to inclusion of activities such as soaks during heatup and power escalation and continuous on-line injection.]

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Reference [41] discusses the chemical and physical properties of boric acid and borates, the effect of boric acid on corrosion of materials, steam generator performance effects, field experiences, and application procedures and guidelines. Utility personnel considering the use of boric acid chemistry should carefully study this document to develop site-specific implementation plans.

Laboratory data at high bulk water sodium concentrations indicate that boric acid is effective in preventing initiation of IGA/SCC and in reducing propagation rates if corrosion is caused by highly caustic environments. The effectiveness in slowing the progression of existing IGA/SCC is dependent on pre-existing crack depth as well as accessibility to the bulk solution.

Accumulation of boric acid in the packed crevices with the highest primary-side temperature may be limited because of the boric acid volatility.

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Based on the data noted above, the following practices relative to boric acid treatment are suggested for consideration:

3.7.1.1 Plant Trip with Recovery of Power—No Cooldown

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3.7.1.2 Plant Trip, Hot Standby Maintained for More than Two Days

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3.7.1.3 Heatup with High Boric Acid for Chemically Cleaned Steam Generators

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3.7.1.4 Supporting Aspects of BAT

- BAT may be effective in preventing initiation of IGA/SCC and slowing the rate of existing IGA/SCC.
- BAT may provide protection against denting as a result of acidic chlorides or sulfates.
- BAT has extensive industry experience and has been demonstrated to have limited downside risks relative to steam generator corrosion.

3.7.1.5 Considerations for Implementing BAT

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- There may be practical limitations for achieving adequate boric acid concentrations in steam generator crevices to inhibit SCC.

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- Additional tanks and pumps may be required for additions. Various plant modifications and procedure modifications may also be required.
- Boric acid will have an impact on condensate and blowdown ion exchanger run lengths.

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- Additional training of personnel may be required for effective implementation.

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3.7.2 Injection of Corrosion Inhibitors

Corrosion inhibitors can react with Alloy 600 surface films at or near the crack tip and affect the anodic reaction (titanium compounds) or slow the cathodic reactions by increasing the resistivity to electron transfer (cerium compounds). In either case, inhibitors must be present at the corroding location to be effective.

The use of inhibitors is expected to have a positive impact on Alloy 600 corrosion without known deleterious side effects.

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3.7.2.1 Supporting Aspects of Chemical Inhibitors

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3.7.2.2 Considerations for Using Chemical Inhibitors

- The benefits of inhibitors have not been conclusively demonstrated in plants to date.
- The maximum possible benefits of using inhibitors may be obtained after chemically cleaning the steam generators.
- Injecting inhibitors without first chemically cleaning the steam generators introduces the uncertainty that long-term use may possibly change the morphology of the corrosion film and metal oxides. The effectiveness of chemical cleaning solvents after long-term use of inhibitors is unknown.
- The effect of blockage of clean or partially filled crevices to produce flow-occluded regions has not been investigated. However, at currently employed addition rates, no detrimental effects are anticipated.
- Low-power soaks or pre-heatup additions are recommended for maximum possible crevice loadings.

3.8 Management of Steam Generator Deposits

Corrosion products deposited in steam generators may create flow-occluded crevices where contaminants in the bulk water can concentrate in a thermodynamically limited fashion [2]. There is also a correlation between the location of pitting and wastage and the sludge deposited on the top of the tubesheet. Hence, the presence of corrosion product deposits is considered a precursor to the development of environments where localized chemistry can be a contributor to corrosion. (Note that tube-to-support contact locations also can be regions where concentrated solutions develop even in the absence of deposits.) Deposits may also be oxidized during layup, especially under uncontrolled, drained conditions, increasing the risks of undesirable oxidizing conditions being present in localized areas and contributing to corrosion during subsequent operation.

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3.8.1 Corrosion Product Transport Control

The primary method of controlling corrosion product transport to the steam generators should be optimization of cycle chemistry to minimize corrosion product transport from cycle materials (within the limits of other chemistry goals). The use of alternate amines, condensate polishers and filters, and directing selected system flows to drains or cleanup systems during startup and transients, should be considered. Also included in the optimization should be an assessment and resolution of FAC concerns, including consideration of replacing materials with more resistant materials. The optimization program should address the generation of corrosion products within the steam generators through lay-up chemistry and shutdown practices. Consideration should also be given to preventing the oxidation of deposits already present in the steam generators and secondary system.

3.8.2 Mitigation of Steam Generator Fouling

Dispersant application during operation to mitigate steam generator fouling from corrosion products entering the steam generator is a promising new technology. Based on the extensive qualification work and the two plant trials at ANO Unit 2 and McGuire Unit 2, sufficient information to support safe and effective long-term use of dispersants for reducing steam generator deposit fouling rates has been developed. The dispersant application sourcebook [44] includes summary discussions of all such technical bases as well as detailed guidance for utilities supporting application of dispersants at one or more of their stations.

3.8.3 Steam Generator Deposit Removal

There are several methods available for removing deposits after they have accumulated in steam generators during operation, including both chemical and hydraulic techniques. These techniques will be discussed in generic terms in the following sections.

3.8.3.1 Chemical Cleaning

The EPRI-SGOG chemical cleaning process has been generically qualified for all PWR steam generators. The process can effectively remove significant quantities of iron and copper deposits from the steam generators, both on tube surfaces and in tube-to-support intersections, although the high-temperature process required for crevice cleaning has not been generically qualified.

Other chemical cleaning processes have been successfully employed as well, including on-line (plant heat) cleanings which have the advantage of greatly reducing the complexity of the cleaning equipment, as well as the outage time consumed in the process. Crevice cleaning is generally better in off-line EPRI-SGOG cleanings than on-line cleanings. Plant heat processes are generally applied at higher temperatures, which can lead to elevated corrosion of SG carbon and low alloy steel internals. Plant heat processes are also generally less effective with respect to copper removal.

Chemical removal of deposits can also be used as a deposit maintenance treatment approach by applying cleaning chemicals during refueling outages (in off-line or plant heat processes), with the frequency determined by transport experienced during the cycle. In this case, deposit removal need not be as complete as in a full chemical cleaning, since removal can be more frequent, with the objective of maintaining SG cleanliness and performance. The advantages of this approach

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It should be noted that chemical cleaning cannot be considered a solution to the chemical concentration process. Without implementation of water chemistry controls to minimize corrosion product transport to the steam generator, development of flow occluded areas (where localized aggressive chemistries can be formed) will be initiated shortly after startup and power operation. Several parameters should be considered relative to when and what process should be considered. Some of these are:

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3.8.3.1.1 Supporting Aspects of Chemical Cleaning

- Cleaning can eliminate, to a great extent, deposit-related locations where significant concentrations of impurities can develop, though complete cleaning of 100% of all tube support intersections is unlikely unless performed prior to the formation of packed crevices.
- Chemical cleaning can also remove deposits that may aggravate steam generator tubing corrosion (e.g., lead).

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3.8.3.1.2 Considerations for Chemical Cleaning

- Chemical cleaning may be expensive and may add to typical refueling schedules. Newly introduced chemical cleaning techniques can significantly reduce the deposit inventory within shorter cleaning times, which may reduce the potential for impact on outage schedule.
- Chemical cleaning must be qualified for each set of plant-specific conditions to ensure compatibility with materials of construction and system design.
- Corrosion allowances for tube-to-support clearance may only permit a limited number of chemical cleanings in a steam generator lifetime, if post-cleaning tolerances approach maximum design criteria. Consideration must be given to vibration-related degradation (fretting/fatigue) when determining plant specific corrosion allowances.
- Chemical cleaning only removes metal and metal oxide deposits that already exist in a steam generator. Additional chemistry controls are required to ensure that accumulation of future deposits is minimized.
- The top of tubesheet crevices are expected to refill with deposits (with the rate of refill depending on corrosion product ingress rates) such that chemical cleaning may not provide a long term benefit for this crevice region.

3.8.3.1.3 Partial Deposit Removal

Relatively dilute chemical agents have been applied to steam generators to enhance mechanical sludge removal. These chemicals are also used to improve heat transfer properties of scale deposits resulting in improved SG performance. Due to the varying nature of scale deposits in different power plants and even within the same steam generators, laboratory bench scale testing is recommended to optimize the process and maximize the effectiveness of the application. Depending on the recommended application temperature, the treatment may be applied during plant cooldown prior to refueling operations or when the plant is at cold shutdown conditions. Even though corrosion rates associated with typical applications are very low, potential system corrosion must be assessed prior to application. This technique is most effective modifying the structure of scale deposits which results in improved SG performance, and rendering these deposits more amenable to removal by hydraulic tube bundle cleaning methods such as in-bundle sludge lancing and ultrasonic energy cleaning.

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3.8.3.2 Top of Tubesheet Sludge Removal

During refueling outages, recirculating steam generators are often drained and opened to permit top of tubesheet (TTS) sludge removal. Various techniques and designs are available with varying degrees of effectiveness for removal of top of tubesheet deposits. At a minimum, most are effective for removing loosely adherent particulate corrosion products and small sludge rocks. Top of tubesheet cleaning techniques only remove deposits from the top of the tubesheet and the first few inches of tubing extending up from the top of the tubesheet.

3.8.3.2.1 Supporting Aspects of Top of Tubesheet Sludge Removal

- Tubesheet sludge has been shown to cause undesirable concentrations of impurities in the steam generator. Removal of tubesheet sludge reduces the extent to which impurities are likely to concentrate in the tubesheet region of the steam generator.
- The hot leg, TTS region is very sensitive to several degradation mechanisms. Sludge removal at this location via various top of tubesheet cleaning methods can be effective in reducing the impact of these degradation mechanisms on steam generator tubing.

3.8.3.2.2 Considerations for Top of Tubesheet Sludge Removal

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Top of tubesheet sludge removal technologies include general sludge lancing, in-bundle lancing, and ultrasonic energy cleaning. These techniques are discussed in more detail below.

3.8.3.2.3 Sludge Lancing

Sludge lancing is typically applied as water jets from either the center tube lane or the tube bundle periphery. Sludge lancing is effective in removing loosely adherent corrosion products and small sludge rocks from the top of the tubesheet. Hard scale deposits and scale collars around the base of the steam generator tubes are not effectively removed by sludge lancing. Square pitch and triangular pitch tubed steam generators typically require different water jet patterns to facilitate sludge removal, either from the center tube lane out to the periphery or from the periphery into the center tube lane. Sludge washed from within the tube bundle is then pumped from these more easily accessed areas and collected by filtration.

3.8.3.2.4 In-bundle Sludge Lancing

In-bundle lancing provides access within the tube bundle utilizing a robotic delivery system for the water jet lance. The high pressure water jets may be applied directly at the location of a heavy tubesheet sludge deposit or scale collar and can be effective in loosening more tightly adherent scale deposits at the tube to tubesheet interface. In bundle high pressure lancing is typically followed by a water spray to work the loosened sludge deposits out of the steam generators in a similar manner to conventional sludge lancing. Benefits of hard scale and sludge removal using in-bundle sludge lancing at various plants were presented at the 1999 SG Sludge Management Workshop [47].

3.8.3.2.5 Ultrasonic Energy Cleaning

Ultrasonic energy cleaning utilizes high power radial field ultrasonic energy to disrupt adherent steam generator tube and tubesheet deposits by causing localized cavitation within the deposit matrix. This mechanical cleaning technique has been applied in water alone and also applied with chemicals in order to enhance deposit removal. Currently developed and qualified for top of tubesheet applications in several steam generator designs, this technique has the potential for use in full bundle cleanings, and also for adaptation to other steam generator designs. It is effective in disrupting more tightly adherent scale deposits in the region of application making removal by subsequent sludge lancing more effective. Successful application has been reported for five units [45].

3.8.3.3 Tube Bundle Sludge Removal Technologies

Sludge accumulations at upper elevations are not addressed by top of tubesheet sludge removal techniques. Techniques for tube bundle sludge removal are effective for a wide range of deposits from loose sludge removal only to removal of hardened deposits within broached flow holes and bridged deposits between tubes. The presence of accumulated, densified deposits on tube and tube support surfaces within the tube bundle have been implicated in tubing degradation, thermal performance reduction, and water level instability. Tube bundle sludge removal technologies include high volume bundle flushing, upper bundle hydraulic cleaning, application of scale conditioning agents, and chemical cleaning.

3.8.3.3.1 High Volume Bundle Flushing

High volume bundle flushing uses water pumped through hoses introduced through the steam generator secondary manway and primary moisture separators above the tube bundle. Flow has also been directed in bundle through a wand placed in an upper bundle penetration. Water is recirculated through the tube bundle and the sludge washed down to the tubesheet is subsequently removed by sludge lancing. This technique is most effective at washing loosely adherent sludge from the tube bundle to the top of the tubesheet. Reported benefits vary from plant to plant depending primarily on deposit morphology.

3.8.3.3.2 Upper Bundle Hydraulic Cleaning

Upper bundle hydraulic cleaning uses a robotic delivery system to place a high pressure hydraulic cleaning head in the tube bundle center tube lane at various support plate elevations. This cleaning head acts in a similar manner to sludge lancing by using high pressure water to dislodge sludge residuals and wash them through flow holes down to the tubesheet. This technique is most effective at dislodging loosely and slightly more adherent scale and sludge deposits. Seabrook reported benefits of upper bundle hydraulic cleaning at the 1999 SG Sludge Management Workshop [47].

3.9 References

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4

METHODOLOGY FOR PLANT-SPECIFIC OPTIMIZATION

4.1 NEI Commitments Regarding Chemistry Control—Strategic Water Chemistry Plan

This Chapter outlines guidance for development and maintenance of the Strategic Water Chemistry Plan (referred to as the "Plan" in the remainder of this Chapter). Development and maintenance of the Plan is a mandatory requirement of these *Guidelines* in accordance with NEI 03-08 and NEI 97-06. The goal of this chapter is to provide guidance for establishing and maintaining a plant-specific Strategic Water Chemistry Plan that will govern the optimization of the plant-specific water chemistry program, not to prescribe the program in detail.

The U.S. nuclear power industry established a framework for increasing the reliability of steam generators by adopting NEI 97-06, *Steam Generator Program Guidelines.* The most recent issue of NEI 97-06 [1] includes the following requirements regarding secondary water chemistry:

- "Each licensee shall have procedures for monitoring and controlling secondary-side water chemistry to inhibit secondary-side corrosion-induced degradation in accordance with the EPRI PWR Secondary Water Chemistry Guidelines."

The U.S. nuclear power industry has more recently produced a policy that commits each nuclear utility to adopt the responsibilities and processes on the management of materials aging issues described in NEI 03-08, *Guideline for the Management of Materials Issues.* NEI 03-08 [2] identifies its objective as follows:

- "The objective of this Initiative is to assure safe, reliable and efficient operation of the U.S. nuclear power plants in the management of materials issues."

In addition, NEI 03-08 "outlines the policy and practices that the industry commits to follow in managing materials aging issues", indicating that "each licensee will endorse, support and meet the intent of NEI 03-08" and further stating that it "commits each nuclear utility to adopt the responsibilities and processes described in this document."

With respect to these *Guidelines*, the scope of NEI 03-08 includes "PWR steam generators" and "chemistry/corrosion control programs". It states that "as deliverables or guidelines are developed, action should be classified as to relative level of importance." In this regard, these *Guidelines* identify Mandatory, Shall and Recommended Elements. Mandatory elements are those that are considered important to secondary system component integrity, including steam generator tube integrity, and should not be deviated from by any utility. Steam generator tube integrity is defined as meeting the performance criteria as specified in NEI 97-06. Shall elements are those that are considered important to secondary system component reliability. It is recognized that Shall elements may be subject to legitimate deviations due to plant differences and/or special situations. Recommended elements are those that are considered good or best practices that utilities should try to implement when practical.

The Mandatory, Shall and Recommended elements in these *Guidelines* are identified in Chapter 8. To be in compliance with NEI 03-08 and NEI 97-06, utilities must meet the Mandatory and Shall elements in these *Guidelines* or provide a technical justification for deviation. Any deviation to a Mandatory or Shall element must be handled in accordance with the guidance in the current revision of the Steam Generator Management Program (SGMP) Administrative Procedures.

4.1.1 Documenting Exceptions to Recommended Elements

Chapter 8 identifies the Recommended elements of these *Guidelines.*

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4.1.2 Maintenance of the Plan

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4.2 Introduction

Due to the wide range of conditions and materials of construction in the secondary system, no single optimum water chemistry program can be specified for all PWRs. Thus, a site-specific Plan governing the optimization of the water chemistry program requires development and maintenance. This Plan should consider factors such as steam generator and BOP component design and operating history and use of condensate and/or blowdown demineralizers.

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The development of a cost/benefit analysis for secondary chemistry is difficult for several reasons. First, the long-term benefits of water chemistry cannot be easily quantified, although the value of minimizing corrosion is well understood. For example, lower steam generator sodium levels are expected to result in reduced steam generator corrosion. Although the potential cost savings cannot be accurately determined, the expense of reducing sodium often can be quantified (e.g., improved condensate polisher regeneration, etc.). In cases where the cost can be quantified but the benefit can be assessed only qualitatively, optimization consists of pursuing the minimum cost water chemistry program which provides the greatest expected benefit (e.g., lowest sodium levels). In other cases, both the costs and benefits can be quantified. For example, several alternate amines can be used for pH control in the secondary system. The costs associated with the amine program can be determined with the aid of EPRI ChemWorks™. A recent software tool developed by EPRI in collaboration with EDF is "CIRCE – PWR Secondary Water Chemistry Optimization Tool" [3] that models not only the chemistry around the secondary system but also the corrosion product transport to the steam generators and resultant steam generator fouling. The value of the benefits can be assumed as a first approximation to be proportional to the feedwater iron concentration achievable with a given amine program. The optimum amine program then would be the lowest cost program which achieved a target iron value. The target iron value would be determined on a more qualitative basis. For plants using condensate and/or blowdown demineralizers, the use of alternate amines could also increase contaminant levels in the system, when demineralizers are allowed to remain in service beyond the amine break. Optimization of the amine program must also at least qualitatively assess the cost of contaminants in the system. This could be achieved by establishing an upper contaminant limit in the system and determining the minimum cost amine program which achieves both the contaminant and iron targets.

The tradeoffs illustrated for the optimization of the pH control program are typical of many secondary water chemistry programs. Optimization for one component or portion of the system can lead to less than optimum conditions in other parts of the system. Therefore, an overall systems approach must be taken in developing the Plan. To do this effectively, a ranking system is provided in this chapter. The ranking system attempts to put the qualitative factors on a firmer basis. The system considers the merits of the secondary water chemistry initiatives presented in Chapter 3. Each utility must evaluate the merits of each initiative relative to plant specific design features, materials of construction, etc. Ultimately, a utility must decide where it sees its greatest risks and potential rewards.

It is suggested that procedures similar to those discussed in this chapter be applied in the plant-specific Plan as a basis for the plant-specific secondary water chemistry program.

4.3 Key Elements of a Strategic Water Chemistry Plan

The items in the list below are recommended elements of the Plan:

- Statement of the objectives of the Plan

- Key plant design parameters, chemistry milestones and significant plant transients
- Evaluation of technical issues, including risk/susceptibility/performance
- Evaluation of chemistry control strategies
- Deviations from Mandatory, Shall, or Recommended Elements
- References

4.3.1 Objectives of the Strategic Water Chemistry Plan

The objectives of the Plan will likely be plant specific, but should be aligned with corporate goals. Examples of such objectives could be:

- Implement water chemistry programs considering relative risk and expected benefits of different chemistry control approaches
- Maximize total avoided costs from material degradation and other performance related issues while minimizing operating costs
- Optimize water chemistry programs balancing plant design and operating considerations along with materials issues
- Align decisions that affect chemistry (and thus systems and components) with overall corporate goals
- Foster understanding and cooperation of chemistry related materials management issues by communicating and coordinating chemistry program actions with other departments (Engineering, Ops, SG Engineer, LLW, etc)

4.3.2 Key Plant Design Parameters, Chemistry Milestones and Significant Plant Transients

The Plan should include a listing of key system materials, plant design parameters and a brief history of key milestones/events, including past secondary chemistry programs. This may most easily be expressed in table format. Table 4-1 presents a generic example of documenting key design and operating parameters. Table 4-2 presents a generic example of documenting plant milestones and events.

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

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Table 4-2
Chemistry and/or Plant Milestones / Events (EXAMPLE)

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4.3.3 Evaluation of Technical Issues, Including Risk/Susceptibility

4.3.3.1 Summary of Approach

The objective of this section is to develop a reasonable framework for ranking the relative susceptibility of various major components/systems to corrosion damage/performance degradation or in some cases their reliability in performing their design function. Only those design features or operating parameters which influence degradation through interaction with the water chemistry program should be considered. The principal idea is to determine the important design and operating parameters of each component/system that will influence which water chemistry programs will be used. When operating conditions or major plant design features change, the Plan should be updated and the impact on the plant-specific water chemistry program re-evaluated.

The following components/systems should be considered during development of the Plan:

Table 4-3
Components/Systems To Be Considered

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For some components/systems, the relative susceptibility to corrosion and/or performance degradation can be defined based on key design features. Each utility should classify the susceptibility of each component as high, medium, or low. For example, a steam generator with

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4.3.3.2 Component Susceptibility

The first step in developing the Plan is to define the relative susceptibility of various component/systems to corrosion damage and/or performance degradation, and to also rank the cost impact of the failure of each major component. Table 4-4 provides an example format for developing this ranking. The goal is to define important design and operating parameters of each component/system which will impact on optimization of the water chemistry program.

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4.3.3.3 Component Reliability

A qualitative ranking of the reliability of components whose failure or performance inadequacies could significantly impact secondary cycle chemistry should be developed.

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Table 4-4
Corrosion Susceptibility of Major Components/Systems

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Table 4-5
Component/System Reliability

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4.3.3.4 Prioritization of Components/Systems

The rankings developed in Sections 4.3.3.2 and 4.3.3.3 provide a qualitative basis for developing an optimized water chemistry program that should focus on the highly susceptible and expensive to replace components. However, it is also important to consider those systems which may be less reliable and have a significant influence on maintaining the water chemistry program goals.

The purpose of this section is to prioritize the importance of the major components/systems in the secondary plant identified in Table 4-4 and Table 4-5. This assessment should go beyond a simple ranking of components based on their maintenance and/or replacement costs. Less tangible but important issues which should be considered in prioritizing components/systems include safety considerations, utility outage goals, etc. The optimum water chemistry program should be weighted towards the highest priority components.

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Table 4-6
Relative Impact of Components/Systems on Establishing an Optimized Chemistry Program

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4.3.4 Evaluation of Chemistry Control Strategies

4.3.4.1 General Considerations

The objective of this section is to discuss the advantages and disadvantages of each chemistry control program option relative to each component/system. Consideration is given to the factors provided earlier **Content deleted - EPRI Proprietary Information**

The section is organized into brief discussions of each major water chemistry initiative presented in Chapter 3. The discussions summarize the influence of each initiative on the major components/systems. This information is summarized in Table 4-7 according to the expected influence of each chemistry control initiative on the major components/systems. As with previous chapters, the discussion as to the merits and interactions of various chemistry programs is illustrative, not exhaustive. Utility personnel should supplement this information with additional site-specific criteria as appropriate. It is expected that a detailed evaluation with supporting information will be given in the Plan.

After consideration of plant-specific design features and completion of the relative ranking in Section 4.3.3.4, the relative merits of each chemistry program option should become clearer within the context of the overall ranking and importance of each component.

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The final outcome should be a list of chemistry control initiatives (e.g., BAT, Dispersant, alternate amines, mid-cycle soaks, etc.) to be included in the Plan.

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4.3.4.2 ALARA Chemistry

In recent years, it has become clear that ALARA chemistry by itself will not prevent corrosion in steam generators where partially flow-occluded crevices are present. As discussed in Chapter 3, the presence of crevices and other regions where impurities can concentrate allows aggressive solutions to form locally. MRC and inhibitors should be considered for use in conjunction with ALARA chemistry when conditions exist for the formation of concentrated solutions. The total quantity or mass of a corrosive species which accumulates in the local crevice regions will be proportional to its steam generator concentration. Since the probability of corrosion increases as the available mass of corrosive liquid increases, ALARA chemistry is prudent even when other measures have been taken (e.g., MRC, BAT, etc).

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4.3.4.3 Molar Ratio Control (MRC) for RSGs

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MRC Guidelines (EPRI TR-104811) [4] were developed for utilities to use in designing a plant-specific program. Little guidance has been provided on whether or not MRC should be implemented as a proactive program for plants with "lower risk" steam generators. Additional information on MRC is provided in a recent report on steam generator hideout return assessments [5].

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4.3.4.4 Integrated Exposure (IE) for RSGs

Research completed under EPRI's Heated Crevice Program, discussed in Appendix A, shows that the mass of accumulated impurities in crevices in RSGs is proportional to the impurity exposure (e.g., the product of impurity concentration and time).

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4.3.4.5 Boric Acid Treatment and Injection of Corrosion Inhibitors

Boric Acid Treatment (BAT) has been used as both a remedial and proactive chemistry control program for steam generator corrosion. Plant data do not allow definitive confirmation of the beneficial effects of BAT. However, it is possible that BAT has had a mitigative effect on both denting and IGA/SCC. **Content deleted - EPRI Proprietary Information**

To consider the use of BAT as a proactive water chemistry program, the risks and possible benefits must be considered. Boric acid, due to its volatility, is transported throughout the system. As a weak acid at elevated temperatures, boric acid has limited impact on the at-temperature pH in the turbine or extraction lines.

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Titanium dioxide, titanium dioxide-silica sol-gel, and a lactate acid titanium chelate (DuPont TYZOR LA®) have been shown to significantly reduce the tendency for IGA/SCC in C-rings as well as constant extension rate tests [7]. Since limited data also indicated that titanium could be accumulated in support plate crevices of model boilers, short term evaluations of titanium compound behavior at operating plants with IGA/SCC were considered justified.

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4.3.4.6 Minimization of Steam Generator Oxidant Exposure

4.3.4.6.1 Elevated Hydrazine

The importance of the electrochemical potential (ECP) to steam generator corrosion was discussed in Chapter 2. The role of hydrazine in maintaining reducing conditions in the steam generator has been discussed in Chapter 3. In many plants, operation with sufficient hydrazine to maintain reducing conditions can be accomplished at minimal cost. However, in some cases, the quantity of ammonia generated from decomposition of hydrazine will compromise condensate polisher operation and, if copper alloys are present in the system, may increase copper transport to the steam generators. The specifications presented in Chapters 5 and 6 for hydrazine provide flexibility in defining the minimum required feedwater hydrazine concentration. When optimizing hydrazine levels, the objective should be to minimize the ingress of oxygen and possibly reducible metal oxides to the steam generators.

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Another concern associated with elevated hydrazine has been the production of reduced sulfur species and their impact on steam generator corrosion (see Sections 2.3.4.1 and 2.4.4). Numerous laboratory tests [10, 11, 12, 13, 14] and evaluation of various samples from plants [5, 15, 16, 17, 18, 19] indicate that sulfate can be reduced to less oxidized species under secondary side conditions.

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4.3.4.6.2 Limiting Exposure to Startup Oxidants

It has been hypothesized that increased exposure of steam generator tubes to oxidizing conditions during startups and early periods of subsequent power operation leads to increased IGA/SCC of the tubes. As such, limiting exposure to and formation of oxidants during startups and early power operation periods as part of efforts to minimize IGA/SCC should be considered. Information regarding strategies to limit exposure to startup oxidants is reviewed in references discussed in Chapter 2 (see e.g., Section 2.5.3). Reference [21] provides a summary evaluation of this issue.

4.3.4.7 Secondary System pH Control

The use of alternate amines for pH control is widespread in US PWRs. The choice of the optimum amine or mixture of amines is strongly dependent upon plant design. The advanced Amines Application Guidelines [22] and EPRI ChemWorks™ should be used in these evaluations. The primary goals of the optimum pH control program are to minimize iron transport to the steam generators and to minimize FAC induced thinning of structurally important parts in the secondary system. Although computer codes can be used to predict the pH and qualitatively evaluate corrosion product transport and FAC risk at various locations in the system (e.g., EPRI's Plant Chemistry Simulator and CIRCE—PWR Secondary Chemistry Optimization Tool), plant experience is required to validate these predictions.

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The use of alternate amines often results in increased organic acid levels in the secondary plant. Evaluations using MULTEQ indicate that the pH_T of the secondary circuit is higher using alternate amines relative to ammonia (for the same $pH_{25°C}$) despite the presence of organic acid decomposition products. These evaluations were performed using conservative bounds on both the amine concentration (evaluated at a lower bound) and the acid concentration (evaluated at the upper bound). This should minimize concerns regarding the potential for an increased risk of acid corrosion in the turbine [23]. Also see Section 2.5.4.

Several plants operating full flow condensate polishers with ethanolamine have observed a loss of resin performance. The severity of the problem has varied from plant to plant with some plants not observing any noticeable effect. Resin fouling has been shown to increase with condensate temperature. The potential and extent of the problem cannot be predicted before a unit converts to ethanolamine or another alternate amine, but a worst case scenario can be evaluated. This worst case scenario might consist of having to replace the resin at an increased frequency based on other plant experience. Plant-specific data could be used after conversion to the alternate amine when evaluating the overall cost impact on the plant. At least one plant has been successful at recovering the resin when ETA was removed and pH controlled with ammonia over the course of a few weeks.

4.3.4.8 Steam Generator Deposit Management

As noted in Chapter 3, a goal of secondary water chemistry is to minimize partially occluded locations within a steam generator (via corrosion product transport and deposition mitigation) thereby minimizing the number and/or extent of regions where solution concentrations increase to thermodynamically limited values. Steam generator deposit management is a methodology to provide appropriate steam generator cleaning operations above and beyond routine chemistry control of corrosion product transport. Plants can adopt a preventative approach to steam generator deposit management (i.e., prior to indications of significant concentrating regions or loss of thermal performance) or a remedial approach (i.e., following the observation of loss of thermal performance or the appearance of corrosion indications that suggest aggressive chemistry environments). The preventative approach can be realized by increasing the at-temperature pH to reduce corrosion product transport, and/or application of PAA dispersant for recirculating steam generators to minimize corrosion product deposition (i.e., maximize removal via blowdown). The remedial approach is realized during plant outages via operations designed to remove at least part of the existing deposit inventory in the steam generators. Steam generator deposit management can be an effective method of minimizing loss of thermal performance or minimizing regions where highly concentrated solutions can develop. Steam generator deposit management involves the use of available steam generator deposit management strategies (see Section 3.8) in a manner most appropriate for plant-specific conditions.

4.3.4.9 Hideout Return Evaluations

Hideout return evaluations are unique opportunities to assess the likely steam generator crevice chemistry as it exists during operation based on data collected during a plant shutdown. During a unit shutdown, steam voids collapse, crevices are rewetted, and impurities diffuse into the bulk water. The evaluation of hideout return data is dependent on the amount and type of data collected and the quantity of impurities that returns to the bulk water. Evaluation of hideout return data is discussed in the EPRI PWR Hideout Return Sourcebook [5]. A screening process has been established to assist in the determination of the scope and type of evaluation that can reasonably be performed on a given set of hideout return data. Additional guidance is given for minimal returns and sampling during a rapid shutdown, particularly for data collected at hot zero power.

Table 4-7
Examples of Secondary Chemistry Initiative Evaluations

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Table 4-7 (continued)
Examples of Secondary Chemistry Initiative Evaluations

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Table 4-7 (continued)
Examples of Secondary Chemistry Initiative Evaluations

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**Table 4-7 (continued)
Examples of Secondary Chemistry Initiative Evaluations**

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4.4 Final Optimization of Secondary Chemistry Program

This section provides guidance for optimizing the chemistry program on a component and system basis. EPRI ChemWorks™ tools can be used to assist in the optimization process. An example flowchart which could be used for the optimization process is shown in Table 4-8. Plant personnel are referred to application guidelines, such as TR-102952, *Amine Application Guidelines* [22], TR-104811, *Molar Ratio Control Application Guidelines* [4], TR-5558, *Boric Acid Application Guidelines* [24], TR-108002, *Titanium Dioxide Application Guidelines* [7], TR-1014985, *PWR Lead Sourcebook* [25], *PWR Hideout Return Sourcebook* [5], and TR-1015020, *PWR Dispersant Application Sourcebook* [25] for detailed optimization strategies. For the Plan, each utility should first prioritize the water chemistry initiatives supported by the assessments captured in Tables 4-1 through 4-6. (In the flow chart, the prioritization is left blank.) After providing the overall prioritization (e.g., 1. pH Optimization, 2. Dispersant, 3. ALARA, etc.), proceed to the appropriate box in the example flowchart for the water chemistry initiative and address how each of the actions will or has been completed and then how each of the optimization options is addressed. Each utility should present a table or flowchart in the Plan that summarizes the response to each of the actions and optimization options. A complete optimization study for a given plant may require significant resources/time.

As part of their optimized water chemistry program, a number of utilities have adopted administratively lower impurity concentration targets than the Action Level 1 values in Chapter 5 for RSGs and Chapter 6 for OTSGs. Examples of these target values are given in Table 4-9 and Table 4-10, respectively. Many utilities have established administrative target or normal operation impurity concentrations below Action Level 1 values with efforts to identify the cause of an abnormal condition initiated before Action Level 1 values are approached.

4.4.1 NEI 03-08 and NEI 97-06 Checklist

Utilities should review the following list to try to ensure that they have met the requirements of these *Guidelines* relative to materials related integrity and reliability. Completing these requirements is necessary in order to be in compliance with NEI 97-06 and NEI 03-08.

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Table 4-8
Flowchart for Site-Specific Chemistry Optimization

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Table 4-8 (continued)
Flowchart for Site-Specific Chemistry Optimization

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Table 4-9
Examples of Plant Specific Administrative Chemistry Targets for RSGs

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Table 4-10
Examples of Plant Specific Administrative Feedwater Chemistry Target Values for OTSG Plants (Power Operation)

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4.5 References

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5

WATER CHEMISTRY GUIDELINES RECIRCULATING STEAM GENERATORS

5.1 Introduction

These guidelines reflect current understanding of the role of chemical transport, impurity concentrations, material selection, corrosion behavior, chemical analysis methods, and industry practices on the operation and integrity of steam generator systems.

The guidelines included in this chapter represent a condensation of the technical bases from Chapter 2, chemical control strategies from Chapter 3, and optimization issues from Chapter 4 into a generic program for recirculating steam generators (RSG). The current understanding suggests that it is the "consequence" of the contaminant concentrations and concentrating mechanisms in the steam generator and the susceptibility of the alloys that establishes the corrosion concern.

It is recognized that steam generator designs vary significantly as do company management philosophies and economic conditions. Therefore, implementation of these guidelines requires "customization" to ensure they are specific to the needs of a given power station. However, as discussed in Chapter 1, this "customization" needs to be accomplished within the framework of meeting mandatory and "shall" requirements, which are identified in Chapter 8.

As noted in Chapter 1, deviations to mandatory and "shall" requirements shall be handled in accordance with the guidance in the current revision of the Steam Generator Management Program (SGMP) Administrative Procedures. Additionally, these Guidelines recommend that any exception to a recommended element (identified in Chapter 8) be documented in the Strategic Water Chemistry Plan (see Section 4.3.1).

This chapter contains shall requirements that must be viewed as boundaries of the envelope within which plant specific optimization should be initiated, and within which plant-specific limits will often be located. However, it is recognized that, in some cases, plant-specific considerations will result in these boundaries being exceeded. This is acceptable, as long as each deviation is appropriately documented and technically justified in accordance with the current revision of the SGMP Administrative Procedures. The discussions in the previous chapters and the flowcharts and tables of example values contained in Chapter 4 should be helpful in the effort to outline the appropriate limits for each plant.

Typical corrective actions are recommended in several portions in this chapter. These corrective actions are not meant to be all-inclusive or universally applicable and should be modified for plant specific concerns.

This chapter presents general guidelines for the addition of various combinations of chemical additives in units with a variety of secondary system materials and demineralization schemes. For some of these chemistry treatment and plant system combinations, extensive field experience and test data exist; for other combinations, this is not the case. The user of these guidelines should evaluate the information available regarding previous experience with these treatments to make an informed decision regarding the selection of any treatment program.

5.2 Control and Diagnostic Parameters

The tables presented in this chapter include chemistry monitoring requirements and recommendations.

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5.2.1 Loss of Monitoring for a Shall Monitoring Requirement

A temporary non-compliance to a shall monitoring frequency requirement, such as a temporary inability to take continuous samples, should not be treated as a deviation per the SGMP Administrative Procedures as long as it occurs as a result of normal maintenance activities (such as calibration or preventive maintenance) or as long as all of the following conditions are met:

- Compliance to the required monitoring frequency is restored as soon as reasonably practical.
- The reasons for the temporary non-compliance, together with the actions taken, are documented in accordance with the station's corrective action program.
- The actions include a sampling and analysis program that quantifies the parameter at a frequency defined as reasonable in plant specific documentation.

5.2.2 Low Power Hold (LPV) and Mid Power Hold (MPV)

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5.3 Action Level Responses

Three Action Levels have been defined for taking remedial action when control parameters are outside the specified operating range. Significant changes from chemistry concentrations normally achieved at a given station should be investigated. Action Levels prescribe threshold values of a parameter beyond which long-term system reliability may be jeopardized. Operating at values such that the Action Level 1 condition is not entered provides a greater degree of assurance that corrosive conditions will be minimized. Action Level 2 is instituted when conditions exist that are known to result in steam generator corrosion during extended full power (100%) operation. Action Level 3 is implemented when conditions exist that will result in rapid corrosion of a significant secondary side component and continued operation is not advisable.

The Action Levels and the associated chemistry limits are considered to be the first line of defense against secondary system and steam generator degradation.

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5.3.1 Action Level 1

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5.3.1.1 "Shall" Requirement Actions

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5.3.2 Action Level 2

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5.3.2.1 "Shall" Requirement Actions

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5.3.3 Action Level 3

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5.3.3.1 "Shall" Requirement Actions

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5.4 Corrective Actions

Typical corrective actions for various plant status modes are presented in the bullets following the next paragraph, and in several tables in the balance of this chapter. These corrective actions are not meant to be all-inclusive or universally applicable but should be considered. It should be noted that impurities may originate from within the system (weld repair, plant modification, component replacement, etc.) or from outside of the system (condenser cooling water leak, makeup water contamination, etc.). Corrective actions vary accordingly.

When chemistry parameters exceed their normal concentrations, corrective actions should be implemented. The corrective actions which should be implemented are parameter- and plant-specific. Each plant should have a predefined course of action that has been developed with attention to specific concerns. The following actions are considered typical:

- Identify and isolate sources of impurity ingress.
- Increase steam generator blowdown to maximum for removal of specific impurities.
- Increase sample and analysis frequencies for short-term trending and confirmatory analyses of critical chemistry parameters.

5.5 Specific Guidelines and Technical Justifications

5.5.1 Cold Shutdown/Wet Layup

5.5.1.1 Guidelines

The guideline parameters for full wet layup are presented in Table 5-1.

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5.5.1.2 Discussion

During outages, wet layup of steam generators with chemically treated water is desirable to minimize corrosion and oxidation during the layup period and also corrosion during subsequent startup and power operation. Protection is provided by an amine for pH control and hydrazine (or other qualified oxygen scavenger) to maintain a protective oxide film and a reducing environment. Plant experience and laboratory studies show that proper layup chemistry can provide corrosion protection for six months or longer [4, 5].

Units with sensitized tubing should exercise special care to avoid conditions which can result in formation of intermediate oxidations state sulfur species since these species can cause rapid attack of sensitized tubing at ambient temperatures. For example, long drained and dry periods without nitrogen cover should be avoided since these can result in oxidation of sulfides in top of tubesheet crevices and sludge piles to more aggressive intermediate oxidation states, and can also concentrate the solutions to more aggressive levels.

Table 5-1
Wet Layup (RCS ≤200°F) Steam Generator Sample

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Mixing of the steam generator bulk solution will assure uniform distribution of chemicals in the bulk water. Nitrogen sparging and/or recirculation [6] and adequate sample line flush times will provide chemistry samples that are representative of steam generator contents (see Section 7.3.1).

Steam generator layup requirements should be a major consideration of outage planning.

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5.5.1.3 Justification for Parameters and Values in Table 5-1

Summary justifications are provided below. Section 2.4 provides more detailed information on the relative corrosion susceptibility of the different steam generator tubing alloys.

5.5.1.3.1 Steam Generator

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5.5.1.3.2 Fill Source/Steam Generator

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5.5.1.4 Corrective Action Guidelines

After verification that a parameter is out-of-guidelines, the following actions should be considered:

Table 5-2
Corrective Action Guidance for Full Wet Layup

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5.5.2 Heatup/Hot Shutdown (RCS >200°F, <MPV Reactor Power)

5.5.2.1 Guidelines

The guideline parameters and values for feedwater and steam generator blowdown during heatup/hot shutdown, as well as those for power escalation greater than the lower power value (>LPV) and greater than the mid power value (>MPV), are given in Table 5-3 and Table 5-4, respectively.

5.5.2.2 Discussion

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Table 5-3
Recirculating Steam Generator Heatup/Hot Shutdown and Startup (RCS >200°F to <MPV Reactor Power) Feedwater Sample (from Steam Generator Feed Source)

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Table 5-4
Recirculating Steam Generator Heatup/Hot Shutdown and Startup (RCS >200°F to <MPV Reactor Power) Blowdown Sample

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5.5.2.3 Justification for Parameters and Values

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5.5.2.4 Corrective Action Guidelines—Heatup / Startup

After verification that a parameter is out-of-guidelines, the following corrective actions should be considered:

Table 5-5
Corrective Action Guidance during Heatup / Startup

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5.5.3 Power Operation

5.5.3.1 Guidelines

Guidelines for ≥MPV reactor power feedwater and blowdown chemistry are given in Table 5-6 and Table 5-7, respectively. Condensate chemistry guidelines at >LPV reactor power are given in Table 5-8.

5.5.3.2 Discussion

The parameters and operating ranges monitored during power operation are those currently considered appropriate to protect the steam generators and balance of plant. Site-specific implementation of these guidelines may result in a more extensive surveillance program or lower levels of impurities to further reduce the likelihood of corrosion degradation.

Guidelines are provided for feedwater, blowdown, and condensate.

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Table 5-6
Recirculating Steam Generator Power Operation (≥MPV Reactor Power) Feedwater Sample

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Table 5-7
Recirculating Steam Generator Power Operation (≥MPV Reactor Power) Blowdown Sample

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Table 5-8
Power Operation (>LPV Reactor Power) Condensate Sample

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5.5.3.3 Justification for Parameters and Values

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5.5.3.4 Corrective Action Guidelines—Power Operation

After verification that a parameter is out-of-guidelines, the following corrective actions should be considered.

Table 5-9
Corrective Action Guidance for Power Operation

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5.6 References

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6

WATER CHEMISTRY GUIDELINES ONCE-THROUGH STEAM GENERATORS

6.1 Introduction

The guidelines presented in this chapter reflect the current understanding of the roles of chemical transport, impurity concentrations, and materials on the operation and integrity of once-through steam generator (OTSG) systems. They also reflect the technical bases of Chapter 2, the chemical control strategies of Chapter 3 and the optimization issues of Chapter 4.

The criteria for the establishment of the guideline parameters were:

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Using these criteria, guidelines have been formulated which provide chemistry control while retaining operating flexibility. These guidelines identify parameters to be measured and recommend actions for off-normal chemistry conditions. Wherever possible, literature sources are cited for justification.

As discussed in Chapters 3 and 4, it is intended that plant-specific optimized strategic water chemistry plans be developed for each plant. It is recognized that steam generator designs vary significantly as do company management philosophies and economic conditions. Therefore, implementation of these guidelines requires "customization" to ensure they are specific to the needs of a given power station. However, as discussed in Chapter 1, this "customization" needs to be accomplished within the framework of meeting mandatory and "shall" requirements, which are identified in Chapter 8.

As noted in Chapter 1, deviations to mandatory and "shall" requirements shall be handled in accordance with the guidance in the current revision of the Steam Generator Management Program (SGMP) Administrative Procedures. Additionally, these Guidelines recommend that any exception to a recommended element (identified in Chapter 8) be documented in the Strategic Water Chemistry Plan (see Section 4.3.1).

This chapter contains shall requirements that must be viewed as boundaries of the envelope within which plant specific optimization should be initiated, and within which plant-specific limits will often be located. However, it is recognized that, in some cases, plant-specific considerations will result in these boundaries being exceeded. This is acceptable, as long as each deviation is appropriately documented and technically justified in accordance with the current revision of the SGMP Administrative Procedures. The discussions in the previous chapters and the flowcharts and tables of example values contained in Chapter 4 should be helpful in the effort to outline the appropriate limits for each plant.

Typical corrective actions are recommended in several sections in this chapter. These corrective actions are not meant to be all-inclusive or universally applicable and should be modified for plant-specific concerns.

Because of the operating characteristics of the OTSG, secondary plant water chemistry requirements differ from those of a recirculating steam generator. This is particularly true during power operation (i.e., >15% reactor power) since there is no blowdown from an OTSG. In addition, since some impurities transported to the OTSG via the feedwater are transported almost quantitatively out of the OTSG by the superheated steam, the turbine rather than the steam generator may be the limiting corrosion concern. These guidelines assume the cycle and equipment design is appropriate for the OTSG system (i.e., full-flow condensate polishers, etc.).

Chemistry limits, responses to abnormal chemistry conditions, and the impact of such considerations on plant operation are discussed in this chapter. The chemistry limits and action levels are considered to be the minimum requirements for protection against steam generator, secondary system, and turbine corrosion. The guidelines are applicable for any cooling water source and are based upon the philosophy that plants should operate with the lowest practicable impurity levels consistent with their circumstances.

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6.2 Control and Diagnostic Parameters

The tables presented in this chapter include surveillance parameter requirements and recommendations.

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6.2.1 Loss of Monitoring for a Shall Monitoring Requirement

A temporary non-compliance to a shall monitoring frequency requirement, such as a temporary inability to take continuous samples, should not be treated as a deviation per the SGMP Administrative Procedures as long as it occurs as a result of normal maintenance activities (such as calibration or preventive maintenance) or as long as all of the following conditions are met:

- Compliance to the required monitoring frequency is restored as soon as reasonably practical.
- The reasons for the temporary non-compliance, together with the actions taken, are documented in accordance with the station's corrective action program.
- The actions include a sampling and analysis program that quantifies the parameter at a frequency defined as reasonable in plant specific documentation.

6.3 Action Level Responses

Three Action Levels have been defined for taking remedial action when monitored parameters are outside the specified operating range. Deviations from chemistry concentrations normally achieved at a given station should be investigated. Action Levels prescribe values of a parameter above which long-term system reliability may be jeopardized. Operating below Action Level 1 values provides a greater degree of assurance that corrosive conditions will be minimized. Action Level 2 is instituted when conditions exist which are more likely to result in steam generator or balance of plant corrosion during extended full power operation. Action Level 3 is implemented when conditions exist which have the potential to result in rapid steam generator or balance of plant corrosion, and continued operation is not advisable.

The Action Levels and the associated chemistry limits are considered to be the first line of defense against secondary system and steam generator degradation.

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6.3.1 Action Level 1

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6.3.1.1 "Shall" Requirement Actions

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6.3.2 Action Level 2

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6.3.3 Action Level 3

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6.3.3.1 "Shall" Requirement Actions:

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6.4 Operating Conditions

These guidelines address steam generator status relative to the thermal and hydraulic conditions within the steam generator, based on the corresponding plant condition, and the consequent effects of the chemical environment. Revision 7 was updated by replacing the operating condition descriptive wording with the applicable temperature and power condition in both the text and tables of Chapter 6. The following operating conditions and corresponding temperature and power conditions were used as the basis:

1. Cold Shutdown/Wet Layup: *RCS ≤ 200°F*
2. Startup: 200°F < RCS ≤ 350°F
3. Hot Standby: RCS > 350°F, Reactor-not-critical
4. Reactor Critical at < 15% Power

5. Power operation: $\geq$ 15% Reactor Power

6.5 Guidelines

6.5.1 Cooldown/Hot Soaks

During plant cooldown, steam generator bulk water may contain significant levels of impurities from hideout return. A site specific plan for maximizing the removal from the steam generators of hideout return impurities during the cooldown should be included in the outage shutdown plan. The plan should also include the development of a hideout return database. (See Chapter 7 for details on evaluating hideout return data.)

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6.5.2 Cold Shutdown/Wet Layup

6.5.2.1 Guidelines

The guideline parameters for wet layup are presented in Table 6-1 and Table 6-2.

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6.5.2.2 Discussion

During outages, wet layup of steam generators with chemically treated water is desirable to minimize corrosion and oxidation during the layup period and also corrosion during subsequent startup and power operation. Protection is provided by an amine for pH control and hydrazine (or other qualified oxygen scavenger) to maintain a protective oxide film and a reducing environment. Plant experience and laboratory studies show that proper layup chemistry can provide corrosion protection for six months or longer [5, 6].

Mixing of the steam generator bulk solution will assure uniform distribution of chemicals in the bulk water. Nitrogen sparging and/or recirculation [7]and adequate sample line flush times will provide chemistry samples that are representative of steam generator contents. (see Section 7.3.1).

Steam generator layup requirements should be a major consideration of outage planning.

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Table 6-1
Wet Layup (RCS ≤200°F) Steam Generator Sample

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Table 6-2
Once-Through Steam Generator Fill Water

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6.5.2.3 Justification for Parameters and Values

Summary justifications are provided below. Section 2.4 provides more detailed information on the relative corrosion susceptibility of the different steam generator tubing alloys.

6.5.2.3.1 Steam Generator

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6.5.2.3.2 Fill Source/Steam Generator

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6.5.2.4 Corrective Actions

After verification that a parameter is not within normal limits, the corrective actions given in Table 6-3 should be considered.

Table 6-3
Corrective Actions during Cold Shutdown/Wet Layup (≤ 200°F)

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6.5.3 Startup, Hot Standby, and Reactor Critical at <15% Reactor Power (RCS >200°F, <15% Reactor Power)

6.5.3.1 Guidelines/Technical Justifications

Feedwater and OTSG chemistry guidelines during startup, hot standby, and low power operation are given in Table 6-4 and Table 6-5, respectively.

Proper feedwater quality minimizes corrosion of the steam generators and produces steam that is suitable for turbine startup and operation. It also reduces fouling of steam generator heat transfer surfaces and support plate flow paths.

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Good water quality reduces the time required to go from system startup to full power operation. It is important to attain the best possible feedwater chemistry during startups to minimize the amount of time in this operating condition.

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Table 6-4
Once-Through Steam Generator RCS > 200°F to Reactor Critical at <15% Reactor Power Feedwater Sample

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Table 6-5
Once-Through Steam Generator RCS > 200°F to Reactor Critical at <15% Reactor Power Blowdown Sample [a]

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6.5.3.2 Parameter Justifications

6.5.3.2.1 Feedwater

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6.5.3.2.2 Steam Generator Bulk Water

It is considered appropriate that the impurity concentration limits between 0% and 15% reactor power should be essentially the same as for recirculating steam generators at full power. Note that these limits are somewhat more conservative for OTSGs both because of the lower temperatures at the tubesheet and the limited time for which these limits apply.

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6.5.3.3 Corrective Actions

After verification that a parameter is not within normal limits, the corrective actions given in Table 6-6 should be considered.

Table 6-6
Corrective Actions during RCS > 200°F to Reactor Critical at <15% Reactor Power

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6.5.4 Power Operation (≥15% Reactor Power)

6.5.4.1 Guidelines/Technical Justifications

Feedwater chemistry guidelines for power operation are given in Table 6-7. Chemistry guidelines for condensate samples are given in Table 6-8. For normal operation, these values represent limits below which little impurity-related corrosion of steam generators or turbines has been noted by the industry. Out-of-guideline conditions should be corrected within the time specified. Higher water quality should be maintained whenever possible.

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Table 6-7
Once-Through Steam Generator Power Operation (≥15% Reactor Power) Feedwater Sample

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Table 6-8
Once-Through Steam Generator Power Operation (≥15% Reactor Power)
Condensate Sample

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Table 6-9
Once-Through Steam Generator Power Operation (≥15% Reactor Power)
Moisture Separator Drain Sample

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6.5.4.2 Parameter Justifications

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6.5.4.3 Corrective Action Guidelines—Power Operation

After verification that a parameter is out-of-guidelines, the corrective actions given in Table 6-10 should be considered.

Table 6-10
Corrective Action during Power Operation (> 15% Reactor Power)

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7

DATA: COLLECTION, EVALUATION, AND MANAGEMENT

7.1 Introduction

The primary purposes of secondary cycle chemistry controls are to minimize general corrosion and prevent localized corrosion of plant materials with the expectation of attaining the design life of all components. The effectiveness of the secondary cycle chemistry control program must be continually evaluated to determine if chemistry conditions in the bulk water are consistent with achieving these goals. During operation, corrosion processes can only be inferred by analyzing treatment additives, impurities, and corrosion products in conditioned samples withdrawn from bulk process streams. Non-representative samples and analysis errors can provide misleading results. A QA/QC program that addresses sampling and analysis issues is necessary.

Recent developments in modeling have enabled chemistry conditions throughout the cycle to be evaluated while minimizing sampling and analytical requirements. In particular, the EPRI ChemWorks™ software can be used for this purpose (see Section 7.4.2). There are also other tools available for assessing local chemistry conditions and component performance. A hideout return study during shutdowns can provide an indication of concentration processes within the steam generators while the system was operating, Inspections of steam generators and other components can indicate the extent and mode of corrosion. Mass balances can be used to evaluate impurity input sources. Once impurity source terms are quantified, corrective measures can be taken to reduce impurity inventories and/or concentrations. The mass balance tool can be used for ionic species as well as corrosion products. For plants that utilize condensate polishers and/or blowdown demineralizers, resin analyses can provide an indication of the performance of the resins and their impact on system chemistry.

In Chapters 5 and 6, secondary water chemistry guidelines are established for units with recirculating steam generators and once-through steam generators. Table 7-1 and Table 7-2 summarize the continuous instrumentation identified for Control (C) parameter monitoring in Chapters 5 and 6, respectively. Diagnostic parameters of Chapters 5 and 6 that can be monitored using continuous instrumentation are designated by (D). Examples of Additional (A) instrumentation that can provide further assistance in assessing chemistry variations and component performance are also given.

Table 7-1
Examples of Continuous Instrumentation for Recirculating Steam Generators

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Table 7-2
Examples of Continuous Instrumentation for Once-Through Steam Generators

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7.2 Data Collection and Analysis

7.2.1 Data Collection

Data collection is performed by grab sampling and by process instrumentation analysis. Both types of analyses are required. For short-term system diagnosis, in-line (continuous process) data typically are used as the initial indication of an event. Grab sample data are typically used for long-term diagnosis and short-term confirmatory information. Data collection frequencies are designated for control parameters in Chapters 5 and 6. Frequencies for diagnostic parameters should be assessed based on the perceived site-specific need for the particular analysis. A site specific plan for contingency sampling when a process instrument is out of service also should be developed (see Chapter 1).

7.2.2 Basis for Generating Chemistry Data of Known Quality

ASTM and other sources have developed specific standards and guidelines for QA/QC practices that are applicable to power plant chemistry programs.

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7.2.3 Data Management

The *PWR Secondary Water Chemistry Guidelines* do not specify explicit requirements for a chemistry data management system, but do identify desirable features which can be incorporated into a plant-specific system. A main feature of a data management system should be retrievability of results in a timely manner. Ideally, the data management system should provide for automated input from chemical process instrumentation and manual input from grab sample analyses. A well designed chemistry data management system should provide the following to enable reviews to promptly identify and assess potential problems:

- System being sampled and sample point
- Plant status (e.g., power level, blowdown flow rate, polisher configuration, etc.)
- Chemistry limits and analysis frequency
- Analysis time
- Results of current and previous samples
- Actions to be taken if limits are not met (e.g., chemical additions, changes in blowdown flow rate or demineralizer/polisher status, etc.)

Ideally, the chemistry data management system would be capable of interfacing with EPRI ChemWorks™ (see Section 7.4.2), linking plant data files to the Plant Chemistry Simulator (PCS) to perform automated evaluations. Other desirable features of the data management system include:

- Graphically display chemistry and operational parameters as a function of time, with real time plots available from process instrumentation
- Perform mass balances for various species
- Graphically display QC results on control charts and evaluate the results for conformance requirements. (A separate data management system can be used to perform this function.)

7.2.4 QC Considerations for Secondary Chemistry Control

An important aspect of the QC program is the analysis of QC samples to verify analytical performance. Analysis of QC samples should reflect the matrix of the samples under analysis unless the matrix is known to not impact the analysis result (i.e., analysis of a QC sample in demineralized water will not necessarily verify the sulfate concentration in a steam generator blowdown sample under layup conditions with 100 ppm hydrazine and 20 ppm ammonia). The following practices are recommended:

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Chemistry process instrumentation should be calibrated and maintained to the degree necessary to provide accurate, real-time data. Additional guidance is provided in ASTM D-3864 [2].

Chemicals used as treatment additives can be a source of impurity ingress to the secondary cycle. Purchase specifications should ensure that sodium, chloride, and sulfate are limited in treatment additives. Impurities such as ethylene glycol should be limited in ETA or as appropriate in other amines.

7.3 Sampling Considerations

7.3.1 General Considerations

Efforts should be made to assure that a sample is representative of the process stream or vessel of interest. Long sample lines and improper sample conditioning can lead to results that do not reflect process stream concentrations. Non-representative samples can result from:

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Existing sampling systems often do not take into account design features presently considered appropriate. Plants upgrading their sampling systems should consider improved sampling practices such as those given by ASTM and ASME [3, 4, 5, 6, 7]. General guidance such as the following is provided in such references:

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Additional considerations relevant to PWR secondary system sampling and analysis are given below:

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A major concern is sampling the steam generators during blowdown isolation or shutdowns. If the plant is at temperature during blowdown isolation, blowdown samples may not be representative as a result of excessive sample transport times. Sample collection time should reflect sample transport time in the sample line if delays are significant. During shutdowns, with or without blowdown isolation, pressure may not be available to provide sufficient head for sample flow, and local samples must be withdrawn for analysis. This is a particular concern during layup conditions. If a recirculation pump is not used, local samples must be collected, and purging requirements should be defined. It is suggested that replicate samples be collected at the highest practicable purge rate to establish sample validity. A particular concern is sampling after a chemical addition during layup without recirculation. In this case, local samples can be non-representative unless nitrogen sparging is used to distribute the chemicals.

7.3.2 Corrosion Products

7.3.2.1 Sampling

Sampling of feedwater, condensate, and blowdown for metal oxides presents significant challenges since a significant fraction of the iron based corrosion products are particulate. Although the particulates may be uniformly distributed in the flowing stream, deposition on sample line tubing surfaces and subsequent release of deposited oxides from the sample line can significantly affect the sample concentration and its relation to the concentration in the process stream. In addition, feedwater and condensate system concentrations during normal operation are generally very low. General guidance on collection of filterable and non-filterable matter in water samples is given in ASTM D 6301-03 [6].

To improve the likelihood of obtaining a representative sample, the following approaches should be considered:

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Table 7-3
Sample Flowrate (kg/min) required to Achieve a Sample Line Velocity of 6 ft/sec

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Table 7-4
Sample Line Velocity (ft/sec) at a Sample Flowrate of 1 kg/min

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Table 7-5
Sample Line Reynolds Number (dimensionless) at a Sample Flowrate of 1 kg/min

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7.3.3 Oxygen

Sampling of feedwater for oxygen requires special consideration. In the past, most feedwater sampling systems were designed with sample coolers and analyzers distant from the sample location. As a result, the feedwater oxygen concentration was routinely underestimated due to its reaction with hydrazine in the sample line prior to sample cooling and analysis. Guidance for obtaining reliable feedwater hydrazine and oxygen concentration data can be derived from the work of Dalgaard [9].

The rate of change of the oxygen concentration in the sample line as a function of the oxygen and hydrazine concentration and temperature can be approximated as follows:

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Where,

Solving this equation for the oxygen concentration at time t (for a small variation in hydrazine concentration),

Where,

This equation is based on data with initial oxygen concentrations in the range of approximately 5 to 100 ppb. It should not be used for estimating reaction rates far outside this concentration range.

Table 7-6 shows an example calculation of oxygen concentration versus time in a feedwater sample line at 204°C (477K) with 40 ppb hydrazine and 5 ppb oxygen.

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Table 7-6
Example Calculation of Oxygen Reduction in a Feedwater Sample Line

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The need to minimize the delay time between the feedwater sample point and the initial sample cooler to obtain reliable oxygen concentration data is clearly illustrated by the Table 7-6 example.

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7.3.4 Sample System Design Consideration

The diagrams shown in Figure 7-1, Figure 7-2 and Figure 7-3 illustrate several suggested approaches to sample system design. The specific configuration shown in Figure 7-4 should minimize fractionation of suspended matter based on the density difference of water and the suspended matter.

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Figure 7-1
Example of Feedwater Sample Line Configuration for Oxygen Sampling

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Figure 7-2
Example of Feedwater Sample Line Configuration for Metal Oxide Sampling

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Figure 7-3
Suggested Feedwater Sample Line Configuration for Oxygen and Metal Oxide Sampling

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Figure 7-4
Example of a Sample Tee Configuration

7.3.5 Sampling for Lead

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7.3.6 Alternative to Continuous Blowdown Sampling for Sodium for OTSGs During Startup

In the case where continuous monitoring of blowdown sodium concentrations cannot be met, an alternate calculational / intermittent measurement approach can be employed based on a mass balance assessment utilizing continuous feedwater measurement of sodium concentrations and grab sample measurements of blowdown sodium concentrations. The following conditions should be employed in this approach:

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It is expected that these criteria will be demonstrated by a suitable evaluation of plant data and analytical capability, and verified by comparing continuous feedwater and grab sample blowdown sodium concentrations, before this alternative approach is employed.

In addition, the following issues should be considered in development of the mass balance assessment:

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7.4 Data Evaluation Tools

7.4.1 Introduction

Data evaluation historically has involved consideration of conformance to specification or target values, comparisons of parameter values at different sampling locations, comparisons of measured pH and conductivity values to values calculated from measured chemical additive concentrations, comparions of measured cation conductivity to that calculated from anion concentration data, etc. Software packages are available to perform these comparisons on a routine basis. Other evaluation tools that may provide valuable information include secondary system mass balances, steam generator hideout return studies, and resin performance testing including resin kinetics, site composition, and capacity.

The initial evaluation of chemistry data should be performed by the person generating the data or recording data from chemical process instrumentation. Investigations should take place if an analysis parameter falls outside of a normally observed range or outside of a control band. Changes in system configuration, plant conditions, or chemical dosing may explain the change in analysis results. The QA/QC program should be designed such that changes in analysis results are not artifacts of the sampling or measurement approach.

To the extent practicable, pH/conductivity/treatment additive concentration relationships and cation conductivity/anion impurity relationships should be automated and biases given. Analysis parameters from different sample points should be consistent with expected relationships. The Strategic Water Chemistry plan or appropriately referenced station document should identify the frequency with which the calculated pH, specific and cation conductivity comparisons should be made with actual data, in different portions of the secondary system. This may require analysis for organic acids as well as the routine anionic contaminants. Computer programs are available for such calculations. QC data should be considered when evaluating the significance of any differences seen in the calculated versus measured values. The acceptable uncertainty of these comparisons can be different for different portions of the secondary systems.

7.4.2 EPRI ChemWorks™ Software

EPRI ChemWorks™ is a series of computer codes developed to aid chemistry personnel in evaluating and interpreting chemistry data and predicting various chemical conditions throughout the secondary cycle. The modules were developed with the idea that computer tools could be used to model the chemistry environment on the basis of design/operational plant parameters and limited measured analysis parameters. The following software models, summarized in Table 7-7, are available as of the publication of these guidelines.

Table 7-7
EPRI ChemWorks™ Software Products

Title	Description	Software Type	Product ID
ChemWorks™ Tools, version 1.0 .	Developed to be the core ChemWorks™ application that contains previously EPRI ChemWorks™ spreadsheet applications. Current version includes MULTEQ 4.0 and Hideout Return Calculator.	Application	1014959
MULTEQ Version 4.0 Desktop Application	Stand-alone version of MULTEQ 4.0, EPRI's high temperature chemistry calculator.	Application	1014414
Plant Chemistry Simulator Version 4.0: PWRSCS 4.0/BWRSIM 4.0	An equilibrium chemistry simulator for the PWR secondary system. See below for a more detailed description.	Application	1006145
CIRCE - PWR Secondary Water Chemistry Optimization Tool Version 1.0	An integrated application that combines the Plant Chemistry Simulator, FAC rate calculations from EPRI CHECworks, and the EDF BOUTHYC model.	Application	1014960
ChemWorks™- Primary to Secondary Leak Calculator Software, Version 2.0	Spreadsheet application to estimate the leak rate from the primary coolant to the secondary circuit.	Excel Spreadsheet	1000989
ChemWorks™ Polisher Performance Calculator (PPC) Software, Version 1.0	A resin management tool that tracks polisher and blowdown vessels, resin charges, and the regeneration frequency and chemical consumption	Application	1007330
ChemWorks™ - AminMOD, Version 4.0	AminMod models the distribution of amines, amine decomposition products, and boric acid at key points in the secondary cycle [12, 31]. More rigorous results are obtained with the Plant Chemistry Simulator, but quick estimates can be performed with basic system design input.	Application	SW-109560-P6
ChemWorks™—Mixed Bed Ion Exchange (MBIE) Version 1.0	Calculates the equilibrium leakage of a condensate polisher or blow down demineralizer based on the ionic loading of the contaminants.	Application	SW-109560-P9DK
Integrated Exposure Calculator (IE Calculator) Version 1.0	Calculates an integrated exposure (IE) and an actual tube exposure factor (TEF) for sodium, chloride, and sulfate [32]. The methods implemented in the IE Calculator are described in Appendix A.	Application	1006143

Below are more detailed descriptions of the most commonly used products for PWR Secondary Chemistry.

7.4.2.1 ChemWorks Tools ™

The ChemWorks™ User's Group and the EPRI Technical Advisory Committee indicated that the preferred method for using EPRI's various ChemWORKS products was to have them combined in a single software application. EPRI has responded to this request by developing ChemWorks™ Tools application, which currently has MULTEQ and the Hideout Return Calculator [34].

7.4.2.2 MULTEQ

MULTEQ is a stand-alone program that calculates the chemical speciation, pH and electrochemical potential of an aqueous solution as it is concentrated up to 10^{10} between 150°C and 335°C. MULTEQ calculates complex chemical interactions of species and allows precipitates to form during the concentration process by assuming that the liquid, vapor, and solid phases are in thermodynamic equilibrium. MULTEQ also calculates the boiling point elevation (BPE) during the concentration process. Calculations at lower temperatures can be performed if the equilibrium and distribution constants are verified and/or modified to be accurate at the specified temperature. Conductivity and pH calculations also can be performed at 25°C. In performing these calculations it should be understood that exactly 25°C must be specified to ensure that the code default values are used.

7.4.2.3 Hideout Return Calculator

The Hideout Return Calculator is now part of the ChemWorks™ Tools Application, which calculates the change in the impurity or boric acid inventory in the steam generators from blowdown and feedwater concentrations, power level, steam generator water level, blowdown flowrate, and feedwater flowrate during a shutdown is also available. Successive summations of the changes in inventory over time provide the cumulative hideout return. The spreadsheet performs the calculations for different steam generator models at varying blowdown and feedwater flowrates. The model will be integrated with MULTEQ in the ChemWorks™ Tools Application [11].

7.4.2.4 Plant Chemistry Simulator

The Plant Chemistry Simulator (PCS) allows the user to model the equilibrium distribution of chemical species, steam generator hideout, chemical decomposition, and condensate polisher/blowdown demineralizer impurity removal for PWRs and BWRs [30]. The distribution of additives and contaminants in the steam cycle is calculated in terms of solute flows in the steam/water system. Phase separations are modeled using the MULTEQ high temperature chemistry calculation. The following components are modeled by the PCS:

- Steam generator*
- Blowdown flash tank*
- Blowdown demineralizer†
- Main steam
- HP turbine*
- Moisture separator*
- LP turbine*
- Steam reheater*
- Boiler feed pump turbine *
- Feedwater heater shells
- Heater shell drain tank
- Heater drain tank*
- Feedtrain tube side
- Condenser*
- Air ejector
- Condensate polisher†

*includes phase separation calculation
†includes ion exchange equilibrium calculation

The model is based on the passage of steam from the steam generator through the high pressure turbine, moisture separators, reheaters, and low pressure turbine to the condenser. Condensate is then returned to the steam generator via the feed train. Plant-specific temperatures and flow rates are used in the model.

7.4.2.5 CIRCE

In 2005, EDF and EPRI began collaborating on the development of the CIRCE research program to evaluate the effects of chemistry on general corrosion, flow assisted corrosion, and steam generator fouling. In 2007, EPRI released the CIRCE v1.0 software application that combined the following models:

- EPRI Plant Chemistry Simulator,
- EDF BOUTHYC Steam Generator Fouling Model
- EPRI ChecWORKS model (or user specified FAC rates)
- Iron Transport Model developed by EPRI and EDF.

The model combines several cycles of operation for a single unit, and can be used to calculated steam generator fouling factors over time [27].

7.4.2.6 Polisher Performance Calculator

Polisher Performance Calculator (PPC) is a stand-alone application that allows the user to employ ion exchange system descriptions, and operations data to estimate system economics, and the performance of each polisher and charge of resin. The PPC provides a consistent, standardized method for tracking polisher system performance for utilities with multiple stations [33].

7.4.3 Calculated Cation Conductivity

Cation conductivity is used to monitor the total concentration of anionic contaminants. Monitoring this parameter requires that the sample be passed through cation resin in the hydrogen form which exchanges cations in the sample with the hydrogen ion:

$$R^-H^+ + Na^+ + Cl^- \rightarrow R^-Na^+ + Cl^- + H^+$$

Since the equivalent conductance of typical cations (such as sodium and ammonium) and anions is 50-80 Siemens-cm^2/equivalent, whereas the hydrogen ion has an equivalent conductance of 350 Siemens-cm^2/equivalent (see Table 7-8), the measurement is more sensitive to strong acid anions than the specific conductivity measurement. Ammonia, hydrazine and amines do not affect the measured cation conductivity since they are removed by the cation resin:

$$R^-H^+ + NH_4^+ + OH^- \rightarrow R^-NH_4^+ + H_2O$$

Table 7-8
Equivalent Conductivities for Some Ions: [Ref. MULTEQ Database]

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Although advanced amine pH treatment additives do not directly contribute to the cation conductivity, their decomposition leads to the formation of short chain organic acid anions such as acetate and formate that elevate cation conductivity. Strongly ionized anions such as chloride and sulfate have been documented to have deleterious effects on steam generator and turbine materials when the anions are present at high concentrations. Anions associated with breakdown of organics and amines (such as acetic and formic acid) have not been shown to impact corrosion of secondary system components within current chemistry control practices. The cation conductivity measured in plant streams reflects a combination of all anions, including borates, fluoride, and organic acid anions. Since complex ionic equilibria govern the behavior of a multi-component system, a simple subtraction of the conductivity contribution of any single component or of several components cannot be made on a linear basis (e.g., taking the ppb times a factor does not properly take into account the effect on solution conductivity governed by complex ionic equilibria).

To demonstrate conformance to control parameter values, the concentrations of chloride and sulfate (and any other strong-acid, non volatile anions, e.g., phosphate) are used to calculate the cation conductivity, taking into account the proper ionic equilibria with water. Calculations of specific and cation conductivity can be performed using MULTEQ.

Increases in cation conductivity above the normal baseline level also can be used as an indicator of possible chloride or sulfate ingress and as a basis for an augmented chloride or sulfate analysis effort. However, the increase cannot be used as a quantitative indicator of the actual chloride or sulfate concentration.

7.4.4 Steam Generator Corrosion Evaluations

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7.4.4.1 Source Term Evaluation

The principle of ALARA chemistry is based on the optimal reduction of source terms. Understanding the sources of the steam generator impurities allows the utility to prioritize resources to address and reduce source terms. Source term identification can be addressed in two ways: through direct analysis of each source or through modeling. Typically, both of these methods are used. The goal of each method is to perform a mass balance of the secondary system impurities to identify and quantify impurity source and removal terms. Table 7-9 gives examples of source and removal terms typically found in PWR secondary systems.

Table 7-9
Typical Source and Removal Terms in PWR Secondary Systems

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At steady state, the source and removal terms must be equal:

$$\Sigma(W_{IN})(C_{IN}) = \Sigma(W_{OUT})(C_{OUT})$$

Where:,

W = Mass flow rate, lbs./hr.
C = Concentration, lbs./lbs.
IN = Sources
OUT = Removal

The difficulty occurs in systems where either the flowrate is not known or the concentration is less than detectable. This is where modeling can greatly help. The EPRI ChemWorks™ Plant Chemistry Simulator (PCS) can be used to perform mass balances for the secondary system and calculate concentrations of streams that are either not able to be sampled or have too low a concentration to measure. Once the concentrations and flows are established, a prioritized listing of each impurity and source can be determined. Table 7-10 gives an example of this technique for sodium for a plant rejecting blowdown to the environment.

Table 7-10
Source and Removal Term Percentages

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In this example, impurity removal and input rates are very similar indicating minimal hideout in the steam generators. Note that some amount of difference is typical and may be due to errors in the measurements or unaccounted for source or removal terms. The utility can use this information to prioritize source term reduction actions as well as to understand the importance of addressing issues such as condensate polisher performance, condenser inleakage, etc.

7.4.4.2 Source Term Contribution from Total Organic Carbon

Secondary systems are susceptible to contamination from organic compounds from a variety of sources: maintenance activities, contaminants in makeup water, degradation of non-metallic secondary system components, and additive chemicals. The principal organic compounds seen in the secondary systems due to amine degradation products are acetates, formates, and glycolates, which are routinely measured in the 1-100 ppb concentration range. The principal effect of these anions is to increase the cation conductivity of secondary system water. To date, there have been no negative effects noted on secondary system component corrosion or reliability due to the presence of these anions. However, the increased cation conductivity caused by the presence of these organic acids decreases the ability to identify ingress of other anionic impurities such as chloride and sulfate.

Increases in blowdown chloride and sulfate concentrations can result from the ingress of chlorine and sulfur bearing organics. Makeup water can be a source of such compounds if the water treatment processes are focused on removing only ionic contaminants. The organic materials may not be detected in the makeup water treatment system effluent because they are non- or weakly ionic, and are at low concentrations. Analysis for specific organic compounds is not practical since there is such a wide variety of possibilities. However, Total Organic Carbon (TOC) analyses are sometimes performed [14].

Several instruments used for this analysis [15] employ the decomposition of carbon compounds into carbon dioxide and water. The methods of organic carbon oxidation include:

- Peroxydisulfate-UV irradiation,
- High temperature oven-oxidant,
- Metal catalyst-UV methods.

In evaluating sources of secondary cycle impurities, transport of organically bound inorganics such as chlorine, sulfur and phosphorus should be considered. For example, chlorination will produce varying concentrations of chloromethane, chloroethane and dichloromethane, depending upon the degree of chlorination and the concentration of organic matter. Water treatment processes that use only ion exchange will not remove these compounds, as they are not ionic. Furthermore, concentrations of these compounds of several hundred ppb will go undetected because the usual methods of demineralized water analysis are directed towards ionic compounds. These compounds undergo rapid degradation in the steam generators when they are exposed to high temperature. The principal degradation product will be chloride. The absence of a corresponding cation (e.g., sodium) is an indication that the source may be organic halides. Several methods of analysis are available to detect low concentrations of these compounds in make up water. Analysis for total organic halides (TOX) can be performed along the lines of the TOC, except that the oxidation products are analyzed for halides by microcoulometric analysis [16]. At BWRs, the presence of organically bound sulfur and chlorine is routinely evaluated by post UV ion chromatographic analyses for sulfate and chloride.

Minor leaks of turbine oils that contain organophosphate compounds can create similar problems. These oils will decompose to yield carbon dioxide, water and phosphate. This may not even be noticed in routine ion chromatographic analysis since HPO_4^{2-} is strongly retained by an ion chromatography column. However, this could show up as a discrepancy between cation conductivity and calculated cation conductivity if phosphate concentrations are significantly elevated.

Organic chemicals also can contaminate make up water when new resins are put into service. One of the final steps in resin production is to swell the beads with an organic compound (1, 3 dichloropropane is a commonly used swelling agent). This material is then flushed from the resin with water and the resins are regenerated and then packed for shipment. Traces of these compounds on the resins will enter the make up water system undetected unless the final make up water is analyzed for TOC/NPOC/POC or POX/NPOX. At least one such event has had a significant effect on plant operation [17]. In this instance, even after resin regeneration and significant volume water flush of the resin (more than 10,000 gallons), between 100 and 400 ppb of dichloropropane was found in the demineralizer effluent.

Plants also experience leaching of organic materials from cation resins in the condensate polisher or blowdown recovery systems. The extent of this leaching depends upon the temperature of the fluid in contact with the resin, the amine used, and its concentration. The principal compounds that are leached are short chain sulfonic acids. These compounds are weakly ionic and do not contribute significantly to either specific or cation conductivity. They are not detectable through normal chromatographic techniques (i.e., ion chromatography for sulfate) since the sulfate is still organically bound. One approach that can be used to determine their presence is to split a sample and analyze the first part for sulfates directly. The second portion is irradiated with a high intensity UV light. This portion is then analyzed by ion chromatography for sulfates. The irradiation process decomposes the organic material into carbon dioxide, water, and sulfate, which also occurs when water processed by demineralizers is fed forward to the steam generators.

Finally, organic compounds are routinely observed during a unit power decrease or shutdown. The acetate, formate and glycolate ions may be returning from hideout regions but they are more likely formed at an increased rate from the pH additives when oxygen enters the system during shutdowns. These compounds can contribute significantly to the cation conductivity.

7.4.4.3 Integrated Exposure Evaluation (for Recirculating Steam Generators)

Research completed under EPRI's Heated Crevice Program, discussed in Appendix A, shows that the mass of impurities accumulated in RSG crevices is proportional to the impurity exposure. Appendix A describes several proposed methods for determining the relative amount of integrated exposure. While these methods do not quantify the actual mass of impurities in the crevice, they do provide a relative indication of the amount of impurities accumulated in the crevice at any point during the cycle. Plant personnel and plant management may find this a useful tool in the decision-making process when considering responses to chemistry transients.

Appendix A also provides examples of how several plants have used the integrated exposure concept. It should be noted that information in these examples does not supersede any Action Levels, requirements, or responses; the plants are still responsible for following procedures when Action Levels are entered. It should also be noted that these models are not applicable to OTSGs. This is due to the manner in which contaminants accumulate in the RSG crevices, which is not the same as for the OTSG surfaces.

7.4.4.4 Hideout Return Evaluations [11]

During a unit shutdown, steam voids collapse, crevices are rewetted, and impurities diffuse into the bulk water. This process is known as hideout return. Return of species from crevice regions, sludge piles and surface deposits is expected to occur. Evaluation of hideout return data is described in various EPRI documents [11, 13, 14, 18] and vendor documents (e.g., for OTSGs and for units with eggcrate tube supports [19]), and these should be evaluated for applicability. Minimum recommendations for the species that should be monitored during hideout return studies are:

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However, any species that returns at a high enough concentration to affect crevice pH should be added to this list.

Hideout return evaluations are unique opportunities to assess the likely steam generator crevice chemistry as it exists during operation based on data collected during a plant shutdown. The evaluation of hideout return data is dependent on the amount and type of data collected, and the quantity of impurities that returns to the bulk water. A screening process has been established to assist in the determination of the scope and type of evaluation that can reasonably be performed on a given set of hideout return data as shown in Figure 7-5 [11]. Additional guidance is given for sampling during a rapid shutdown, particularly for data collected at hot zero power. Evaluation of hideout return data is discussed in the EPRI PWR Hideout Return Sourcebook [11].

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Figure 7-5
Hideout Return Sampling and Evaluation Processes [11]

For hideout return studies to be valid, it is essential that the sample results match steam generator temperature and conditions at the time the sample resided in the steam generator. When sample line delays are significant, sample collection time should be corrected to accurately reflect the time at which the sample was in the steam generator.

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Plant strategies for minimizing outage length are challenging the established hideout return study time frames. Shorter outage times reduce the time during the shutdown to grab samples, and there generally are no hold points. The PWR Hideout Return Sourcebook [11] should be consulted on how and when to conduct a HOR study under these circumstances. Some utilities have expanded the temperature range for prompt return to include data at temperatures around 50°F (28°C) below hot zero power.

Experience with new steam generators indicate that there is minimal hideout. Low values for HOR indicate generally clean crevices. However, plants should continue HOR evaluations to establish a baseline for future assessments of steam generator health. Note that as a result of the small amounts of hideout return currently being experienced in many operating units, it is important that make up water flow rates and impurity concentrations be monitored during the hideout return evolution and that the impurity input rate from this source be subtracted from the apparent hideout return. When minimal amounts of cumulative mass return are observed, e.g., as indicated by blowdown concentration increases of less than 1 or 2 ppb for the highly soluble species, performing evaluations such as MULTEQ modeling may not provide reasonable results due to the significant uncertainty in the data, and thus may not be justified. However, trending the total return is always suggested as a reasonable method for assessing changes in the hideout characteristics of the steam generators over time. See reference [11] for more details.

7.4.4.5 Deposit Chemistry Evaluation

The deposits in contact with the steam generator tubes can have a direct effect on the corrosion rate. A mass balance of the metals and metal oxides such as iron and copper in the feedwater and blowdown during startup and power operation can be used to calculate the total amount of deposits in the steam generators.

$$M = \Sigma(W_{FW}C_{FW} - W_{BD}C_{BD} - W_{MS}C_{MS})$$

Where,

M = accumulated mass in the steam generators (lb)
W = mass flow rate (lb/hr)
C = concentration (lb/lb)
FW = final feedwater
BD = blowdown
MS = main steam

Steam transport is generally neglected, unless plant specific data show otherwise.

Estimated deposit magnitudes should be compared to in-service inspection results and visual examinations of the steam generators to assess the impact of the deposits on steam generator performance and corrosion. Trending of tube deposit analysis results can be used to better understand the potential influences of lead, copper, sulfur, and alumino-silicates [20].

7.4.4.6 Sludge Analysis and Monitoring

The characterization of the chemical and structural composition of deposits removed from steam generators during sludge lancing can provide valuable insights into the potential for steam generator corrosion and thermal performance degradation. The presence of deposits on the secondary side of steam generators and the corrosion of steam generator materials and loss of thermal efficiency are intimately related. It is the solution chemistry within steam generator deposits and the properties of deposits adjacent to tube surfaces that primarily influence corrosion and heat transfer.

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Sludge lancing provides an excellent opportunity to retrieve representative deposits from various regions in the steam generator. Traditionally, sludge deposit analysis often focused on the chemical composition of loose powdered sludge samples because they are easily gathered. However, the analyses of loose powdered sludge may not be as meaningful as the analyses of tube scale flakes and "collar" samples, which reflect prevailing conditions in the vicinity of the tube wall. Steam generator deposits are not homogeneous in chemical or structural composition.

An improved assessment of the steam generator conditions can be developed by selecting a variety of samples for analysis, consisting of tube scale flakes, "collars", and powdered sludge. Microscopy (optical microscopy and scanning electron microscopy) of tube scale flakes and "collars" can identify consolidation layers, porous layers, and heterogeneous inclusions (such as copper) in the deposit and locate these regions with respect to their proximity to the tube wall. This structural information taken together with elemental analysis and compound identification across the cross-section of the deposit provides a more meaningful representation of conditions in the vicinity of the tube wall, which sheds light on the potential for future corrosion. Furthermore, tube scale thickness, porosity, and structure can shed light on the progression of thermal performance: dense deposit layers generally impede thermal transport while the boiling effects in porous deposit layers can enhance thermal transport.

A number of outside laboratories have the analytical equipment needed to perform a comprehensive characterization of sludge deposits and the expertise to interpret the analytical results. The comprehensive characterization of sludge deposits should provide detailed compositional and structural information; however, there are various sets of analyses that can lead to this end. Examples of types of analyses used in the characterization of sludge and scale deposits collected from sludge lance filters and grit tank screens are provided below [21, 22]:

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7.5 Balance of Plant Corrosion Concerns

Maintaining low corrosion rates in the BOP minimizes repairs to plant equipment and reduces the transport of metal oxides to the steam generators. The following techniques can be used to monitor and evaluate BOP corrosion concerns.

7.5.1 pH Control and Corrosion Product Transport

The at-temperature pH, pH_T, has a large effect on the corrosion rates of plant equipment. Optimizing pH_T for the metallurgy of the unit will minimize the amount of corrosion products being transferred to the steam generator. For all ferrous plants, typically the higher the pH_T, the lower the iron transport to the steam generator. For plants with mixed metallurgies (i.e., iron and copper), a balance must be reached between the optimal iron and optimal copper pH_T.

To optimize the pH control program, plants should develop a profile of corrosion product transport throughout the balance of plant. The EPRI ChemWorks™ Plant Chemistry Simulator (PCS) can be used to determine the appropriate amine(s) that optimize pH_T in all areas of the secondary plant [23, 24, 25, 26]. In addition, a recent software tool developed by EPRI in collaboration with EDF (CIRCE—PWR Secondary Water Chemistry Optimization Tool [27]) models not only the chemistry around the secondary system (as with PCS) but also the corrosion product transport to the steam generators and resultant steam generator fouling.

In assessing the program, utilities should consider the following data shown in Table 7-11:

Table 7-11
pH Control Program Data Trends

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Initially, these data can be used to establish the sources of iron and copper at the applied amine and ammonia concentrations using the mass balance methodology, e.g., the feedwater mass transport rate can be expressed as follows:

$$M_{FW} = W_{FW} C_{FW}$$

Using similar relations, the amount of transport at each location can be evaluated for a given feedwater system chemistry. A sample calculation is shown in Table 7-12.

Table 7-12
Sample Calculation for Iron and Copper Transport

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Examples of conclusions that can be developed from the above mass transport summary are as follows:

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7.5.2 Integrated Corrosion Product Loading

Plants should maintain an estimate of integrated corrosion product loading (or deposit loading) in steam generators for evaluating the need for mechanical or chemical cleaning and for assessing performance and chemical control issues. For example, B&W [28, 29] recommended steam generator chemical cleaning when steam generator deposit loading is between 10 and 14 grams per square foot of steam generator tube surface area. Deposit loading is the estimated steam generator deposit (or the integrated transport of corrosion products into the steam generator less removal by blowdown and sludge lancing) divided by the steam generator tube surface area. It should be noted that this is an average number; actual deposition may be significantly different across the steam generator. Deposit loading should be estimated during each cycle and totaled over multiple cycles to determine cumulative deposit loading.

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Table 7-13
Example Data on Steam Generator Deposit Loading

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7.6 Technical Assessments

Assessments should be performed routinely to evaluate the impact of secondary chemistry on system materials. These should consider In-Service Inspection (ISI) and Non-Destructive Evaluation (NDE) data, chemistry program data, and operational data. It is suggested that assessment results be documented in an end-of-cycle report. They also may be captured in other evaluations during the cycle. Recommendations from this assessment should be compared with the current strategic water chemistry plan and changes made to the plan to address any adverse conditions and to identify program improvements for extending component life and improving system performance. Examples of areas for consideration are:

7.6.1 Contaminant Ingress Control (Ionic Contaminants)

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7.6.2 Contaminant Ingress Monitoring (Oxidants)

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7.6.3 Corrosion Product Transport

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7.6.4 Steam Generator Corrosion

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7.6.5 System/Component Observations

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7.6.6 Demineralizer/Filter Performance

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7.6.7 Process Instrument Performance and Reliability

7.6.8 Hideout Return

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7.7 References

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8

MANDATORY, SHALL AND RECOMMENDED ELEMENTS

8.1 Introduction

Chapter 8 captures all of the specific elements contained within these *Guidelines* that are identified as mandatory, shall or recommended, consistent with NEI 03-08 and NEI 97-06. Each element is captured in Section 8.2, along with any needed supporting information related to the element. The Guidelines Revision 7 Committee evaluated and concurred with the inclusion of each element.

All mandatory, shall and recommended elements are identified in this Chapter 8.

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8.2 Mandatory, Shall and Recommended Elements

8.2.1 Mandatory Element

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8.2.2 Shall Elements

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8.2.3 Recommended Elements

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[1] Note that Table 5-8 and Table 6-8 identify condensate dissolved oxygen as a Control Parameter. However, as indicated in footnote (a) of each table, plants may consider condensate dissolved oxygen as a Diagnostic Parameter (with no associated Action Level value) if they meet the requirement outlined in the footnote.

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A
INTEGRATED EXPOSURE

A.1 Introduction

This appendix was created to document the concept of integrated exposure, its basis, and methodologies that can be used to evaluate integrated exposure of tubes to impurities. In addition, this appendix demonstrates how some plants have used integrated exposure in practice. Plant personnel and plant management may find integrated exposure a useful tool in the decision-making process to evaluate the response to chemistry transients.

The following items are covered in this appendix:

- Integrated Exposure Technical Basis
- Integrated Exposure Methodologies
- Integrated Exposure Plant Examples

It should be noted that information in this Appendix does not supersede any guideline Action Levels, requirements, or responses; meaning that the plants are still responsible for following requirements defined in Chapters 5, 6, and 8 when Action Levels are exceeded.

A.2 Integrated Exposure Technical Basis

Research completed under EPRI's Heated Crevice Program, cosponsored by several Japanese utilities, has shown that the mass of accumulated impurities in crevices is proportional to the exposure [1, 2]. In order to research crevice chemistries, investigators used two heated crevice systems. Both systems were of similar configuration, but one system was fed faulted bulk water chemistry in a laboratory while another was set up in Ohi Unit 1. Figure A-1 is a schematic showing the integrated autoclave-heated tube-ring assembly, consisting of an Alloy 600 tube surrounded by a 405 stainless steel ring to form the crevice. In most investigations involving packed crevices, the packing material was diamond powder due to its dielectric and chemical properties. However, in cases where the Raman probe was used, alumina powder was substituted for the diamond to minimize back reflections.

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Figure A-1
Conceptual Design of Heated Crevice Device Showing the Autoclave Heated Tube and Simulated Support Plate [2]

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In Figure A-2, the bold black line labeled "predictions" is based on a thermal hydraulic model of crevice solution concentration developed by an EPRI program at MIT [1]. Based on the application of energy, mass, and momentum conservation laws for transport processes within fouled crevices and sludge, the model predicts that the rate of accumulation of impurities will depend on crevice parameters such as temperature, crevice packing, bulk water concentrations, etc.

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Figure A-2
Amount of Accumulated Sodium as a Function of Exposure to Sodium in the Feedwater [1]

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A.3 Integrated Exposure Methodologies

*A.3.1 Method A (ppb*days)*

The simplest method of calculating integrated exposure is to integrate the impurity concentration over the number of days the crevice is exposed (continuous cycle length). This integration is just the area under the curve of a plot of the time during the cycle vs. the product of concentration of impurity and power and is easily calculated with the use of a computer spreadsheet. Shown below in Figure A-3 is an example of what the spreadsheet might look like.

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Figure A-3
Spreadsheet Used to Calculate Integrated Exposure by Simple Integration Method

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Figure A-4
Sample Sodium IE Calculation for Plant with High Impurity Exposures During Startup

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Figure A-5
Plant Exposure at Normal Operation vs. Reference Plant Exposure

A.3.2 Method B (Tube Exposure Factor)

A second method of calculating integrated exposure, which takes into account both the time the crevice is exposed to the impurities and the amount of tubing surface area that is exposed, is also easily calculated with a computer spreadsheet. This tube exposure factor calculation is suggested as an option, because the simple integration method described above does not distinguish between impurity exposures earlier or later in the cycle. For example, Figure A-6 shows three scenarios of contaminant bulk water concentrations over a 100 day period.

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Figure A-6
Three Cases with Similar Cumulative Mass Accumulation Over the Cycle Length

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Figure A-7
Relative Tube Surface Area Wetted for Three Different Cases where Cumulative Mass Accumulation at the End of the Cycle is the Same

The next few paragraphs detail how the tube exposure factor is calculated for a drilled hole crevice geometry.

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Figure A-8
Drilled Hole Crevice Geometry

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Figure A-9
Relationship between Surface Area Wetted vs. Volume Filled for an Eccentric Crevice

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Figure A-10
Relative Tube Exposure Factor Illustrating Differences in Exposure for Cases where Total Cumulative Mass Accumulation Over the Cycle Length is the Same

The spreadsheet used to calculate the tube exposure factors is also easy to set up. Figure A-11 depicts a sample spreadsheet.

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Figure A-11
Sample Spreadsheet Used to Calculate Tube Exposure Factors

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Figure A-12
Example Relative Tube Exposure Factor for an Actual Operating Cycle Showing the Effect of the Startup Transient

A.3.3 Method C (CREV-SIM)

A third possible method that can be used to calculate integrated exposure is by means of CREV-SIM. CREV-SIM is a part of the EPRI ChemWorks™ family of codes and was originally developed to model PWR steam generator chemical hideout and to provide a basis for predicting crevice chemistry from blowdown chemistry data. This estimate of crevice inventory is calculated from measured blowdown concentrations and an estimated hideout rate constant for each impurity, with this constant determined by chemical injection or blowdown flowrate variation tests. Similar to method A, the accumulated crevice inventory is reset to zero after shutdowns and hideout returns.

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A CREV-SIM manual is available to explain how to use the code and what parameters are needed.

A.4 Integrated Exposure Plant Examples

Three plant examples of integrated exposure use are provided in this section. Other plants have indicated use of the integrated exposure concept as part the process to evaluate the transient chemistry conditions but perform these evaluations on a case-by-case basis, when applicable, rather than having defined processes.

A.4.1 Integrated Exposure 1: Utilization of Integrated Exposure Limits to Control Molar Ratio

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A.4.2 Integrated Exposure Example 2

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A.4.3 Integrated Exposure Example 3

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PWR Secondary Chemistry Operating Guideline

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Operating Philosophy

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Content deleted - EPRI Proprietary Information

<u>Basis</u>

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Operating Methodology

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A.5 References

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B

PWR STEAM CHEMISTRY CONSIDERATIONS

B.1 Introduction

This appendix contains an assessment on the subject of steam chemistry that was originally prepared for and presented to the Revision 6 Committee. This appendix was reviewed and edited as part of the Revision 7 process.

B.2 PWR Steam Chemistry Considerations

B.2.1 Introduction

This appendix reviews the key issues associated with steam chemistry in PWR's. Over the past several years, EPRI and other international organizations have sponsored a research program focused on steam chemistry within power plant steam cycles. This work resulted in the lowering of steam impurity limits in the EPRI Cycle Chemistry Guidelines for Fossil Plants [1]. The BOP and OTSG subcommittees of the EPRI Secondary Water Chemistry Guideline Committee requested that this body of research be reviewed to determine if changes to the PWR water chemistry guidelines were needed during the Revision 6 process. It has subsequently been reviewed and edited as part of the Revision 7 process. The following documents were reviewed as a basis for this paper:

1. *EPRI Cycle Chemistry Guidelines for Fossil Plants: All-Volatile Treatment*, EPRI, Palo Alto, CA: 2002.1004187. [1].
2. *The Volatility of Impurities in Water/Steam Cycles*, EPRI, Palo Alto, CA: 2001. 1001042. [2].
3. *Turbine Steam Path Damage: Theory and Practice, Volume 1: Turbine Fundamentals*, EPRI, Palo Alto, CA: 1999. TR-108943 V1. [3].
4. *Turbine Steam Path Damage: Theory and Practice, Volume 2: Damage Mechanisms*, EPRI, Palo Alto, CA: 1999. TR-108943 V2. [4].
5. *Steam, Chemistry, and Corrosion in the Phase Transition Zone of Steam Turbines*, EPRI, Palo Alto, CA: 1999. TR-108184 V1. [5].
6. Deposition of Corrosive Salts from Steam, EPRI, Palo Alto, CA: 1983. NP-3002. [6].
7. Solubility of Sodium Salts in Superheated Steam and Related Deposition Processes, published in TR-114837, August 2000 [7].

Revision 5 of the EPRI Secondary Water Chemistry Guidelines address steam purity considerations indirectly. In RSG's, steam chemistry limits can be inferred from the blowdown limits based on an assumed moisture carryover and the estimated vaporous carryover for impurities and additives. In OTSGs, steam concentrations of inorganic impurities will be equal to or less than those in the feedwater. Concentrations of organic acids could slightly exceed those in feedwater due to thermal decomposition of amine additives in the OTSG. In both RSGs and OTSGs the blowdown and feedwater limits have been set more restrictively to protect the SG's.

B.2.2 Recommendations

Based on this review, no changes to the EPRI PWR Secondary Water Chemistry Guidelines are recommended at this time. Many utilities have chosen to include specific steam chemistry specifications based on turbine vendor recommendations and warranty requirements. This practice is expected to continue in the future.

Additional research would be needed to determine if changes in water chemistry would improve turbine performance.

B.2.3 Discussion

Steam chemistry is controlled in power plants for several reasons; to prevent or control deposition of impurities on turbine blades, to minimize erosion of turbine blades and to control general and localized corrosion of turbine blades and discs, cross over piping and extraction lines. In well operated nuclear plants, the major consideration for steam chemistry control is the environmentally assisted cracking of turbine blade/disc attachments and FAC of piping in two phase regions of the BOP. The latter consideration is addressed through pH control by organic amines and/or ammonia based AVT. pH control practices will not be discussed further, other than by reference to the generation of organic acids and their influence on cracking processes.

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B.2.4 Deposition Processes in Turbines

In order to establish acceptable steam impurity limits, the processes by which impurities accumulate in steam turbines must be established. It is readily accepted that impurities enter the steam through mechanical carryover of liquid droplets from the steam generator and through direct volatilization to the steam phase. In OTSGs the latter mechanism is responsible for transporting nearly all of the feedwater impurities (less hideout) to the superheated steam leaving the OTSG.

The transport of impurities in the turbine cycle is driven by both thermodynamic and kinetic processes. These processes are dependent on the local temperature and pressure, the degree of saturation of the steam and the concentration of the impurities.

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Figure B-1
Mollier Diagram Showing Sodium Solubility in Steam and OTSG Turbine Expansion Lines (Based on Reference [9] and Reference [10])

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Figure B-2
Location of Salt Concentration in LP Turbines

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B.2.5 Steam Chemistry Guidelines

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Table B-1
Reheat Steam Limits in Drum Units

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B.2.5.1 Acceptability of this Approach to Setting PWR Guidelines

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Figure B-3
Steam Expansion Path for Fossil and Nuclear Steam Cycles (LP = Low Pressure, IP = Intermediate Pressure, HP = High Pressure, and η is the turbine efficiency)

B.3 References

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D

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ORGANIZATION(S) THAT PREPARED THIS DOCUMENT

Electric Power Research Institute (EPRI)

加圧水型原子炉二次系統の水質に関する指針– 改訂７版

1016555

最終報告書、2009年２月

報告書の要約

最高水準の水化学プログラムは、機器の腐食を減らし、蒸気発生器の信頼性を強化する。業界の専門家委員会は、二次系統の腐食と性能問題に関する最新の実働データと実験室データを連携させるために、「PWR二次系統の水質指針」改訂版を作成した。加圧水型原子炉（PWR）の事業者は、この指針を用いて、二次冷却系の水化学プログラムを更新することができる。

背景

EPRIは、新しい情報が利用できるようになると、業界向け水化学指針を定期的に更新する。「PWR二次系統の水質指針」の以前のバージョンは、研究およびフィールド情報のその時点での理解と一貫していると見なされた詳細な水科学プログラムを明確にしてきた。各バージョンは、こうした指針がプラントの運転に与える影響を議論し、指針の実施に当たっては、電力会社がプラント特有の評価に従って指針プログラムの改訂を望むだろうと記している。2004年１２月の改訂６版の公表以後、電力会社からのフィードバックは、評価および恐らくは指針改訂を必要とするその他の分野を明らかにした。

目的

PWR二次系統の水質指針– 第６版を更新すること。

方法

電力会社のスペシャリスト、原子力用蒸気供給系統のメーカ代表、INPO（原子力発電運転協会）代表、コンサルタント、EPRIスタッフから構成される電力業界の専門家委員会が、二次系統の水質と二次系統の腐食に関して利用できるデータを協同で検証した。こうしたデータに基づき、同委員会は、電力会社がすべてのPWR原子力発電プラントに採用できる水質指針を作成した。原子力発電プラントの所有者がそれぞれ独自の設

計、運転、企業としての懸念を持っていることを認識した上で、同委員会は、プラント固有の最適化のための方法論を開発した。作成された文書は、厳格なレビューを受け、蒸気発生器管理プログラム（SGMP）を経由する採用プロセスで処理された。

結果

PWR二次系統の水質指針– 第7版は、すべてのメーカおよび設計のPWR二次系統の水質用指針を提供しており、次の章が含まれる：

- 第１章には、経営者の責任のリストが挙げられ、原子力エネルギー協会（NEI）９７－０６とNEI０３－０８に適合するための二次系統水化学プログラムの要求事項を取扱っている。
- 第２章には、蒸気発生器管と補助系設備材料に関する腐食データのまとめが提示されている。この情報は、具体的なパラメータと文書に詳述されているプログラムのための技術的な基礎として役立つ。
- 第３証では、蒸気発生器の局部区域での濃縮プロセスの役割と、この濃縮区域内の結果として起こる水質を修正するために利用できる化学的「ツール」が議論されている。この議論は、こうした化学的体制を採用する際の役立つ側面と考慮すべき事項を簡潔に説明している。また、化学的な戦略の適用のためのより詳細な文書が読者に示されている。
- 第４章では、最適化されたプラント特有の水質プログラムを決定するための詳細な方法論が提示されている。
- 第５、６章はそれぞれ、再循環蒸気発生器（RSG）と貫流蒸気発生器（OTSG）のための水化学プログラムを示している。この２章は、化学担当者が最も頻繁に参照する章である。この２章に示されている表は、第４章で説明されているプラント特有の最適化手順の限度を提供する。
- 第７章は、データ収集、評価、管理に関する情報を示す。この章は、プラントデータを評価して、サイクル全体を通じた高温の化学的環境を予測するためのEPRI ChemWorks ™モジュールを用いる方法を解説する。

- 第８章は、こうした指針に含まれる特定の要素すべてを記録している。これらの要素は、NEI０３－０８およびNEI９７－０６と一致することが必須、義務、勧告されていると見なされるものである。
- 付録Aは、総合被ばくプログラムを実施するための方法論の例を提示する。
- 付録Bは、PWR蒸気の化学的考慮の評価を示す。

EPRIの考え方

この「PWR二次系統の水質指針 - 第７版」は、EPRI蒸気発生器管理プログラムの電力会社役員により支持されている。この文書は、二次系統の劣化を制限または管理するためのプロアクティブな化学プログラムを維持する上でさらに一歩前進したことになる。なぜなら、企業の資源およびプラント特有の設計 / 運転懸念に配慮がなされているからである。電力会社はそれぞれ、プラント特有の状況を検討して、この指針がどのようにしたら最高の形で実施できるかを決定すべきである。

キーワード

PWR
水化学
腐食保護
原子力用蒸気発生器
二次冷却材の回路

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表リスト

가압경수로 이차계통수 화학지침 —개정 제7판

1016555

최종보고서, 2009년 2월

보고서 요약

최첨단 계통수 화학 프로그램에 의하여 장비의 부식은 감소되고 증기발생기의 신뢰도는 증진된다. 업계 전문가들로 구성된 위원회는 최신 분야와 이차시스템 부식과 성능 문제를 통합하기 위해 이와 같이 개정된 *가압경수로 이차계통수 화학지침을* 작성하였다. 가압경수로(PWR) 운전자들은 자신들의 이차계통수 화학 프로그램을 업데이트하기 위해 이러한 지침을 사용할 수 있다.

배경

EPRI는 새로운 정보가 입수됨에 따라 업계의 이차냉각수 화학지침을 주기적으로 업데이트하고 있다. 이러한 *PWR 이차계통수 화학지침*의 선행 버전들은 그 당시의 연구 및 현장 정보를 파악하고 있는 것과 일치하는 것으로 보이는 자세한 계통수 화학 프로그램을 규명하였다. 각각의 버전에서는 전력회사들이 시행에 대한 발전소별 평가에 따라 지침 프로그램을 개정하고자 할 수도 있다는 것에 주목하면서, 발전소 운전에 미치는 이러한 지침의 영향을 논의하였다. 2004년 12월 개정 제6판이 발간된 이후 전력회사의 피드백으로부터 평가와 잠재적인 *지침* 개정이 필요한 추가 영역이 밝혀졌다.

목적

- *PWR 이차계통수 화학지침—개정 제6판*을 업데이트하기 위함.

방법

전력회사 전문가, 핵증기 공급시스템 판매회사 담당자, 미국 원자력발전 운전협회 담당자, 컨설턴트 및 EPRI직원을 포함한 업계 전문가들로 구성된 위원회는 이차계통수 화학작용 및 이차 순환주기 부식에 관하여 입수한 데이터를 검토하는데 있어 협력하였다. 이러한 데이터에 근거하여, 위원회는 전력회사가 모든 PWR

원자력발전소에서 채택할 수 있는 계통수 화학지침을 작성하였다. 원자력발전소 소유회사는 회사마다 특유의 설계, 운전 및 우려사항이 있다는 사실을 인지하고, 위원회는 발전소별 최적화를 위한 방법을 개발하였다. 그런 다음 그 문서는 증기발생기 관리프로그램 (SGMP)을 통하여 엄격한 검토와 채택과정을 거쳤습니다.

결과

PWR 이차계통수 화학지침 개정 제7판은 PWR 모든 제작과 설계의 이차시스템 화학작용에 대한 지침을 제공하며, 다음의 장들을 포함한다:

- 제1장은 관리 책무 목록을 포함하며, 원자력 에너지 연구소의 NEI 97-06과 NEI 03-08의 준수를 위한 이차계통수 화학 프로그램을 역점을 두어 다룬다.
- 제2장은 증기발생기 전열관과 원전 보조기기 자재에 대한 부식 데이터가 편찬되어 있다. 이 정보는 문서에서 자세히 기술된 특정 변수 및 프로그램에 대한 기술적 근거로서 소용이 있다.
- 제3장은 증기발생기의 국소 부분에서의 농축 과정의 역할과 이러한 농축 부분내에서 초래되는 화학 기전을 변화시키는데 쓰이는 화학 " 도구" 에 관해 논의한다. 본 장에서는 이러한 화학 기전의 채택이 뒷받침하는 면과 그러한 채택을 위한 고려사항을 간략하게 규명한다. 본 장에서는 독자에게 화학 전략의 적용하기 위하여 더 상세한 문서를 참조하라고 한다.
- 제4장은 최적화된 발전소별 화학 프로그램을 결정하기 위한 상세한 방법이 나와있다.
- 제5장과 6장은 재순환 증기발생기(RSG: recirculating steam generator)와 관류형 증기발생기 (OTSG: once-through steam generator)에 대한 화학 프로그램이 나와있다. 본 장들은 화학담당 직원들이 가장 빈번하게 참조하는 장들이다. 본 장들에 나와있는 표들은 제4장에 기술한 발전소별 최적화 절차에 대한 한계를 나타낸다.
- 제7장은 데이터의 수집, 평가 및 관리에 관한 정보를 제공한다. 본 장은 발전소 데이터를 평가하고 순환주기 내내 고온 화학 환경을 예측하기 위한EPRI ChemWorks ™ 모듈 사용법을 기술하고 있다.

- 제8장은 NEI 03-08 와 NEI 97-06에 부합하는 필수 원소, shall 원소 또는 권 고 원소로서 규명된 것으로서 이러한 지침내에 포함된 모든 특정 원소를 갈무리한다.
- 부록 A는 집적 노출량 프로그램을 시행하기 위한 방법의 예가 나와있다.
- 부록 B는 PWR 증기화학 고려 사항에 대한 평가가 나와있다.

EPRI 전망

*PWR 이차계통수 화학지침*의 본 개정 제7판은 EPRI 증기발생기 관리 프로그램을 담당하는 전력회사의 임원들이 승인한 것이다. 본 문서는 회사 자원과 발전소별 설계/운전에 관한 우려사항을 고려하면서, 이차시스템의 성능저하를 제한하거나 제어하기 위한 선행적 화학 프로그램을 유지하는데 있어서 다른 하나의 단계를 설명한다. 각 전력회사는 본 지침이 어떻게 하면 가장 잘 시행될 것인지를 판단하기 위하여 자신의 발전소에 관한 상황을 조사하여야 한다.

주요 단어

PWR
계통수 화학
부식 방지
원자력 증기발생기
이차냉각제 순환로

목차

그림 목차

표 목차

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