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Technical Guidance Document: Steam Purity for Turbine Operation

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This technical guidance document considers steam turbines from power plants using fossil, combined cycle, nuclear, alternative and geothermal energy, including turbines in industrial applications. It is emphasized that this is an IAPWS technical guidance document and that, depending on local requirements, the normal or target values will need to be customized for each case, depending on the actual conditions of operation, the type of generation and use of the steam, and the power cycle chemistry.

Further information about this technical guidance document and other documents issued by IAPWS can be obtained from the Executive Secretary of IAPWS or from http://www.iapws.org.

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1 Nomenclature and Definitions

Term	Alternative or Acronym	Definition
All-volatile Treatment	AVT AVT(R) AVT(O)	Conditioning regime in which only volatile alkalizing agents are added to the feedwater (commonly ammonia, but volatile amines may also be employed) May be either: Reducing conditions (added reducing agent) or Oxidizing conditions (without reducing agent)
Attemperator		Device for controlling superheater and reheater outlet temperature by spraying feedwater (or condensate or degassed demineralized water) into steam
Condensate		Water that derives from condensation of steam after expansion in a steam turbine and passage through a condenser or process heat exchanger
Conductivity	Specific Conductivity Direct Conductivity	Electrical conductivity of the water sample as measured directly without any treatment[1]
Conductivity after cation exchange	CACE Cation Conductivity Acid Conductivity	Conductivity of a water sample after passage through a strongly acidic cation exchanger in the hydrogen form
Caustic Treatment	CT Hydroxide Dosing	Involves addition of NaOH to the boiler or HRSG evaporator
Corrosion Fatigue	CF	Mechanical degradation of a material under the combined action of corrosion and cyclic loading
Degassed conductivity after cation exchange	Degassed Cation Conductivity	Conductivity after cation exchange of a sample from which volatile weak acids (predominantly carbonic acid) have been stripped
Drum boiler or HRSG (drum-type)		Boiler in which steam (generated in heated evaporator tubes) is separated from water in an unheated horizontal pressure vessel (drum). The liquid phase is recirculated to the evaporator.
Feedwater		Water that is pumped into a boiler or HRSG to balance the steam production

Term	**Alternative or Acronym**	**Definition**
Flow-accelerated Corrosion	FAC	In this document it is understood as accelerated chemical dissolution of magnetite on the surface of carbon steel components as a result of flow
Heat Recovery Steam Generator	HRSG	Steam generator using heat transfer from the exhaust gas of a combustion (gas) turbine
High Cycle Fatigue	HCF	Cracking induced by frequent reversals of stress such as vibration of turbine blades
Ion Chromatography	IC	An analytical technique to analyze for cations and anions in water
Once-through boiler or HRSG		Boiler in which output steam is generated from input water by complete evaporation. There is no recirculation of boiler water.
Oxygenated Treatment	OT	Conditioning regime in which oxygen and ammonia are added to the feedwater
Parts per billion Parts per million	ppb, µg/kg ppm, mg/kg	In this document, computed as mass fraction of a constituent in steam or in water (mass of constituent per total mass)
Phase-transition Zone	PTZ	Region in low pressure steam turbine where liquid droplets begin to form from the steam
Pitting		Extremely localized corrosion that leads to the creation of holes in the metal
Phosphate Treatment	PT	Conditioning regime for drum boilers in which alkalinity is achieved by dosing the boiler water with tri-sodium phosphate
Stress Corrosion Cracking	SCC	A cracking mechanism that occurs in the steam turbine phase transition zone.
Swallowing capacity	Flow passing ability	A measure of the volumetric capacity of the turbine to accept a steam flow, usually referred to the maximum possible steam flow at nominal pressure and temperature.
Tri-sodium phosphate	TSP	Alkalizing boiler water treatment chemical

2 Introduction: Purpose of Document and How to Use it

The purpose of this document is to provide guidance on the development of steam purity limits to assist operators of a broader suite of generating plants in minimizing equipment damage and loss of efficiency, and in maximizing plant reliability.

The guidance document can form the basis of, but should not restrict, other derivative guidelines around the world.

IAPWS has issued a series of Technical Guidance Documents for the steam cycle chemistry control of conventional fossil and combined cycle plants.[2,3,4,5] The volatile treatment and phosphate/caustic documents include limits for steam purity. The purpose of this document is to provide further guidance on the development of steam purity limits to assist operators of a broader suite of generating plants in minimizing equipment damage and loss of efficiency, and in maximizing plant reliability. To avoid the major types of damage in the steam turbines, equal emphasis must be given to the operating as well as to startup and shutdown environments, and these are discussed within this document. The guidance can be used directly by chemists and plant operators, and to develop international, national, company and manufacturer's guidelines. It should be noted that the guidance for feedwater and boiler treatments of conventional and combined cycle/HRSG plants have been published in other IAPWS Technical Guidance Documents[4,5] and the Normal/Target values for feedwater and boiler water remain the same.

The primary purposes of this document are to: a) highlight the problems which can exist in steam turbines, b) indicate how these problems occur and can be avoided, c) provide a set of normal steam purity limits that will provide optimum protection for power plants using fossil, nuclear, alternative and geothermal energy, including turbines in industrial applications, and d) provide sufficient discussion that the reader can customize these normal values to actual plant configurations.

The IAPWS experiences with steam purity are covered within this document, but a number of initial general principles and comments are delineated here:

a) The success of any steam purity guidance and limits ultimately depends on the operating experience and the lack of any serious failures, damage and deposits. Thus the guidance must be linked closely with comprehensive inspections during shutdown periods. Deposit samples should be carefully taken from each turbine stage, and analysis results should include elemental, compound and metallurgical assessments.

b) It is important to note the locations and topography of deposits when they are removed. In the low pressure (LP) turbine it is important to note both the stage in relation to the Mollier diagram for expansion and the locations on the blade profile.

Any signs of pitting should also be recorded. The locations of deposits in high pressure (HP) and intermediate pressure (IP) sections should also be noted carefully.

c) For drum type units, it is of paramount importance that carryover is measured on a frequent basis according to the IAPWS Technical Guidance Document.[2] This is particularly important when phosphate and NaOH alkalizing chemicals are added to the boiler/HRSG evaporator water, because elevated carryover can be a major source of corrosive impurities in the steam. Carryover is a function of drum pressure and therefore is more important at high steam pressures.[2]

d) Operators of all units must recognize that attemperation water injected directly into the steam is often a source of impurities, including oxides/hydroxides from the feedwater system.

e) The IAPWS solid alkali Guidance Document[5] is based on more than 20 years of excellent experience worldwide using tri-sodium phosphate and NaOH. Use of PT and CT chemistries outside the dosing limits for phosphate and NaOH additions will require careful review and modification of the suggested steam purity limits presented in this document

f) Plant operators must have knowledge of every chemical added to the cycle to ensure that the correct steam purity limits are selected and applied. The effects of proprietary chemicals of undisclosed composition and of their decomposition products must be known.

The development of operating steam purity guidance requires several steps. The starting point in this document is Section 5.1, which contains the Tables of Normal/Target chemistry limits. Customization to specific plant conditions or plant types (industrial, geothermal, nuclear etc.) is done within Section 6.

It is emphasized that this is an IAPWS Technical Guidance Document representing the cumulative experience of IAPWS PCC Working Group members, and as such should be regarded as guidance for operating cycle chemistry limits for plants under stable operating conditions. This guidance is customizable to units that cycle and those that have extensive shutdown periods. This guidance document can form the basis of, but should not restrict, other derivative guidelines around the world.

Experience has indicated that the Normal/Target values in Section 5.1 will provide good reliability and availability if they are customized for each plant to account for actual conditions of operation, the equipment installed, the materials used at different locations in the cycle, the chemical treatments, and the condenser cooling media. Customization is accomplished in two steps. The first step is to develop Action and Shutdown Levels, which require the plant operator or chemist to take some avoiding or corrective action. The second step customizes the tables to specific unit conditions, materials, chemistry, and possible damage mechanisms following the roadmap approach in Section 6.

It is further emphasized that these guidance values should not be considered as manufacturer's guarantees. Each manufacturer should provide a set of target values representing the plant as designed, and these may be slightly different than the operating guidance provided in this document.

Throughout this document, conductivity limits are provided in units of µS/cm. It is recognized that conductivity units of mS/m are preferred in the SI system; this document uses µS/cm to be consistent with the most common industrial practice worldwide. All conductivities and pH values in this document refer to water samples cooled to 25 °C.

3 Background

Impurities in the steam may cause deposits and corrosion in steam turbines that adversely affect their operation. These problems can usually be avoided by following the guidance in this document.

The three most important corrosion-related failure mechanisms in any low pressure steam turbine are pitting, corrosion fatigue and stress corrosion cracking. The local steam environment determines whether these damage mechanisms occur on blade and disk surfaces. The phase transition zone (PTZ), where the expansion and cooling of the steam leads to condensation, is particularly important. A number of processes that take place in this zone, such as precipitation of chemical compounds from superheated steam, deposition, evaporation, and drying of liquid films on hot surfaces, lead to the formation of potentially corrosive surface deposits. Understanding the processes of transport, droplet nucleation, the formation of liquid films on blade surfaces, and concentration of impurities is vital to understanding how to avoid corrosion-related damage, and to improve unit efficiency/capacity.

Over the last 20 years, the understanding of the driving force behind these damage mechanisms has changed. About 30 years ago, major research concluded that turbine corrosion mechanisms were driven by high oxygen levels in concentrated solutions containing extreme levels (up to almost 30%) of chloride, sulfate, and hydroxide.

Recent improved understanding of the turbine environment has identified the following as significant factors relevant to turbine corrosion:

- The dynamic environment during turbine operation. These are the local conditions formed by the condensation of steam as it expands through the PTZ of the turbine, and by the deposition of salts, oxides and other contaminants directly onto steam path surfaces. It has now been shown that there is no oxygen in the liquid films during operation (i.e., when the damaging stress is applied).
- The environment produced during shutdown. These are the conditions that occur during unprotected shutdown when oxygenated moist/liquid films form on steam path surfaces as a result of hygroscopic effects. These films are directly caused by inadequate shutdown practices adopted by the turbine operator. They can lead to pitting, which is most often the precursor to the corrosion mechanisms.

- Steam purity and shutdown conditions are only two of the parameters that lead to the corrosion damage. Adequate materials properties (composition, structure, internal stresses, etc.) and design (temperature, stresses, crevices, etc.) also play essential roles.

Thus, if adequate layup protection (dehumidified air) is not guaranteed, serious corrosion damage may occur even with the best operating chemistry, materials, design, and with only few major deposits. It is recognized that pitting can possibly also initiate during operation in crevice areas such as blade attachments.

The purity of turbine steam controls most corrosion processes and is vital to plant reliability. The goals of developing steam purity guidance are to minimize equipment damage and loss of efficiency, and to maximize reliability. Additionally, the recommendations must be practically achievable and incorporate targets that can be measured by existing monitoring devices.

3.1 Chemical Environment in the Steam Turbine

3.1.1 Path of Impurities into the Steam

Impurities can enter the steam by the following processes:

- Carryover of boiler water
- Volatility in evaporating boiler water
- Injection of feedwater into the superheater or reheater for attemperation

3.1.2 Nucleation of Early Condensate Droplets

As superheated steam enters a fossil or combined cycle LP turbine and expands, it approaches and crosses the saturation line where droplets of moisture are nucleated heterogeneously on ions (Figure 1). In other plants covered in this IAPWS document (nuclear, industrial, geothermal), the saturation line may be not be in the LP turbine. Numerous investigations of these “first (or early) condensate” droplets have given a good understanding of their nature and effects. They are typically about 0.1 µm in diameter. They concentrate ionic impurities, which are usually present in low concentrations in superheated steam, by factors of about 150-200.[6,7] When they concentrate anionic impurities, early condensate droplets have a reduced pH.

Another fact about the droplets that is crucial to understanding the mechanisms of PTZ failure is that they contain low levels of dissolved oxygen (< 1 µg/kg). This low oxygen in the early condensate is due to partitioning of oxygen to the steam phase. This is true for units operating on AVT(R) and for units operating on oxygenated treatment with well over 150 µg/kg of oxygen in the steam

Formation of the droplets is associated with a high electrostatic charge which has been found to be a function of the operating chemistry on the unit.[8,9]

As the expansion proceeds through the turbine, the impurity concentrations are diluted as the droplets add moisture and grow. For drum and once-through/supercritical units, at the exit of the turbine there is about 7-11 % of moisture depending on the efficiency of the turbine and cycle. In other plants included in this IAPWS document, the moisture percentage will be different, but should be known. After the last turbine stage, this mixture usually flows to a condenser where the associated sub-cooling causes the remaining vapor to nucleate and condense homogeneously. In industrial plants this mixture might provide process steam.

3.1.3 Formation of Liquid Films on PTZ Surfaces

Liquid films form on the steam turbine materials as the steam flows through the PTZ. These films can be up to 100-120 μm in thickness,[6] and form either by collision of the liquid droplets or by heterogeneous nucleation on the blade/disk material itself. They may be subject to reheating due to heat transfer across a turbine disk or shaft and result in concentration of ionic impurities by up to a factor of about 1000 times the levels found in bulk steam. In the case of anionic impurities, the pH of the liquid film may have a low or even acidic pH.

It is important to note that the levels of dissolved oxygen in these liquid films are very low, usually < 1 μg/kg, even when the oxygen levels in the steam are in the hundreds of μg/kg. The low oxygen concentration limits the corrosiveness of anions in the liquid films.

It should also be mentioned that these liquid films flow off the surfaces, break up, and form droplets up to 100 μm in size which is considerably larger than the nucleated “early condensate” droplets discussed in the previous section. These larger droplets not only cause the erosion of blades in downstream turbine stages, but they also can cause liquid impingement damage (or low temperature FAC) in water- and air-cooled condensers. The overall flow of the two-phase liquid out of the turbine consists of a large fraction (>90%) of very small droplets (on the order of 0.1 μm) and a smaller fraction (< 10%) of the large droplets (up to 100 μm).

These liquid films play an important role in PTZ failure mechanisms in that both corrosion fatigue and stress corrosion cracking require an aqueous electrochemical solution for crack growth to occur during operation. The liquid films that span the PTZ form tortuous paths across steam path surfaces that are unique to each machine. Thus a number of blade and diaphragm stages in the PTZ are always “touched” by these liquid films, and unless measurements are made with laser probes, the film profiles can only be modeled or inferred. Sometimes observations of “stains” and “water lines” on PTZ surfaces during inspections can provide information about the operational liquid films.[7] The film profiles certainly include rotor blades and attachment points where cracking and damage take place in the PTZ. From the standpoint of blade design, it is important to consider wetness profiles so that an approximation can be made of the moisture percentage at potential damage locations. The lower the concentration of moisture, the more concentrated are the harmful anions.

It should be mentioned that liquid films are not restricted to the PTZ. Solutions with an elevated boiling point, such as concentrated solutions of NaOH, may form corrosive liquid films in the HP or the IP turbine, well within the superheat area of the Mollier diagram.[7] When the turbine is shut down, these NaOH films turn white when they are carbonated by exposure to air. Such films and deposits are usually harmless, but are an important indicator of carryover and poor operation with NaOH or phosphate treatments. For susceptible materials however, hot NaOH solutions induce severe corrosion even in the absence of oxygen (Section 3.2.2).

3.1.4 Influence of Steam Purity on Early Condensate Nucleation and Liquid Films

It is important to emphasize that the formation of droplets and liquid films are natural processes governed by the thermodynamics of steam expansion. The concentration mechanisms discussed in this Section occur in all types of steam turbines in generating situations included in this IAPWS Technical Guidance Document, even on fossil and combined cycle units with world-class cycle chemistries. In all cases, anions entering a turbine with steam will concentrate in droplets and liquid films by the multiplication factors indicated in the previous sub-sections for fossil and combined cycle plants.

3.1.5 Deposition

In parallel with the formation of droplets and liquid films, deposits form on steam-path surfaces throughout the PTZ, and indeed throughout the other pressure stages of the turbine. The deposit formation process is complex, involving impaction of crystals of salts, oxides and other compounds, as well as deposit formation due to thermophysical and chemical processes such as precipitation from superheated steam, evaporation of moisture, adsorption of impurities and decrease of compound solubility. Deposition is strongly influenced by the surface finish of the PTZ blades/disks.

Deposition on these surfaces plays an important role in the dynamic process that can result in damage and failure. Deposits become moist during periods of non-protected shutdown and lead to passivity breakdown and pitting which are key parts of every initiating event for corrosion fatigue and stress corrosion cracking, and often, even for high cycle fatigue (HCF) on last stage blades.

The most common corrosive deposits are salts of chloride and sulfate. Obviously, the cleaner the steam, the less deposition occurs; however, an international collaboration in the 1990s[10] found that deposits (including salt crystals) can form on any turbine surface during operation even in fossil and combined cycle units with the best cycle chemistries and cleanest steam. This finding led to the steam limit of 2 μg/kg for sodium in the IAPWS Technical Guidance Documents covering superheated steam for fossil and combined cycle plants.[4,5] The same limit is also provided for chloride and sulfate, though the continuous measurement of these parameters is not usually performed and values have not been included in the IAPWS Instrumentation Guidance Document.[3] Thus the intent of the limit on these deposit-forming species is to minimize deposition on blade/disk surfaces, while recognizing that some deposition is inevitable in every steam turbine, and to an even greater extent in industrial and geothermal turbines. Further, it is expected that deposition will be more pronounced on surfaces within the steam flow, and that deposits will form in crevice areas, such as those between the blade and the steeple. The pits that initiate damage and failure can form at all of these deposit locations.

The solubility of impurities in steam generally decreases as the steam expands. When the solubility of an impurity falls below the impurity's concentration in steam, it may precipitate and form a deposit. Deposits reduce steam passage and steam flow at the turbine blades, and, when in substantial thickness, impair turbine capacity and efficiency. Examples of deposits that can form in a steam turbine include salts, copper oxides and hydroxides, sodium phosphates, silica and sodium silicates, aluminum hydroxides, etc. Many types of deposits are also corrosive when they become moist.

Deposition throughout the steam turbine can be controlled by keeping the impurity concentration in steam below its solubility limit. Figure 2 and Figure 3 give examples of the solubility limits of SiO_2 and NaCl under various steam conditions. It is seen that in order to prevent deposits of pure silica, the SiO_2 concentration in steam should be < 10 μg/kg, while for NaCl a much lower concentration, on the order of 0.01 μg/kg, might theoretically be required.

The solubility of NaOH is thought to be similar to NaCl, and it is undisputed that the solubility of Na_2SO_4 is considerably lower than that of NaCl. Similar information has also been researched for other substances, but the experimental data deviate such that an error of up to two orders of magnitude is possible[11,12] and therefore no data will be given in this guidance document.

Such solubility curves are valid only at equilibrium conditions, which are hardly expected given the rapid steam expansion in the turbine.[13] Further, when an impurity does precipitate from steam, a large fraction of it passes along with the steam as dust and possible heterogeneous nuclei for the upcoming steam condensation, rather than depositing on turbine component surfaces. Experience, however, indicates that at least for silica, Figure 2 is not far from representing in-plant conditions of occurrence and location of the deposits.[14]

As mentioned above, cleaner steam yields fewer deposits. Similarly, deposition from steam with a high concentration of impurity yields thicker deposits than deposition from steam with a low impurity concentration. In the latter case, the steam holds a lower quantity of substance that is available for depositing.

Although it would be desirable to have zero deposition in the turbine, this is generally not practicable. For example, the solubility of sodium chloride in low pressure turbine steam at 0.1 MPa is approximately 0.01 μg/kg. Maintaining steam purity at this concentration is unlikely, but the rate of deposition from higher concentrations, such as 1 μg/kg, may be acceptable. Results from the 1990s International Collaboration Study on fossil-fired utility power plants[10] have indicated that limits of < 2 μg/kg for Na, Cl, and SO_4 are a reasonable balance between the ideal scenario of zero deposition and actual operating experience and the relation of cost-to-benefit.

3.1.6 Shutdown Environment

When a plant is not operating, no droplets or liquid films are formed on the PTZ surfaces. But the deposits formed during prior operation remain on the blade/disk surfaces and in the blade/steeple crevices. These deposits become of critical importance during shutdown depending on whether the PTZ is protected. Under non-protected shutdown, steam path surfaces are exposed to ambient conditions and the deposited crystals absorb moisture from the atmosphere, resulting in conductive conditions locally. Unlike what happens during operation, the solutions that form are oxygenated, and a local corrosive anodic environment can form at the deposit/blade interface. Such reactions will usually not take place if the moisture level of the flowing dehumidified environment over the blade surfaces is kept below 40%. This is the basis for protecting steam path surfaces by flowing dehumidified air.

The turbine environment during shutdown ultimately controls whether corrosion damage/failures will occur in the PTZ. Other processes (droplet nucleation, liquid films and deposits) are unavoidable consequences of thermodynamics and solubility. Shutdown protection, however, is within the control of the operator.

3.2 Damage Mechanisms in the Steam Turbine

3.2.1 Deposits

Mechanical blockage can occur as a result of deposits. Although rare, blockages at sensitive locations usually have severe consequences. For example, even small deposits on the stem of a turbine check valve can interfere with its function. In the event of a turbine trip, a malfunctioning check valve may lead to continued steam flow, an overspeed event, and destruction of the turbine. Also, deposits on stationary parts, if thick and strong enough, may impede blade movement, presenting a particular risk of mechanical damage to small blades.

Plugging of the steam flow path changes the pressure relations in the turbine in a way that can cause an axial shift of the shaft. This can lead to contact between rotating and stationary parts, with the potential for severe failure. Such conditions are usually detected and avoided by monitoring the turbine pressures.

A more frequent, but less consequential result of steam flow plugging is a reduction of the flow passing ability (“swallowing capacity”) of the turbine, and the change in effective steam flow profile on the turbine blades. These changes result in a reduction of steam flow and consequently power output of the turbine, and a degradation of turbine efficiency. Common examples are deposits of copper and aluminum species in the HP turbine, and silica deposits in the IP and LP turbine.

Corrosion is the most common damage mechanism resulting from deposits. It is discussed in other parts of Section 3 of this document.

3.2.2 Corrosion

Pitting and localized corrosion are important precursors to more extensive damage from CF and SCC, although extensive pitting of blades can cause significant loss of stage efficiency or, in extreme cases, weaken component integrity to the point of failure.

Pitting and localized corrosion are unlikely to originate during turbine operation due to the absence of oxygen in the liquid films on the turbine surfaces during operation. Rather, pitting results from corrosive deposits absorbing moist air during turbine shutdown.

During non-protected shutdowns where the blade/disk surfaces are open to the atmosphere, any deposits, particularly chloride or sulfate, which have formed on steam-path surfaces during operation can become moist and lead to local, conductive, aqueous environments that contain ppm levels of oxygen. These local environments initially lead to breakdown of the blade metal passivity, then to metastable pit formation, and finally to stable pits after repeated shutdown cycles.[15] Each shutdown period is followed by operation where the dynamic situation of droplet formation, liquid films and deposition occur as described in Section 3.1. Once a turbine has resumed operation, liquid films can repassivate areas where passivity was lost during shutdown and metastable pits had formed. However, deposition continues to occur during operation as described in Section 3.2, and deposits associated with a loss of passivity that caused a metastable pit during one unprotected shutdown will lead to further growth of that pit during the next extended unprotected shutdown. Repetition of this process will eventually lead to a stable pit. Most often, these pits are not visible, but because they have resulted from an active corrosion mechanism during shutdown the internal surfaces will be rather irregular. So the different environments which exist during the repetitive operation and shutdown periods eventually lead to the initiation and growth of a number of pits on the surface. Analysis needs to be conducted of the surface geography of the blades and disks in the PTZ rows.

Corrosion Fatigue (CF) and Stress Corrosion Cracking (SCC) of turbine components have been consistently identified among the main causes of turbine unavailability. Both phenomena are characterized by two stages: initiation and propagation.

In steam turbines, initiation most frequently occurs at microcracks that emanate from pits that form when deposits become corrosive during unprotected shutdowns. Cracks can, however, also initiate on locations of fretting, manufacturing defects, inclusions, microscopic imperfections, and at areas where specific absorption of species has locally reduced surface energy. These locations are where deposition will be preferential. Increased surface roughness acts to increase deposition.

In addition, liquid films of hot NaOH solution can induce severe SCC, even in the absence of oxygen. At special risk are Stellites and austenitic steels, especially under high internal or external stresses. Low alloy and carbon steel are also at risk at weld joints when no or inadequate stress-relief heat treatment has been performed.

Propagation of CF and SCC is driven by cyclic or steady stress situations only in regions where dynamic liquid films are present.

Turbine components may also be attacked by Flow-accelerated Corrosion (FAC) when liquid films form on turbine components in the presence of two-phase wet steam. Poor steam purity can cause low pH in such films, and thus trigger or enhance FAC. The use of Cr-alloyed steels can mitigate and even prevent FAC.[16]

Solid particle erosion. This is commonly caused by iron oxide particles that scour the surface of blades, mainly in the initial stages of the HP and IP turbine. The source of such particles is oxide on superheater and reheater tubes and piping that exfoliates during transient operation such as startup and shutdown. The growth and exfoliation of these oxides is not related to steam chemistry.

4 Guidance to Limit the Effects of Poor Steam Chemistry

4.1 Steam Purity Parameters

4.1.1 Impurities

Conductivity after cation exchange (CACE) gives direct, but unspecific information on the presence of anionic species in steam purity. It is the key monitoring parameter for steam. Feedwater and condensate purity is discussed in another IAPWS Guidance Document.[3] In previous IAPWS documents, a practical limit value of <0.2 µS/cm was given to provide adequate protection for many types of power plants, as seen in the Tables of Section 5. Although this limit does not fully prevent deposits or corrosion, it serves as a general indicator of steam and water purity. For fossil and HRSG plants operating on oxygenated treatment (OT), the steam purity limit is < 0.15 µS/cm, because of the feedwater requirement.

Degassed CACE is a measurement of CACE after processing the steam sample through a device that strips away most of the carbonic acid, leaving behind nearly all of the strong inorganic acids and most of the weak organic acids.[17] Because the separation is non-quantitative and incomplete, Degassed CACE cannot be compared directly with specification limits for CACE. It is however a useful indicative parameter in specific cases to supplement the other instrumentation (Section 4.2).

Carbon dioxide is an impurity that enters the steam / water system mostly as air in-leakage or by decomposition of organic matter (impurities or added treatment chemicals). It is considered non-corrosive to the steam turbine, when its concentration is within reasonable limits[18] (e.g., CACE in steam <0.5 µS/cm), but it increases CACE and masks the presence of other impurities.

Sodium is an indicator of the presence of common salts and of NaOH. According to equilibrium solubility data, a limit of < 0.01 μg/kg would be required to prevent deposits in the LP turbine (Figure 3), but dynamic effects indicate that higher concentrations are more realistic.[13] A practical limit was found to be < 2 μg/kg for fossil and combined cycle/HRSG plants.[10] This limit may, however, not be achievable for other steam turbines included in Section 6 of this IAPWS document (e.g., industrial or geothermal plants).

Chloride and sulfate are the anionic partners of corrosive salt deposits. When there is no matching cation, these species are volatile and concentrate in the early condensate as explained in Sections 3.1.2 and 3.1.3.

Silica deposits can obstruct steam flow, impairing the flow capacity and efficiency of the turbine. According to equilibrium solubility data, a limit of < 10 μg/kg is required to prevent deposits in the LP turbine (Figure 2), but if traces of NaOH are present, Na-silicates form that have a lower solubility. Silica deposits are not corrosive, but may need to be removed by mechanical cleaning if they have become excessive.

Copper deposits originate from volatile species that have accumulated in the superheater and migrated into the turbine. As with silica, they can impair steam flow, but more important with copper is that the deposits increase the blade path surface roughness, which leads to efficiency degradation. They can be removed by foam chemical cleaning. As the transport of copper from the superheater is a function of steam density (pressure), copper deposits only form at high steam pressures (greater than about 17 MPa).

Iron. Solid particle erosion is caused by steam-grown oxide exfoliation from superheater and reheater internal surfaces during periods of transient operation. There is no effect of steam chemistry on oxide growth or exfoliation. Methods to detect bursts of solid particles require special Solid Particle Detectors,[19] which is not within the scope of this IAPWS Steam Purity Technical Guidance Document.

Aluminum deposits originate from volatile species that have migrated from the boiler into the turbine. They impair steam flow and can only be removed by mechanical cleaning. Aluminum deposits in the turbine have been found in power cycles with major components made of aluminum, especially at higher boiler pressures. Aluminum can also enter power cycles in cooling water, from coal ash, and from coagulant use in some water treatment plants.

Organic matter, if not ionized, is not damaging for the steam turbine and its operation. However, such matter is usually subject to decomposition in the boiler. Their decomposition products may be acidic and cause low pH conditions at early condensation in the PTZ. They also elevate the background CACE and mask the contribution to CACE from corrosive constituents, such as chloride and sulfate. It is important to note that organic reducing agents and amines added to fossil and combined cycle plants as part of the chemistry regime also decompose and form breakdown products that produce large increases in steam CACE. This subject needs careful consideration because the large number of such compounds are usually proprietary chemicals, and the operators of plants that use them often do not know what they contain (Section 6.11).

Organics can be a particular problem in industrial plants, where condensate is often recovered (Section 6.4).

Oxygen has no general relevance in the turbine during operation. In superheat steam, oxygen content is not relevant for oxide growth.[20] In wet steam, due to the large partition coefficient for oxygen, liquid films have very low oxygen content even when the steam contains hundreds of µg/kg of oxygen. However, steam produced by Boiling Water Reactors, and steam at any plant under conditions of high oxygen partial pressure in the condenser (broken vacuum conditions), liquid films can have significant oxygen concentration that influences corrosion behavior (Sections 6.1 and 6.7).

4.1.2 Conditioning Agents

Solid conditioning agents, such as sodium phosphate and sodium hydroxide, used for boiler water treatment may cause deposits in the turbine and therefore need to be considered as potentially corrosive impurities.

Volatile conditioning agents, on the other hand, may separate to some extent into the liquid phase in the PTZ and provide the possibility for protection. In the superheat part of the turbine they do not provide any protection.

Ammonia is the most common conditioning agent in the steam/water cycle. Due to its volatility and relatively weak dissociation, it provides only moderate alkalization in the liquid films in the turbine to counteract anionic impurities. Care should be taken to avoid impurities in chemicals added to the cycle, including ammonia, as these could be a source of chloride.

Reducing Agents. Hydrazine is used in many steam/water cycles where a reducing environment is required. It decomposes rapidly at temperatures above 400 °C and, therefore, hydrazine is present in steam only in such plants with lower steam temperatures or when injected directly into the steam. Due to its low volatility, it partitions at condensation preferentially into the water phase and thus provides better alkalization of the liquid phase than ammonia.

There are alternative reducing agents, but as these are organic compounds which decompose, they tend to lead to an increase in CACE in steam.

Amines. Selected amines such as cyclohexylamine, morpholine, ethanolamine and others offer the possibility of greater partitioning into the liquid phase in the phase transition zone, as well as stronger alkalization, and thus perhaps better corrosion protection of turbine components. However, the balance of alkalization between amine and its possible acidic decomposition products must be considered.

4.2 Monitoring Instrumentation

The instrumentation for monitoring steam chemistry should follow the IAPWS Guidance Document “Instrumentation for monitoring and control of cycle chemistry for the steam-water circuits of fossil-fired and combined-cycle power plants”[3] for all plant types considered in the present Steam Purity Guidance Document, except where explicitly specified otherwise.

4.3 Layup

Conservation of the turbine during shutdown with dry air (relative humidity less than 40%) is of utmost importance to avoid corrosion during off-line periods, which can further develop into serious damage during subsequent turbine operation (Sections 3.1.6, 3.2.2 and 6.2).

4.4 Mitigating Consequences of Sub-optimum Steam Chemistry

First commissioning

During initial commissioning or after extensive boiler modifications, it is often difficult to achieve the values given in this Guidance Document. These values can be attained and risk of damage to the turbine can be minimized by adequately cleaning the water / steam circuit.

Unforeseeable situations

Unexpected events, such as cooling water leakage or attemperation injection of contaminated feedwater, may cause the limits to be exceeded and increase the risk of deposits and corrosion in the turbines. The contamination and its cause must therefore be identified and eliminated as soon as possible and the consequences minimized by taking preventive measures.

Impurity deposits in the turbine, insoluble in water

Impurity deposits in the turbine like metallic oxides, silica, hardness residues, etc. can cause poor operating behavior and decreased efficiency of the turbine. These deposits can usually be removed by specific measures, e.g., sandblasting.

Impurity deposits in the turbine, soluble in water

Deposits of water-soluble and hygroscopic materials may cause corrosion during shutdown periods if humidity exists. Dry air preservation is required for long periods of shutdown. The cause of the deposits should be eliminated. Depending on the nature, severity and frequency of occurrence of the deposits it may be recommended to wash the turbine, either with water or with wet steam.

Impurity deposits in the turbine valves

Impurity deposits in turbine valves can cause blockage of the turbine steam strainers and sticking / seizure of the stop and control valves. This also occurs when voluminous oxidation or corrosion products deposit between a valve shaft and its bushings. If such a situation cannot be reasonably excluded, valve function must be checked daily.

Acid conditions

Acid conditions can promote severe corrosion and must be avoided. Acids can enter the steam/water circuit via makeup water or the water polishing plants, and they can also form within the circuit by thermal decomposition of organic material or salts from seawater in-leakage. Acids can also form by ingress of cooling water into the condensate polishers when the anion exchanger has a larger ionic leakage than the cation exchanger. Most anions of concern are volatile in steam generators with volatile conditioning, and condense in the steam turbine, creating a corrosive environment. Once acid corrosion has taken place, it may be necessary to perform component repair, as well as to reduce the risk of further attack. When acidic conditions are present, the addition of alkalizing chemicals may reduce their symptoms, but does not eliminate their cause.

This risk of acid corrosion can be substantially reduced by observing the Steam Purity limits (Sections 5 and 6) and by appropriate design and operation of the water/steam cycle with regard to excluding sources of acids such as those mentioned above. Complete detection of acidic conditions in steam turbines requires techniques that are not available to routine chemistry monitoring.

Degradation of the water/steam separation

Degradation of the water/steam separation in drum boilers may cause excessive carryover of boiler water droplets (i.e., dissolved solids), and even of boiler water itself in the case of a rapid pressure drop. Water/steam separation must first be ensured by design measures, then subsequently verified through periodic inspections and maintenance of the separators, the water level instrumentation, etc.

5 Table of Chemistry Limits

5.1 Table of Steam Purity Limits

These Tables refer to steam at the turbine inlet and cover all downstream parts of the HP, IP, and LP turbines.

If steam or attemperation water is injected downstream of this reference point, then its quality should be such that it does not compromise the steam purity as listed in the Tables.

5.1.1 Condensing Turbines with Superheated Steam

Parameter	Unit	Normal / Target Values
Conductivity after cation exchange @ 25 °C	µS/cm	< 0.20
Sodium as Na	µg/kg	< 2
Silica as SiO_2	µg/kg	<10

Table 1. Steam purity for condensing utility turbines with superheated steam, applicable for steam temperature below 600 °C.

5.1.2 Condensing Turbines with Saturated Steam

Parameter	Unit	Normal / Target Values
Conductivity after cation exchange @ 25 °C	µS/cm	< 0.30

Table 2. Steam purity for condensing utility turbines with saturated steam without reheat.

In the event that the steam dries locally, e.g. by expansion in the turbine inlet valve, the specification for superheated steam should be used.

5.2 Limits for Normal Operation

The normal or target values in Table 1 and Table 2 represent the accumulated experience of the IAPWS Power Cycle Chemistry (PCC) Working Group with representation from 17 countries. The limits on these tables after modification through use of Section 6 are considered as the normal operating values during stable operation. They represent the current state of knowledge and research worldwide to avoid the damage mechanisms delineated in Section 3. They are therefore consistent with long-term plant reliability.

5.3 Development of Limits for Startup

At startup, cycle chemistry is usually not within specification and requires some time to stabilize toward normal operating values. In order to minimize deposits and corrosion during this period, a certain degree of steam purity should be met, and specifications developed for each specific case. Requirements may depend on the length of the shutdown period and on scenarios that influence steam purity. For example, a plant with a seawater-cooled condenser requires more careful scrutiny of CACE than a plant with an air-cooled condenser.

As a starting point, the basic steam purity outlined below can be used for guidance. Chemical analysis of steam during startup as well as inspections of the turbine give information for determining whether these values are suitable, or should be tightened or relaxed. Such decisions may also be based on fleet experience with similar power cycles. Chemical analysis of the steam should include measurement of sodium, anions and cations with IC, CACE, and Degassed CACE if it is available. Inspections of the turbine can, of course, only be made during shutdown, and only when accessible. The main focus of inspections is on the occurrence, location and extent of deposits and corrosion.

Basic steam purity for startup

In the case of a warm start, the values for normal operation (Section 5.2) should be attained within 2 hours, and in the case of a cold start within 8 hours. During startup, the impurity concentrations should show a decreasing trend.

Steam should not be sent to the turbine if the concentration of sodium exceeds 20 μg/kg. The immediate need at startup to ensure compliance with this limit requires a sodium monitor for steam, as specified in the IAPWS Guidance on Instrumentation for Cycle Chemistry.[3]

Steam should not be sent to the turbine if the CACE exceeds 0.5 μS/cm. Allowance may be given to possible contributions from carbon dioxide (Section 6.10), but at most to the extent of the limits in Table 3. The actual contribution of carbon dioxide must be measured and regularly verified for the specific plant. Degassed CACE can help to estimate the contribution of carbon dioxide.[21]

Na μg/kg	**CACE *** μS/cm	**Restrictions**
> 20	> 2	Do not pass steam to turbine
10 … 20	1 … 2	- Steam production < 40% nominal - Max 30 min per startup
n … 10	*n* … 1	Max 8 hours per startup

Table 3. Na and CACE during startup; *n* = normal operation value.
* maximum permissible allowance for carbon dioxide (on-line instrument readings).

The instruments for monitoring Na and CACE must be in functional condition at startup. During shutdown, the main steam pipe and sampling line usually fills with air that will enter the monitor when the plant resumes operation. Adequate venting and flushing of the cation resin can reduce the dead time until CACE starts giving good values.[21]

5.4 Development of Action Levels

If steam purity is outside normal operation levels, then the reason for the degraded purity must be determined, and corrective action taken to restore operation within the normal limits as soon as is practicable.

It is strongly suggested that each plant operator, chemist, or owner develop a set of Action Levels that define when the operators must take action in response to values outside the limits. Determination should be made whether to include two or three Action Levels with gradually increasing values. Because adequate research has not been conducted, most organizations find it acceptable to double the normal/target value for the First Action Level, and then double that value for the Second Action Level.

It is recognized that it is always desirable to operate with the lowest achievable impurity levels for the longest time. These alarmed limits should be available for the unit operator in the control room.

5.5 Development of Shutdown Limits

In addition to developing a set of Action Levels, it is also necessary to define a set of cycle chemistry conditions under which a unit must be shut down because of severe contamination. For the turbines that are the focus of the Tables in Section 5.1, shutdown conditions usually involve defining a CACE that indicates serious acidic contamination. Typically, a value of 1 µS/cm can be used under conditions that coincide with other upset conditions in the steam/water cycle. Carbon dioxide from air in-leakage or certain conditioning agents may warrant a less stringent CACE (Section 6.10).

6 Road Map Approach to Customize Steam Purity Limits to Plants with Specific Features

The road map is illustrated in Figure 4. If a specific case fits into more than one of the listed features, then the customizations may be combined accordingly.

6.1 Turbines for Cycling or Peaking Operation

Load changes should not result in major deviations in steam purity. However, if load changes are accompanied by significant steam purity transients then this could be an indication of deposits in the boiler mobilized by the transient, of drum boiler carryover, or of inadequate attemperation water purity. Such situations require an expert analysis about the type, quantity, and effects of deposits, drum furniture, and the associated mitigating actions as described in Section 4.4.

Startups. Turbines for cycling operation will have frequent short shutdowns and associated startups. There is the question of what risks can occur to the cycle chemistry during such shutdowns. Following such a risk assessment, a plant-specific startup steam purity specification can be tailored following Section 5.3.

It can be useful to define Action Levels (Section 5.4) with a limit of permitted cumulative hours for each level. Such limits should be based either on experience with proper plant operation, or on fleet experience with similar plants.

The use of Degassed CACE can indicate the time CACE is showing values elevated by carbon dioxide.[22]

Shutdowns also require special attention. When condenser vacuum is broken, normally dry salt deposits may become wet and aerated, creating an aggressive environment. This is a significant issue with turbines that are subject to frequent startups/shutdowns. It is recommended that the turbine be coasted completely down, as quickly as possible. In addition, any water injection into the turbine (hood spray) should be avoided if possible, and certainly limited to the time it is actually necessary to control exhaust temperature.

Periods of layup are handled in Section 4.3 and 6.2. However, in plants with cycling operation, shutdown periods are usually too short, for example overnight, to apply dehumidified air treatment. In such cases, it is recommended to maintain full condenser vacuum during shutdown. This necessitates maintaining sealing steam, some of which enters the turbine, and is therefore only applicable as long as the turbine stays at a temperature above 100 °C. This is usually the case over night or over a weekend. For shutdowns that exceed 3 days, when the turbine cools down appreciably, dehumidified air treatment should be applied.

6.2 Turbines with Extended Periods of Shutdown

The criticality of providing an appropriate shutdown environment was discussed in Section 3.1.6, and the sequence of damage leading to failure in situations without shutdown protection was provided in Section 3.2.2.

The main tool for preserving the turbine during an extended shutdown is to subject it to a controlled and monitored flow of dehumidified air.[23]

In case of mothballing for very long or indefinite period of time, additional techniques can be considered:

- If the turbine has been subjected to severe deposition with hygroscopic deposits (such as NaCl), it is recommended to clean and dry again the turbine beforehand
- Mobile turbine components (rotors, upper casings) can be relocated to a storage house with a controlled environment. If a protective oil coating is applied, it must be completely removed before re-assembly of the turbine
- Application of VCI (Vapor Conditioning Inhibitors) is only to be done in addition to dehumidified air treatment. Strict management of the VCI containers is required to ensure complete removal at the end of conservation
- Periodic inspections indicate whether the applied conservation is adequate

6.3 Backpressure Turbines

Condensing backpressure turbines

Steam purity should follow the specifications given in Section 5.1.

Non-condensing backpressure turbines

Volatile acids in steam are separated with the first condensate. There will therefore be no acid corrosion in backpressure turbines if the exhaust steam is sufficiently superheated. Note: acids begin to condense above the steam saturation line. Sulfuric acid may already condense at temperatures above 300 °C.

Solid materials deposit if their solubility limit in steam is exceeded. Solubility decreases during steam expansion. Note: NaOH may already produce highly concentrated liquid films at temperatures above 300 °C.

In the case of non-condensing backpressure turbines, some of the values mentioned in Section 5.1 may be exceeded under certain circumstances. However, this is only permitted if the composition of the steam is known and in accordance with the steam data at the turbine exhaust. These values must be developed on a plant-specific basis.

6.4 Turbines for Industry and Process Supply

The category “Industrial Turbines” ranges from turbines in small but otherwise conventional power plants to turbines in plants with specific features like:

- contaminated return condensate due to extraction of heating or process steam
- elevated levels of carbon dioxide and/or organic decomposition products
- varying steam production and frequent shutdowns
- common steam supply with other, independently operating components

Although industrial turbine inlet steam conditions may differ from those in utility power plants, the expansion in the LP turbine is similar (Figure 1). Therefore the discussion of the PTZ in Section 3.1 also applies for these turbines. The potential consequences of operation with contaminated steam for the turbine as such may be less drastic for industrial turbines because of the smaller size of the turbine itself, but the direct and indirect cost for shutdown of a large process dependent on steam from an industrial turbine may be very high indeed. The concentration of critical contaminants in the steam should therefore, if possible, be lower than their practical solubility in superheated steam, especially at the area of any phase transition zone between dry and wet steam.

The position suggested for industrial turbines is to maintain steam chemistry in line with the limits in Section 5.1. These limits however, especially the limit for CACE, are difficult and sometimes impossible to meet in many industrial applications, and can be customized with the options provided in the other parts of Section 6.

There are a few rules that should in any case be applied to every industrial turbine:

- Efforts to achieve good steam purity should be supplemented by analysis of steam turbine deposits that indicate if steam chemistry has been adequate. A chemist or operator responsible for the plant chemistry should be the first to view cylinders whenever the turbine is opened, and should take representative photos and samples. The geography of deposits and pits on these surfaces should also be noted. If available, analysis of the samples by XRDA (X-Ray Diffraction Analysis) is useful because it can identify the individual species present. This analysis should be followed by quantitative chemical analysis. Finding in the sample fractions of sodium chloride, sodium hydroxide or a mixture of the two in amounts above 0.25% is generally cause for concern.[24]

- In all turbines, trip and throttle valves should be exercised at least once a week to avoid valve freezing due to deposit buildup. Turbine stage pressures should also be checked regularly, as deposits on the rotating blades lead to axial shift that may cause contact between the rotating and stationary parts (Section 3.2.1).

- If there are indications of deposit buildup, washing of the turbine (on-line or off-line), or other off-line deposit removal options as appropriate (e.g., foam cleaning, sand blasting) should be considered.

- The importance of proper layup must be taken into account. Lack of protection (dehumidified air) during shutdown is the main reason for failure / damage in these turbines.[23]

Examples

1. Plants with significant amounts of contaminated return condensate, resulting in high CACE or other steam chemistry deviations. It is possible to produce steam fulfilling the limits in Table 1 and Table 2 with a feedwater quality corresponding to softened water, provided the feedwater is not used for steam attemperation. But this approach is usually more difficult and costly than with feedwater based on demineralized makeup water, and it requires a sufficiently low mechanical carryover of boiler water.
2. Plants where the preferred water treatment is based on organic additives as well as plants where the use of organic additives is due to outsourcing of the management of water and steam chemistry to chemical vendors, either to save the cost for chemists or because of a lack of qualified chemists. Thermal decomposition of such organic additives often results in high steam CACE (Section 6.11).
3. Plants with high and/or persistent in leakage of air, e.g., cycling units. This may result in high CACE in steam because of high levels of carbon dioxide (Section 6.7).
4. Some industrial plants with a boiler water treatment based on the use of solid alkalizing agents like Na-Phosphates or NaOH may have difficulty meeting the sodium limit because of the mechanical carryover of boiler water. This is usually less critical for plants with pure Na_3PO_4 treatment where a higher Na limit can be considered (Section 6.9) than for plants with a treatment based on sodium hydroxide (Section 3.2.2) or phosphate blends. Hydroxides do not add to the measured CACE value so a low value does not exclude an excessive content of, e.g., sodium hydroxide in the steam. This is one of the reasons why sodium should always be measured online together with CACE. If the limits cannot be met, the following rules mentioned earlier in this section are of great importance.
5. Industrial turbines are dependent on the operating modes of the industrial process and are often supplied by varying steam production. If peaking steam production is accompanied by increased boiler water carryover, it is useful to inspect the turbine more frequently for deposits. This inspection can be performed, for example, with a suitable endoscope, without the need to open the turbine.
6. Many industrial turbines are subject to frequent or extended shutdowns. Sections 4.3, 6.1 and 6.2 outline measures for the protection of the turbine during these periods.
7. Frequently, industrial turbines have a common steam supply with other, independently operating components. If the turbine is shut down, care must be taken to ensure that no steam can leak from the supply header into the turbine. Such steam leaks create a moist atmosphere and lead to severe corrosion attack of the turbine. When there are

such leaks, normal layup procedures are overwhelmed by the steady supply of moisture.

8. Industrial plants with copper alloy heat exchangers can have problems with copper deposition in the same way as discussed in Sections 4.1.1 and 6.13. However, because few industrial turbines operate above 17 MPa, the harmful effects of copper will not be in the turbine. Plants may see deposits in the boiler waterwalls, and as already mentioned in the primary superheater of all plants independent of the pressure.

6.5 Turbines with Solar and Biomass Steam Generating Systems

The requirements for these turbines are basically the same as for all other steam turbines, given in Section 5, with customization for special features given in Section 6. For solar turbines, Section 6.1 (Turbines for Cycling or Peaking Operation) is of particular relevance.

6.6 Turbines with Geothermal Steam

There are 3 basic types of geothermal power plants. The use of each type of plant is dependent on many factors; however, the condition (e.g., enthalpy, pressure) of the fluid extracted from the well may preclude the use of some plants (e.g., direct steam).

(1) Direct steam plants that deliver either superheated or saturated steam directly to a steam turbine

(2) Flash plants that flash geothermal fluid at a lower pressure and separate the steam that is then delivered to a steam turbine

(3) Binary power plants in which geothermal fluid is used to heat and vaporize a secondary working fluid. The secondary working fluid is then expanded through an expander or turbine to generate power.

Steam Purity

Steam purity is an important consideration for geothermal direct steam and flash plants as the geothermal steam contacts the steam turbine directly. Contaminants in geothermal steam are often significantly higher than the contaminant levels experienced in thermal plants. As such, fouling and corrosion of geothermal steam turbines is commonplace. Steam purity is less of a concern in binary plants where geothermal fluid does not come into contact with a steam turbine.

The steam chemistry in geothermal power plants is a product of the geochemistry of the fluid that is extracted from the geothermal reservoir for use in the power plant. The fluid geochemistry can vary significantly from country to country, field to field, and also between wells in the same field. Fluid geochemistry can also change over time within the same well as fluid is extracted. The differences in fluid chemistry can result in significant changes in steam purity at a given level of moisture carryover.

The ability to improve steam purity at direct steam plants may be limited to solid particle removal, although the development of dry steam scrubbing technologies (adsorbent and absorbent) is continuing. Direct steam plants may utilize wet steam scrubbing systems if adequate moisture removal systems are also used and the enthalpy loss of using such systems is tolerable. Direct steam plants may experience steam purity issues related to high concentrations of chloride (corrosion) and silica (deposition) among others, while acidic steam (containing chloride and/or fluoride) can also be of concern and may require neutralization.

Steam purity at flash plants is largely influenced by the efficiency of the steam separation system. Steam purity can be further improved with the implementation of steam washing systems, which usually involve the injection of a small amount of water into the steam and its later draining to assist in contaminant removal. Flash steam plants may experience steam purity issues related to high concentrations of chloride (corrosion) and silica (deposition) among others.

Steam purity in many geothermal power plants is unlikely to meet the steam purity requirements set out in Sections 5.1 and 6. Geothermal steam turbines are often designed to handle lower steam purity than that experienced in thermal plants, however the corrosion and fouling of geothermal steam turbines is still commonplace. Measures to manage the lower levels of steam purity often include the use of higher grade alloys within the steam turbine, regular on-line and off-line washing of turbines and regular turbine outages for inspection and repair.

Due to the lower steam purity experienced in geothermal power plants, the implementation of the correct turbine shutdown and storage conditions as described in Sections 4.3 and 6.2 is essential for minimizing offline corrosion and damage.

Other features mentioned in Section 6.4 on Industrial Turbines may also be of relevance.

Developing steam purity specifications

As discussed above, steam purity is largely given by the geothermal source, and techniques to influence it are limited. This results in a wide range of varieties that cannot be fitted into a simple standard.

A plant steam purity specification will therefore start with the values used for the design of the turbine. Steam purity monitoring can identify any deviations and in such cases give the basis for additional corrective measures, as described above and in Section 4.4.

6.7 Turbines with Steam Generated in Nuclear Power Plants

Although HP turbine inlet steam conditions are quite different from those in fossil-fired utility power plants, the expansion in the LP turbine is similar (Figure 1). Therefore, the discussion on the PTZ in Section 3.1 also applies for turbines in nuclear power plants.

There is, however, one particularly important factor. The steam generating systems in Boiling Water Reactors as well as in Pressurized Water Reactors are much more sensitive to corrosion and deposits than fossil-fired boilers. Therefore these nuclear steam generating systems are operated with water purity unmatched in fossil-fired boilers. As a consequence, the nuclear generated steam has a higher purity and the steam purity specification can be reduced to a few key parameters.

Superheated steam from nuclear power plants

Steam purity should follow the specifications given in Table 1, monitoring steam chemistry should follow Section 4.2.

Saturated steam from Boiling Water Reactors (BWR)

In a BWR, steam is generated directly in the nuclear reactor. Cycle chemistry is characterized by the use of neutral feedwater and reactor water, with no alkalizing agents. There is no capacity for neutralizing volatile acidic impurities that may condense in the turbine and can provide a corrosive environment.[25] This is aggravated by the oxidizing environment in the turbine. Without hydrogen chemistry, the oxygen concentration in steam is up to 10-20 mg/kg, resulting in 100-200 µg/kg in the water film at HP turbine inlet and on the order of 1 µg/kg at the beginning of condensation in the LP turbine. With hydrogen reactor water chemistry, the oxygen levels are lower, but still high enough to produce an oxidizing environment in the turbine.

Table 4 gives a specification to limit acidic corrosion. Carryover is to be limited in order to avoid excessive contamination of the turbine by non-volatile activation products like Co-60. A lower value may be considered depending on feedback from experience of similar BWR plants.

As the cycle operates under all volatile and neutral water chemistry, the instrumentation for monitoring steam chemistry can be reduced to a measurement of direct conductivity.

Parameter	**Unit**	***N***
Conductivity @ 25 °C	µS/cm	< 0.10
Mechanical Carryover *	%	< 0.1

Table 4. Steam purity for boiling water reactors (*N* = normal operation limit).
* Percentage of reactor water carried along in the live steam.

Saturated steam from Pressurized Water Reactors (PWR)

In a PWR, steam is generated in the steam generators, which isolate the nuclear reactor from the steam/water cycle. PWR cycle chemistry is characterized by the use of volatile alkalizing agents for feedwater, usually in combination with a reducing agent like hydrazine. The alkalizing agent provides some protection against acidic environments. On the other hand, specific treatments like the addition of boric acid to the steam generator water (boric acid is very volatile), and the use of amines that decompose to organic acids have added another dimension to steam turbine chemistry.[25]

Table 5 gives a specification to limit acidic corrosion. A less stringent specification for cation conductivity may be considered when using amines for water treatment; in such cases the conditions specified in Section 6.11 should be observed.

Additional requirements should be considered if dissolved solids or compounds of boron are used as a conditioning agent at any place in the secondary circuit.[25] The requirements regarding Na (Table 5, Sections 4.2 and 6.11) and carryover (Table 5) may be omitted if only AVT is used for steam generator water treatment.

Parameter	**Unit**	***N***
Conductivity after cation exchange @ 25 °C	µS/cm	< 0.20
Sodium as Na	µg/kg	< 10
Mechanical Carryover *	%	< 0.5

Table 5. Steam purity for pressurized water reactors with saturated steam (N = normal operation limit).
* Percentage of steam generator water carried along in the live steam.

6.8 Ultrasupercritical Turbines with Steam Temperatures above 600 °C

There is no comprehensive experience with this type of turbine. The main issues to be considered have been compiled in IAPWS Certified Research Need 21.[26]

6.9 Turbines in Plants with Boilers using Phosphate Treatment

With drum boilers using solid alkalizing agents like Na_3PO_4 or NaOH it may be difficult to meet the sodium limits given in Section 5.1 because of carryover of the boiler water, which becomes especially significant at higher boiler pressures.[2]

Tri-sodium phosphate (TSP) is not known to be corrosive in the turbine either as a deposit or in a liquid film. For such cases, a relaxed sodium limit in steam is possible.

Inspections of the high pressure turbine as well as fleet experience can indicate which quantities of Na_3PO_4 carryover lead to excessive turbine deposits. Because such supporting information is not commonly available, the sodium concentration in steam could be limited in this case to <5 µg/kg.

There is a risk for corrosive deposits with Caustic Treatment (CT), or when products other than only Na_3PO_4 are used or present in the boiler water, e.g., phosphate blends, NaOH, free caustic, and proprietary products. In such cases, the limits given in Section 5.1 apply, and should not be relaxed. This is also a reason why plant operators and chemists should always know exactly what compounds are added to the boiler, and always follow the guidance on measuring carryover.[2]

6.10 Turbines with Steam containing Elevated Levels of Carbon Dioxide

At temperatures found in the PTZ, carbon dioxide has a high volatility[27] and a weak dissociation.[28] Consequently, moderate quantities of carbon dioxide do not significantly influence the pH in the PTZ of alkalized steam.[29] There is no definitive evidence that carbon dioxide is directly responsible for turbine damage. In case of increased CACE due to carbon dioxide, it is therefore possible to give a discreet additional allowance to the CACE limits in Section 5.1.

Such allowance will however decrease the sensitivity of CACE to the presence of more corrosive contaminants like chlorides and sulfates. A moderate increase of CACE due to the presence of carbon dioxide can only be tolerated as long as it can be shown that the high value is caused solely by carbon dioxide (or rather carbonic acid). In such cases, a Degassed CACE analysis may be of use as an indicative tool (Section 4.1.1).

With Degassed CACE, most of the carbonic acid in the sample is removed during this measurement, while nearly all of the strong inorganic acids and most of the weak organic acids remain.[17] Depending on the origin of the organic acids, they may or may not be corrosive (Section 6.11). This is a reason always to include online monitoring of sodium in steam as a complement to CACE, and why an IC analysis is needed to identify the organic acids/compounds as well as trace amounts of chlorides and sulfates.

IC analysis is, however, a relatively costly analytical method. It requires qualified chemists, and is therefore not available in all power plants, especially in those that do not have a chemistry laboratory. If IC analysis cannot be performed with the plant resources, it can be contracted from a specialized laboratory. This is the price required for taking an additional allowance to the CACE limits.

This additional allowance for carbon dioxide should be restricted such that in no instance may CACE exceed 2 μS/cm. If the alkalization of steam is low (circa pH<8.5), then the pH in the PTZ will also be low and no additional allowance for carbon dioxide shall be given.

6.11 Turbines with Steam containing Organic Decomposition Products

Organic matter in the steam/water circuit decomposes to short-chain organic acids, most prominently acetic acid, as well as other products. The speed and degree of decomposition depends strongly on the nature of the species, as well as the residence time and the temperature in the boiler. Decomposition becomes especially prominent at temperatures greater than 400 °C.

Depending on its origin, a decomposition product has the following influences in the PTZ:[18]

A. Amines used for feedwater treatment. Acidic decomposition products partition in the PTZ into the liquid phase, lowering pH and thus increasing corrosiveness. However, depending on the boiler temperature, some of the amine may pass straight on to the steam and may neutralize or even over-compensate the effect of the acid in the PTZ.

B. Natural organic matter from the makeup water or cooling water ingress; water treatment chemicals that do not have alkalizing properties (e.g., many boiler water dispersants and organic oxygen scavengers). Unlike amines, there is no cation that can compensate the effect of the acid in the PTZ.

As long as it can be shown that the acidity of the decomposition product in the PTZ is at least compensated by other products (case A), the acidic decomposition product may be acceptable, and an additional allowance for CACE can be given. In order to take such an allowance, plant operators and chemists must know exactly what compounds are added to the water/steam cycle, and analyze what organic decomposition products are present in the steam. This is a reason to always include online monitoring of sodium in steam as a complement to CACE, and why an IC analysis is needed to identify the organic acids/compounds as well as trace amounts of chlorides and sulfates, as outlined in Section 6.10.

This additional allowance should be such that in no instance will CACE exceed 1 µS/cm.

If adequate chemistry information is not available, it is advised to give no extra allowance in the CACE limits of Section 5.1 for organic decomposition products.

Consideration should also be given to the effect of steam with acidic products on other equipment of the steam/water cycle, e.g., condenser, feedwater heaters, economizer, etc.[18]

6.12 Turbines with Steam containing Elevated Levels of Silica

Silica has a significant volatility[30] and as a consequence is a prominent compound in steam. The value listed in Table 1 controls silica deposits such that in the long term no substantial deposits will occur.

In the event that this limit is not practicable in a specific case, operation with higher silica concentration in steam is possible. Operation with elevated silica may, however, lead to buildup of silica deposits. Such deposits are by themselves not corrosive, but they impair the flow-passing ability and efficiency of the turbine, and can result in axial thrust on the turbine shaft. If they become excessive, they must be removed by mechanical cleaning, which requires opening the turbine. The necessary frequency of turbine cleaning can be determined by routinely checking turbine pressure and efficiency.

In no case should the silica concentration in steam be above 100 µg/kg, except for short transient periods and first commissioning.

6.13 Turbines in Power Cycles containing Major Components with Copper or Aluminum

Plants with Copper Alloys in Feedwater and Condensate Components

Many fossil and industrial plants have copper alloy feedwater heaters, supplementary heaters and condensers. Copper can cause a number of problems and has a major influence on availability and performance at several water/steam cycle locations, primarily in the feedwater system, boiler, and in the HP steam turbine.[31] The various aspects of copper in the water-touched components have been covered in the IAPWS Technical Guidance Document for Volatile Treatments[4] where it states that in order to achieve a level for copper of <2 μg/kg at the economizer inlet, the use of a reducing environment (AVT(R)) is required. This Guidance Document on Steam Purity only covers prevention of copper deposits on the HP steam turbine components. Such deposits impair the flow-passing ability and efficiency of the turbine, and can result in axial thrust on the turbine shaft. If they become excessive, they must be removed by specialized chemical cleaning processes (e.g., foam cleaning), which can be performed without opening the turbine.

The dominant copper species in steam are cuprous and cupric hydroxides ($Cu(OH)$ and $Cu(OH)_2$). The partitioning constants for both into saturated steam are relatively high across the temperature range 100–350 °C, which includes unit startup conditions. The concentrations are independent of pH of the boiler water. Copper deposits in the primary superheater as a crystalline growth of CuO and Cu_2O as the saturated steam changes to superheated steam. There is an increasing solubility for both copper hydroxides with pressure in superheated steam, and the level in steam at 17 MPa is about 3–4 μg/kg. Below this pressure, both copper hydroxides have much lower solubilities. Thus at pressures $\leq$ 17 MPa, copper remains in the superheater and does not transport significantly to the turbine. Above this pressure, the copper will transport to the turbine and deposit on the initial HP stages because of the decreasing solubility with decreasing pressure as the steam expands.

The methodology of controlling copper deposits in turbines operating in units with drum pressures above 17 MPa is to control the economizer inlet copper levels to less than 2 μg/kg by optimizing the reducing potential and minimizing air in-leakage.[31] It should be recognized that increasing the steam pressure above 17 MPa (such as overpressure operation) will result in higher levels of copper transport from the primary superheater to the turbine. Once the optimum feedwater chemistry of a plant is achieved and copper deposition is lowered in the primary superheater, then copper levels in saturated steam and main steam should consistently be less than 2 μg/kg. This is not meant to be a manufacturer's guarantee, only a statement of fact for optimized feedwater and boiler water treatments. Monitoring copper in steam should be conducted at the unit's maximum operating pressure.

Plants with Sources of Aluminum in the Cycle

Fossil and industrial plants with aluminum feedwater and condensate tubed heat exchangers are much rarer than those with copper alloys. However, aluminum is present in a number of other sources in various plants. Some dry cooling systems that are used in fossil and combined cycle plants have aluminum tubes. Other plants use aluminum for water storage tanks, and aluminum compounds are present in plant cooling water, coal ash, and potentially in boiler makeup water. Operators should be cognizant of any forms of aluminum in a plant. The earliest papers on this subject were related to the use of aluminum brass condenser tubes.[32] The understanding of aluminum compounds around generating plants is not as well developed as for copper compounds, but it is known that aluminum oxides / hydroxides are transported in condensate and feedwater as soluble compounds, and have significant volatility in steam.[30] Aluminum has been a concern for fossil plant chemists for a number of years because of the possible deposition of aluminum oxides and/or hydroxides on the HP surfaces of the steam turbine. As with copper deposits they are found mainly in the HP turbine and impair the flow-passing ability and efficiency, and can result in axial thrust on the turbine shaft. Unlike copper deposits, they can only be removed by mechanical cleaning.

In one case in the 1970s, it was identified that the aluminum value in superheated steam under supercritical conditions was about 5 μg/kg.[33,34] More recent information suggests that a limit of less than 5 μg/kg should be used for plants operating up to about 17 MPa and less than 3 μg/kg for plants operating above this pressure. These values should be regarded as tentative limits until more research is undertaken as suggested in ICRN-26.[35] It is clear however, that as with plants with copper, regardless of the aluminum source, any significant concentration of aluminum in the feedwater will transport as a soluble aluminum oxide through to the boiler and may deposit in the turbine. At a pH (25 °C) of 8 or higher, the dominant dissolved aluminum species is the aluminate anion. As the pH is lowered below 8, the dissolved species become predominantly cation. The key to success will be the ability to remove the aluminum prior to the feedwater circuit.

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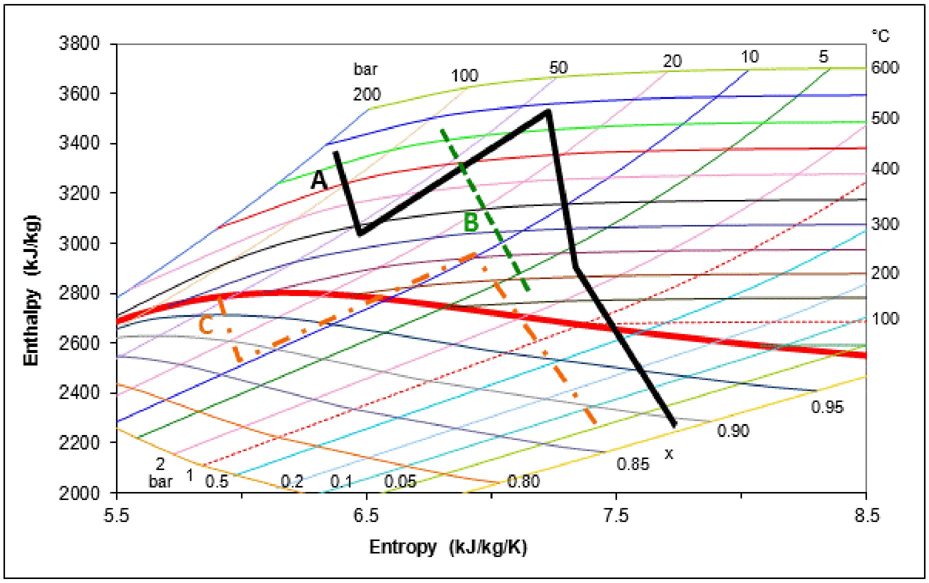

Figure 1.

Mollier diagram with three typical turbine cycles (symbolic presentation):

A reheat turbine in fossil fired plant

B backpressure turbine

C reheat turbine in a nuclear LWR plant

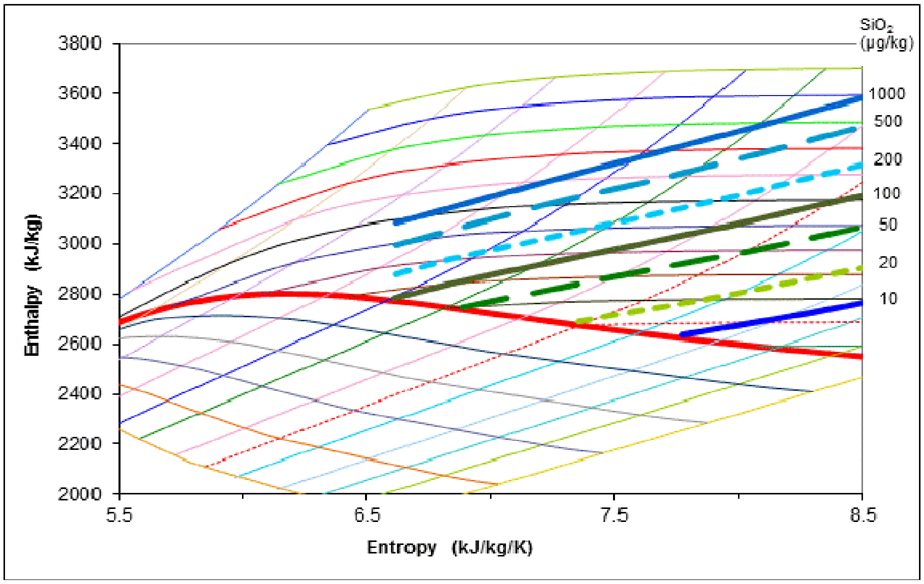

Figure 2.

Solubility limits of SiO_2 at various steam conditions; evaluation of literature data[11,14]

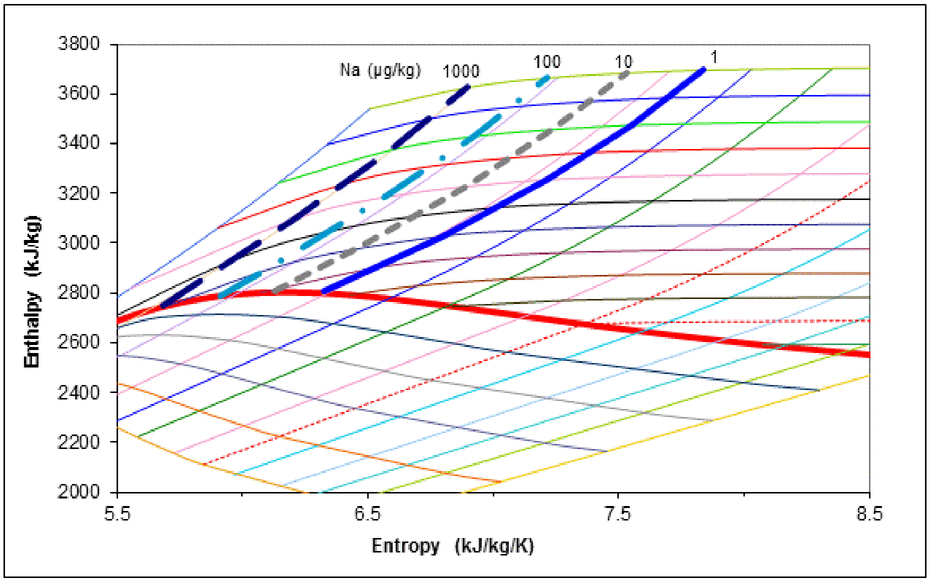

Figure 3

Solubility limits of NaCl at various steam conditions; evaluation of literature data[11,14]

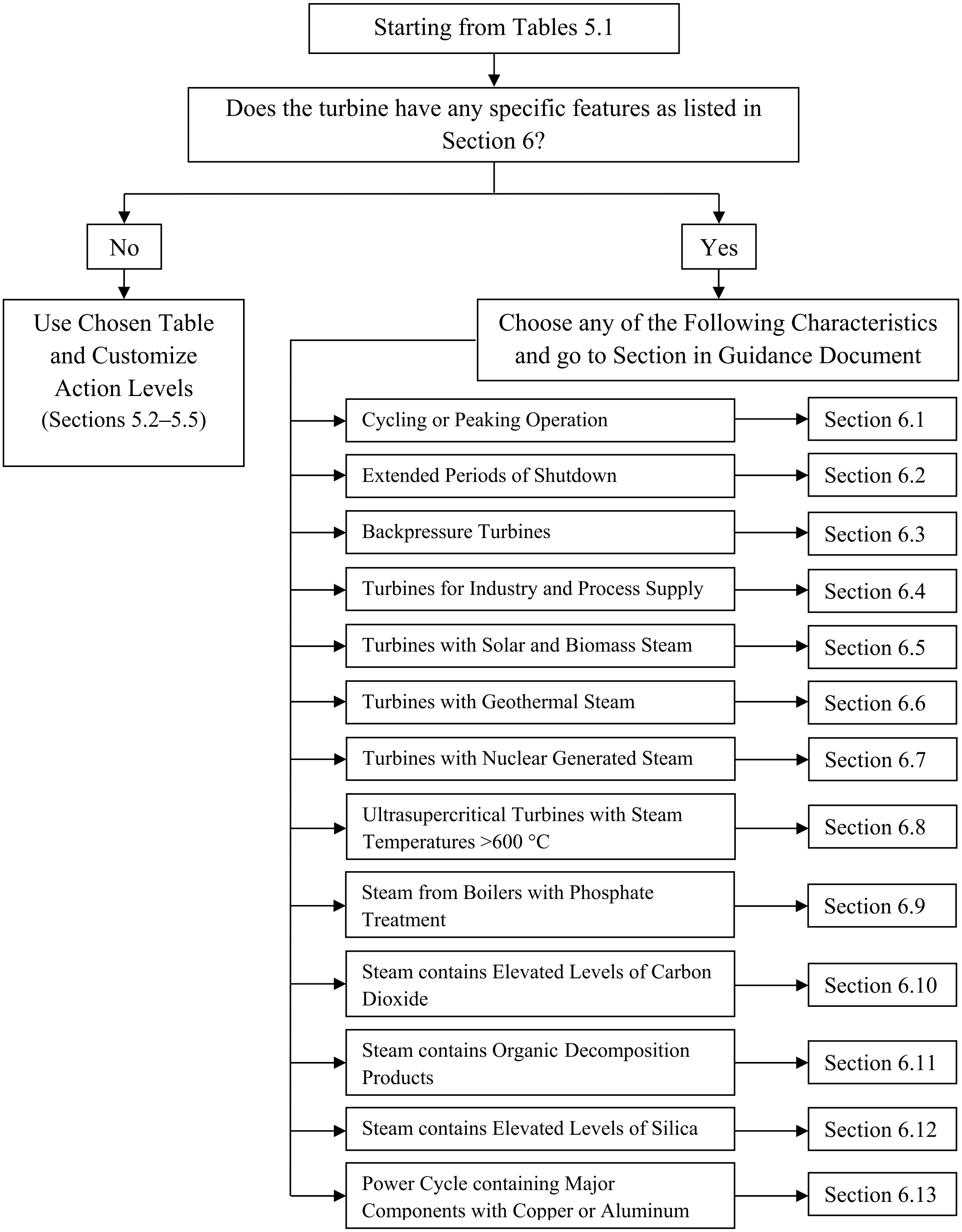

Figure 4. IAPWS Roadmap to Develop Steam Purity Limits from the Base Table 1 to Specific Configurations. If a specific case fits into more than one of the listed features, then the customizations may be combined accordingly.