Nuclear Plant Makeup Water Chemistry Guideline

Gap Analysis

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EPRI Project Manager

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PRODUCT DESCRIPTION

This report provides an assessment of the current makeup water treatment guidance available to nuclear power plants. The assessment evaluated the acceptability of existing makeup water treatment guidance for nuclear plants. The assessment also evaluated the makeup water treatment guidance developed specifically for fossil plants in EPRI report 1019635, *Guidelines for Makeup Water Treatment, Conventional Fossil and Heat Recovery Steam Generator Water/Steam Cycle Makeup*, and this document's applicability for nuclear plants.

Background

Only somewhat dated information is available to the nuclear stations with respect to makeup water chemistry guidance. In particular, EPRI report NP-6377-M, *Guidelines for the Design and Operation of Makeup Water Treatment Systems,* June 1989, is one of the few reference documents providing makeup water chemistry guidance. This guidance was developed as two volumes: volume 1 – design information for the implementation of a new system and volume 2 – operation of makeup water treatment systems. While comprehensive and certainly reflective of the state of the technology at the time, these volumes provide little useful information for today's nuclear power plant chemist. The guideline provides effluent water quality targets, as shown in Table 2-1, but these are not acceptable in today's nuclear plants.

Approach

The project team used a document review to document the assessment in this report. The assessment also includes survey input from several nuclear plant members.

Results

The results reveal that significant guidance related to makeup water treatment design and operation is found in the fossil station guidelines. The results also point to certain makeup water treatment effluent chemistry limits that can be found in other documents available to the industry.

Applications, Value, and Use

This report is applicable to nuclear power plant and station personnel interested in applicable guidance related to makeup water treatment.

Keywords

Makeup water
Demineralization

EXECUTIVE SUMMARY

This report provides an assessment of the current makeup water treatment guidance available to nuclear power plants. The assessment evaluated the acceptability of existing makeup water treatment guidance for nuclear plants. The assessment also evaluated the makeup water treatment guidance developed specifically for fossil plants in EPRI report 1019635, *Guidelines for Makeup Water Treatment, Conventional Fossil and Heat Recovery Steam Generator Water/Steam Cycle Makeup*, and this document's applicability for nuclear plants.

This report presents the bases for the following conclusions:

1. As identified in section 3.0 of this report, EPRI report 1019635 [6] provides a discussion of treatment methods for producing high quality demineralized water that is directly applicable to nuclear stations. In the absence of similar guidance specifically for nuclear plants, it is suggested this document be used for such guidance. In particular, the guidance provided in the referenced report appears satisfactory for the design of makeup water processes and the operation of water treatment equipment in nuclear stations.
2. As identified in section 3.0 of this report, the limits for chemical impurities in the effluent of makeup water treatment processes presented in EPRI report 1019635 [6] are not commensurate with the current needs of makeup water purity at nuclear plants.

The overall need for generating new makeup water treatment guidance is not necessarily driven by an absence of technical information. EPRI report 1019635 [6] provides design and operation guidance, equally applicable to both nuclear and fossil generating stations. Current chemistry impurity limits for nuclear plant makeup water treatment effluent samples can be found in Institute of Nuclear Power Operations (INPO) documents.

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1

INTRODUCTION

Makeup Water Production in Nuclear Stations

High purity makeup demineralizer (MUD) water at nuclear stations is an essential element of a chemistry program at nuclear plants. The term *makeup*, in this report, refers specifically to the high-purity water supply for the steam/water cycle of nuclear plants. It should not be confused with makeup to other auxiliary systems using water, such as open/closed cooling water. Improper control of makeup water purity can result in adverse effects on chemistry within the plant systems. As a minimum, increased impurity levels in the treated makeup tend to reduce the operational capability to meet chemistry control criteria at other points in the plant. In PWR plants, it might be necessary to increase steam generator blowdown rates, thereby increasing energy consumption and cost of operation. Condensate polishers (where applicable) effectively remove impurities introduced with treated makeup, but at the expense of increased frequency of regeneration.

Chemistry guidelines developed for industrial fossil units have generally refrained from inclusion of any detailed criteria for treated makeup. Instead, the prevailing philosophy has been that makeup purity should be satisfactory to attain applicable limits for steam generator water or reactor water chemistry. This is due to the variety of system designs for industrial facilities.

Another variable that influences treated water purity requirements in industrial applications is the amount of makeup required by the system. In traditional utility cycles, the makeup rate is typically less than 2% of steam flow. In industrial systems, makeup rates are usually higher; they can be as high as 50% to 100% in applications where there are substantial losses from the cycle.

Purity Needs

The makeup water purity at nuclear plants is driven by the need to satisfy chemistry constraints in the systems supplied by the makeup water. These chemistry constraints are dictated by the governing chemistry guideline [1, 2, 3]. Yet, nuclear plants target impurity concentrations in these systems at much lower values. For example, most PWR plants have accepted a threshold of 0.8 ppb sodium in steam generator blowdown water. The EPRI PWR Secondary Water Chemistry Guidelines [2] establish an Action Level 1 value for sodium as 5ppb. Thus, given the current chemistry control targets, makeup water-borne impurities can have a significant impact upon the plant's ability to meet the target values.

Generally, plants will establish makeup water impurity limits for sodium, chloride, sulfate, silica, total organic carbon (TOC), and specific conductivity. Some plant's specifications will include parameters for chloride and sulfate after treatment with ultraviolet light. Plant specifications also may include limits for suspended solids, potassium, fluoride, nitrate, phosphate, and pH and hardness ions. These additional parameters are tailored to either challenge in removal from the raw water, and/or particular needs within the plant. For example, a plant challenged to assure hardness cations are maintained low due to elevated RCS silica may need to closely monitor aluminum, calcium, and magnesium in the makeup water. Likewise, a plant that has found excessive aluminum contamination in steam generator sludge samples may place focus on makeup water aluminum contamination.

As many/most nuclear plants rely on contracted mobile water treatment and demineralization, chemistry limitations for treatment stages ahead of the final effluent bear no importance. The pretreatment and subsequent stages become an economic priority only for the contractor. As such, these limitations are not discussed in this report.

Volume/Flowrate Constraints

The makeup water flowrates for nuclear plants vary from station to station. Some plants have made system leakage a priority and have very low makeup rates. Makeup rates at these plants are as low as 10 gpm. Other plants, due to system design, or other reasons, may have very high makeup rates. PWR plants that do not recover steam generator blowdown water and discharge this water to the environment, may have makeup water flowrates of over 300 gpm on a long-term continuous basis.

Many plants will perform routine mass balances to determine the chemical contaminant contribution of potential sources such as makeup water, main condenser inleakage, and chemical additions feed equipment. Certainly, a plant with a low makeup flowrate will tend to have a lower contribution of contaminates to the overall mass balance from the makeup water. Plants in this situation have a higher tolerance for chemical contaminates in the makeup water.

Other design features will also play a role in makeup water chemical contamination tolerance. Plants with full flow condensate polishers can tolerate high makeup water contribution as the condensate polishers can be relied upon to removal most of this contamination. Likewise, PWR plants designed with large capacity steam generator blowdown treatment equipment, as a fraction of main feedwater flowrate, may also have a higher tolerance for makeup water chemical contamination.

To incorporate the above noted rationale for high chemical contamination tolerance into a makeup water chemical limitations specification becomes very difficult. As such, no makeup water guidance to date has attempted to capture this methodology into its specifications. This approach also becomes difficult for the plant when it’s related situation changes. For example, a plant designed with low flowrate steam generator blowdown treatment equipment and no condensate polishers, and a low makeup flowrate, may accept certain elevated makeup water chemical contamination. Yet when makeup flowrate is temporarily elevated due to startup or other transient situations, this tolerance is changed. Thus, determining makeup water chemical limits inclusive of flowrate considerations becomes difficult to impossible.

Conclusions

This report presents basis for the following conclusions:

1. As identified in section 3.0 of this report, reference 8 provides a discussion of treatment methods for producing high quality demineralized water that is directly applicable to the nuclear stations. In the absence of similar guidance for the nuclear plants, it is suggested this document be used for such guidance. In particular, the guidance provided in reference 8 appears satisfactory for the design of makeup water processes, and the operation of water treatment equipment in nuclear stations.

2. As identified in section 3.0 of this report, the limits for chemical impurities in the effluent of makeup water treatment processes presented in reference 8 are not commensurate with the current needs of makeup water purity at nuclear plants.
3. The overall need for generating new makeup water treatment guidance is not necessarily driven by an absence of technical information. The reference 8 provides design and operation guidance, equally applicable to both nuclear and fossil generating stations. Current chemistry impurity limits for nuclear plant makeup water treatment effluent samples can be found in INPO documents.

2
NUCLEAR PLANT MAKEUP WATER CHEMISTRY GUIDANCE

Historical Chemistry Guidance

Available to the nuclear stations with respect to makeup water chemistry guidance is only somewhat dated information. In particular, the EPRI report, “Guidelines for the Design and Operation of Makeup Water Treatment Systems”, June 1989 [4], is one of few reference documents providing makeup water chemistry guidance. This guidance was developed as 2 volumes: volume 1 – design information for the implementation of a new system; and 2 – operation of makeup water treatment systems. While comprehensive and certainly reflective of the state of the technology at the time, these volumes provide little useful information for today’s nuclear power plant chemist. The guideline provides effluent water quality targets, as shown in Table 2-1, but these are not acceptable in today’s nuclear plants.

Table 2-1
Effluent Water Quality Targets

Parameter	**Concentration**
Sodium	< 3 ppb
Chloride	< 5 ppb
Iron	< 10 – 20 ppb
Copper	< 2 ppb
Dissolved Oxygen	< 5 ppb
Total Organic Carbon	< 100 ppb
Dissolved Silica	< 20 ppb
Suspended Solids	< 10 ppb

Other makeup water treatment guidelines available to the industry have been INPO guidance documents. These documents have provided the US nuclear industry makeup water treatment system effluent targets for chemistry parameters important to plant waters.

Current Chemistry Guidance

Current industry guidance for makeup water treatment chemistry control at nuclear plants is very limited. The nuclear steam supply system (NSSS) designers provided chemistry manuals which include some makeup water operational guidance; however, this information is quite dated and does not represent the state of the art with respect to makeup water quality needs.

The new Advanced Nuclear Technology plants are provided with some operational guidance. An example is the AP-1000 Design Control Document [5] which contains some very limited chemistry control guidance.

Plant representatives from various BWR, PWR, and CANDU plants provided input as to the need for new Makeup Water Chemistry guidance as part of Technical Strategy Group meetings. Appendix C provides a summary of this input. The survey response was mixed: approximately equal input that a new makeup water chemistry guideline for the nuclear stations is needed, and not needed. The responses opposed to the new guidance included the following as reasons:

- Enough industry and vendor experience that seems to be doing fine as is.
- Most plants use vendor trailers due to economics of maintaining the equipment and the ability to use the maintenance and operations staff for in-plant work.
- From the BWR perspective, I don’t see much need for makeup water guidelines. I would rather see this effort applied to the radwaste side of water processing.
- I don't think this is a worthy area in which to spend time. We need to meet demineralized water standards for the DWST and that translates to the makeup system pretty easily.
- The guidance in BWRVIP-190 [3] Table E-1 is adequate. I do not think the limits need to be changed.
- No need, we already have Westinghouse guidance.

The responses in favor of new guidance stated the need for updated technical bases for limits, and the utility of the guideline when preparing contract specifications for mobile water processing.

3

APPLICATION OF FOSSIL STATION GUIDANCE

The Generation sector of EPRI has recently updated the makeup water treatment guidance for fossil generating stations. The resulting document, Guidelines for Makeup Water Treatment, Conventional Fossil and Heat Recovery Steam Generator Water/Steam Cycle Makeup (EPRI 1019635) [6] was published in 2010. This document, while tailored to the fossil generating plants, has information pertinent to nuclear stations as well. This guideline is analyzed in the sections below for applicability to the nuclear plants.

3.1 Makeup Limits and Guidance Overview

This section provides suggested impurity limits for makeup water. The rationale for the selection of the limits is presented below:

> *Linking makeup guideline values to steam purity limits for sodium, chloride, sulfate, silica and total organic carbon (TOC) provides ultimate flexibility to operating units to continuously meet the required steam purity limits, even in upset conditions. For systems that do not meet these purity guidelines, Section 2 provides a method for evaluating the plant-specific potential consequences and establishing plant-specific limits (see Section 2.10, Purity Guidelines for Existing Systems).*

Table 3-1 presents the limits as suggested in the report.

Table 3-1
EPRI Guideline Values for Treated Makeup to Fossil Units

Constituent	**As**	**Type of Boiler/Heat Recovery Steam Generator Treatment**(a)	
		Phosphate (Low), Caustic, All-Volatile, and Oxygenated	**Phosphate (High)**
Sodium(b)	ppb Na	≤ 2	≤ 3
Chloride(b)	ppb Cl	≤ 2	≤ 3
Sulfate(b)	ppb SO_4	≤ 2	≤ 3
Silica(b)	ppb SiO_2	≤ 10	≤ 10
Total Organic Carbon(b)	ppb total organic carbon (TOC)	≤ 100	≤ 100
Conductivity	µS/cm at 77°F (25°C)	0.1	0.1
Dissolved Oxygen(c)	ppb dissolved oxygen	≤ 100	≤ 100

(a)For systems in which a common makeup plant serves boilers/HRSGs where different treatments are in use, the higher purity criteria should be applied.
(b)Equivalent to steam purity limits for various treatments.
(c)Maximum dissolved oxygen to minimize risk of corrosion fatigue damage for filling shutdown equipment.

3.1.1 Adequacy Fossil Limits for Nuclear Plants

The makeup water purity at nuclear plants is driven by the need to satisfy chemistry constraints in the systems supplied by the makeup water. These chemistry constraints are dictated by the governing chemistry guideline [1, 2, and 3]. Yet, nuclear plants target impurity concentrations in these systems at much lower values. For example, most PWR plants have accepted a threshold of 0.8 ppb sodium in steam generator blowdown water. The EPRI PWR Secondary Water Chemistry Guidelines [2] establish an Action Level 1 value for sodium as 5ppb. Thus, given the current chemistry control targets, makeup water-borne impurities can have a significant impact upon the plant's ability to meet the target values. Table 3-2 presents typical makeup water limits used at nuclear power stations. These values were obtained from the review of several plants' procedures.

Table 3-2
Typical Makeup Water Treatment Effluent Limits

Constituent	**Effluent Limit**
Sodium (ppb)	0.1
Chloride (ppb)	1.0
Sulfate (ppb)	1.0
Silica (ppb)	5.0
Total Organic Carbon (ppb)	30
Conductivity (µS/cm at 77°F (25°C))	0.06
Dissolved Oxygen (ppb)	30

Some specifications will include parameters for chloride and sulfate after treatment with ultraviolet light. Plant specifications may also include limits for suspended solids, potassium, fluoride, nitrate, phosphate, pH and hardness ions. These additional parameters are tailored to either challenge in removal from the raw water, and/or particular needs within the plant. For example, a plant challenged to assure hardness cations are maintained low due to elevated RCS silica may need to closely monitor aluminum, calcium, and magnesium in the makeup water. Likewise, a plant that has found excessive aluminum contamination in steam generator sludge samples may place focus on makeup water aluminum contamination.

In comparing Table 3-1 with Table 3-2, it is observed that the limit values are all lower in Table 3-2. The process and equipment used to produce makeup water in nuclear and fossil stations is the same for each. For example, most PWR plants have accepted a threshold of 0.8 ppb sodium in steam generator blowdown water. The fossil station chemistry guideline [7] includes a sodium target limitations that vary from 0.4 to 0.8 ppb, depending on the treatment chemistry. Another notable difference is that the fossil stations place much weight on the steam chemistry purity, while BWRs perhaps place most weight on the reactor water chemistry, and PWRs steam generator blowdown chemistry.

As many/most nuclear plants rely on contracted mobile water treatment and demineralization, chemistry limitations for treatment stages ahead of the final effluent bear no importance. The pretreatment and subsequent stages become an economic priority only for the contractor. As such, these limitations are not discussed in this report.

3.1.2 Limits Based Upon Flowrate Considerations

The makeup water flowrates for nuclear plants vary from station to station. Some plants have made system leakage a priority and have very low makeup rates. Makeup rates at these plants are as low as 10 gpm. Other plants, due to system design, or other reasons, may have very high makeup rates. PWR plants that do not recover steam generator blowdown water and discharge this water to the environment, may have makeup water flowrates of over 300 gpm on a long-term continuous basis.

Many plants will perform routine mass balances to determine the chemical contaminant contribution of potential sources such as makeup water, main condenser inleakage, and chemical additions feed equipment. Certainly, a plant with a low makeup flowrate will tend to have a lower contribution of contaminates to the overall mass balance from the makeup water. Plants in this situation have a higher tolerance for chemical contaminates in the makeup water.

Other design features will also play a role in makeup water chemical contamination tolerance. Plants with full flow condensate polishers can tolerate high makeup water contribution as the condensate polishers can be relied upon to removal most of this contamination. Likewise, PWR plants designed with large capacity steam generator blowdown treatment equipment, as a fraction of main feedwater flowrate, may also have a higher tolerance for makeup water chemical contamination.

To incorporate the above noted rationale for high chemical contamination tolerance into a makeup water chemical limitations specification becomes very difficult. As such, no makeup water guidance to date has attempted to capture this methodology into its specifications. This approach also becomes difficult for the plant when it’s related situation changes. For example, a plant designed with low flowrate steam generator blowdown treatment equipment and no condensate polishers, and a low makeup flowrate, may accept certain elevated makeup water chemical contamination. Yet when makeup flowrate is temporarily elevated due to startup or other transient situations, this tolerance is changed. Thus, determining makeup water chemical limits inclusive of flowrate considerations becomes difficult to impossible.

3.2 Makeup Treatment Process Selection and Evaluation

This section of the report provides the information needed to make proper judgments regarding selection of the various processes described in the makeup water guideline [6]. Also provided are the criteria to be applied to assemble the various unit processes into workable, effective treatment systems. This section considers the unit processes comprising makeup treatment plants as a system. Detailed information on design and operation of individual unit processes can be found in this report. The extent and complexity of the makeup water treatment facility will depend to a large degree on both composition of the water supply and its source.

3.2.1 Makeup Plant Capacity Assessment

The majority of this section of the fossil guideline is dedicated to the evaluation of the plant’s raw water and the selection of optimum treatment processes. This subsection addresses the appropriate sizing of a new makeup water treatment facility and equipment. While the details are specific to fossil stations in some examples, the overall message and calculations are directly applicable to nuclear stations.

3.2.2 Guidelines for Control of Dissolved Oxygen

The detailed examples are specific to fossil stations. Yet, the overall message and deoxygenation principles and technologies are applicable to nuclear stations.

3.2.3 Evaluation of Existing Systems

This section provides methodology to evaluate the appropriateness of modification to existing makeup water treatment systems in order to address water quality and/or water quantity improvement needs. The examples used are mainly specific to fossil plants, but include some nuclear experience and are directly applicable to nuclear stations.

Interestingly, the section addresses outsourcing water treatment to a mobile or on-site company. The discussion provides the details to be considered when a plant is evaluating this as an option to operating plant-installed equipment.

3.3 Biological Control and Oxidation

Makeup water treatment systems must maintain some level of biological control. Also, oxidants are sometimes required to oxidize either heavy metals (as an aid to coagulation) or corrosive gases (such as hydrogen sulfide). In the past, biological control was nearly universally achieved through chlorination with either chlorine gas or sodium hypochlorite. The oxidation of metals was most commonly achieved through chlorination in conjunction with aeration and/or permanganate addition. However, multiple options now exist for biological control and oxidation. This section reviews the available technology and provides guidance for some of the more established methods.

3.3.1 Effectiveness and Application of Oxidizing Biocides

This section provides an excellent discussion of the chemistry technology of the processes involving with applying oxidizing biocides as a pre-treatment stage of water treatment. The discussion is completely relevant to nuclear plants. The only possible omission relative to nuclear plants, is the topic of potential to impact control room habitability. Information on this topic can be found in reference [8].

3.4 Clarification and Chemical Softening

The clarification of water is a process applied mostly to surface waters for the removal of suspended solids, finely divided particles present as turbidity or color, and other colloidal materials. Conventionally the clarification process involves coagulation, flocculation, and sedimentation. The primary function of the clarification process is liquids/solids separation. Clarification occurs as a result of increasing—through interparticle surface reactions—the size and density of particles in the dispersed phase such that they separate and settle from the bulk liquid. Recently, the feasibility of using membrane technology (e.g., microfiltration) for direct clarification of raw water has been demonstrated at several power plants.

The design, operation and troubleshooting portions of this section pertain equally to nuclear as it does fossil generating stations.

3.5 Granular Media Filtration

Filtration is a unit operation for separating fluid/solid mixtures by passage through a porous element (filter medium) which retains a percentage of the suspended matter. The fraction of solids retained by the filter depends on the pore size of the medium and the dimensions of the particles. Screens, cloth, paper, synthetic fibers, and beds of solids (rigid porous and granular) are among the typical filter media used for retaining particle sizes greater than 0.5 µm. The development of synthetic membranes made possible the economic retention and separation of particles smaller than 1 µm—including dissolved ionic species—through membrane processes such as microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO), and electrodialysis (ED).

This section, including the design, operation and troubleshooting discussions pertain equally to nuclear as it does fossil generating stations.

3.6 Removal of Oxidants and Oxidation Byproducts

Ion exchange resins and membranes used for reverse osmosis (RO), electrodialysis reversal, continuous electrodeionization and ultrafiltration are subject to oxidation by chlorine and other oxidants. In recent years, membranes have been developed which have improved resistance to chlorine and/or chloramine residuals below a specific value either by controlling the oxidant feed rate or by oxidant removal techniques. However, in most instances, it is recommended to eliminate oxidant residuals in the supply to protect sensitive membranes. Some methods of oxidant removal can also reduce levels of oxidation byproducts such as chlorite, bromated, trihalomethanes (THMs) and other organic species.

This section pertains equally to nuclear as it does fossil generating stations.

3.7 Membrane Ultrafiltration and Microfiltration and Cartridge Filtration

Filtration removes suspended or other materials from water based on particle size. In ASTM D6161 [9]—the current ASTM glossary of terminology for MF, UF, NF, and RO—MF extends from 2 µm down to 0.05 µm and UF is anything less than 0.1 µm that "will retain nonionic solutes based primarily on physical size, not chemical potential." The *Membrane Filtration Guidance Manual* (EPA 815-R-06-009) [10] defines MF as having a pore size range of approximately 0.1–0.2 µm (nominally 0.1 µm) and UF as having a pore size range of 0.01–0.05 µm (nominally 0.01 µm). The American Membrane Technology Association (AMTA, FS-1) [11] defines MF as having pore sizes down to 0.1–0.2 µm and UF as having pore sizes down to 0.005–0.010 µm.

This section pertains equally to nuclear as it does fossil generating stations.

3.8 Reverse Osmosis and Nanofiltration

The RO process uses selective semipermeable membranes and elevated pressures to remove dissolved solids from a solution. In this process, water is forced to flow through a selective membrane by applying a pressure greater than the sum of the osmotic pressure of the solution and any permeate pressure. The membrane rejects the solute molecules that concentrate in the high pressure chamber, and purified water is collected on the low-pressure product water side of the membrane. In typical RO applications, the solute molecules are of about the same size as the solvent molecules. The first RO membranes were developed in the late 1950s and have been greatly improved since their introduction.

This section, including the design, operation and troubleshooting discussions pertain equally to nuclear as it does fossil generating stations.

3.9 Electrodialysis

Electrodialysis (ED) is a membrane process for the selective removal of dissolved, charged contaminants (ions). Ions with a positive charge—such as sodium (Na^+), calcium (Ca^{+2}), manganese (Mn^{+2}), and so on—are called *cations*. Ions with a negative charge—such as chloride (Cl^-), sulfate (SO_4^{-2}), acetate (CH_3COO^-), and so on—are called *anions*. Ions are separated (removed) from feedwater by using an alternating combination of anion- and cation-transport membranes in conjunction with a dc electric field. The electric field provides the driving force that causes the ions in solution to migrate toward the electrode having the opposite electric charge. Positive ions (cations) migrate to the negative electrode (cathode) and negative ions (anions) migrate to the positive electrode (anode).

The applied electric field affects only ions. Uncharged contaminants are not attracted to the electrodes and pass out in the waste stream. ED, therefore, is not suitable for separating nonionized (uncharged) and weakly ionized species such as silica, colloids, and organic matter from feedwater.

This section, including the design, operation and troubleshooting discussions pertain equally to nuclear as it does fossil generating stations.

3.10 Ion Exchange

Ion exchange equipment is typically an integral part of makeup water treatment systems regardless of the water supply source. The proper ion exchange system may be selected and sized based on influent water quality, desired effluent quality, and flow rate.

This section, including the design, operation and troubleshooting discussions pertain equally to nuclear as it does fossil generating stations.

Some areas where this section could be enhanced for applicability to nuclear plants are:

1. A table is provided titled, “Monitoring Instrumentation—Cation/Anion/Mixed Bed Demineralization System”. The table includes suggested monitoring frequencies for parameters important to makeup water treatment. This table suggests that sodium, sulfate, TOC, and pH are optional monitoring parameters.
2. The suggested monitoring technique for sodium and silica is in-line or grab. Practice at nuclear stations is to monitor all of these parameters. Analysis for sodium, silica, and TOC is typically via in-line monitors (continuous).

3.11 Electrodeionization

Electrodeionization (EDI) is a technology that has experienced considerable advances since it’s commercialization in the 1980s. It is capable of producing makeup water quality equivalent to that of a conventional mixed bed ion exchange demineralizer when supplied with a comparable inlet water quality. Another term used, especially by one EDI unit manufacturer, to describe this technology is *continuous electrodeionization (CEDI)*, to differentiate a continuous process versus a batch process. The term *EDI* is more commonly used in the industry. One of the primary advantages of this technology is that, unlike conventional ion exchange processes, it requires no additions of regenerate acid and caustic. The required hydrogen and hydroxide regenerant ions are generated from water molecules by an applied direct current within the process. To produce high-purity water and minimize resin beads and membrane fouling potential within EDI units, the process is preceded by reverse osmosis (RO) membrane treatment.

This section, including the design, operation and troubleshooting discussions pertain equally to nuclear as it does fossil generating stations.

3.12 Degasification

Degasification equipment can reduce the anionic loading on (and thus the cost of) anion exchangers through carbon dioxide removal and/or it can reduce the dissolved oxygen content of the makeup water. Since carbon dioxide removal is most efficient at low pH values, it is typically performed after a cation exchanger or reverse osmosis (RO) unit. Carbon dioxide removal is often attractive if the bicarbonate or carbonate alkalinity of the water supply is above 50–100 ppm and the flow rate are above 11.5–23 m3/day (50–100 gpm). For many years, carbon dioxide removal was conducted using either a forced draft (FD) decarbonator or a vacuum degasifier. Both devices remove carbon dioxide to about 5–10 ppm as CO2. The advantage of vacuum degasifiers lies primarily in their ability to remove dissolved oxygen down to as low as 20–50 ppb. In cases where dissolved oxygen in the makeup water is not a concern, then a decarbonator often is selected because of its lower capital costs.

In recent years, use of membrane technology has been advanced as an alternative to decarbonators and degasifiers. Initial use of the so-called gas transfer membranes was restricted to low-volume applications such as laboratories. A major advantage of the new technology is the relatively small space requirements, as compared to conventional decarbonation and degasification towers. This has made the use of gas transfer membranes especially attractive to firms which provide mobile water treatment systems. In addition, use of membranes in favor of traditional tower packings allows better dissolved oxygen removal efficiency (with reported effluent oxygen concentrations of <1 ppb) than attainable with conventional vacuum degasifiers. This potential benefit has resulted in use of permanent gas transfer membrane systems in a variety of applications, including the electronics, power generation, pharmaceutical and beverage industries.

This section, including the design, operation and troubleshooting discussions pertain equally to nuclear as it does fossil generating stations.

3.13 Evaporation

Evaporation is the term often employed to describe the process for concentrating solutions of nonvolatile solutes through the vaporization of the volatile solvents. When more than one component in solution can vaporize, the process is referred to as distillation. In the utility industry, evaporation was widely used for boiler makeup water production until the early 1960's. The development of more energy-efficient technologies such as ion exchange and membrane processes, have limited the applicability of evaporation in new makeup treatment systems to seawater and wastewater feed supplies. However, evaporators are also used in the chemical process, food and pharmaceutical industries. In recent years, the drive towards zero liquid discharge facilities has resulted in the usage of evaporation technology for treating waste waters, which in turn has resulted in increased usage of this technology as part of the boiler makeup production system. The re-introduction of this technology as part of the boiler makeup water production system is driven by the high quality distillate byproduct, often produced in evaporation processes designed to eliminate a facilities liquid discharges.

While not typically used at nuclear plants, evaporation processes hold some potential. This section, including the design, operation and troubleshooting discussions pertain equally to nuclear as it does fossil generating stations.

3.14 Treated Water Storage

Makeup water storage facilities typically include storage tanks for two types of service.

- Filtered water for granular media (or membrane) filter backwash operations and othermiscellaneous service water uses such as pump seal water.
- Demineralized water and/or condensate. (The demineralized makeup water tank andcondensate tank are often one in the same. In the event that they are separate tanks, theforegoing discussion applies to both.)

In addition, plants operating non-continuous pretreatment such as reverse osmosis (RO) or other membrane filtration process usually will require a product water storage tank to ensure continuity of feed to ion exchange equipment. In cases where water supply quality has been observed to periodically deteriorate (plants using river water near the coastline where tidal effects could alter salinity of the feedwater), raw water tanks have been used to accumulate acceptable quality water (during low tide), which is then consumed during periods of unacceptable water quality (during high tide).

Primary emphasis in this section is on tanks used for storage of product water from the plant makeup water treatment system. The main purpose of such tanks is to provide sufficient volumes of treated water to meet demands of the generating units under most, if not all, operating conditions. Useful criteria for determination of water storage requirements are provided in subsections 14.2 (Design Criteria) and subsection 2.6 (Makeup Plant Capacity Assessment – in Section 2 of this guideline).

With proper storage, there is no significant change in the composition of the water. In the case of condensate storage tanks, with the exception of the influence of ammonia or other treatment chemical(s), the purity of water directed to the generating units should be essentially equivalent to that of water leaving the treatment system. With conventional storage tank designs (vented and open to the atmosphere), this is typically the case with respect to dissolved solids. However, exposure to the surrounding atmosphere during storage can allow contamination by dissolved gases (including oxygen and carbon dioxide) and combustion product gases (such as sulfur dioxide).

This section, including the design, operation and troubleshooting discussions pertain equally to nuclear as it does fossil generating stations.

3.15 Resin Selection Guidelines

It is the intent in this section to provide the investigator some insight into ion exchange resin alternatives available for the demineralization process and to indicate criteria for the selection of appropriate types and combinations of resins within a treatment scheme. Emphasis is placed on differing characteristics of similar types of resin and components of the water supply which affect the selection process. More detailed discussion on selection of an ion exchange process and actual application of resins is included in Sections 10 and 2 of this guideline. Discussion is limited to ion exchange resins most widely utilized in water treatment applications. Integral to the ion-exchange-resin-based demineralization process are cation and anion resins. The most widely utilized resins are strong acid cation and strong base anion. However, depending on concentration and distribution of constituents in the supply, additional resin alternatives are available, and combinations of different cation and anion resins can be included in the demineralization process.

A survey of fossil-fueled power plants in North America is presented in this guideline and found that only about 5% of them use weak acid resin. Approximately 15% of the survey participants indicated that weak base resin is employed in the primary demineralization step either as an adjunct to or instead of strong base resins. Weak acid and weak base resin usage is much more prevalent in Europe.

This section provides basic information as to the selection of resin types. This discussion pertains equally to nuclear as it does fossil generating stations. Nuclear plants can also utilize the resin specification found in Information Regarding Procurement Specifications for Nuclear Power Plant Bulk Chemicals, EPRI 1022558 [12].

3.16 Membrane Selection and System Evaluation Guidelines

This section focuses on the selection of membranes for RO, NF, UF, and MF applications. It does not cover the selection of materials for cartridge filters. Information on cartridge filter material selection is covered in Section 7 of this guideline.

The first steps in selection of RO/NF/UF/MF membrane is to clearly define the characteristics of the raw water supply and to provide detailed product (permeate) water specifications. Based on these criteria, the appropriate RO/NF/UF/MF membrane process, or combinations thereof, can be selected. The ranges of applicability of each membrane process depend on the molecular size, shape, and ionic characteristics of the feedwater supply constituents and the objectives of the treatment program. There are also economic constraints that favor or disfavor the use of certain technologies at different dissolved solids concentration levels.

This section provides basic information as to the selection of resin types. This discussion pertains equally to nuclear as it does fossil generating stations.

3.17 Performance Monitoring Guidance

When properly designed and operated, the fossil plant makeup water system is generally quite reliable in providing a product meeting the requirements of the plant with respect to both quantity and purity. At many utilities, the makeup system is taken for granted except when the water produced does not meet the needs of the units. Many of the problems that might arise are quite distinct and readily recognized by routine surveillance, which usually permits initiation of an appropriate action by responsible station personnel. Examples of these distinct problems include clarifier carryover, ineffective demineralizer regeneration, and media plugging. Sections 3–14 of this guideline describe some of the more common problem areas and remedial actions that can be taken.

More difficult to detect are the relatively subtle and gradual changes in performance of the makeup treatment system. Examples include fouling of ion exchange resins and membranes, degradation of resins or other sensitive media by debris or other contaminants, and minor leakage at valves, pump seals, and other points of potential contamination. Because these phenomena occur so gradually, the system can continue to operate and meet plant specifications for treated makeup. However, during this time, there is often a small, albeit detectable, decrease in system efficiency—rates of water production decrease, levels of impurities increase, and both occur simultaneously. These changes are often, and in some cases correctly, attributed to variations in raw water supply characteristics and effects of aging on resins and membranes. Close scrutiny is needed to distinguish preventable decreases in system performance from those that are inevitable.

This section provides basic information such as media and flowrate monitoring. This discussion pertains equally to nuclear as it does fossil generating stations.

3.18 Requirements for Chemicals and Media Used in Makeup Water Treatment Systems

Unit processes used in makeup water treatment systems require various chemicals and other media. Proper selection of these materials is essential to the assurance of reliable equipment operation to provide a treated water consistent with desired purity criteria. In Appendix A of this guideline, desirable characteristics of these materials are reviewed and, where possible, generic specifications are given.

This discussion is based on the experience of the author’s personnel with fossil plants and is supplemented by chemical suppliers’ product literature. Nuclear plant personnel are encouraged to instead consult reference [12] for chemicals and media used in makeup water treatment systems.

3.19 Materials of Construction for Makeup Treatment Systems

Reliable operation and maximum availability of fossil plant cycle makeup treatment systems require specification of appropriate materials of construction. The tables which follow provide guidelines on preferred materials for the various environments (including aqueous chemical solutions and waters of different purity) which might be encountered in the unit processes comprising a particular system.

This discussion pertains equally to nuclear as it does fossil generating stations.

4

CONCLUSIONS

The review of the fossil chemistry guidelines for makeup water, Guidelines for Makeup Water Treatment, Conventional Fossil and Heat Recovery Steam Generator Water/Steam Cycle Makeup [6] and the document's relevance to nuclear plant chemistry control, results in the following conclusions:

1. As identified in section 3.0 of this report, reference 8 provides a discussion of treatment methods for producing high quality demineralized water that is directly applicable to the nuclear stations. In the absence of similar guidance for the nuclear plants, it is suggested this document be used for such guidance. In particular, the guidance provided in reference 8 appears satisfactory for the design of makeup water processes, and the operation of water treatment equipment in nuclear stations.
2. As identified in section 3.0 of this report, the limits for chemical impurities in the effluent of makeup water treatment processes presented in reference 8 are not commensurate with the current needs of makeup water purity at nuclear plants.
3. The overall need for generating new makeup water treatment guidance is not necessarily driven by an absence of technical information. The reference 8 provides design and operation guidance, equally applicable to both nuclear and fossil generating stations. Current chemistry impurity targets/limits for nuclear plant makeup water treatment effluent samples can be found in pertinent INPO documents.

5

REFERENCES

1. EPRI PWR Primary Water Chemistry Guidelines, EPRI
2. EPRI PWR Secondary Water Chemistry Guidelines, EPRI
3. EPRI BWR Water Chemistry Guidelines, EPRI
4. Guidelines for the Design and Operation of Makeup Water Treatment Systems”, June 1989
5. AP-1000 Design Control Document
6. Guidelines for Makeup Water Treatment, Conventional Fossil and Heat Recovery Steam Generator Water/Steam Cycle Makeup (EPRI 1019635)
7. Comprehensive Cycle Chemistry Guidelines for Fossil Plants, EPRI 1021767
8. EPRI Open Cooling Water Chemistry Guidelines, EPRI
9. ASTM D6161
10. The *Membrane Filtration Guidance Manual* (EPA 815-R-06-009)
11. American Membrane Technology Association (AMTA, FS-1)
12. *Information Regarding Procurement Specifications for Nuclear Power Plant Bulk Chemicals*, EPRI 1022558

A

SURVEY RESULTS

Members of the BWR and PWR Chemistry TSGs were surveyed as to the need for new Makeup Water Chemistry Guidelines. The below table provides the results of the survey.

Plant	Is there a need for makeup water system operational guidance?	Is there a need for makeup water system design information?	Can makeup water system limits be optimized?	Comments
A	No	No		Enough industry and vendor experience that seems to be doing fine as is.
B	I don't think this is a worthy area in which to spend time. We need to meet demineralized water standards for the DWST and that translate to the makeup system pretty easily.			There are a lot of systems out there. The newer systems have a lot of bells and whistles but the water quality is unchanged.
C	No. Most plants use vendor trailers due to economics of maintaining the equipment and the ability to use the maintenance and operations staff for in-plant work.	No.	For BWRs, makeup is a small amount of the impurities in the plants but for PWRs it is a much larger source.	
D	From the BWR perspective, I don’t see much need for makeup water guidelines. I would rather see this effort applied to the radwaste side of water processing.			
E	Yes	Yes	Yes	

F	Not for Quad Cities. Quad Cities uses GE Mobile Water trailers to provide our makeup water. I believe that the majority of the industry is headed towards vendor mobile trailers to process makeup water.	Not for Quad Cities. Our vendor is able to meet all the limits in BWRVIP-190 Table E-1.	The guidance in BWRVIP-190 Table E-1 is adequate. I do not think the limits need to be changed.	
G	No need, we already have Westinghouse guidance.			
H	I understand there is a gap in the guidelines since there are no written makeup water chemistry guidelines and consistency would say that this gap needs to be filled. Given the role that INPO has played and the market for vendors to bring in their own equipment and produce makeup water for plants using ever-improving equipment, I'm just wondering whether it is worth the time and money to work on this.			Technically based makeup water chemistry limits (as opposed to INPO based limits getting the limits as low as possible) would seem to be somewhat site specific based on the calculated mass input of each impurity of concern at the maximum reasonably expected makeup rate to a system at the maximum calculated impurity concentration that contributes only a small fraction of the total system concentration in the system where that impurity is the most limiting based on industry guidelines for that system and the impurity removal capabilities for that plant. A technically based guideline would probably justify higher limits for some makeup water chemistry parameters than what would be permitted by the INPO approach of everyone achieving as low of impurity concentrations as the state of the technology can achieve. However, in the current nuclear culture of trying to see how low impurity limits can be driven and maintained regardless of whether there is a technical basis for driving the limits that low, a technically based makeup water chemistry guideline based on the most limiting water chemistry limits in the secondary,

				primary, and closed cooling water chemistry guidelines, may be of limited value since I doubt anyone will argue for raising their makeup water chemistry limits. If the guidelines document would only document what the currently achievable makeup water chemistry limits are, then those limits will change with time as the technology improves and would seem to duplicate what INPO is already doing or has done.
I	I would like to see something from EPRI regarding MU water quality. Not trying to turn this into a big-deal, but I believe that the lack of MU water specifications is a small hole in EPRI's water chemistry program.			It would be a good point of reference for utilities to use when developing purchase specifications, and would also let the vendors know that there is a benchmark. That along with the INPO proposed change to Condition 4 to lower the steam generator sodium value from 0.8 ppb to 0.6 ppb, will make makeup water quality more important. With an approximate 100 X concentration factor in steam generators, and a 0.6 ppb sodium CEI "trigger", makeup water needs to be better than 6.0 ppt. What other parameters are important to monitor in MU water, what reactor coolant system concerns need to be considered?
J				KEPCO follows old EPRI guidelines and uses both RO and IX.

K				We know utilities are investigating modernizing makeup water based on improving secondary side chemistry. Some plants have significant Al and silica deposits that are related to makeup water. This is a rationale for RO rather than IX for makeup water.
L	Has been looking for documents just like, but all he has found are fossil reports which could only be used as a starting point. Recommendations should consider source of water.			
M				One issue will be that requirements differ from plant to plant and will result in significant variation; e.g., is there blowdown, is there a condensate polishing, is water recovered, etc. It will be hard to set limits because a lot of it will be based on what is achievable based on the water system at each plant. There is a need for a guideline, but limits might be difficult.
N	Fossil plants use demineralizers and may be able to achieve different results. What EPRI is doing is good, but it doesn't need to be 300 pages.			Limits on current reverse osmosis (RO) systems may be based on what is reasonably achievable with the technology.

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