CONSENSUS ON OPERATING PRACTICES FOR CONTROL OF WATER AND STEAM CHEMISTRY IN COMBINED CYCLE AND COGENERATION POWER PLANTS

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Prepared by the
Heat Recovery Steam Generator Chemistry
Limits Task Group and the Water Technology
Subcommittee of the
ASME Research and Technology
Committee on Water and Steam
in Thermal Systems

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❐ FOREWORD ❐

The Water Technology Subcommittee of the ASME Research and Technology Committee on Water and Steam in Thermal Systems, under the leadership of David Daniels, Mechanical & Materials Engineering, has established a “Consensus on Operating Practices for Control of Water and Steam Chemistry in Combined Cycle and Cogeneration Power Plants.”

This publication is an important companion to previously published documents prepared to inform and educate the reader and to develop good chemistry control and operating practices for steam and water usage in thermal systems. The earlier publications are “Consensus on Operating Practices for the Control of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers”; “A Practical Guide to Avoiding Steam Purity Problems in the Industrial Plant”; “Consensus for the Lay-up of Boilers, Turbines, Turbine Condensers, and Auxiliary Equipment” and “Consensus on Operating Practices for the Sampling and Monitoring of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers.”

This consensus was prepared by a task group of this subcommittee under the guidance of David Daniels. The task group consisted of representatives of manufacturers, operators and consultants involved with the design, manufacture, operation and monitoring of industrial and utility boilers, steam generators and associated equipment.

The ASME Research Committee will review, revise and reissue this document from time to time as necessary to comply with advances in technology in the design of these units and the water treatment options.

Edward Beardwood
Chair, ASME Research and Technology
Committee on Water and Steam in
Thermal Systems

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❒ PREFACE ❒

The ASME Research Committee on Water and Steam in Thermal Systems previously published an “Operating Consensus for the Control of Water and Steam Chemistry in Modern Industrial Boilers,” ASME Publication CRTD-34. That document has been widely applied by designers and operators of these boilers to establish critical monitoring parameters and normal operating limits that will minimize deposits and corrosion in the boiler and subsequent steam-driven equipment.

Combined cycle power plants, consisting of combustion turbines (CTs) and heat recovery steam generators (HRSGs), have chemical operating requirements that are significantly different from those for industrial or power boilers. Due to a lack of contrary evidence at the time of issuance, ASME CRTD-34 included HRSGs in the same classification as industrial watertube drum type generators. In 2001 errata were published to exclude HRSGs from the original consensus for industrial boilers.

At that time the Committee also formed a task group with the goal of generating an operating chemistry consensus specific to the needs of combined cycle plants. This document is the product of that task group’s efforts together with solicited input from members of the HRSG Users Group and manufacturers.

English units have been used throughout this document with metric equivalents in parentheses. Also in this document mg/L and μg/L are assumed to be equivalent to ppm and ppb respectively.

❐ SECTION 1 ❐

INTRODUCTION

The Combined Cycle Task Group of the ASME Research and Technology Committee on Water and Steam in Thermal Systems has prepared the following set of chemical operating limits specifically to address the requirements for heat recovery steam generators.

A common configuration for power generation utilizes a natural gas-fired combustion turbine (CT) coupled with a heat recovery steam generator (HRSG) that extracts heat from the gas turbine exhaust to produce steam for a separate steam turbine/generator set. Often multiple CT/HRSG units feed a single steam turbine. Some combustion turbines can use fuel oil as either the primary or back up fuel. If steam or hot water is exported to an industrial user, the plant is typically known as a cogeneration facility.

Combined cycle (CT plus HRSG) systems are extremely efficient, with the newest configurations approaching twice the heat rate of conventional fossil fuel-fired power plants. Since the plants are typically powered by natural gas, the need for sulfur emission control technologies is almost always eliminated. For these reasons, the combined cycle power plant has become an extremely common configuration for new generating capacity. Though such arrangements were first conceived and built in the mid-1950s, it was not until the mid-1970s that advances in high-temperature materials and air cooling of gas turbine blades made the combined cycle power plant commercially viable.

Simple cycle gas turbines have long been used to provide peaking power generation due in part to their fast response time. Some owners have operated their combined cycle units in a similar mode and many of these units undergo hundreds of starts a year. In addition, nitrous oxide (NO_x) emissions limits often require that the units be ramped quickly to approximately 50% of full load, or higher, imposing thermal strains on the HRSG.

HRSGs, sometimes referred to as waste heat boilers, have long been used in industrial applications to recover heat from exothermic processes and to generate steam for use elsewhere in the process. The industrial units differ from their power generating counterparts. The industrial HRSG is typically in constant operation (does not cycle) and the steam is ultimately used for plant processes or to feed a non-condensing steam turbine before use in the process.

The HRSGs used for power generation, often more complex and operating at higher pressures than their industrial counterparts, may have up to three steam drums each operating at different pressures in addition to superheat and reheat steam sections. The newer units may also have significant makeup water demands caused by 1) the unrecoverable use of steam in NO_x-emissions control; 2) the use of high purity water for air cooling and direct injection into the gas turbine; 3) the loss of steam that may be exported at a cogeneration facility.

Closely spaced finned heat exchange elements in the HRSG produce exit gas temperatures that are much lower than those from a conventional boiler. The final tube bundles typically act as a feedwater heater but, at those low temperatures, some or all deaeration must be accomplished in the condenser under vacuum. If a discrete deaerator (DA) is provided, it is often located directly on top of the low pressure (LP) drum, in effect using the LP drum as the DA storage tank. In these cases, steam for deaeration is provided by the HRSG itself. This arrangement can result in excessive dissolved oxygen concentrations in the feedwater during start-up when neither pressure nor vacuum deaeration is yet possible. Another configuration employs a completely separate pressure deaerator and feedwater storage tank with steam provided from the LP drum.

Combined cycle plants designed strictly for power generation typically are constructed with all- ferrous materials such as carbon steel, low alloy steel and stainless steel. Cogeneration plants often have copper alloys as well as ferrous alloys in the steam/condensate cycle. Plants with a mixture of ferrous and copper-bearing alloys in the steam/water cycle are referred to as mixed metallurgy cycles. Since the optimal treatment regime is different for all-ferrous and mixed metallurgy systems, chemistry limits are generally segregated by these two generalized categories of system materials. Titanium may be present in any of these configurations without affecting the choice of the treatment regime.

Though originally designed to absorb heat from gas turbine exhaust only, many HRSGs are being built for the regular use of duct burners that can generate significantly higher temperatures than those typical of turbine exhaust gas. The use of duct burners can change the operating pressure of the HRSG and more than double the steaming rate.

Considering their relatively short operating history, HRSGs have seen more than their share of failures. While a few of the common failure mechanisms are strictly mechanical, most have a significant water/steam chemistry component. The reliable operation of the combined cycle power plant is predicated on stringent control of water and steam chemistry throughout the steam cycle.

❒ SECTION 2 ❒

SCOPE

While the main focus on water and steam chemistry in the new combined cycle plant is on the HRSG and steam turbine, chemistry limits are also important for water that is used to cool air feeding the gas turbine and water directly injected into the gas turbine. The limits suggested herein address all these water uses in a combined cycle plant. Small, low pressure HRSGs operating with soft water makeup are included in the document, although the suggested chemistry limits for these units are the same as for industrial watertube boilers. This document does not cover HRSGs used for enhanced oil recovery or thermal in-situ operations.

❒ *TYPES OF HRSGS*

Many HRSG configurations create very complex flow patterns. During start-up, some tubes in the HRSG may remain stagnant or even flow in the opposite direction from operation. Lay-ups, particularly those in hot standby condition (daily cycling), are common and chemistry during this time is also important. These conditions dictate chemical operating limits that more closely approximate those for large, fossil-fuel boilers than the drum pressures would indicate.

Most recently built combined cycle power plants use demineralized water makeup. However, some existing units, primarily in industrial settings, operate at low pressures and use softened water makeup. Units operating at higher pressures and using demineralized makeup are more sensitive to some types of corrosion than those on softened water. For example, softened water units rarely have issues with flow accelerated corrosion (FAC). Since the chemistry limits of HRSGs using softened water and demineralized water are significantly different, they are detailed in separate tables in this document.

Once-through heat recovery steam generators are HRSGs that do not include a conventional steam drum for the separation of water and steam. Water is pumped into the unit as a subcooled liquid and passes over the HRSG heat exchange surfaces where it is converted to steam. Since this HRSG design does not include provisions for concentration and mechanical removal of impurities in the system, feedwater quality in these units must match superheated steam purity requirements. Specific guidelines on water chemistry operating limits for these units should be obtained from the manufacturers.

❒ *DESIGN CONSIDERATIONS*

When specifying a new HRSG unit, owners and/or engineering procurement contractors (EPCs) prepare detailed technical specifications to which original equipment manufacturers (OEMs) are expected to bid. Without specific requirements, bidders will always choose the least expensive capital cost approach. Some decisions can be made by the customer at this stage that can provide substantial payback in the unit's useful life and reliability, even though initially appearing slightly more expensive. A few of these design considerations are listed below.

❒ *HRSG CHEMICAL TREATMENTS*

A number of possible chemical treatment regimes are discussed in this document but no single set of chemistry parameters can be correct for all HRSGs. This document is intended to provide sufficient information to allow HRSG owners or their consultants to select chemistry control limits suited to the particular configuration of their own plant. Since some of these parameters can be determined only after commissioning, a set of conservative chemistry limits using general assumptions is also suggested for use during commissioning until more refined limits can be established.

During start-up and shutdown, chemistry may drift outside of the established limits and it will be important to define the allowable deviations. Particularly during start-up, grab sample testing and on-line analysis should be used as soon as possible to determine the actual chemistry of the water and steam in the unit. Prompt action can then be taken to reach normal operating limits as soon as possible.

Considering the complex nature of HRSG piping combined with the cycling service under which many units operate, serious consideration should be given to the potential hazards of the misapplication of high concentrations of phosphates, chelants, polymers, or complex organic treatments. If contaminants that require precipitation, complexation, or dispersion regularly enter the HRSG, all possible steps should be taken to improve the condensate return and feedwater quality instead of attempting to remedy the problem internally after the water has entered the HRSG.

However, for HRSGs that use softened water make up, a variety of traditional chemistry programs may be used.

Copper materials in the feedwater and steam systems limit the feedwater pH. The lower pH required makes the HRSG more susceptible to flow accelerated corrosion (FAC). It is strongly recommended that copper materials not be used in combined cycle plants. Aluminum alloys should never be used **ANYWHERE** in the HRSG water and steam cycle including the makeup water system.

❐ SECTION 3 ❐

OBJECTIVES OF HRSG STEAM/WATER CYCLE CHEMISTRY

The primary objective of any water treatment program is the long-term reliability and health of all materials in the steam/water cycle. This requires that water and steam purity be constantly monitored and controlled to prevent corrosion and deposition. Corrosion and deposition are often related; corrosion in one area of the steam/water cycle often results in deposition further downstream in the process. An accumulation of deposits can, conversely, promote corrosion of the underlying metal.

Chemical control limits are of little value without frequent and accurate monitoring to ensure compliance. The use of continuous on-line monitoring of pH, specific conductivity, cation (acid) conductivity, sodium, and dissolved oxygen is highly recommended as opposed to grab sample testing once a shift or daily. Such manual testing is insufficient if the plant is to be protected from damage caused by chemistry excursions.

On-line monitors must be specified prior to construction, installed during construction, and put into service and calibrated during commissioning. Once the reliability of an on-line analyzer has been verified, grab sampling and accurate analysis is required occasionally to confirm the on-line readings. It is important to realize that the results of grab sample analyses may be more prone to errors than those of on-line monitors.

Refer to the ASME "Consensus on Operating Practices for the Sampling and Monitoring of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers" (CRTD-81) and "Steam and Water Sampling, Conditioning, and Analysis in the Power Cycle" (ASME PTC 19.11-2008) for specifics of on-line and grab sample analysis.

❐ SECTION 4 ❐

SCOPE DESIGN CONSIDERATIONS

Decisions made during the design and construction phase of the HRSG can have a tremendous impact on the chemistry control that can be used to prevent corrosion.

Auxiliary Steam Generating System - steam from auxiliary boilers may be used for brief periods at start-up, used to maintain vacuum during longer outages or used for sparging of the HRSG. Purity of steam from auxiliary boilers should be the same as that of steam produced in the HRSG. Contaminants in auxiliary steam may make cleanup of the steam/water cycle more difficult at a subsequent start-up.

Cascading Drum Blowdown - in multi-pressure steam drum HRSG units, cascading of steam drum blowdown is a common design configuration. Cascading blowdown generally refers to the process in which the continuous blowdown from a steam drum is discharged into a lower pressure steam drum to capture blowdown energy and improve cycle efficiency. In a three-pressure HRSG unit, the receiving drum for high-pressure (HP) blowdown is normally the intermediate-pressure (IP) drum. In a dual pressure HRSG unit, the receiving drum would be the low- pressure (LP) drum. In many HRSG designs, LP drum water is used for steam attemperation purposes. In this case, cascading to a LP drum is unacceptable. Although cascading blowdown improves overall plant efficiency, it can result in chemistry-related concerns and issues that must be addressed at the design phase. For example, low molecular weight organic acids produced from degradation of certain organics in the HP steam drum can cause low drum water pH in the receiving drum.

Drums receiving blowdown from a higher pressure drum must themselves have a blowdown system adequate for appropriately controlling their own drum water chemistry. For start-up and emergency operation, provision should be made for independent control and discharge to waste of normally cascaded blowdown.

Condensate/Process Return Polishing - condensate filters/polishers can be very effective for removing contaminants and corrosion products from the feedwater thereby minimizing deposits in the HRSG. Their inclusion is considered standard practice for once-through HRSGs, for drum HRSGs that operate on an oxygenated treatment (OT) program, and for units that collect condensate from an industrial process or from a central heating system. They should also be strongly considered for HRSGs that operate at greater than 1800 psig (12.5 MPa) or on any HRSG that will operate on an all-volatile treatment (AVT) program. These systems should be equipped with adequate monitoring of returned condensate and reliable systems for quick dumping of out-of-specification condensate upstream of the polishers to avoid contamination of not only the steam/water cycle, but the condensate polishers as well. See Table 8b.

Condensers - chemical treatment is greatly simplified if there are no copper alloys in the system including the steam condenser. Copper alloys possess excellent heat transfer characteristics but are susceptible to ammonia attack on the steam side, chemical and biological attack on the water side, and have lower allowable maximum flow velocities than ferrous alloys. If copper alloys are not present in the combined cycle plant system or in a steam host's system, where such exists, the feedwater pH can be raised above 9.3 using ammonia or amines to minimize flow accelerated corrosion (FAC).

In selecting replacements for copper alloys, stainless steel alloys are often considered. Stainless steel, however, is susceptible to attack by chlorides and microbiologically influenced corrosion (MIC) from cooling water. Additionally, some stainless steel condenser tubes have suffered pitting damage if the cooling water contains even trace amounts of manganese. Titanium alloys eliminate these issues, however, titanium tubed condensers may be more costly and tubes must be shop-welded into the tube sheets to minimize leaks. Both titanium and stainless steel alloys offer superior erosion resistance as compared to copper alloys, allowing the use of higher maximum cooling water flow velocities. Cost, size, velocity, and cooling water chemistry are all factors that must be considered in the selection of condenser materials.

Chemical Feeds - the proper feed and control of chemical treatment is critical to the successful operation of any steam generator. In HRSG systems it is important to provide the capability to feed treatment chemical to each individual steam drum. This will enable the adjustment of individual unit chemistry as required by varying operating conditions. The treatment chemicals should be fed downstream of any economizers and injected so that they are mixed thoroughly with the incoming feedwater. This can be accomplished by feeding through a chemical feed quill of suitable alloy into the center of the feedwater line prior to its entry into the steam drum, or by feeding a high volume dilute solution of chemical into a suitably designed and positioned distribution header within the steam drum.

Feedwater and condensate system pH control chemicals such as ammonia and amines should be fed where they will provide pH control for all carbon steel and copper alloy components in the makeup and feedwater systems. Feed into the condenser hot well or to the condensate pump discharge will serve this purpose in many systems. In facilities with condensate polishers, feed should be to the discharge of the polishers.

For those systems requiring an oxygen scavenger (reducing agent), the feed of chemical into the condensate pump discharge is preferred. In facilities with condensate polishers, feed should be to the discharge of the polishers.

Low-pressure HRSG systems operating with lower quality feedwater (e.g. softened makeup or low-quality process condensate return) typically use different treatment injection points. Oxygen scavenger (reducing agent) and amine treatments are usually injected into the deaerator storage section while the boiler water treatment chemicals are injected into the feedwater.

Cycling Operation Considerations - since many HRSGs and combined cycle plants are developed to operate as cycling units, several additional points need to be addressed in the design phase to plan properly for this mode of operation. The HRSG blowdown and blowoff treatment and disposal system should be sized to accommodate and safely dispose of blowdown at a rate of at least 5% of design steam flow. The sizing criteria for cycle chemical feed pumps should be based not only on the normal operating feed requirements, but also on start-up feed requirements which can occur on a daily basis in a cycling unit. The pumps should be sized for the start-up drum blowdown rate of 5% of design steam flow in addition to the normal operating steam drum blowdown conditions.

Deaerator - combined cycle units are normally supplied with feedwater deaeration systems in one of three basic configurations. Pressure deaeration may be accomplished with a stand-alone deaerator or a deaerator integral to the HRSG. The integral pressure deaerator design utilizes the LP steam drum as the feedwater storage tank. Vacuum deaeration is achieved through the use of a special deaeration section and spargers located internally in the condenser.

It is recommended that the HRSG be furnished with a separate stand-alone deaerator that is designed to remove dissolved oxygen in the feedwater under all conditions, particularly during start-up. The stand-alone deaerator provides benefits that are not available when an “integral” type deaerator, integral either to the HRSG or the condenser, is utilized.

Steam produced in an auxiliary boiler or steam from an alternate source can be beneficial for short-term lay-up and start-up of an HRSG. A stand-alone deaerator can operate with auxiliary steam to produce deaerated feedwater prior to the firing of the combustion turbine. Auxiliary steam also provides other advantages such as maintaining heat in the HRSG and vacuum in the steam turbine condenser in a cycling plant.

A stand-alone deaerator can also provide steam attemperation water that allows for the use of solid-alkali treatment to mitigate two-phase FAC in the LP evaporator.

Documentation Requirements - as a minimum, all critical parameters including all on-line analyzer data (see Table 2) should be recorded every two hours, including during the commissioning period prior to commercial operation. The preferable method is to retain chemistry data electronically. All treatments, blowdown settings, and pump settings should also be regularly recorded.

Duct Burners - HRSG operation with and without the need for duct burners in service should be carefully reviewed and evaluated at the design stage. In some cases, HRSG chemistry requirements and system operating conditions will be different when the duct burners are in service as compared to operation with no duct burners. Different rates of firing may produce alternate scenarios that need to be considered; especially since duct burners generally do not distribute heat evenly across the HRSGs' heat transfer surfaces. The chemical treatment program should be developed considering the worst-case scenario of the various anticipated operating scenarios for each particular unit.

Depending on the HRSG design, high rates of firing with duct burners have been known to create chemical hideout, particularly in HP evaporator tubes. A low solids (or no solids) treatment program may be required to prevent deposit accumulations when the HRSG is being fired with duct burners. Since the utilization of the duct burners is not predictable, prudence requires that the treatment program be designed for the most severe (i.e., highest heat flux/pressure) conditions. This optimum chemistry must be determined by performance testing.

Plant Materials - corrosion generally is affected by conductivity, pH, and oxygen concentration. In systems with mixed materials, high pH and oxygen may lead to corrosion of the copper and copper alloys, while low pH leads to corrosion of carbon and low alloy steels. If the pH and oxygen are low, the steels are subject to flow accelerated corrosion (FAC). For all- ferrous systems, the level of dissolved oxygen typically present in the effluent of a properly functioning deaerator (< 7µg/L) may be acceptable without the addition of chemical oxygen scavengers (reducing agents). High pH values in the feedwater that protect ferrous alloys create amounts of ammonia that may be corrosive to copper alloys.

Flow accelerated corrosion (FAC) has been found in many HRSGs. Testing and experience has shown that mild steel alloys that contain chromium are far less likely to develop FAC.

Owners/Engineers should specify use of alloys containing a minimum of 1.25% chromium in the areas susceptible to FAC. The primary areas for FAC in HRSGs are all economizers and the LP evaporator. Chromium-containing alloys will significantly improve FAC resistance in systems.

The HP and IP evaporator feedwater lines and attemperator piping may also be susceptible to FAC depending on design, materials, and operation.

Copper-alloyed materials in the condenser, or in a host's steam system, limit the feedwater pH that can be used. This lower pH makes the HRSG more susceptible to flow accelerated corrosion (FAC). It is strongly recommended that copper materials not be used in combined cycle plants. Aluminum alloys are unacceptable in the HRSG water and steam cycles.

Makeup Water Treatment System - combined cycle plants are subject to frequent start-up/shutdown cycles and the makeup water treatment system and related storage facilities must be designed and sized accordingly. Ideally, the makeup treatment systems for a cycling unit should be sized for the highest demand during start-up and maximum steaming rate. The start-up case should include an initial blowdown rate of 5% of design steam flow as well as any other potential water consumption that may be required during start-up operations. The maximum operating case should include blowdown, steam to hosts, sampling, and miscellaneous cycle losses, as well as any additional water uses such as combustion turbine inlet fogging, combustion turbine steam power augmentation, and steam injection for NO_x control. In situations where other considerations dictate that a smaller makeup water treatment system be installed, storage facilities must be sized to provide sufficient water at the rate and volume required during peak demand periods.

The design must include adequate makeup treatment capacity to allow continuous operation during normal and abnormal circumstances, such as the loss of returned condensate from the steam host or mechanical problems with the water treatment system. Adequate treated (softened or demineralized) water storage should provide the plant with sufficient response time for corrective action.

In design and specification of the equipment required for processing plant makeup water, care must be taken to ensure that representative source water analyses are obtained and provided to the manufacturers prior to procurement. These water analyses should include seasonal variations in water quality parameters including historical data for at least two years. The more water data that are provided the more satisfactorily the equipment can be designed to meet the specific needs of the plant. Crucial parameters that should be included in all water testing for design of these systems include pH, seasonal temperature variations, organic concentrations, alkalinity, hardness, full ionic analysis, total dissolved solids, reactive and total silica, total suspended solids, oil and grease contaminants, and heavy metals.

***Purity Requirements for Chemicals* -** the chemicals for the steam/water cycle have to fulfill the following purity requirements to avoid impairment of the recommended quality of steam and water as shown in Table 1. The purity may be proven either with certification by the chemical supplier or with laboratory analyses. Dilution water should be high-purity demineralized water. Trisodium phosphate is the only phosphate recommended. Trisodium phosphate could be supplied as a dry powder or as solution. If supplied as a solution, the user should request a Certificate of Analysis to ensure that it does not contain contaminants.

Table 1.

Typical Purity of Aqueous Ammonia (10-29%)

Chloride as Cl	<2.0 ppm (mg/l)
Sulfate as SO_4	<1.5 ppm (mg/l)
Sodium as Na	<1.0 ppm (mg/l)
Iron as Fe	<2 ppm (mg/l)
Copper as Cu	<0.05 ppm (mg/l)

Typical Purity of Trisodium Phosphate

Na_3PO_4 content as Na_3PO_4	>44%, if water of crystallization included
	>98%, if expressed as calcined product
Water insoluble substances	<0.05%
pH of 1 wt% solution, at 25°C	11-12

Sample Conditioning and Continuous Analyzers - proper sampling and sample conditioning is critical to reliable monitoring of the water and steam chemistry parameters in the unit. Proper sample conditioning includes dual sample coolers for all high-pressure/high-temperature samples so that the sample lines can operate continuously while maintaining 77°F (25°C). Sampling and sample conditioning guidelines published by ASME and ASTM should be followed.

Critical control parameters should be monitored continuously on any HRSG that produces steam for a steam turbine, regardless of the operating pressure of the HRSG. These are shown in Table 2.

Table 2. Measurement Testing Frequency

Parameter	On-Line Measurement Location (1-2)
Silica	Makeup water
	HP drum water
	Main or reheat steam
Specific Conductivity	HP drum water (phosphate treatment)
	IP drum water (phosphate treatment)
	Makeup
	Feedwater downstream of ammonia feed (for alternative pH determination)
	Process condensate returns
Cation Conductivity (3)	Condensate pump discharge
	HP feedwater (BFP discharge or economizer inlet)
	Main steam or reheat steam
	HP drum (for units on AVT)
Dissolved Oxygen	Condensate pump discharge
	Feedwater pump discharge
TOC	Process condensate returns
ORP	Feedwater pump discharge
Sodium	Condensate pump discharge
	HP feedwater (feed pump discharge)
	Main or reheat steam (4)
	HP drum (for units on AVT)
pH	HP, IP, LP drum (blowdown)
	LP, HP feedwater
	Process condensate returns

(1) It is preferred that each of the parameters in this table have dedicated analyzers for each sample point. A list of analyzers that can be shared can be found in Table 3.
(2) Continuous analyzers should be verified by grab samples or by comparison with other analyzers at least daily. Increase manual testing frequency to every two hours if a continuous analyzer is not working.
(3) The on-line direct measurement of anions by on-line ion chromatography (IC) is an acceptable alternative to cation conductivity.
(4) Monitoring the HP and IP saturated steam and attemperation water (e.g., economizer inlet) can provide equivalent information as the main steam or reheat steam sample if steam and attemperation flow rates are known.

Certain sampling points should have a dedicated analyzer, but other sampling points can be connected to a **shared analyzer.** Shared analyzers reduce capital costs and ongoing operating and maintenance costs. The sampling frequency will vary depending on whether the plant is being operated in a cyclic or base-loaded mode.

Table 3 identifies which of these sample points can utilize a shared analyzer. The shared analyzer can be manually valved to each sample or can be cycled through all points by means of an automatic sequencer. If sample points are to be manually valved, they should be set to operate as outlined in Table 3 during normal operation.

Table 3. Sampling Points with Shared Analyzers

Measurement	Samples Sharing Analyzer	Set for Normal Operation
TOC	Makeup, process return condensate	Process return condensate
Dissolved Oxygen	Feedwater heater inlet HP/IP economizer inlet	HP economizer inlet
Silica	LP saturated steam (stand-alone system) IP saturated steam Hot reheat steam HP main steam	HP main steam
Sodium	Makeup Hot reheat steam HP main steam HP saturated steam IP saturated steam LP saturated steam	HP main steam or hot reheat
Cation Conductivity	LP saturated steam IP saturated steam HP saturated steam	HP saturated steam
Phosphate	LP drum water (stand-alone) IP drum water HP drum water	sequenced

Since there are many different plant configurations, additional sample points may be needed to continuously monitor a system, provide chemistry control and identify contamination ingress. For example, additional on-line analyzers would be needed for any condensate process returns. The user should examine their specific system when considering what parameter(s) to monitor and the required sampling point(s).

For additional discussion on this topic, refer to the ASME "Consensus on Operating Practices for the Sampling and Monitoring of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers" (CRTD-81) and "Steam and Water Sampling, Conditioning, and Analysis in the Power Cycle" (ASME PTC 19.11-2008).

Steam Purity - The required steam purity for the steam turbine or any process equipment must be defined clearly in the project design stage. Critical decisions regarding makeup treatment and condensate treatment will all be determined by the required steam purity.

Unit Commissioning Considerations - Timely and successful unit commissioning is highly dependent on proper planning in the pre-design and design stage. Provisions for chemical cleaning need to be evaluated and factored into the design of piping and system equipment in the plant design stage. All required connections should be accessible once construction is complete and any connections that will remain as part of the system after commissioning should be completely drainable.

Early design of chemical feed systems can save money later in the project. The options for chemical treatment for the HRSG should be evaluated early in the project and a plan of treatment (i.e. selection of chemicals, chemical injection locations, and anticipated chemical feed rates) chosen in the design phase. Chemical feed equipment can then be properly specified to avoid problems of inadequate feed systems (i.e. oversized pumps, undersized pumps, wrong type of pumps) during unit commissioning.

Sampling systems (conditioners and analyzers) must be functional prior to introducing steam into the turbine, while venting steam or bypassing to the condenser, so that chemistry can be monitored. Refer to the ASME "Consensus on Operating Practices for the Sampling and Monitoring of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers" (CRTD-81) and "Steam and Water Sampling, Conditioning, and Analysis in the Power Cycle" (ASME PTC 19.11-2008)

❒ SECTION 5 ❒

DERIVING CHEMISTRY OPERATING LIMITS

Specific HRSG configurations impose equally specific requirements for water and steam chemistry. The operating chemistry limits in this document are meant to provide a starting point from which each plant can develop its own plant-specific limits. Lower pressure HRSGs that provide process steam have very different requirements from high-pressure HRSGs that drive steam turbines for power generation. Selection of appropriate plant chemistry limits is greatly influenced by the presence of those pieces of equipment that are particularly sensitive to deposits and corrosion, the first and foremost being the steam turbine.

❒ *STEAM TURBINE*

The steam turbine may be fed with steam from HP, IP and LP superheaters of one or more HRSGs and the purity of steam supplied to the turbine is one of the most critical parameters in the plant. The objective of the steam chemistry program is to prevent corrosion and deposits in the steam turbine. The presence of sodium hydroxide (caustic soda), sulfate, or chloride in the steam can cause turbine blade or rotor failures from stress corrosion cracking. Chlorides may also lead to pitting and corrosion fatigue.

The formation of deposits reduces turbine efficiency by creating turbulence and restricting flow and may become so severe that blades fail because of deposit-caused vibrations. Recent research shows that deposits and corrosion can occur over a broader range in the turbine than previously thought. Areas of high flow rate can become subcooled to the point that condensation begins on blades that otherwise would be above the condensation line. Flow stagnation can lead to areas of superheat in cooler sections of the turbine.

The steam chemistry is the fixed point in the cycle. Regardless of the operating pressure, source of the steam, attemperator water flow, number of drums or makeup system, the steam chemistry limits must be met to maintain the reliability of the turbine. For reference, limits from various turbine manufacturers are shown in Table 4. These limits apply to condensing steam turbines, not back-pressure turbines. The chemistry requirements of back-pressure turbines are less stringent.

Table 4. Comparison of OEM Steam Chemistry Limits for Condensing Steam Turbines under Normal Operating Conditions

Steam (HP, IP, LP)	Alstom	GE (1)		Mitsubishi	Fuji	Siemens
		Reheat	No reheat			
Specific conductivity at 25°C, µS/cm	3-11	NS	NS	NS	NS	NS
Cation conductivity at 25°C, µS/cm	< 0.2	≤ 0.15	≤ 0.25	< 0.3	<0.3	< 0.2
pH at 25°C	9.0-9.6 (2)	NS	NS	NS	9.0-9.3	NS
Silica as SiO_2, ppb (µg/kg)	<20	≤ 10	≤ 20	< 10	<10	<10
Total iron as Fe, ppb (µg/kg)	<20	NS	NS	< 20	<20	<20
Total copper as Cu, ppb (µg/kg)	<3	NS	NS	< 2	<3	<2
Sodium as Na, ppb (µg/kg)	<10	≤ 3	≤ 6	< 5	<10 (3)	<5
Chloride as Cl, ppb (µg/kg)	NS	≤ 3	≤ 6	< 5	NS	NS
Sulfate as SO_4, ppb (µg/kg)	NS	≤ 3	≤ 6	NS	NS	NS
Oxygen as O_2, ppb (µg/kg)	NS	NS	NS	< 10	<10	NS
TOC as C, ppb (µg/kg)	NS	≤ 100	≤100	NS	NS	NS

(1) Using phosphate treatment (greater than 2.6 Na:PO4 molar ratio) or AVT
(2) pH 9.0 – 9.3 with copper-alloy condensers
(3) Na + K
NS is not specified

The most critical of these parameters are sodium, silica, chloride and sulfate. Chloride and sulfate concentrations are typically measured indirectly by determining the cation conductivity of the steam. Cation conductivity is also influenced by organic and inorganic anions, such as acetate and carbonate. Unlike chloride and sulfate, carbonate species are volatile and can be removed by heating or purging the sample with an inert gas prior to measuring the cation conductivity. When so treated, the parameter is referred to as *degassed* cation conductivity. The general consensus is that degassed cation conductivity is valuable during commissioning and for troubleshooting. The most direct and accurate method for measuring chloride and sulfate is by ion chromatography.

❒ *MAKEUP WATER AND CONDENSATE RETURN*

Makeup water and condensate return for cogeneration units should be sufficiently pure to meet the feedwater requirements when these streams are introduced into the HRSG, Tables 6-9. Water treatment equipment such as filters and ion exchange polishers may be required to treat condensate prior to returning it to the HRSG. As a minimum, each source of process return should be monitored continuously for specific conductivity, pH, turbidity, or other parameters specific to the anticipated impurities.

❒ *LP DRUM CHEMISTRY*

In some configurations, each of the HRSG drums in a multi-drum configuration is fed in parallel from the hotwell. In others, the LP drum is the feedwater source for higher pressure sections and the drums are in series to one another. The chemical treatment of the LP drum varies according to the specific configuration. Where water from the LP drum is used for attemperation, it must meet the same chemical purity standards as the steam limits. Attemperation rates during startup may be very high (>10%) and may significantly affect the purity of the steam.

In cases where demineralized makeup is used and the feedwater to and blowdown from the LP drum are in parallel with those of the other drums, that is to say that water from the LP drum does not feed any other higher pressure location, the LP drum can be treated with phosphate. The use of solid alkali will mitigate two-phase FAC in the low-pressure evaporator.

In systems containing copper alloys, the LP drum should not be the source of feedwater to the higher pressure drums. Ammonia cannot be used to maintain sufficiently high pH to prevent corrosion (FAC) in the LP drum if copper is used in the steam turbine condenser or in steam host systems.

❒ *AMMONIA AND AMINE USAGE*

Many combined cycle power plant designs contain no copper alloys in the steam/water cycle. In these cases, and where superheated steam is attemperated with feedwater, ammonia or high-basicity amines are recommended to maintain the feedwater pH sufficiently alkaline to maximize formation of protective iron oxide and minimize iron transport.

For plants that contain copper alloys in either the steam condenser or in process components (in cases of a steam host), there is a variety of amines that may be considered as an alternate to ammonia, as excessive ammonia causes grooving and stress corrosion cracking in copper alloys.

In systems with mixed materials, the feedwater must also be maintained in a lower range of 8.8-9.3 pH. Air inleakage and potential organic compound degradation, including the degradation of amines and oxygen scavengers may increase the amount of amine required to maintain this pH range and increase the likelihood for corrosion of copper components.

As superheated steam temperatures approach or exceed 1000°F (540°C), owners/operators must be aware that any organic compound, naturally occurring or intentionally added for chemistry control - including amines, can degrade to form acetates, formates and other organic acids. These breakdown products may increase cation conductivity to the point where the value is higher than the recommended normal operating limits.

❒ *TOTAL ORGANIC CARBON*

Organic carbon may decompose to form acetic, formic, and other carboxylic acids, as well as carbon dioxide in the steam cycle. These anions raise cation conductivity. The rate of conversion of organic carbon to acidic species depends on many parameters.

Organic compounds may also contain other elements such as chlorine and sulfur. For example, if the water source from the plant is treated wastewater, it is often highly chlorinated and charged with halogenated organic compounds. These compounds are often non-ionic species that can slip through conventional water pretreatment systems. At elevated temperature and pressure these can breakdown into chloride and sulfate in the steam.

In particular, halogenated organic compounds in the pretreatment and demineralized water should be quantified and steps taken to reduce these to the lowest level possible.

If the cation conductivity exceeds normal values, elevated TOC should be considered as a possible cause. Even with TOC < 300 ppb, high cation conductivity in condensate or steam may require that water treatment equipment be added to remove sufficient TOC to reach acceptable cation conductivity.

Continuous monitoring for organics, (i.e. TOC), may be required on process return condensate if cation conductivity or pH measurement does not detect potential organic contamination. These limits are excluding any TOC added via organic treatment chemicals.

❐ *HP AND IP DRUM CHEMISTRY*

Steam purity requirements and the amount of carryover, mechanical and vaporous, of the evaporator water into the steam will dictate the chemistry of the IP and HP drums. The vaporous carryover is a function of the total dissolved solids and other contaminant concentrations in the drum, operating pressure of the drum and the pH of the evaporator water. The mechanical carryover is a function of the drum design and condition of the steam/water separators, the operating pressure, the drum water level control, the steam header pressure stability, the steaming rate and the magnitude of sudden surges in the steaming rate.

Conventional water-tube boilers are conservatively designed to produce steam that contains less than 0.1 to 0.2% mechanical carryover for a drum operating between 1001-2400 psig (7.0-16.6 MPa), according to American Boiler Manufacturers Association (ABMA) standards. Measured carryover is typically lower as long as the drum is operating at the design level and the separation equipment is working properly. The percent mechanical carryover from any drum that supplies steam to the turbine should be checked every six months by comparing the sodium in the drum water (grab sample) versus the sodium in the saturated steam (on-line analyzer).

Attemperation or desuperheating water provides a direct route for possible additional steam contamination. Depending on the purity of the feedwater and the amount of attemperation needed during start-up, duct burner use, or other operating conditions, the amount contributed from this source can be significant.

Species such as chlorides, sulfur compounds, and hydroxides in steam can cause corrosion of steam turbine materials. Other species such as silica and copper compounds can cause deposits and reduce turbine efficiency. There are various chemical regimes for the feedwater and drums that can be used to achieve the steam chemistry requirements listed in Tables 10 and 11. The selection of a chemical regime is a site-specific decision based on a number of factors including:

- Configuration (number of drums)
- Materials of water- and/or steam-touched equipment
- Operating pressure of HP and IP drum
- Operating Conditions (base-load, cycling, peaking)
- Balance of plant equipment

The advantages and disadvantages of common chemical treatment regimes are discussed below.

❒ *ALL-VOLATILE TREATMENT*

All-volatile treatment is only applicable to units using demineralized water (< 0.1 µS/cm specific conductivity) makeup, excellent control over feedwater purity, and continuous monitoring to ensure that feedwater and steam purity is maintained.

If the unit suffers even minor contamination while using AVT, corrosion of the HRSG tubes is likely. Also, the use of AVT presumes that tube surfaces are clean. Changing from another treatment to AVT or using AVT on an HRSG that was not chemically cleaned prior to commissioning is inadvisable.

All-volatile treatment (AVT) has a long history of successful use in conventional fossil-fired watertube boilers and is applicable to HRSGs where feedwater purity is consistent with Table 9a. In conventional boilers the treatment regime consists of the use of ammonia or volatile amine and a volatile oxygen scavenger such as hydrazine. In HRSGs, concerns about FAC typically preclude the use of oxygen scavengers during continuous operation for units with all-ferrous materials. As long as the HRSG contains only ferrous materials, the pH should be raised sufficiently to maintain a pH greater than 9.4 at 25°C in the LP drum to minimize FAC. The LP feedwater prior to the LP drum should always be maintained at a pH greater than 9.6 at 25°C.

Ammonia is the simplest volatile compound for raising the pH of the feedwater in the economizers and evaporators. Neutralizing amines have also been used but there are some disadvantages. All neutralizing amines contain carbon and, depending on system temperature and pressure, may eventually break down into ammonia, carbon dioxide, and organic acids such as acetic acid. All of these, except ammonia, will increase the cation conductivity of the feedwater and steam. The cation conductivity limits in steam were established assuming only a small contribution from organic acids or carbon dioxide. Plants that use amines may find that they have difficultly determining whether an elevated cation conductivity of the steam results from organic acids or to the presence of chloride and sulfate in the steam.

Many of the commonly used neutralizing amines have a higher preference for the liquid phase than ammonia and will condense preferentially from the steam into the first condensate, increasing the pH to protect the turbine or condenser materials. Often, a combination of two or more amines is used to cover a variety of conditions in the steam/water cycle. Proper selection and application of volatile alkalizing agents is important to reduce the rate of FAC in HRSGs.

Ammonia effectiveness at pH elevation is reduced at high temperatures because the ammonia is primarily present in molecular form, and therefore may not protect the HRSG materials. Any acid forming species, i.e. chloride, can cause corrosion in the tubing even when the sample pH at 25^{o}C indicates the drum water is alkaline if the rise in pH is strictly from ammonia. Therefore, it is strongly recommended that before choosing AVT treatment, steps be taken to ensure the consistent purity of plant feedwater. Such steps may include use of a titanium-tubed condenser and/or full-flow condensate polishing.

High pH in the feedwater from ammonia will cause ion exchange polishers in the system, including cation conductivity resin columns, to exhaust more quickly since non-ammoniated resin removes the feedwater ammonia. Resin exhaustion should be considered when setting the upper limit for feedwater pH and selecting the operating form of the resin in the condensate polisher.

❒ *PHOSPHATE TREATMENTS*

In developing phosphate treatment guidelines for HRSGs it was assumed that the HRSG would have and use duct burners. The risk of phosphate hideout and the potential for phosphate gouging are much higher when duct burners are in use. HRSGs that do not have duct burners may be operated with higher phosphate concentration or with congruent phosphate-pH control in the HP drum.

Both low-level and equilibrium phosphate treatments have been successfully used in HRSGs. Low-level phosphate treatments usually limit the range of phosphate between 2-6 ppm (mg/l) whereas equilibrium phosphate (EPT) typically maintains a lower phosphate concentration of less than 2 ppm (mg/l). Low-level phosphate treatments were designed for high-pressure fossil-fired boilers that experience or are susceptible to phosphate hideout. Hideout may be a precursor to phosphate gouging. Feedwater purity requirements for EPT-treated systems are comparable to those for AVT systems.

The most common cause of phosphate hideout for a HRSG is the operation of the duct burner. Depending on the capacity of the duct burner, different degrees of hideout are possible. Testing during duct burner operation is necessary to determine the appropriate chemistry range to use.

Using the drum pH, ammonia, and phosphate concentration, an estimate of the sodium:phosphate molar ratio can be developed from the following equation (Hull, et al.):

$$R = (1/P_t)\{K_w/H+3P_t/D+2HP_t/DK_3+H^2P_t/((DK_3)K_2) - H - A_t K_b/[(K_w/H)+K_b]\}$$

Where:

R = Sodium to phosphate molar ratio
H = Hydrogen ion concentration = 10^{-pH}
A_t = Ammonia concentration in moles/l = (ppm NH_3)/ (17,030.61)
P_t = Phosphate concentration in moles/l = (ppm PO_4)/ (94,971.4)
K_w = Dissociation constant for water at 25°C = 1.008×10^{-14}
K_b = Dissociation constant for ammonia at 25°C = 1.7742×10^{-5}
K_1 = First dissociation constant for phosphoric acid at 25°C = 7.1121×10^{-3}
K_2 = Second dissociation constant for phosphoric acid at 25°C = 6.2373×10^{-8}
K_3 = Third dissociation constant for phosphoric acid at 25°C = 4.571×10^{-13}
D = Ionization fraction = $H^3/(K_1K_2K_3) + H^2/(K_2K_3) + H/K_3 + 1$

To use the complete equation, the ammonia concentration in the HRSG must be determined by separate analysis. The above equation assumes that ammonia is used to control the feedwater pH. If high concentrations of amines are in use, the effect of the amine on the drum pH may affect the accuracy of the sodium:phosphate molar ratio. In these cases, the amine supplier should furnish the proper correction factors.

A separate equation can be used to calculate the amount of free sodium hydroxide:

ppm free NaOH = (R-3) x (ppm PO_4) x 0.42139

The minimum sodium:phosphate molar ratio (R in the above equation) recommended is 2.8, with an upper limit of 3.0 +1 ppm sodium hydroxide per the equation. This should be achieved by the addition of trisodium phosphate only. Some may advise a minimum molar ratio of 3.0. Normally trisodium phosphate is the only solid alkali chemical required. The use of caustic as a treatment chemical is not recommended with a phosphate program; however, there may be circumstances where it is required.

There are a few cooling waters that will increase the pH of the drum water if they contaminate the condensate. If this occurs, blowdown should be increased to maintain boiler water chemistry within the prescribed limits. If drum water chemistry cannot be controlled in this manner, shutdown to avoid both HRSG and steam system damage should be considered.

The selection of the phosphate concentration in high pressure HRSG's must take into consideration carryover limits and potential for phosphate hideout. Phosphate treatment is not advised for HRSG drums operating above drum pressures of 2400 psig (16.6 MPa).

If the HP drum operates above1500 psig (10.3 MPa), the use of organic polymers as iron dispersants is not recommended due to increased concerns with thermal degradation. If iron corrosion products from process return condensate are a problem, other means should be used to remove the iron prior to its reintroduction into the HRSG. When considering the use of iron-dispersing polymers in HRSGs operating between 900-1500 psig (6.3-10.3 MPa), the risk of FAC from any acid by-products should be evaluated. At less than 900 psig (6.3 MPa) the use of polymers is a common practice, however, HRSGs operating with less than 1% blowdown get little benefit from iron-dispersing polymers. Preventing iron corrosion products from entering the HRSG is **much** more effective.

❐ *GAS TURBINE INJECTION WATER*

The gas turbines/generators in a combined cycle power plant are often responsible for producing two-thirds of the total power generation. As such, their reliable operation may be considered as more critical than that of the steam turbine. Water may be injected into a gas turbine for NO_x control and/or to increase its generating capacity. This water must be of sufficient purity to ensure that significant deposits will not accumulate and corrosion will not occur in the combustion path. Deposits can critically affect heat transfer across the blades. Corrosion of the refractory coatings on the blade and the blade itself can occur if significant amounts of fluxing chemicals such as sodium and potassium are added to the gas. Potassium levels in makeup water are typically not an issue and therefore sodium is the critical parameter monitored. Table 12 shows an example of suggested limits for gas turbine NO_x control injection water.

❐ *EVAPORATIVE COOLING WATER*

Gas turbines often operate during the summer peak power generation period. One constraint on the amount of power that can be generated is the density (temperature) of the air at the turbine intake. To generate more power during hot summer temperatures, the inlet air to gas turbines is often cooled with evaporative cooling systems. Water may be sprayed directly into the inlet air stream (fogging) or cascade~~d~~ across loose media perpendicular to the air flow (evaporative) to reduce the air temperature. As with the gas turbine injection water, any corrosive or deposit-forming species in the water are a concern. An example of the suggested limits for direct injection water used for inlet air cooling is provided in Table 13. In addition, demineralized water may leach chemicals from fibrous cooling media in an evaporative system resulting in material breakdown, carryover, or loss of media strength. Some units establish the proper amount of dissolved solids in the water to prevent problems with the media, and then add demineralized water to replace water lost to evaporation. Table 14 shows an example of evaporative cooling water limits.

❒ Section 6 ❒

UPSET CONDITIONS AND COUNTERMEASURES

The first action to be taken in case of exceeding specified chemical limits is to check the sampling system for the following:

- Adequate sample flow
- Correct sample temperature
- Exhausted cation exchanger cartridge
- Out-of-calibration analyzer (oxygen, silica, pH, conductivity, sodium)

Table 5 lists some of the more typical problems, their causes and the necessary countermeasures. Use of blowdown as a corrective action should be a temporary action until the chemistry parameter is brought back into conformance. NOTE: This list is an example only and may be incomplete. Each deviation from a specified value requires careful investigation.

Table 5. Upset Conditions and Countermeasures

Out of limit condition	Possible Cause	Possible Troubleshooting Actions
High feedwater oxygen concentration (separate deaerator)	Condenser air inleakage	Verify condensate pump discharge oxygen concentration
		Check air ejector flow rate compared to design
	Poor deaerator performance	Verify oxygen concentration in deaerator outlet
		Check deaerator vent
		Check deaerator temperature and pressure
		Check deaerator internals
High feedwater cation conductivity	Condenser leak	Check for contamination. If condensate or demineralizer storage is free of contamination, increase the blowdown
		If chemistry limits for drum pH or steam chemistry cannot be maintained, shut down unit

High feedwater cation conductivity	Makeup contamination	Check makeup treatment plant operation
		Determine the source and amount of contamination and isolate makeup system
		If chemistry limits for drum pH or steam chemistry cannot be maintained, shut down unit
	Process return condensate contamination	Dump process return condensate
	Contamination by organics	Decrease TOC of feedwater. Determine source and correct
High drum water specific conductivity	Contamination entering the system or lack of blowdown	Check for contamination. If condensate storage and/or demineralized water storage is free of contamination, increase blowdown
	High treatment concentration	Decrease treatment feed rate
Low drum water specific conductivity	Excessive blowdown	Decrease blowdown flow
	Low treatment concentration	Increase treatment feed rate
Drum water pH at 25°C low but > 8.0 If drum pH at 25°C is <8.0, shut down	Contamination	Minimize superheat and reheat attemperation
	Condenser tube leak	Check for condensate storage contamination, if condensate purity is good, increase blowdown
		If drum pH or steam chemistry limits cannot be maintained, shut down unit
	Makeup contamination	Determine the source and degree of contamination and isolate
		If steam chemistry limits cannot be maintained, shut down unit
	Process return condensate contamination	Increase blowdown
		Determine the source and amount of contamination and dump the contaminated condensate

High drum water pH at 25°C (>11.5 for demineralized water systems)	High phosphate	Decrease caustic and phosphate dosing
		Increase blowdown
	Contamination	Check makeup treatment plant and condensate storage
		Check steam chemistry. If limits cannot be maintained shut down unit
High saturated steam cation conductivity	Condenser leak	Check for condenser contamination
		Check condensate storage. If purity meets limits, increase blowdown
	Makeup contamination	Determine the source and degree of contamination and isolate
		If steam chemistry limits cannot be maintained, shut down unit or bypass the steam turbine
	Process return condensate contamination	Isolate process return condensate
	Contamination by organics	Apply technologies to maximize TOC removal in pretreatment equipment
	Mechanical carryover	Verify by checking saturated steam sample for sodium concentration
		Reduce drum level and check for improvement
		Reduce steam flow by throttling the turbine
		Shut down and inspect drum internals
High silica in saturated steam	High boiler water silica concentration	Increase blowdown
	Condenser leak	Check condensate storage. If purity meets limits, increase blowdown
		Check other parameters such as cation conductivity and sodium for evidence of contamination
	Makeup contamination	Check for colloidal silica in makeup
		Check makeup treatment plant
	Process return condensate contamination	Dump contaminated condensate

High sodium in steam	Attemperator problems	Check attemperator operation
		Check attemperation source (feedwater) for contamination
	Mechanical carryover	Check steam separation and steam drum level
	Contamination	Check attemperation source (feedwater) for contamination
		If steam chemistry limits cannot be maintained shut down the unit
	Condenser leak	Check condensate storage. I If purity meets limits, increase blowdown
	Makeup contamination	Check for caustic in makeup
		Check makeup treatment plant operation
	Process return condensate contamination	Dump contaminated condensate

❒ SECTION 7 ❒

LAY-UP AND START-UP PRACTICES

Lay-up and start-up of a combined cycle power plant are particularly important as the plants are often cycled regularly to meet peak demands. Start-up is not gradual, as in a conventional fossil-fired boiler, but very sudden because the combustion turbine exhaust gases produce very rapid heating of the tubes.

Combustion turbine purge cycles that occur just prior to ignition exacerbate the situation by pushing cold air through the HRSG followed by the engine ignition and sudden temperature rise. These factors can produce condensate in superheaters that can result in thermal low-cycle fatigue. This result can be minimized with proper design and operational procedures.

Start-up practice should ensure that oxygen is less than or equal to 10 ppb in the feedwater and any other water that will be fed to the HRSG before the deaerator is operational. This stipulation applies to water in the HRSG drums and the condenser hotwell and may even extend to the condensate storage tanks in some configurations. The purity of steam supplied by auxiliary boilers to a HRSG should be the same as that of steam produced by the HRSG.

Additional information on proper lay-up practices can be found in the ASME publication “Consensus for the Lay-up of Boilers, Turbines, Turbine Condensers, and Auxiliary Equipment” (CRTD-66).

❐ SECTION 8 ❐

RECOMMENDED WATER/STEAM CHEMISTRY LIMITS FOR HRSG

There are a variety of HRSG configurations and operating pressures. For the purposes of this document two configurations have been considered: an industrial HRSG and a three-drum HRSG where the steam is used in a steam turbine to generate electrical power. These are shown in Figures 1-2. The chemical limits are always dictated by the steam purity requirements, the highest drum pressure on the HRSG, and, if applicable, by the highest pressure at the duct-fired condition.

Although the temperature of the turbine exhaust is much lower than the flue gas temperatures in an equivalent water-tube boiler, sudden heat flux changes and inefficient circulation in HRSGs, particularly during start-up, require a higher purity feedwater and a lower chemical treatment rate than would typically be associated with the respective operating pressures.

Depending on the configuration, the LP drum may be isolated from the higher-pressure drums and require its own chemistry or may be, in effect, a feedwater heater that feeds all the higher-pressure drums in the unit. In the latter case, only volatile chemicals can be used for treatment in the LP drum as water from the LP drum is often used as attemperation water for superheat and reheat. The intermediate pressure (IP) drum often receives blowdown from the high-pressure (HP) drum, therefore the IP drum chemistry is to a certain extent set by the HP drum chemistry. The HP drum chemistry is determined by its operating pressure when operating at its highest capacity.

The term “drum water” is equivalent to “boiler water” for the purposes of this document.

Tables with suggested limits can be found at the end of this document. These limits do not contain any safety factor to provide reasonable response time for an excursion.

Recommendations regarding sampling and analysis can be found in the ASME “Consensus on Operating Practices for the Sampling and Monitoring of Feedwater and Boiler Water Chemistry in Modern Industrial Boilers” (CRTD-81) and “Steam and Water Sampling, Conditioning, and Analysis in the Power Cycle” (ASME PTC 19.11-2008).

Figure 1. Sampling Points for HRSG with a Steaming Deaerator (LP Drum Water is Used to Feed Higher Pressure Parts on the HRSG)

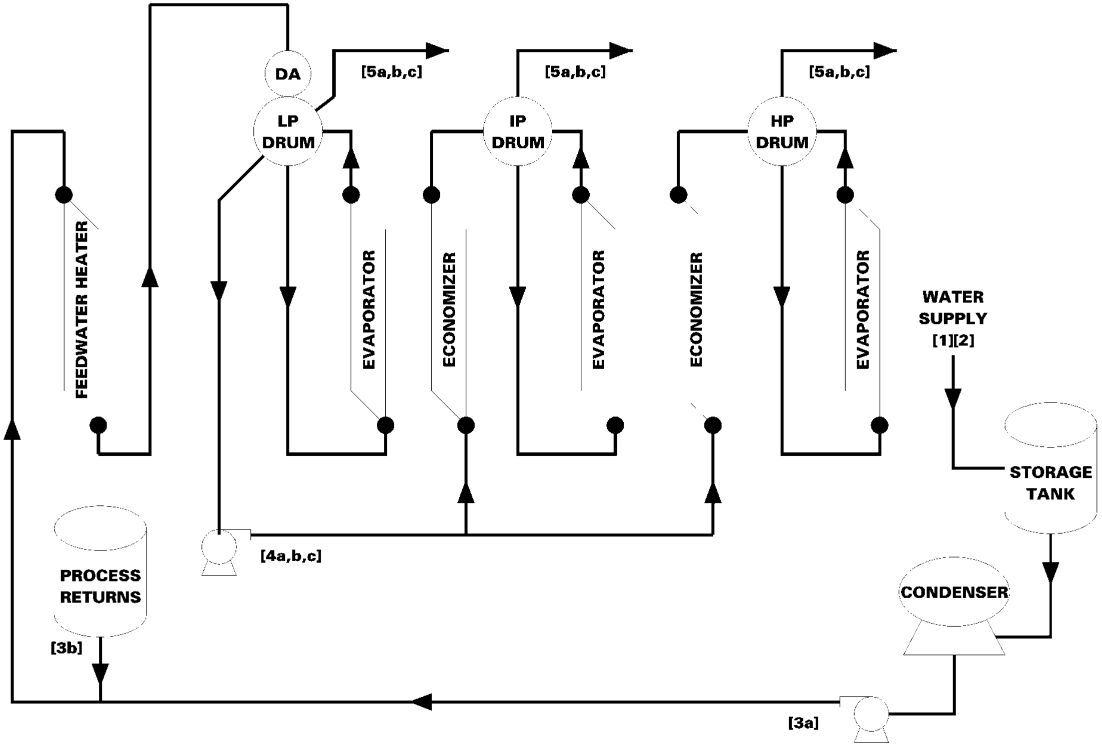

Figure 2. Sampling Points for HRSG with a Self-Contained LP Drum (LP Drum Water is not used to Feed Higher Pressure Parts on the HRSG)

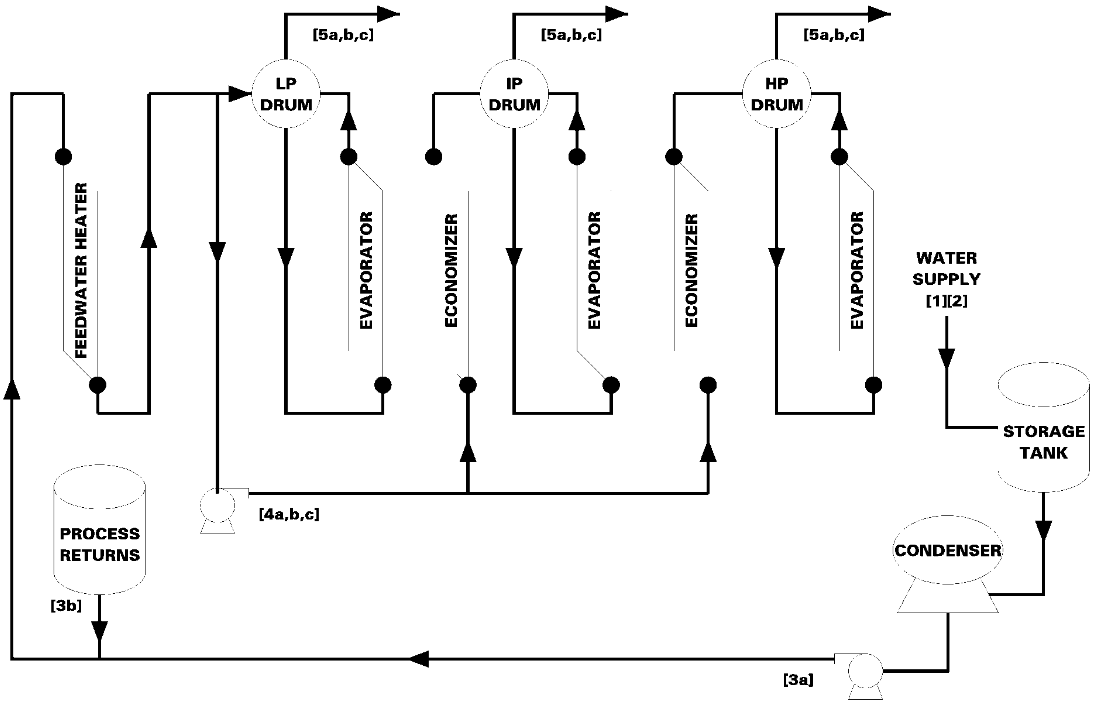

Table 6. Demineralized Water to Storage Tank

Parameter	Normal	Comments
Specific conductivity at 25°C, µS/cm	<0.1	Carbon dioxide will absorb into demineralized water upon standing and will increase the conductivity. High conductivity can be due to acid or caustic contamination
Silica as SiO_2, ppb (µg/l)	<20	Once-through HRSG require <10 ppb
Sodium as Na, ppb (µg/l)	<5	
TOC as C, ppb (µg/l)	<300	

Table 7. Soft Water to Storage Tank (1)

Parameter	Normal	Comments
Unneutralized specific conductivity at 25°C, µS/cm	<120% of incoming water conductivity	
Total hardness as $CaCO_3$, ppm (mg/l)	<0.2	Some on-line hardness analyzers measure calcium and not total hardness
(1) Water should be free of hydrogen sulfide		

Table 8a. Condensate Pump Discharge (from condensing turbine hotwell)

Parameter	Normal		Comment
Materials	Mixed	All Ferrous	Mixed metallurgy systems contain copper and iron alloys
Cation conductivity at 25°C, µS/cm	<0.2	<0.2	Assumes no contribution from treatment chemicals
pH at 25°C	8.8-9.3	9.4-10.0	Higher pH values may be required to produce a pH of 9.4 in the LP drum
Unneutralized specific conductivity at 25°C, µS/cm	Specific conductivity should be consistent with the pH (1)		
Silica as SiO_2, ppb (µg/l)	<10 (2)	<10 (2)	Limit shall be consistent with OEM purity requirements (2). Cation conductivity is the primary method for detecting inorganic contaminant inleakage but will not detect silica. Silica testing may be required for troubleshooting purposes.
Iron as Fe, ppb (µg/l)	<10	<10	
Copper as Cu, ppb (µg/l)	<3	Not Applicable	
Dissolved oxygen as O_2, ppb (µg/l)	<20	<20	
Sodium as Na, ppb (µg/l)	<5	<5	
TOC as C, ppb (µg/l)	<300	<300	Excludes contributions from treatment chemicals. Plant experience will dictate

(1) $pH=\log_{10}(SC-0.3CC)+8.57$; where SC is specific conductivity and CC is cation conductivity

(2) Refer to Table 4 or your specific OEM limits

Table 8b. Process Return Condensate (Feedwater limits for individual parameters must be met (1))

Parameter	Normal		Comment
Materials	Mixed	All- ferrous	Mixed metallurgy systems contain copper and iron alloys
Cation conductivity at 25°C, µS/cm	<0.4	<0.4	For demineralized makeup, assumes no contribution from treatment chemicals
Sodium as Na, ppb (µg/l)	<5	<5	For demineralized makeup
pH at 25°C	8.8-9.3	9.4-10.0	
Unneutralized specific conductivity at 25°C, µS/cm	Normal HRSG feedwater +5 µS/cm (for soft water makeup)		
Silica as SiO_2, ppb (µg/l)	<10 (2)	<10 (2)	Limit shall be consistent with OEM purity requirements (2). Cation conductivity is the primary method for detecting inorganic contaminant inleakage but will not detect silica. Silica testing may be required for troubleshooting purposes.
Turbidity, NTU	<1	<1	Provides on-line trending for particulate excursions such as iron, but is not a replacement for specific analyses
Iron (3) as Fe, ppb (µg/l)	<20	<20	
Copper as Cu, ppb (µg/l)	<10	Not Applicable	
TOC as C, ppb (µg/l)	<300	<300	Excludes contributions from treatment chemicals

(1) The above values represent typical contaminant values and will vary by application. Ultimately, feedwater limits for individual parameters must be met. Condensate with high contaminant levels or high percentage condensate return may require some form of polishing to be acceptable as feedwater. Actual acceptable values must be determined on an individual site basis.

(2) Refer to Table 4 or your specific OEM limits

(3) Low pH of the return condensate increases iron contamination in the HRSG. Additional steps may be required to ensure an elevated condensate return pH.

Table 9a. Feedwater (Demineralized Makeup)

Parameter	Mixed	All-ferrous	Comments
Dissolved oxygen (1) as O_2, ppb (µg/l)	<10	2-10	Mixed system presumes oxygen scavenger is added.
ORP (1), mV	-100 to -350	0 to 50	Optimize for minimal iron and copper pickup. Values based on saturated KCl, Ag/AgCl-reference electrode at 25°C at the feed pump discharge
Total iron as Fe, ppb (µg/l)	<10	<10	As low as possible
Total copper as Cu, ppb (µg/l)	<3	<3	As low as possible
TOC as C, ppb (µg/l)	<300	<300	
pH at 25°C	8.8-9.3	9.6-10.1 (2)	Specific conductivity should be consistent with the pH (3)
Cation conductivity at 25°C, µS/cm	<0.2	<0.2	Degassed cation conductivity may be used for diagnostic purposes.
Silica as SiO_2, ppb (µg/l)	<10 (4)	<10 (4)	Limit shall be consistent with OEM purity requirements (4). Cation conductivity is the primary method for detecting inorganic contaminant inleakage but will not detect silica. Silica testing may be required for troubleshooting purposes.

(1) Critical in this area is the control of oxidation-reduction potential and pH. Excessive use of chemical oxygen scavengers can create an environment where flow accelerated corrosion can occur
(2) For units operating with AVT chemistry, the feedwater pH must be greater than 9.4 to obtain an LP drum pH >9.4 to minimize FAC
(3) $pH=\log_{10}(SC-0.3CC)+8.57$; where SC is specific conductivity and CC is cation conductivity
(4) Refer to Table 4 or your specific OEM limits

Table 9b. Feedwater for HRSGs using Softened Water

Drum Operating Pressure, psig (MPa)	psig 0-300 (MPa 0-2.07)	301-450 (2.08-3.10)	451-600 (3.11-4.14)	601-750 (4.15-5.17)	751-900 (5.18-6.21)	Comments
Dissolved oxygen ppm (mg/l)	< 0.007	< 0.007	<0.007	<0.007	<0.007	
Total iron as Fe, ppm (mg/l)	≤0.1	≤0.05	≤0.03	≤0.025	≤0.02	
Total copper as Cu, ppm (mg/l)	≤0.05	≤0.025	≤0.02	≤0.02	≤0.015	
Total hardness as $CaCO_3$, ppm (mg/l)	≤0.3	≤0.3	≤0.2	≤0.2	≤0.1	
pH at 25°C	8.3-10.0	8.3-10.0	8.3-10.0	8.3-10.0	8.3-10.0	
TOC as C, ppm (mg/l)	<1	<1	<0.5	<0.5	<0.5	Excludes added treatment chemicals. Carryover or foaming may require lower TOC values

Table 10a. Drum Water for Multi-Drum HRSG using Demineralized Water and Phosphate-based Treatment (1, 2)

Parameter	Drum pressure, psig (MPa)					Comments
	<75 (0.52 MPa)	76-300 (0.52-2.1 MPa)	301-900 (2.1-6.2 MPa)	901-1550 (6.2-10.7 MPa)	1551-2400 (13.8-16.6 MPa)	For units that increase operating pressure when they are duct-fired, use limits associated with >1500 psig
pH at 25°C (3)	9.8-10.5	>9.0 and phosphate feed consistent with residual found in drum				The HRSG must come off line in an orderly manner as quickly as possible if the pH cannot be maintained above 8
Phosphate (4) as PO_4, ppm (mg/l)	10-20	5-20	2-15	2-10	0.2-3	See Section 5 for further discussion of sodium:phosphate molar ratio

Minimum $Na:PO_4$ molar ratio	2.8					
Maximum free caustic (5) as NaOH, ppm (mg/l)	8	4	2	1		1 ppm maximum NaOH (as NaOH) conforms to phosphate continuum at all pressure levels.
Unneutralized specific conductivity at 25°C, µS/cm	<140	<120	<75	<50	<30	Determine by operating experience.
Silica as SiO_2, ppm (mg/l)	Per silica curves shown in Figures 3-4 (6)					

(1) For cases where the LP drum does feed other drums, the chemistry of the LP drum should be the same as the feedwater chemistry. Recommendations assume that the LP drum is on a separate steam circuit from higher pressure drums i.e., LP drum does not feed the IP or HP drum. If LP drum feeds attemperation—no phosphate should be added.

(2) Phosphate treatment is not recommended for units operating above 2400 psig (16.6 MPa)

(3) The pH at 25°C of the drum should always be greater than 9.0 after the effect of ammonia is accounted for. See text for calculation.

(4) Phosphate residual should be adjusted to prevent hideout.

(5) Lower caustic levels may be required for units with severe concentrating mechanisms or mechanical carryover. Captive alkalinity requires $Na:PO_4$ molar ratios less than 3.0. See phosphate treatment discussion for exceptions to the recommended treatment ratio.

(6) Calculated from formulas presented by Beardwood, E. S., "Silica in Steam Generating Systems," Proceedings of the International Water Conference, 2008, Paper No. IWC-08-12.

Table 10b. Drum Water for Multi-Drum HRSGs (all-ferrous systems) using All-Volatile Treatment (AVT) (1)

Parameter, Units	LP Drum, if LP Drum Feeds Other Drums	HP and IP Drums, All Configurations and LP Drum that Does Not Feed Other Drums		
		Normal Values (Cation Conductivity <1 µS/cm)	Limits if IP and HP drum cation conductivity is >1 µS/cm	
Drum pressure, psig (MPa)	All pressures, all drums	All pressures, all drums	<1800 psig (<12.4 MPa)	1800-2400 psig (12.4-16.5 MPa)
Cation conductivity at 25°C, µS/cm	Approximately same as feedwater	<1	<5	<3
pH at 25°C (minimum)	Approximately same as feedwater (specific conductivity and pH can be lower due to ammonia loss in the steam. Minimum pH 9.4)	Consistent with drum pH and ammonia/amine feed	Consistent with ammonia/amine volatility. Usually 0.1-0.2 pH units less than the feedwater pH, preferably at economizer outlet	
Unneutralized specific conductivity at 25°C, µS/cm			Consistent with drum pH and ammonia/amine levels	
Silica as SiO_2, ppb (µg/l)	Approximately same as feedwater	Per silica curves shown in Figures 3-4 (2)	Per silica curves shown in Figures 3-4 (2)	Per silica curves shown in Figures 3-4 (2)

(1) For cases where the LP drum does feed other drums, the chemistry of the LP drum should be the same as the feedwater chemistry. The use of AVT on an isolated LP drum is NOT recommended. In systems containing copper alloys, the LP drum should not be the source of feedwater to the higher-pressure drums if the unit is operating on AVT. Consistent high-purity feedwater is critical when using this treatment. Condensate polishers are highly recommended.

(2) Calculated from formulas presented by Beardwood, E. S., "Silica in Steam Generating Systems," Proceedings of the International Water Conference, 2008, Paper No. IWC-08-12.

Figure 3. HRSG Drum Water Silica Limits to Produce 10 ppb Silica (as SiO_2) in Steam

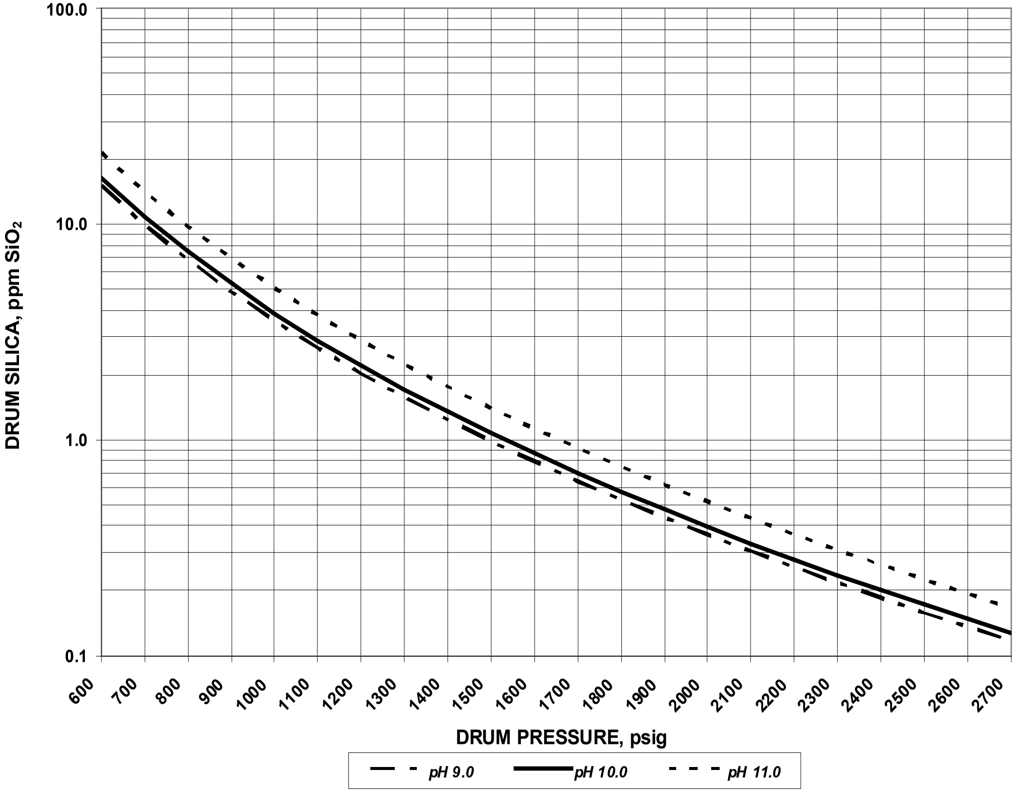

Figure 4. HRSG Drum Water Silica Limits to Produce 20 ppb Silica (as SiO_2) in Steam

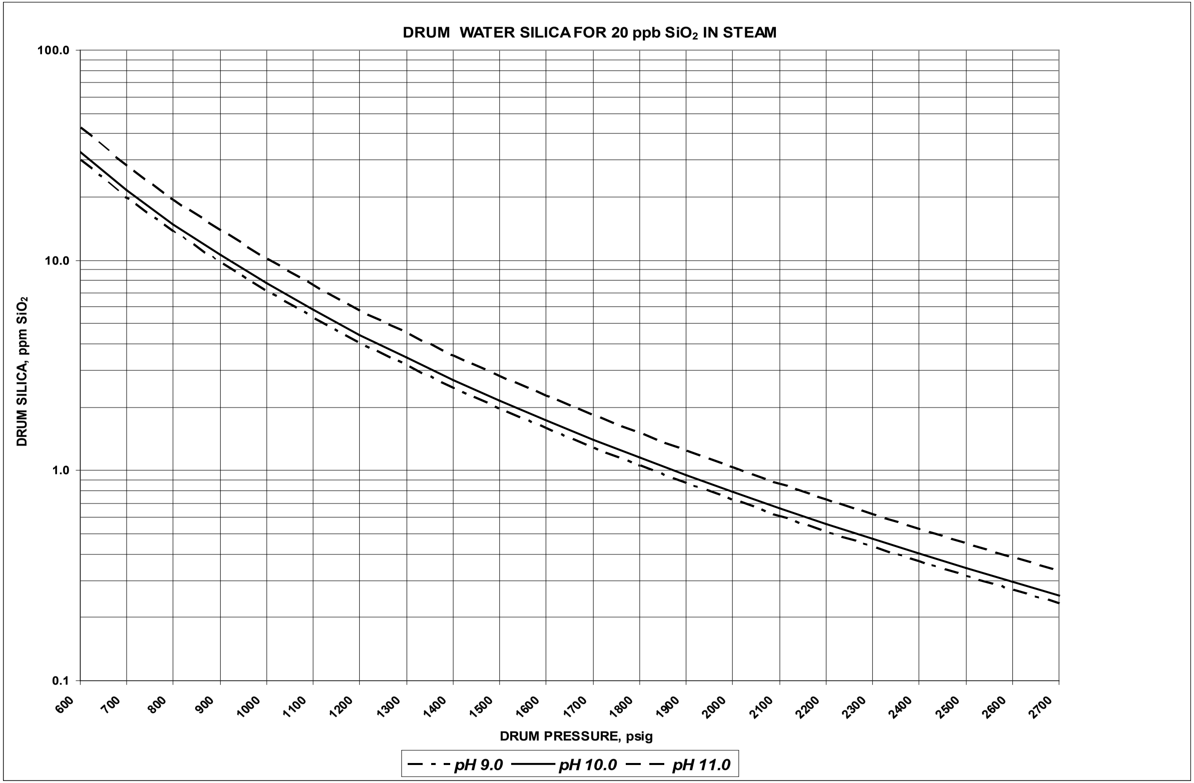

Table 11. HRSG Drum Chemistry Limits for Units using Softened Water and Without Condensing Turbines

Drum Operating Pressure	psig 0-300 (MPa) (0-2.07)	301-450 (2.08-3.10)	451-600 (3.11-4.14)	601-750 (4.15-5.17)	751-900 (5.18-6.21)
Silica as SiO_2, ppm (mg/l)	≤150	≤90	≤40	≤30	≤20
Total alkalinity (2) as $CaCO_3$, ppm (mg/l)	<700	<600	<500	<200	<150
Free OH alkalinity (1) as $CaCO_3$, ppm (mg/l)	Not Specified	Not Specified	Not Specified	Not Specified	Not Specified
Specific conductivity (3) at 25°C, µS/cm	5400-1100	4600-900	3800-800	1500-300	1200-200
Total dissolved solids in steam (4,5,6), ppm (mg/l)	1.0-0.2	1.0-0.2	1.0-0.2	0.5-0.1	0.5-0.1

(1) Minimum hydroxide alkalinity concentrations in boilers below 900 psig (6.21 MPa) must be individually specified by a qualified water treatment consultant with regard to silica solubility and other components of internal treatment.

(2) Maximum total alkalinity consistent with acceptable steam purity. If necessary, should override conductivity as blowdown control parameter.

(3) Maximum values are often not achievable without exceeding maximum total alkalinity values, especially in boilers below 900 psig (6.21 MPa) with >20% makeup of water whose total alkalinity is >20% of total dissolved solids (TDS) naturally or after pretreatment by sodium cycle ion exchange softening. Actual permissible conductivity values to achieve any desired steam purity must be established for each case by careful steam purity measurements. Relationship between conductivity and steam purity is affected by too many variables to allow its reduction to a simple list of tabulated values.

(4) Achievable steam purity depends on many variables, including Evaporator water total alkalinity and specific conductivity as well as design of steam drum internals and operating conditions [Note (3)]. Since HRSGs require a high degree of steam purity for protection of the superheaters, more stringent steam purity requirements such as process steam restrictions on individual chemical species or restrictions more stringent than 0.1 ppm (mg/l) TDS turbine steam purity must be addressed specifically.

(5) As a general rule, the requirements for attemperation spray water quality are the same as those for steam purity. In some cases boiler feedwater is suitable; however, frequently additional purification is required. In all cases the spray water should be obtained from a source that is free of deposit forming and corrosive chemicals such as sodium hydroxide, sodium sulfite, sodium phosphate, iron, and copper. The suggested limits for spray water quality are <30 ppb (µg/l) TDS maximum, <10 ppb (µg/l) sodium as Na maximum, <20 ppb (µg/l) silica as SiO_2 maximum, and essentially oxygen free.

(6) TDS expressed as ppm (mg/l) in steam is proportional to TDS expressed as specific conductivity in the boiler water in each pressure range. For example, 5400 µS/cm in the boiler water is expected to produce 1 ppm (mg/l) TDS in the steam and 1100 µS/cm in the boiler water is expected to produce 0.2 ppm (mg/l) TDS in the steam for boilers operating at 0-300 psig.

Table 12. Example of Gas Turbine Injection Water for NO_x reduction in combustion section (1)

Parameter	Normal
Unneutralized specific conductivity at 25°C, µS/cm	0.5
Cation conductivity at 25°C, µS/cm	<0.5
Silica as SiO_2, ppb (µg/l)	<100
Na + K, ppb (µg/l)	<20
Calcium as Ca, ppb (µg/l)	400
Chloride as Cl, ppb (µg/l)	250
Fe + Cu, ppb (µg/l)	10
(1) Water must contain no suspended solids	

Table 13. Example of Direct Injection Fogging Water (1)

Parameter	Normal	Comments
Cation conductivity, µS/cm	<0.25	If higher cation conductivity is experienced, degassed cation conductivity values can be used. Makeup tank specification must also be met.
Silica as SiO_2, ppb (µg/l)	≤20	
Sodium as Na, ppb (µg/l)	<10	
(1) Water must contain no suspended solids		

Table 14. Example of Evaporative Cooling Water with Fibrous Fill (1)

Parameter	Normal
Calcium as $CaCO_3$, ppm (mg/l)	50-100
Total alkalinity as $CaCO_3$, ppm (mg/l)	50-100
Chloride as Cl, ppm (mg/l)	<50
Silica as SiO_2, ppm (mg/l)	<25
Total iron as Fe, ppm (mg/l)	<0.2
Total petroleum hydrocarbons as hexane extractables, ppm (mg/l)	<2
Total dissolved solids, ppm (mg/l)	30-500
Suspended solids, ppm (mg/l)	<5
pH at 25°C	7.0-8.5
(1) Other fills may have different water requirements. See manufacturers' recommendations.	

GLOSSARY OF TERMS

All-volatile treatment program (AVT) – A treatment program in which all of the treatment components are fully volatile.

Cascading blowdown - Cascading blowdown generally refers to the process in which the highest-pressure drum continuous blowdown is directed to a lower-pressure steam drum to improve cycle efficiency.

Cation conductivity – The conductivity of a sample after passing it through an acid- form strong acid cation resin column, whereby all cations have been replaced by hydrogen ions.

Combined cycle – A combined cycle is any combination of a gas turbine, steam generator (or other heat recovery equipment), and steam turbine used to improve cycle efficiency in the power generation process.

Combustion turbine (CT) – Gas turbine. A turbine that uses the products of combustion to spin the turbine.

Combustion turbine steam power augmentation – The practice of injecting steam to increase the mass flow through the combustion turbine.

Cycling service – Operation at variable load.

Degassed cation conductivity – Degassed cation conductivity either heats the sample to boiling or purges the sample with nitrogen prior to the measurement of cation conductivity, thereby driving off gases and other volatile components.

Dry running condition – Condition of running without water in the tubing of once- through steam generators, especially during start-up.

Duct burner – A supplemental burner located within the gas turbine exhaust used to increase exhaust temperature and the amount of steam which can be produced by the heat recovery steam generator.

Equilibrium phosphate treatment (EPT) – A phosphate-pH control treatment program that typically maintains a phosphate concentration <2 ppm (mg/l).

Evaporative cooling – The practice of cascading water across loose media perpendicular to the airflow to reduce the air temperature. Used to cool combustion turbine inlet air.

Flow accelerated corrosion (FAC) - A process whereby the normally protective oxide surface dissolves into a moving fluid. Metal loss occurs by the interaction of electrochemical and physical effects. In the case of carbon steels, this occurs under very specific, well-defined conditions. When the rate of oxide growth is unable to keep up with the metal dissolution rate, then rapid corrosion rates can ensue. The phenomenon typically occurs in areas of high local flow turbulence.

Fluxing chemical – A chemical that removes surface metal oxides.

Grab sample – A grab sample is a sample collected over a single, relatively short, interval of time.

Heat recovery steam generator (HRSG) – A steam generator that sits in the gas turbine exhaust and is designed to recover the thermal energy remaining after the gas turbine.

Hideout – Apparent loss of boiler water phosphate in high-pressure water-tube boilers operating under high load conditions. The salts reappear when the load is reduced.

Inlet fogging – The practice of spraying water directly into the turbine inlet air stream.

Integral deaerator – A deaerator that sits on top of the low-pressure drum and uses its drum for storage.

Low-level phosphate treatment – A phosphate-pH control treatment program that usually operates with a range of phosphate between 2-6 ppm (mg/l).

Once-through steam generating units (OTSGs) –The water is pumped into the unit as a subcooled liquid, passes over the heating surfaces, and is converted to steam as it absorbs the heat. There is no recirculation of the water within the unit and no conventional drum for the separation of water and steam. Water flows sequentially through the economizer, evaporator and superheater.

Oxygenated treatment program (OT) - A treatment program that uses oxygenated high-purity water to minimize corrosion and/or flow assisted corrosion in the feedwater train. It can only be used in all-ferrous systems with feedwater cation conductivity ≤ 0.15 µS/cm.

Mixed metallurgy - Plants with a mixture of ferrous and copper-bearing alloys in the steam/water cycle.

Phosphate Gouging – The dissolution of carbon steel by localized high concentrations of mono- or disodium phosphate to form maricite ($NaFePO_4$) and other sodium iron phosphate compounds. Crusty alternating black-and-white layered deposits may remain with knife-edge-like surfaces in the gouged area. Corrosion also requires a phosphate concentrating mechanism, such as steam blanketing or boiling within porous deposits, and buildup of a thermal barrier from the boiler water.

Simple cycle gas turbine – A combustion gas turbine without a heat recovery steam generator.

Steam host – A user of the steam produced by a combined cycle system.

Steam purity – Steam purity is an expression of the quantity of non-water components contained in the steam. These components can be dissolved in the steam, dissolved in water droplets entrained in the steam, or carried as discrete solid particles with the steam.

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