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Technical Guidance Document: Phosphate and NaOH treatments for the steam-water circuits of drum boilers of fossil and combined cycle/HRSG power plants

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This technical guidance document considers fossil and combined cycle/HRSG plants and identifies the normal target values for each plant type when operating with a phosphate or NaOH (caustic) treatment. 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 plant depending on the actual conditions of operation, the equipment and materials installed, and the condenser cooling media.

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
Acid phosphate Corrosion	APC	A boiler/HRSG under-deposit corrosion (UDC) tube failure mechanism where acid phosphates (di- and/or mono-sodium phosphate) concentrate beneath deposits
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
Caustic gouging	CG	A boiler/HRSG under-deposit corrosion (UDC) tube failure mechanism where NaOH concentrates beneath deposits
Condensate Polishing Plant	CPP	System containing ion exchange resins to purify condensate. Can also include a filtration system
Condensate Pump Discharge	CPD	
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	Boiler/HRSG tube failure mechanism
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
Di-sodium phosphate	DSP	

Term	Alternative or Acronym	Definition
Dissolved Organic Carbon	DOC	A convenient measure of dissolved organic components in the water or steam
Drum boiler		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.
Economizer		First heat transfer section in boiler or HRSG to heat feedwater located in the cold end of the plant
Feedwater		Water that is being pumped into a boiler or HRSG to balance the steam production
Flow-accelerated Corrosion	FAC	Accelerated chemical dissolution of magnetite on the surface of carbon steel components in the feedwater system and HRSG evaporators, typically occurring at locations of turbulence in the flow
Heat Recovery Steam Generator	HRSG	Plant that generates steam using heat transfer from the exhaust gas of a combustion (gas) turbine
Hydrogen damage	HD	A boiler/HRSG under-deposit corrosion (UDC) tube failure mechanism where acidic conditions concentrate beneath deposits
Makeup Water	MU	Water which is added to compensate for losses of water and steam from the system
Mono-sodium phosphate	MSP	
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 ammonia and oxygen are added to the feedwater
Phase-transition Zone	PTZ	Region in low-pressure steam turbine where superheated steam changes to moisture
Phosphate Treatment	PT	Conditioning regime for drum boilers in which alkalinity is achieved by dosing tri-sodium phosphate to the boiler water
Preheater		A circuit in an HRSG prior to the economizer and LP drum to preheat condensate
Tri-sodium phosphate	TSP	
Total Organic Carbon	TOC	A convenient measure of total organic components in the water or steam
Under-deposit Corrosion	UDC	Boiler/HRSG tube failure mechanism, Three UDC mechanisms are: hydrogen damage (HD), Caustic gouging (CG) and acid phosphate corrosion (APC)
Water Treatment Plant	WTP	Facility where high-purity water is prepared and stored

2. Introduction: Purpose of Document and How to Use it

Phosphate and caustic treatments are common forms of chemical treatments for drum boilers of conventional fossil plants and for the multi-pressure drums in combined cycle/HRSG plants. They are the subject of this part of the suite of IAPWS Technical Guidance Documents [2-4]. The purpose of this document is to provide guidance on the selection of the most appropriate chemical addition for these boiler/HRSG drums to provide maximum corrosion protection. 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 feedwater treatments for these units have been published in a previous IAPWS Technical Guidance Document [2] and the Normal/Target values for feedwater in this document [Tables 1-4] in Section 5 remain the same.

With all-volatile treatment (AVT), ammonia is added to the feedwater to provide chemical conditions that protect the feedwater heaters, boiler, superheater, reheater and turbine against corrosion, without further chemical additions.

AVT can be used in "conventional" and HRSG drum-type boilers, provided high purity feedwater is available and the build-up of impurities in the boiler/evaporator water can be strictly controlled. However, ammonia is a poor alkalizing agent and does not give much protection against corrosion, due to the ingress of corrosive salts, or to flow-accelerated corrosion (FAC), which tends to occur over the temperature range 110–200 °C. FAC is particularly prevalent in the low pressure stages of HRSGs and in carbon steel feedwater heater components of conventional plants, which operate in this temperature range.

While the addition of a solid alkalizing agent, such as sodium phosphate or sodium hydroxide, reduces the effects of corrosive impurities and flow-accelerated corrosion, the use of phosphate (PT) and NaOH treatments in the boiler/HRSG evaporator can lead to a number of other operating and corrosive situations if not applied optimally. In brief, both treatments are designed to help address contamination in the boiler/HRSG evaporator and to prevent the serious under-deposit corrosion (UDC) mechanism hydrogen damage [5], but if not applied properly can result in other problems and damage mechanisms. For instance, phosphate treatments often result in hideout and hideout return in higher pressure boilers/evaporators (>10.4 MPa, 1500 psi), and some treatments can result in a UDC tube failure mechanism, acid phosphate corrosion [6]. Phosphate is also sometimes difficult to control. Caustic treatment (CT), with NaOH dosing, can be destructive and result in another UDC mechanism, caustic gouging [7], if not used in the optimal range and particularly if dryout occurs in the boiler/evaporator. Both treatments have to be monitored very carefully to avoid carryover into steam [3], which can result in steam turbine deposition and stress corrosion cracking in the superheaters and steam turbine.

The primary purposes of this document are to: a) highlight the problems which can emerge from non-optimum phosphate and NaOH dosing, b) provide a set of normal cycle chemistry values to provide optimum protection for fossil and combined cycle/HRSG plants, and c) provide sufficient discussion that the reader can customize these normal values to actual plant configurations.

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

- a) Unlike AVT, phosphate and NaOH treatments are only applicable to drum-type boilers and must not be used for once-through boilers.
- b) In HRSGs, neither solid alkali is used in the LP evaporator of units where the LP drum feeds the IP and HP feedpumps and attemperation. In these units, solid alkali can be used in the IP and HP evaporator circuits.
- c) Phosphate and caustic treatments allow a greater tolerance than AVT to boiler/HRSG evaporator water impurities such as chloride and sulfate, to initiation of corrosion, and to under-deposit corrosion. The tables of normal values in Section 5 have been developed for both treatments at levels of pH, phosphate and NaOH as a function of operating drum pressure to control the levels of contaminants which are considered within boundaries to prevent UDC in tubing and steam turbine problems.
- d) As mentioned above, the concentrations of the phosphate and NaOH alkalizing chemicals in the boiler/HRSG evaporator water need to be carefully controlled to ensure that excessive concentrations do not occur, which could lead to caustic corrosion in the boiler and to the carryover of corrosive impurities into the steam.
- e) Based on more than 20 years of excellent experience worldwide, this Technical Guidance Document recommends only the addition of tri-sodium phosphate within the bounds of a sodium-to-phosphate molar ratio of 3:1 and the sodium-to-phosphate molar ratio of 3:1 plus 1 mg/kg NaOH and with a minimum pH of 9.0 and minimum phosphate of 0.3 mg/kg. However, Section 4.2.1 does include comment on the use of traditional phosphate treatments outside of this molar ratio range such as coordinated, congruent and equilibrium phosphate treatments.
- f) Section 4.1 indicates that this IAPWS Technical Guidance Document covers drum pressures up to 16.5 MPa (2400 psi) for CT and up to 19.3 MPa (2800 psi) for PT. But depending on the specific plant, problems with phosphate hideout and return can occur as low as 10.0 MPa (1450 psi).

The development of operating cycle chemistry guidance for fossil and combined cycle/HRSG plants should follow a number of steps. The starting point in this document is Section 5, which contains the Tables of Normal/Target chemistry limits for four of the most common combinations of fossil/HRSG plants.

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. The guidance document can form the basis of, but should not restrict, other derivative guidelines around the world. Experience has indicated that, depending on local requirements, the normal or target values for phosphate or caustic treatments presented in Tables 1-4 for the four base plants (Section 5) will provide good reliability and availability if they are customized for each plant depending on the actual conditions of operation, the equipment installed, the materials used in different parts of the cycle, and the condenser cooling media. This customization is accomplished in two steps. The first step involves developing a set of Action and Shutdown Levels, which will require the plant operator or chemist to take some avoiding action. The second step involves customizing these tables to the specific unit conditions, materials and possible damage mechanisms, following the suggested 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.

It should be noted that low pressure industrial steam raising plants are not covered within this IAPWS Technical Guidance Document.

Throughout this document, conductivity limits are provided in units of $\mu\text{S}/\text{cm}$. It is recognized that conductivity units of $\mu\text{S}/\text{m}$ are preferred in the SI system; this document uses $\mu\text{S}/\text{cm}$ to be consistent with the most common industrial practice worldwide. All conductivities and pHs in this document refer to water samples cooled to 25 °C.

3. Background to Corrosion in the Water/Steam Circuits of Power Plants

The purpose of good cycle chemistry is to prevent and/or reduce corrosion in the water/steam circuit of power plants. A combination of techniques is used to achieve this.

Fossil and combined cycle/HRSG plants operate at different temperatures and pressures. Both once-through and drum boilers coupled to high pressure (HP), intermediate pressure (IP) and low pressure (LP) steam turbines are employed in traditional fossil-fired plants. Multi-pressure drum-type heat recovery steam generators (HRSGs) are normally used in combined cycle plants, but there are also a number of HRSGs with once-through HP or HP/IP circuits.

Mild and low alloy steels are used mainly in the construction of boilers, HRSG evaporators and feedwater heaters, although copper alloys can be used for condensers. Copper alloys were also extensively used in the feedheating systems of some older plants, but are not used in modern plants and, therefore, these materials are covered by exception in Section 6.7 in this document.

High alloy steels and austenitic stainless materials are used in superheaters, reheaters and steam turbines. They are also used for feedwater heater tubing. Protection against corrosion is provided by the protective oxides which grow on the surface of all these materials.

In conventional fossil and HRSG plants, a number of corrosion mechanisms can occur in the water/steam cycle, which are influenced by the cycle chemistry treatment. These include:

- Under-deposit corrosion (UDC). This is an on-load phenomenon, which can lead to hydrogen damage [5], caustic gouging [7], and acid phosphate corrosion [6].
- Flow-accelerated corrosion (FAC), due to the accelerated dissolution of the protective oxide (magnetite) on the surface of carbon steel components controlled by the cycle chemistry and located by areas of flow turbulence [8].
- Corrosion fatigue (CF), due to repetitive applied stress causing damage to the protective oxide layer (magnetite) [9].
- Pitting corrosion due to inadequate shutdown procedures throughout the cycle, and

- Stress corrosion cracking (SCC) of sensitive steel components in the superheater, reheater and steam turbine due to the presence of impurities, such as sodium hydroxide and chloride.

The feedwater system is the major source of corrosion products, which can flow into the fossil boiler or HRSG evaporator and then deposit on the heat transfer surfaces of the water/steam cycle. Corrosion is increased by the presence of impurities in the feedwater and cooling water and can also be exacerbated by flow-accelerated corrosion (FAC).

The build-up of deposits in the steam generating tubes of the boiler or HRSG, in combination with the presence of impurities, can lead to under-deposit corrosion (UDC) during operation and pitting during shutdown.

The carryover of impurities into the steam can lead to deposits in the steam turbine, stress corrosion cracking in the superheaters and steam turbines, and pitting (particularly in reheaters) during off-load conditions.

Leaks in water-cooled condensers are a common source of impurities, such as chloride and sulfate, entering the water/steam circuit, whereas air-cooled condensers are subject to flow-accelerated corrosion and can be a source of high levels of corrosion products and air ingress [10].

3.1 Chemical Conditioning to Minimize Corrosion

Chemical conditioning is applied to both the feedwater and boiler water for plants conditioned with solid alkalis. Guidance limits have to be developed to control the corrosion processes mentioned above.

The first requirement is for high purity feedwater recycled from the condenser, or added as makeup. The purity is monitored by measurement of the conductivity after cation exchange (CACE) of the condensate, feedwater, boiler/evaporator water and steam. These measurements include contributions from corrosive species such as chloride, sulfate, carbon dioxide and organic anions. The higher the temperature and pressure of operation, the higher the purity of water required to prevent corrosion and, thus, the lower the CACE allowed.

A volatile alkalizing agent, preferably ammonia, is added to the feedwater to increase the pH. In some specific cases, an organic amine can be added instead [11, 12].

There are three variations of volatile conditioning that can be applied to the feedwater (Section 4 of the IAPWS Technical Guidance Document for All-Volatile Treatment [2] includes descriptions of all three treatments):

- Reducing all-volatile treatment (AVT(R)),
- Oxidizing all-volatile treatment (AVT(O)), and
- Oxygenated treatment (OT)

All-volatile treatment (AVT(R), AVT(O) or OT) has to be used for once-through boilers and is used without any further addition of chemicals in the boiler. AVT(R), AVT(O) or OT can also be used for drum boilers of fossil plants or combined cycle/HRSGs without any further addition of chemicals to the boiler/HRSG drum. However, impurities can accumulate in the boiler water of drum-type boilers and it is necessary to impose restrictive limits on these contaminants as a function of drum pressure to both protect the boiler from corrosion and limit the amount of impurities possibly carried over into the steam.

Ammonia is a rather poor alkalizing agent at high temperatures and offers very limited protection against corrosive impurities. It should be recognized that AVT has essentially no capability to neutralize or buffer feedwater/boiler water dissolved solid contaminants, and also provides reduced capability to provide protection in the two-phase regions.

For some drum-type boilers, the addition of solid alkalizing to the boiler/HRSG water may be necessary in order to improve the tolerance to impurities and reduce the risk of corrosion. In cases where the steam content might be limited (e.g., due to restrictions for extraction steam), the ammonia concentration in feedwater may be much too low in order to reduce the risk of FAC. For these situations, tri-sodium phosphate (phosphate treatment (PT)) or sodium hydroxide (caustic treatment (CT)) are recommended as the alkalizing agent. The two can also be used in combination. The amount of sodium hydroxide added has to be strictly limited to avoid excessively alkaline conditions, which can result in another UDC mechanism (caustic gouging) in the boiler/evaporator, which destroys the protective oxide layer. The amounts of both sodium hydroxide and tri-sodium phosphate added to the cycle also have to be controlled to avoid an increase of carryover of these conditioning chemicals into the steam. However, a certain amount of tri-sodium phosphate and/or sodium hydroxide has to be added to the boiler water just to elevate the pH.

AVT(R) has to be used for plants with copper alloys in the feedheating systems, but copper alloys are not used in this location in modern plants. OT can only be used in drum-type boilers, where high purity conditions can be guaranteed [2]. Thus, the recommended feedwater conditioning method used for drum-type boilers is AVT(O) for Phosphate (PT) and NaOH (CT) treatments, as described in this part of the IAPWS Technical Guidance.

4. Descriptions of Chemistries (Phosphate Treatment (PT) and Caustic Treatment (CT))

4.1 Introduction for PT and CT

Boiler and HRSG evaporator treatments are critical to the overall reliability of fossil and HRSG plants as they control and influence not only the major tube failure mechanisms but also a number of damaging mechanisms in the steam turbine. Corrosion takes place in the feedwater system (heaters and interconnecting pipework), and the associated corrosion products flow into the boiler/HRSG where they may deposit in various areas. These deposits can act in the boiler/HRSG evaporator as initiating centers for many of the tube failure mechanisms, and in the steam turbine as a source of either efficiency losses or blade/disk failures. Thus it is of primary concern that the IAPWS Volatile Guidance Document [2] is considered

to optimize the feedwater treatments and to minimize any deposition in the boiler/HRSG evaporator tubing.

The choice of boiler/evaporator chemistry treatment of either phosphate (PT) or NaOH (CT) depends on a number of important factors:

- a) For PT, the addition of only tri-sodium phosphate (TSP) is considered in the base tables of this IAPWS document. If phosphate hideout occurs with the addition of only TSP, then no harmful corrosion situations can occur, whereas some of the problems associated with use of other traditional phosphate treatments are discussed in Section 4.2, especially those where mono- and/or di-sodium phosphate is added. There are, however, some cases where congruent phosphate treatment is still used successfully in boilers/evaporators operating with drum pressures below 17 MPa (2465 psi) and where deposits are controlled.
- b) Drum pressure limits the use of CT up to 16.5 MPa (2400 psi). Special care should be given to combined cycle/HRSG units with duct burners to ensure that their use does not cause the HP drum pressure to exceed the 16.5 MPa limit. Here special problems might be hot spots with local dryout and concentration leading to local caustic gouging.
- c) Although PT is used up to drum pressures of 19.3 MPa (2800 psi), there are numerous observations that PT becomes difficult to control above drum pressures in the range 10–10.5 MPa (1450–1500 psi) due to hideout and hideout return. Using TSP precludes any corrosion reactions being associated with the phenomena, but as outlined in Section 6.4 a simple test should be undertaken to determine that the boiler/evaporator can maintain the >0.3 mg/kg (0.3 ppm) of phosphate considered to be needed for minimum protection.
- d) The cooling water source. Observations suggest that well controlled phosphate and NaOH treatments can manage chloride contamination.
- e) There are many successful examples of addressing FAC in the lower pressure circuits of HRSGs by using either PT or CT [8].
- f) The optimum location for injection of either phosphate or NaOH is into the drum and not into other plant locations such as the economizer/preheater of HRSGs. Just upstream of the drum (but downstream of the economizer/preheater in HRSGs) is also acceptable. Other exceptions are discussed in Section 6.6.
- g) LP boilers/HRSG evaporators that provide saturated steam and are dosed with NaOH have experienced stress corrosion cracking on downstream stainless piping/components in dry/wet regions. Application of CT needs to be done carefully in these cases where PT may be the preferred treatment. Carryover must always be measured on a frequent basis [3].
- h) Leakage of fresh alkaline cooling water into the boiler/HRSG evaporator can produce sodium hydroxide and raise the pH. CT may not be appropriate in these cooling water situations. If a condenser leak occurs, then the boiler water caustic limit (or corresponding pH) should not exceed 1 mg/kg (1 ppm). This may also be an application where mono- and di-sodium phosphate additions can be used.

4.2 Description of PT

4.2.1 Introduction to PT

Phosphates of various types are the bases of the most common boiler/HRSG evaporator treatments worldwide. However, historically there has been a multitude of phosphate compounds and mixtures blended with other treatment philosophies, which have resulted in a wide range of control limits for the key parameters (pH, phosphate level, and sodium-to-phosphate molar ratio) and a number of reliability issues. Some of the traditional phosphate treatments such as congruent phosphate treatment (CPT), coordinated phosphate treatment, and equilibrium phosphate treatment (EPT) have been used over the last 50 years across the fleet of fossil boilers and HRSG evaporators, sometimes successfully, sometimes resulting in tube failures and other problems. Use of CPT, where mono- and/or di-sodium phosphate are used to develop operating control ranges below sodium-to-phosphate molar ratios of 3:1, has resulted in serious acid phosphate corrosion (APC) in boilers/HRSG evaporators which have heavy deposits and have experienced phosphate hideout [6]. Use of EPT, which eliminated the possibility of APC and has some good operating experiences in mostly alkali cooling waters, forced operators to use very low levels of phosphate (<0.2 mg/kg), which essentially provided poor protection in the cases of acidic contaminants such as seawater and resulted in hydrogen damage [5].

More recently, for more than 20 years, consolidated good operating experiences have led to the recognition that tri-sodium phosphate (TSP) should be the only phosphate chemical added to a boiler/HRSG. Thus, the IAPWS guidance in this document suggests that the operating range should be bounded by sodium-to-phosphate molar ratios of 3:1 and TSP + 1 mg/kg NaOH with a pH above 9.0 and a lower phosphate limit above 0.3 mg/kg. This precludes addition of mono- and/or di-sodium phosphate and thus eliminates the possibility of APC. Also, by setting a minimum level for phosphate in the boiler/HRSG evaporator, this should eliminate operating in a regime with so little phosphate that there is not enough protection against contamination and thus hydrogen damage. It should be emphasized that the 0.3 mg/kg level is regarded as a minimum and that better protection will be afforded by operating at as high a level of phosphate as possible without exceeding the steam sodium limits.

Thus, there are two approaches to controlling the complications resulting from phosphate hideout and hideout return, and the effects these phenomena can have on boiler water pH. The first is congruent phosphate treatment (CPT), where a mixture of tri-sodium and di-sodium phosphate is used, in an attempt to counteract the effects on boiler water pH of hidden-out phosphate, and the risks of acid phosphate corrosion. A second, more recent approach is trying to minimize the corrosion aspects by addition of only TSP and to use lower levels of phosphate to minimize hideout. CPT is used successfully in certain parts of the world, but the higher concentrations of sodium phosphate often used in the boiler water can lead to higher sodium concentrations in the steam, due to mechanical carryover. Also, some operators do continue to use CPT without tube failures in boilers which don't

experience hideout and where deposits are controlled at low levels through optimum feedwater treatments and/or frequent chemical cleaning [13].

As with all-volatile treatment [2], ammonia in the feedwater exerts an effect on boiler water pH, so that, even without any phosphate present, the boiler water pH, as measured at 25 °C, is likely to be above 9.0. However, as stated in Section 3.1, ammonia is a relatively weak alkali. The addition of stronger alkalis, such as tri-sodium phosphate, to the boiler water suppresses its effect on pH. Also, the dissociation of ammonium hydroxide becomes significantly weaker at temperatures above 100 °C and, thus, its ability to influence the bulk water pH at boiler operating temperatures, and hence to control corrosion risks, diminishes.

PT can be used in a wide range of drum units up to high pressures (19 MPa, 2800 psi), so it is often the only alkali treatment available as IAPWS does not suggest using CT above 16.5 MPa (2400 psi). However, it will be recognized that hideout and hideout return become more prevalent with increasing pressure. Hideout and hideout return are always associated with large swings of pH causing control problems, but if only TSP is used, then no harmful corrosion reactions can be initiated as was experienced with CPT using sodium-to-phosphate molar ratios above 3:1. Sometimes hideout can be so bad that operating phosphate levels are reduced to below the minimum level (0.3 mg/kg) suggested in this PT guidance. In this case, it may be necessary to supplement the TSP with NaOH but always keeping within the pH/phosphate boundary range and below the sodium-to-phosphate molar ratio line of TSP + 1 mg/kg of NaOH. Some boilers/HRSG evaporators also need a small addition of NaOH (<1 mg/kg) to elevate the pH into the required range (>9.0).

For multi-pressure HRSGs, PT can also be used in each of the pressure cycles, but use of PT here is for different reasons depending on the pressure of the circuit. At high pressure (HP drums >10.3 MPa (1500 psi)), the addition of TSP is basically to address contamination in the same way as for conventional fossil plants, and the operating chemistry ranges are developed as above. In the lower pressure circuits, with temperatures below 250 °C, PT is used to control two-phase FAC much as CT is used in these circuits. Of course neither solid alkali is used in the LP evaporator in units where the LP drum feeds the IP and HP feedpumps and attemperation.

There needs to be an upper limit for addition of TSP which is set by the allowable sodium concentration in steam due to carryover. Vaporous carryover of phosphate is unlikely at pressures up to 17 MPa (2500 psi), however there is always a risk of mechanical carryover from drums [3]. It is most important that, when operating with any phosphate treatment, carryover is measured on a frequent basis, and sodium in steam (saturated or superheated) is confirmed to be below the applicable steam purity limit.

4.2.2 Monitoring PT

As already mentioned above, there should be no risk of any corrosive reactions if hideout occurs on units where only TSP is added. Careful monitoring and control of the boiler/HRSG evaporator water pH, conductivity and CACE should be

undertaken using on-line instrumentation according to the IAPWS Instrumentation Technical Guidance Document [4].

The contribution of anion impurities (chloride, sulfate) to the monitored conductivity and CACE is more complicated than for CT because of the phosphate anions in the water. However, CACE is regarded as the key instrument to provide overall protection for the high pressure boiler/HRSG evaporator, and hence knowledge of the contribution by the level of phosphate alone is required as well as the Normal/Target levels for chloride (and sulfate) in the boiler. Thus, the conductivity and CACE Normal/Target values in Tables 1, 3 and 4 in Section 5 are derived using the Normal/Target levels for anion impurities such as chloride and sulfate, which are considered to be harmless in terms of any concentrating reactions. It is recognized that chloride is only part of the anions present, and to take this into account sulfate concentrations up to twice those of chloride were considered in developing the CACE values. The values of conductivity and CACE in these tables must be used in conjunction with the other monitored parameters of pH and phosphate to ensure optimum protection. When acid contamination enters the plant, it will be expected that CACE will increase above Normal/Target levels in the tables, and, depending on the size of the contaminant, the boiler/HRSG evaporator pH will decrease as well as the CACE increasing at other cycle locations. The concentration of chloride as the typical anion impurities can be determined by analyzing samples of boiler/evaporator water or by using an on-line instrument.

Finally, for PT in the ranges shown in Tables 1, 3 and 4, the ammonia level in the boiler/HRSG evaporator water from the volatile feedwater treatment has an increasing influence on the pH monitored, particularly as the phosphate levels decrease from 3 to 0.3 mg/kg. Above about 3 mg/kg, there is little influence.

4.3 Description of CT (NaOH dosing)

4.3.1 Introduction to CT

Caustic treatment (CT) can be used in “conventional” and HRSG drum-type boilers to reduce the risk of on-load corrosion and hydrogen damage, due to chloride contamination, and in HRSGs for controlling flow-accelerated corrosion, where all-volatile treatment has proved ineffective, or where PT has been unsatisfactory due to hideout or has experienced difficulties of monitoring and control.

The addition of sodium hydroxide to the boiler/evaporator water has to be carefully controlled to reduce the risk of caustic gouging in the boiler and carryover into the steam, which could lead to damage of steam circuits and turbine due to stress corrosion cracking. Of primary risk are austenitic materials, stellite, and all steels with residual stresses (e.g., welds without heat treatment) in superheaters, steam piping and headers, turbine control and check valves, as well as components in the steam turbine. Ideally, caustic addition should be linked to chloride concentration for effective inhibition of under-deposit corrosion. CT is easy to monitor, and the absence of the complications due to the presence of phosphate allows on-line conductivity and CACE measurements to be used for control purposes.

Many of the features for the feedwater and steam for AVT for drum boilers/HRSG evaporators will also apply to CT. However, these need to be supplemented by additional considerations for the boiler water and steam. It is particularly important that CT only be used on units with good circulation, and where there is no possibility of dryout.

4.3.2 Guidance for CT

With CT, the concentration of sodium hydroxide in the boiler water has to be carefully controlled. There should be sufficient alkalinity to achieve the recommended pH, and to minimize the corrosive effects of salt impurities and inhibit FAC in high flow rate or turbulent zones at critical temperatures in the low pressure circuits of multi-pressure HRSGs. However, there should not be so much sodium hydroxide that there is a risk of caustic gouging in the boiler or damage to the turbine due to carryover into the steam. It is most important that, when operating with NaOH treatment, carryover is measured on a frequent basis, and sodium in steam (saturated or superheated) is confirmed to be below the applicable steam purity limit.

Thus, in addition to the alkalization provided by the ammonia in the feedwater, a certain amount of sodium hydroxide has to be added to the boiler water to achieve the recommended boiler water pH and provide protection against corrosion, but not so much as to risk causing caustic gouging. This is determined by the concentration factor in the boiler water/tube oxide interface. It is likely to be plant-specific and, generally, is not known. Areas of dryout would be even worse. However, such problems can normally be avoided simply by setting an upper limit to the boiler water pH and, hence, boiler water sodium hydroxide concentration. It should be noted that, above about 1.5 mg/kg of NaOH, the ammonia will have little effect on the pH.

The upper limit for sodium and other ions in the boiler water is also set by the allowable concentrations in steam. Both vaporous and mechanical carryover occur in drum boilers and HRSGs. Vaporous carryover of sodium hydroxide is unlikely to be a major problem at pressures up to 17 MPa (2500 psi), since it has a low volatility. Thus, strict limits for sodium in steam are required to reduce the risk of damage to the superheaters and turbine.

The concentration of sodium hydroxide in the boiler water should be sufficient to “neutralize” the effects of the anions present. This results in a band of operating conditions, with upper and lower limits for pH and sodium hydroxide. In the event of contaminant ingress, especially chloride, maximum effort should first be given to eliminating or minimizing the chloride content as discussed in the IAPWS Volatile Treatment Document [2]. In parallel, another approach is to increase the concentration of sodium hydroxide in the boiler water to 2.5 times the chloride concentration, up to that set by the upper pH limit [14].

The normal operating limits for chloride are set by the “neutralizing” capacity of the sodium hydroxide. The corresponding limits for sodium, and conductivity and CACE, can be derived from these data and used to assist in chemical control.

All of the above aspects are covered by the Normal/Target values and ranges for CT in the Tables 2-4 in Section 5. It should be noted that IAPWS suggests that NaOH only be used in boilers/HRSG evaporator circuits where the drum pressure is <16.5 MPa (2400 psi) due to lack of research above this pressure and a number of serious carryover and steam turbine deposition problems.

4.3.3 Monitoring CT

With CT, it is particularly important to avoid dryout in the boiler and carryover of boiler water impurities and conditioning chemicals into the steam. Careful monitoring and control of the boiler water pH, and conductivity and CACE measurements should be undertaken using on-line instruments according to the IAPWS Instrumentation Technical Guidance Document [4]. Sodium in steam should also be monitored using on-line instruments.

The contribution of anionic impurities (e.g., chlorides and sulfates) to the conductivity can be obtained directly from the CACE, since there is no complicating anion such as phosphate present. It is recognized that chloride is only part of the anions present, and to take this into account sulfate concentrations up to twice those of chloride were considered in developing the CACE values. The conductivity, after correction for the contribution for the anionic impurities, as indicated by the CACE, can then be used to calculate the pH. Conductivity measurements can often give a more reliable indication of pH than direct measurements and, in any case, should be used to confirm the value given by the pH meter.

The chloride concentration can be determined by analyzing samples of boiler/HRSG evaporator water, or by using an on-line instrument. If the proportion of chloride in the total anions of the boiler water is known to be steady during the various plant operating conditions, a good indication of the chloride concentration can be obtained from the CACE. The equivalent sodium hydroxide concentration can be obtained by titration of samples of boiler water, calculated from the conductivity and CACE, or derived from the boiler water pH.

5. Tables of Chemistry Limits

5.1 **Four Tables of Cycle Chemistry Limits.** Four tables of cycle chemistry limits have been included in this IAPWS Technical Guidance Document for PT and CT as Tables 1-4. These base tables cover the most common units and cycle chemistries in use around the world in conventional fossil and multi-pressure combined cycle/HRSG plants. Variations to the limits in these base tables are included in Section 6. Such variations might be a seawater cooled plant, a plant with copper alloys in the feedwater heaters, or a plant with a condensate polisher. The operator or chemist should determine which variation(s) to use by following

the Road Map in Section 6 and customizing the appropriate base table. The base tables include the following:

- a) Table 1. IAPWS Guidance for Phosphate Treatment (PT). Applicable to fossil plants with drum units, with drum pressure ~17 MPa (~2500 psi), all-ferrous feedwater systems, non-copper tubed condensers, without a condensate polisher, and not cooled by seawater or brackish water. Only tri-sodium phosphate additions to the boiler/HRSG circuit with phosphate levels between 0.3–1.5 mg/kg (ppm). See Section 4.2.1 on the minimum level of phosphate. See Section 5.2 for normal levels of pH, phosphate, and chloride used in developing this Table.
- b) Table 2. IAPWS Guidance for Caustic Treatment (CT). Applicable to fossil plants with drum units, with drum pressure ~16.5 MPa (~2400 psi), all-ferrous feedwater systems, non-copper tubed condensers, without a condensate polisher, and not cooled by seawater or brackish water. NaOH levels between 0.5–1.2 mg/kg (ppm). See Section 5.2 for normal levels of pH, NaOH, and chloride used in developing this Table.
- c) Table 3. IAPWS Guidance for Phosphate Treatment (PT) and Caustic Treatment (CT). Applicable to multi-pressure combined cycle/HRSG drum units, no copper alloys, independently fed low pressure (LP), intermediate pressure (IP) and high pressure (HP) circuits, no condensate polisher, no reducing agent added to the cycle, and not cooled by seawater or brackish water. The drum pressures on this base case are considered to be LP 0.5 MPa (70 psi), IP 2.4 MPa (350 psi), and HP 14 MPa (2000 psi). For PT, only tri-sodium phosphate additions to the boiler/HRSG circuit. See Section 5.2 for normal levels of pH, phosphate, NaOH, and chloride used in developing this Table.
- d) Table 4. IAPWS Guidance for Phosphate Treatment (PT) and Caustic Treatment (CT). Applicable to multi-pressure combined cycle/HRSG drum units, no copper alloys, with the LP drum feeding the IP and HP circuits, no condensate polisher, no reducing agent added to the cycle, and not cooled by seawater or brackish water. The drum pressures on this base case are considered to be LP 0.5 MPa (70 psi), IP 2.4 MPa (350 psi), and HP 14 MPa (2000 psi). For PT, only tri-sodium phosphate additions to the boiler/HRSG circuit. See Section 5.2 for normal levels of pH, phosphate, NaOH, and chloride used in developing this Table.

5.2 Normal Limits for PT and CT in Tables 1-4. In the IAPWS Volatile Technical Guidance Document [2], Normal/Target values developed for boiler/HSRG evaporator water were simply dependent on the ammonia added to the condensate or feedwater, and to immediately identifying contaminant ingress by monitoring CACE in the boiler/HSRG evaporator water and comparing the value to a normal level of contaminant. As discussed in Section 4, the solid alkali treatments, PT and CT, are a little different from the volatile treatments where there is no addition to the boiler/HRSG evaporator water. For these treatments, to develop the Normal/Target values it is necessary to define the level of phosphate and NaOH added to the boiler/HRSG evaporator and a normal level of chloride (and sulfate), which can be maintained without causing UDC and damaging carryover. The

development of a CACE Normal/Target value for PT needs to also include the effect of phosphate level.

For PT at the drum pressure defined for Table 1 (17 MPa, 2500 psi), the range is bounded by the sodium-to-phosphate molar ratio curves of 3:1 and TSP + 1 mg/kg NaOH with a minimum pH of 9.0 and a minimum level of phosphate of 0.3 mg/kg to a maximum of 1.5 mg/kg. The CACE value of <10 $\mu\text{S}/\text{cm}$ is for normal levels of chloride up to 150 $\mu\text{g}/\text{kg}$ and twice as much sulfate. The effect of drum pressure is discussed in Section 6.1.

For CT at the drum pressure defined for Table 2 (16.5 MPa, 2400 psi), the Normal/Target range for pH is from a minimum of 9.1 to a maximum of 9.5. This corresponds to a level of NaOH up to 1.2 mg/kg (1.2 ppm). The CACE of <9 $\mu\text{S}/\text{cm}$ includes a Normal/Target level of chloride up to 320 $\mu\text{g}/\text{kg}$ (320 ppb) and twice as much sulfate.

For the two HRSG cases in Tables 3 and 4, the same derivations have been conducted. The following ranges of phosphate and NaOH have been used for the PT and CT columns respectively: a) LP with pressure of 0.5 MPa (70 psi): 0.3–8.0 mg/kg phosphate, 2–4 mg/kg NaOH; b) IP with pressure of 2.4 MPa (350 psi): 0.3–7.0 mg/kg phosphate, 2–3.5 mg/kg NaOH; c) HP with pressure of 14 MPa (2000 psi): 0.3–2.0 mg/kg phosphate, 0.7–1.5 mg/kg NaOH. The conductivity and CACE values in Tables 3 and 4 have been developed using the following “normal” levels of chloride for each pressure: a) for the PT three pressure levels (LP, IP, HP) respectively: 3000, 2500 and 280 $\mu\text{g}/\text{kg}$, and b) for the CT three pressure levels (LP, IP, HP) respectively: 1500, 1200 and 400 $\mu\text{g}/\text{kg}$. In each case, the CACE value indicated also includes a contribution from twice the level of sulfate.

5.3 Chemistry Limits for Requisite Parameters at Specified Locations. Each table contains the cycle chemistry limits for the requisite parameters at prescribed locations from Table 1 of the IAPWS Instrumentation Technical Guidance Document [4].

Each of Tables 1-4 does not include a condensate polisher under these base conditions, so each plant is reliant on the phosphate or NaOH addition to address contaminant, and on CACE to identify the most serious contaminant in these cycles: ingress of a high level of chloride through a condenser leak. As discussed in the IAPWS Instrumentation Technical Guidance Document [4], for these cases, especially those that are seawater cooled, additional instruments are often included to provide extra security against contaminant entering the boiler/HRSG evaporator circuits. Suggestions here include CACE and sodium in the condenser hotwell and chloride in the boiler/HRSG evaporator on the respective blowdowns. Normal/Target values for chloride for each of the Tables is included in Section 5.2.

Similarly, as mentioned in the Instrumentation Technical Guidance Document [4], targets can be set for silica in the boiler/HRSG evaporator, but it is generally more directly appropriate to monitor silica in steam because it can cause a reduction in steam turbine efficiency. If an organization chooses this option, then an appropriate operating level for Normal/Target level is <10 $\mu\text{g}/\text{kg}$.

- 5.4 Development of Action Levels.** The normal or target values in Tables 1-4 represent the accumulated experience of the IAPWS Power Cycle Chemistry (PCC) Working Group with representation from 15 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. It is strongly suggested that each plant operator, chemist or owner develops a set of Action Levels, which define when the operators need to take some avoiding action in response to values outside the limits. It should be decided 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.** As well as developing a set of Action Levels, there will be a need to also define a set of cycle chemistry conditions when a unit will need to be shut down because of severe contamination. For the fossil and HRSG drum units that are the focus of this IAPWS Technical Guidance Document, this will usually relate to defining a pH or a CACE that indicates serious acidic contamination. Typically, a pH of 7 or 8 can be used under conditions which are coincident with a continuously decreasing boiler or HRSG evaporator water pH. It should be recognized that the local pH will be much lower at or in porous fossil waterwall or HRSG HP evaporator deposits.
- 5.6 Dealing with Condenser Leaks.** Contaminant ingress (such as contaminated feedwater) or out of limits chemistry anywhere in the plant should be dealt with through the development of Normal and Action Levels (Sections 5.2 and 5.4). For fossil drum boilers and the HP drum/evaporator on multi-pressure HRSGs operating with either PT or CT, the most important developments of guidance customization are for the case where the unit develops a condenser leak, which may be acidic or alkaline depending on the cooling water source, and may contain high levels of organics. In cases where the unit has no condensate polisher, this is obviously of paramount importance. There are two extremes. The first is where there is a major condenser leak perhaps of multiple tubes; this case should be dealt with expeditiously by the unit operator responding to an immediate shutdown limit as described in Section 5.5. The second is where there are persistent smaller leaks (multiple times per year) which exceed the Level One Action as described in Section 5.4. In the important case of an acidic in-leakage, as with seawater, the preferred option is to increase the dose of solid alkali (either tri-sodium phosphate or NaOH) into the drum. However, it must be remembered that this will only increase the boiler/HRSG evaporator pH and can only suppress under-deposit corrosion in the boiler/evaporator if applied at the right level. It is very well understood that hydrogen damage can occur with high chloride levels in the boiler/HRSG evaporator under insufficiently alkaline conditions and that caustic gouging can develop if NaOH is over dosed. The leaking condenser tubes must be identified and plugged; ultimately the condenser may need to be retubed.

Table 1. IAPWS Guidance for Phosphate Treatment (PT). Applicable to fossil plants with drum units, with drum pressure ~17 MPa (~2500 psi), all-ferrous feedwater systems operating on AVT(O), non-copper tubed condensers, without a condensate polisher, and not cooled by seawater or brackish water. Only tri-sodium phosphate additions are made to the boiler/HRSG circuit with phosphate levels between 0.3–1.5 ppm. (See Section 5.2 for normal levels of chloride (and sulfate) used in developing this table).

Locations / Parameters	Normal / Target Values
	PT
Condensate Pump Discharge (CPD)	
Conductivity after Cation Exchange, $\mu\text{S}/\text{cm}$	< 0.3
Dissolved Oxygen, $\mu\text{g}/\text{kg}$	< 10
Sodium, $\mu\text{g}/\text{kg}$	< 3
Economizer Inlet (EI)	
Conductivity, $\mu\text{S}/\text{cm}$	Consistent with pH
Conductivity after Cation Exchange, $\mu\text{S}/\text{cm}$	< 0.3
pH	9.2 – 9.8
Dissolved Oxygen, $\mu\text{g}/\text{kg}$	< 10
Boiler Drum / Blowdown (BD) / Downcomer (BDC)	
Conductivity, $\mu\text{S}/\text{cm}$	< 8
Conductivity after Cation Exchange, $\mu\text{S}/\text{cm}$	< 10
pH	9.0 – 9.3
Phosphate, mg/kg	0.3 – 1.5
Saturated Steam (SS)	
Conductivity after Cation Exchange, $\mu\text{S}/\text{cm}$	< 0.2
Sodium, $\mu\text{g}/\text{kg}$	< 2
Main Steam (MS) / Reheat Steam (RHS)	
Conductivity after Cation Exchange, $\mu\text{S}/\text{cm}$	< 0.2
Sodium, $\mu\text{g}/\text{kg}$	< 2
Makeup (MU)	
Conductivity, $\mu\text{S}/\text{cm}$	< 0.1
Conductivity after Cation Exchange, $\mu\text{S}/\text{cm}$	< 0.1
SiO_2 , $\mu\text{g}/\text{kg}$	< 10

Table 2. IAPWS Guidance for Caustic Treatment (CT). Applicable to fossil plants with drum units, with drum pressure ~16.5 MPa (~2400 psi), all-ferrous feedwater systems, non-copper tubed condensers, without a condensate polisher, and not cooled by seawater or brackish water. NaOH levels between 0.5–1.2 ppm. (See Section 5.2 for normal levels of chloride (and sulfate) used in developing this table).

Locations / Parameters	Normal / Target Values
	CT
Condensate Pump Discharge (CPD)	
Conductivity after Cation Exchange, $\mu\text{S}/\text{cm}$	< 0.3
Dissolved Oxygen, $\mu\text{g}/\text{kg}$	< 10
Sodium, $\mu\text{g}/\text{kg}$	< 3
Economizer Inlet (EI)	
Conductivity, $\mu\text{S}/\text{cm}$	Consistent with pH
Conductivity after Cation Exchange, $\mu\text{S}/\text{cm}$	< 0.3
pH	9.2 – 9.8
Dissolved Oxygen, $\mu\text{g}/\text{kg}$	< 10
Boiler Drum / Blowdown (BD)	
Conductivity, $\mu\text{S}/\text{cm}$	3.5 – 9.5
Conductivity after Cation Exchange, $\mu\text{S}/\text{cm}$	< 9.0
pH	9.1 – 9.5
Saturated Steam (SS)	
Conductivity after Cation Exchange, $\mu\text{S}/\text{cm}$	< 0.2
Sodium, $\mu\text{g}/\text{kg}$	< 2
Main Steam (MS) / Reheat Steam (RHS)	
Conductivity after Cation Exchange, $\mu\text{S}/\text{cm}$	< 0.2
Sodium, $\mu\text{g}/\text{kg}$	< 2
Makeup (MU)	
Conductivity, $\mu\text{S}/\text{cm}$	< 0.1
Conductivity after Cation Exchange, $\mu\text{S}/\text{cm}$	< 0.1
SiO_2 , $\mu\text{g}/\text{kg}$	< 10

Table 3. IAPWS Guidance for Phosphate Treatment (PT) and Caustic Treatment (CT). Applicable to multi-pressure combined cycle/HRSG drum units, no copper alloys, independently fed low pressure (LP), intermediate pressure (IP) and high pressure (HP) circuits, no condensate polisher, no reducing agent added to the cycle, and not cooled by seawater or brackish water. The drum pressures on this base case are considered to be LP 0.5 MPa (70 psi), IP 2.4 MPa (350 psi), and HP 14 MPa (2000 psi). For PT, only tri-sodium phosphate additions are made to the boiler/HRSG circuit. (See Section 5.2 for normal levels of chloride (and sulfate) used in developing this table).

Locations / Parameters	Normal / Target Values	
	PT	CT
Condensate Pump Discharge (CPD)		
Conductivity after Cation Exchange, $\mu\text{S/cm}$	< 0.3	< 0.3
Dissolved Oxygen, $\mu\text{g/kg}$	< 10	< 10
Sodium, $\mu\text{g/kg}$	< 3	< 3
Economizer Inlet (EI), Preheater Inlet or Feed Pump Discharge		
Conductivity, $\mu\text{S/cm}$	Consistent with pH	Consistent with pH
Conductivity after Cation Exchange, $\mu\text{S/cm}$	< 0.3	< 0.3
pH	9.2 – 9.8	9.2 – 9.8
Dissolved Oxygen, $\mu\text{g/kg}$	< 10	< 10
LP Drum (0.5 MPa, 70 psi) Blowdown (LPBD) / Downcomer (LPDC)		
Conductivity, $\mu\text{S/cm}$	< 45	15 – 45
Conductivity after Cation Exchange, $\mu\text{S/cm}$	< 80	< 45
pH	9.0 – 9.9	9.7 – 10.0
Phosphate, mg/kg	0.3 – 8.0	<i>Not applicable</i>
IP Drum (2.4 MPa, 350 psi) Blowdown (IPBD) / Downcomer (IPDC)		
Conductivity, $\mu\text{S/cm}$	< 45	10 – 35
Conductivity after Cation Exchange, $\mu\text{S/cm}$	< 80	< 40
pH	9.0 – 9.8	9.6 – 9.9
Phosphate, mg/kg	0.3 – 7.0	<i>Not applicable</i>
HP Drum (14 MPa, 2000 psi) Blowdown (HPBD) / Downcomer (HPDC)		
Conductivity, $\mu\text{S/cm}$	< 15	4 – 12
Conductivity after Cation Exchange, $\mu\text{S/cm}$	< 20	< 15
pH	9.0 – 9.4	9.2 – 9.5
Phosphate, mg/kg	0.3 – 2.0	<i>Not applicable</i>

Locations / Parameters	Normal / Target Values	
	PT	CT
Saturated Steam on LP, IP and HP Drums		
Sodium on LP Drum, µg/kg	< 3	< 2
Sodium on IP Drum, µg/kg	< 3	< 2
Sodium on HP Drum, µg/kg	< 2	< 2
HP Steam / RH Steam		
Conductivity after Cation Exchange, µS/cm	< 0.2	< 0.2
Sodium, µg/kg	< 2	< 2
Makeup (MU)		
Conductivity, µS/cm	< 0.1	< 0.1
Conductivity after Cation Exchange, µS/cm	< 0.1	< 0.1
SiO ₂ , µg/kg	< 10	< 10

Table 4. IAPWS Guidance Document for Phosphate Treatment (PT) and Caustic Treatment (CT). Applicable to multi-pressure combined cycle/HRSG drum units, no copper alloys, with the LP drum feeding the IP and HP circuits, no condensate polisher, no reducing agent added to the cycle, and not cooled by seawater or brackish water. The drum pressures on this base case are considered to be LP 0.5 MPa (70 psi), IP 2.4 MPa (350 psi), and HP 14 MPa (2000 psi). For PT, only tri-sodium phosphate additions are made to the boiler/HRSG circuit. (See Section 5.2 for normal levels of chloride (and sulfate) used in developing this table).

Locations / Parameters	Normal / Target Values	
	PT	CT
Condensate Pump Discharge / Economizer (Preheater Inlet)		
Conductivity after Cation Exchange, $\mu\text{S}/\text{cm}$	< 0.3	< 0.3
Dissolved Oxygen, $\mu\text{g}/\text{kg}$	< 10	< 10
Sodium, $\mu\text{g}/\text{kg}$	< 3	< 3
Feed Pump Discharge / IP/HP Economizer Inlet (LP Boiler Water)		
Conductivity, $\mu\text{S}/\text{cm}$	Consistent with pH	Consistent with pH
Conductivity after Cation Exchange, $\mu\text{S}/\text{cm}$	< 0.3	< 0.3
pH	9.2 – 9.8	9.2 – 9.8
Dissolved Oxygen, $\mu\text{g}/\text{kg}$	< 10	< 10
IP Drum (2.4 MPa, 350 psi) Blowdown (IPBD) / Downcomer (IPDC)		
Conductivity, $\mu\text{S}/\text{cm}$	< 45	10 – 35
Conductivity after Cation Exchange, $\mu\text{S}/\text{cm}$	< 80	< 40
pH	9.0 – 9.8	9.6 – 9.9
Phosphate, mg/kg	0.3 – 7.0	<i>Not applicable</i>
HP Drum (14 MPa, 2000 psi) Blowdown (HPBD) / Downcomer (HPDC)		
Conductivity, $\mu\text{S}/\text{cm}$	< 15	4 – 12
Conductivity after Cation Exchange, $\mu\text{S}/\text{cm}$	< 20	< 15
pH	9.0 – 9.4	9.2 – 9.5
Phosphate, mg/kg	0.3 – 2.0	<i>Not applicable</i>
Saturated Steam on IP and HP Drums		
Sodium on IP Drum, $\mu\text{g}/\text{kg}$	< 3	< 2
Sodium on HP Drum, $\mu\text{g}/\text{kg}$	< 2	< 2
HP Steam / RH Steam		
Conductivity after Cation Exchange, $\mu\text{S}/\text{cm}$	< 0.2	< 0.2
Sodium, $\mu\text{g}/\text{kg}$	< 2	< 2

Locations / Parameters	Normal / Target Values	
	PT	CT
Makeup (MU)		
Conductivity, $\mu\text{S/cm}$	< 0.1	< 0.1
Conductivity after Cation Exchange, $\mu\text{S/cm}$	< 0.1	< 0.1
SiO ₂ , $\mu\text{g/kg}$	< 10	< 10

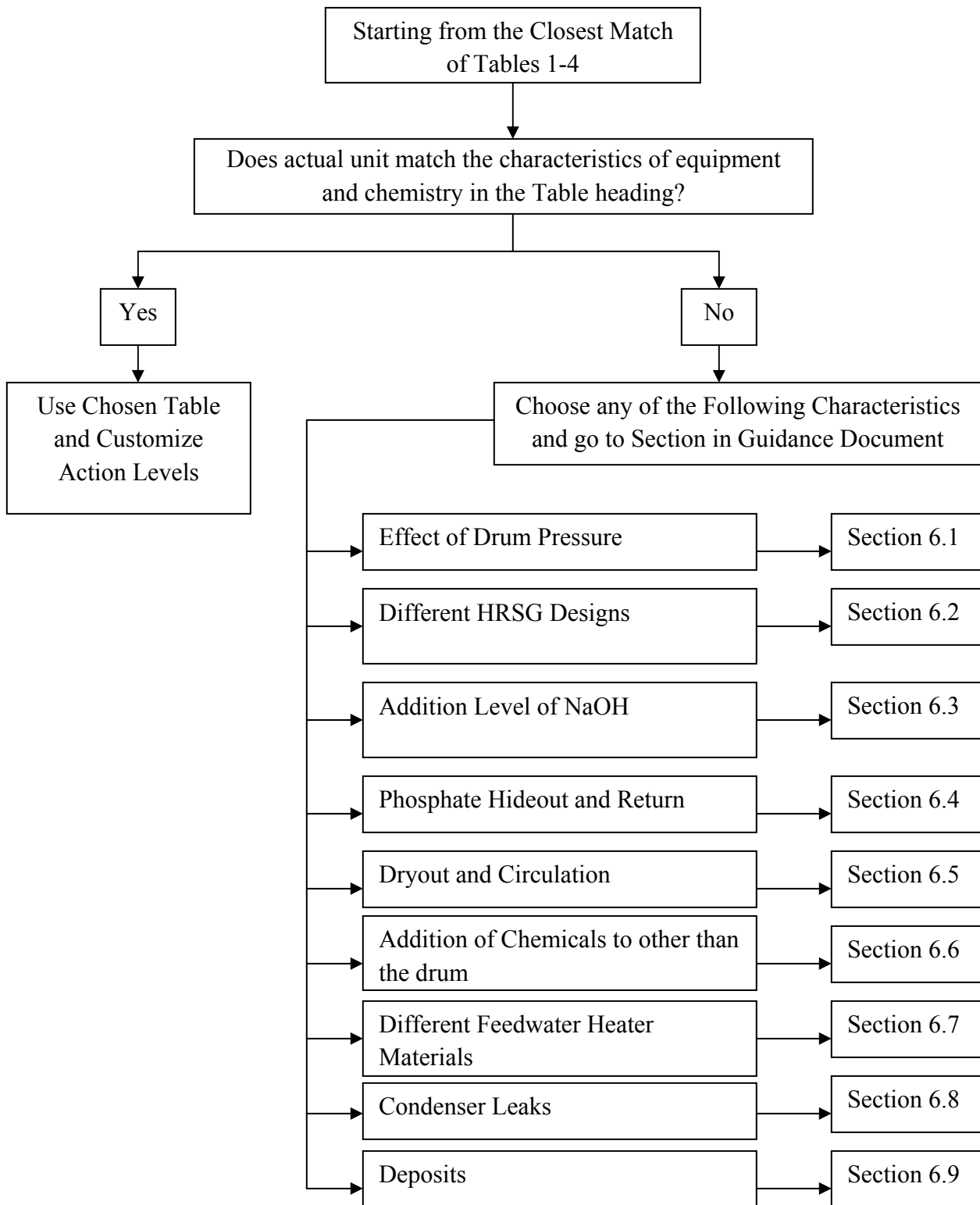
6. Road Map Approach to Reach Optimum PT and CT for Fossil and Combined Cycle/HRSG Plants

Tables 1-4 will provide general guidance for the wide majority of fossil and combined cycle/HRSG plants around the world. **However, it is emphasized that this is an IAPWS Technical Guidance Document and that, depending on local requirements, the Normal/Target values presented in Tables 1-4 will need to be adapted to each plant as there are no sets of tables of cycle chemistry limits which can be applied to every plant worldwide.** This customization of Tables 1-4 is the most important step in deriving cycle chemistry limits for plants with different operating pressures, unique equipment, materials and possible damage/failure mechanisms applicable to that plant. The most common of these features constitute the topics in Sections 6.1 to 6.9.

As each plant is unique, the IAPWS Road Map (Figure 1) provides the approach envisioned. This will identify the necessary customizations required and assist in moving from one of Tables 1-4 to a set of limits that more accurately addresses the actual unit. For units that match the descriptions of the base plants and chemistries in Tables 1-4, the only customization required will be to develop operating chemistry limits that include Action Levels (Section 5.4) and a specific set of Shutdown Limits (Section 5.5). For units that have operating regimes or include equipment outside of the descriptions and chemistries for plants in Tables 1-4, some further customization will be required to ensure that cycle chemistry influenced damage will not occur. Alternatively, a plant might already have experienced some of the damage or failure associated with the additional categories and the current cycle chemistry limits will thus need optimization.

For this PT and CT Technical Guidance Document, the following sections deal with the customizations that will need to be made to make the guidance directly applicable to each plant where phosphate or NaOH is added to the boiler/HRSG evaporator water. However, the customizations relating to feedwater and condensate within the Volatile Treatment Document [2] will also need to be applied for each plant.

Figure 1. IAPWS Roadmap to Develop Cycle Chemistry Limits from the Base Tables 1-4 to Actual Unit Operating Pressure, Specific Configuration and Limits.



6.1 Customization of Base Tables to Include the Effect of Drum Pressure

Some of the customizations related to varying drum pressure were included in the Volatile Technical Guidance Document [2] but become additionally important for the current document because of the possible carryover of phosphate or NaOH into steam, protection of the steam turbine from damage and/or failure, and in helping to eliminate the conditions which lead to under-deposit corrosion in the waterwalls of fossil drum boilers and the HP evaporators of HRSGs. The fossil limits in Tables 1 and 2 are for boilers with drum pressure of ~17 MPa (~2500 psi) and 16.5 MPa (2400 psi), respectively. The HRSG limits in Tables 3 and 4 are for units with HP drum pressure of ~14 MPa (~2000 psi). The following features need to be considered for drum pressures varying from these values.

- a) Carryover, both volatile and mechanical, increases with increasing pressure (see the IAPWS Technical Guidance Document on Carryover [3]). Most importantly, only above pressures of about 16 MPa (2300 psi) does vaporous carryover become significant for most of the solids dissolved in boiler water. Below about 17.2 MPa (2500 psi), the vaporous carryover of phosphoric acid (H_3PO_4) and of NaOH are very low, with mechanical carryover being the dominant transport mechanism. Sodium control in the boiler/HRSG evaporator water is critical when using CT, as nearly all sodium present in the steam is likely to be present as sodium hydroxide; it is for this reason that an upper operating pressure limit of 16.5 MPa (2400 psi) on the drum is imposed on CT in Tables 2-4. Sodium in steam could also be a concern with PT used at sodium-to-phosphate molar ratios above 3:1 but below TSP + 1 $\mu\text{g}/\text{kg}$ NaOH at pressure above 17.2 MPa (2500 psi) as the volatility of NaOH increases. Of course silica and the copper hydroxides are transported into steam as volatile compounds across the range of pressures applicable to fossil and HRSG plants. Thus, the addition of phosphate and NaOH to the boiler/HRSG evaporators in PT and CT, and the possible mechanical carryover of phosphate and NaOH into steam provide additional emphasis on the need to measure the total carryover. There are two aspects which need to be addressed. The first is to identify any deficiencies in the drum furniture or the development of welding defects allowing salts to bypass the separation devices. The second is with regards to adding too much phosphate or NaOH to the drum for control purposes over and above the levels suggested for Tables 1-4. The result in either case may be white deposits on the IP or LP turbine. The total carryover should be measured initially during the process to assign the optimum alkali level to the drum. The steam limits included in Tables 1 and 2 have been derived to control the risk of deposition of harmful salts (chlorides, sulfate, etc.) in the phase transition zone of the steam turbine, and these limits are directly related to carryover and deposition. However, it is recognized that the Normal/Target values for CACE and chloride in boiler/HRSG evaporator water for both PT and CT in Tables 1-4, and as a function of pressure in Section 5.2, will also provide protection against initiation of UDC in the boiler/HRSG evaporator. For any drum pressure, it is important to know the total carryover and check it every 6-12 months as part of the steam turbine and superheater/reheater protection. At drum pressures above ~17 MPa (~2500 psi) on fossil and HRSG HP drums, the steam volatility of solutes becomes increasingly significant. For units with mixed-metallurgy feedwater

systems, operating above this pressure will cause an increasing solubility of copper hydroxides in steam which will be transported to, and deposit in, the HP turbine.

- b) The important tube failure mechanisms of under-deposit corrosion (UDC) are a function of pressure and can be experienced in the waterwalls of fossil plants operating at drum pressures above ~8 MPa (~1100 psi) and in some severe cases at lower pressures, and similarly on the leading HRSG HP evaporator tubes (closest to the gas turbine). These mechanisms involve two parallel aspects: i) increasing deposits on the internal heat transfer surfaces and ii) concentration of contaminants (chloride or sulfate) or incorrect boiler/HRSG evaporator chemicals (acid phosphates or excessive amounts of NaOH). The higher the pressure of the fossil/HRSG drum, the greater is the risk of damage, which relates to an increased concentration factor within the deposit. For this current PT and CT Technical Guidance Document, there is a particularly serious concern with CT of adding NaOH only up to levels that should not lead to caustic gouging tube failures. Tables 2-4 have taken this into account for the pressures applicable to those tables; suggested values at alternate pressures are included in Section 5.2. This is also the reason that TSP is the phosphate addition of choice in PT, because additions of mono- and di-sodium phosphates in Congruent Phosphate Treatment for high pressure boiler/HRSG evaporators (above ~8 MPa (~1100 psi)) have resulted in serious acid phosphate corrosion in situations with hideout [6]. These are applicable to lower sodium-to-phosphate molar ratios (<3:1).

With regards to deposition in fossil high pressure boiler waterwalls, there is a need to keep the feedwater corrosion products at or below those suggested in Sections 6.2 and 6.3 of the Volatile Treatment Technical Guidance Document [2]. In combined cycle/HRSG cycles, the corrosion products in the LP circuits become the controlling feature, and it is well understood that keeping the total iron below 2 µg/kg in the feedwater and below 5 µg/kg in each drum will provide the cleanest evaporator circuits with minimum risk of UDC occurring in the HP evaporator.

- c) Items a) and b) require that the CACE and chloride Normal/Target limits for fossil boilers in Tables 1 (at 17 MPa, 2500 psi) and 2 (at 16.5 MPa, 2400 psi) and for HRSG HP evaporators provided in Tables 3 and 4 (at 14 MPa, 2000 psi) are customized to actual operating drum pressures as indicated in Section 5.2.

6.2 Customization of Base Tables to Deal with Different HRSG Designs

The most widespread HRSG design is the horizontal gas path (HGP) with triple-pressure drum boilers with vertical tube arrangements and natural circulation. Base Tables 3 and 4 cover the worldwide experiences gained with this design. However, the following represent several other HRSG designs and features which are available and in operation, and where careful customization of the parameters in the tables may be required based on review of the design:

- a) Vertical gas path (VGP) HRSGs with horizontal tube arrangement and natural circulation. Here the risk is a low circulation rate at low loads which will lead to steaming in evaporator tubes with local deposition and possible concentration of phosphates or caustic.
- b) HRSG with duct burners. Here the risk is of hot spots with local dryout with deposition and consequent local concentration of phosphates or NaOH.
- c) HRSG with cascading blowdown. Here the risks are associated with control of alkalization, the risk of over-alkalization in the LP, and control of impurity levels in the LP evaporator.
- d) HRSG where the LP drum acts as a Deaerator / Feedwater Tank. In this case, no solid alkalization of the LP drum is permitted.
- e) HRSGs where the LP boiler blowdown feeds gas turbine cooling air coolers. The design features of the air cooler must be considered because the material is mostly austenitic. The tube heat exchanger may have crevices, which can lead to local concentration of phosphate or caustic.
- f) HRSGs with vulnerability to dryout in the peripheral tubes of the assembly.
- g) Double-pressure HRSGs with the LP drum feeding the HP economizer. In cases where the pH may not be high enough in the LP evaporator to counteract two-phase FAC, a small flow from the HP drum to the LP drum will elevate the LP drum pH. This can only be applied if the LP drum does not provide attemperation for the HP superheater.

6.3 Customization of Base Tables to Deal with the Addition Level of NaOH

CT is suitable for use on boilers/HRSG evaporators without internal thick oxide deposits. Compared with AVT, where ammonia is the only alkalizing agent, the addition of sodium hydroxide to the boiler/HRSG water increases the tolerance of the boiler to potentially corrosive anions, such as chloride as is discussed in Section 5.2.

The amount of NaOH that can safely be added depends on the operating pressure. Higher concentrations can be added to lower pressure plants than to higher pressure plants (see Section 5.2). A minimum concentration (for example, 0.5 ppm NaOH for high pressure plants) is required to achieve pH and give some protection against the initiation of corrosion (UDC) by chloride. A maximum concentration (for example, 1.2 ppm NaOH for high pressure plants [16.5 MPa (2400 psi)]) is set to minimize the risk of causing caustic gouging in the boiler and excessive carryover into the steam.

There needs to be sufficient NaOH present to minimize risks from chloride and UDC. One method used to achieve this is to ensure that the concentration of NaOH in the boiler water is at least 2.5 times the chloride concentration [14]. (The excess allows a degree of alkalization to cover other anions typically present.) There are upper limits for NaOH and pH, interdependent with the upper limit for chloride. As with the limits for NaOH and pH, the limit for chloride is also pressure dependent (see Section 5.2); for example, the limit is 0.32 mg/kg chloride for high pressure plants. Excessive concentrations of NaOH, over that required by chloride, are unnecessary and should be avoided.

It is important to know the range of chloride concentrations likely to be encountered during normal (and abnormal) operation of the plant and use these data when

selecting the limits. It is necessary to monitor conductivity and CACE to confirm that correct conditions are being achieved, and then use this information for routine control purposes.

6.4 Customization of Base Tables to Deal with Phosphate Hideout and Hideout Return

Phosphate hideout and return have been identified as serious chemical control problems for as long as phosphate treatments have been used in fossil plants. It is particularly prevalent in boilers and HRSG evaporators operating above ~10 MPa (~1500 psi), and users of this Technical Guidance Document need to be cognizant of how to identify the phenomenon and how to rectify it. It needs to be recognized when the decision is made to operate a boiler/HRSG evaporator on PT. It has also been clearly identified [6] that, if an incorrect phosphate treatment is used, hideout and hideout return can result in major tube failure problems, with acid phosphate corrosion (APC) being the predominant mechanism.

The solubility of sodium phosphate in boiler/evaporator water decreases with increasing temperature (retrograde solubility). It is important to note that both the precipitation (phosphate hideout) and the hydrolysis (phosphate hideout return) are incongruent reactions in which the composition of the reaction products differs from that of the reactants. Basically, with increasing drum pressure, hideout of the phosphate within the boiler/HRSG evaporator occurs with concomitant pH changes dependent on the type of phosphate treatment being used. The two extremes are: a) in the case of only adding tri-sodium phosphate (TSP), a pH reduction on startup (increasing pressure) is observed and an increase on shutdown, whereas b) in the case of addition of mono- and/or di-sodium phosphate with a sodium-to-phosphate molar ratio less than 3:1, a pH increase occurs on startup and a decrease on shutdown. When hideout involves the latter case under conditions of higher pressures and dirty waterwalls (heavy deposits), then the acidic phosphate compounds interact with the magnetite and sometimes with the tube surface to the extent that APC becomes predominant [6]. Choice of the former eliminates the possibility of UDC but can cause large pH swings to occur.

An operator should conduct a simple test to determine the approximate level of phosphate that can be maintained in a boiler/HRSG evaporator without hideout. At a pressure below maximum operating pressure, a couple of mg/kg of TSP should be added to the boiler/HRSG evaporator with the blowdown closed; the pressure is increased to maximum and the remaining phosphate level determined. Attention should be given to the accumulated phosphate in the circuit when the quality of makeup water and feedwater is poor. Trying to operate with a phosphate level above this will result in phosphate hideout, hideout return and accompanying pH changes. If this level is below the value of 0.3 mg/kg suggested in Tables 1, 3 and 4, then consideration must be given to: a) continuing to operate with control problems above 0.3 mg/kg, b) operating with CT providing the operating pressure is below 16.5 MPa (2400 psi), or c) operating with AVT as in the Volatile Technical Guidance Document [2] with additional precautions against contaminant ingress.

When the phosphate control limits are exceeded (the boiler shows significant signs of hideout return), the phosphate dosing should be stopped and the control parameters carefully monitored. As the actual phosphate inventory has not decreased in the boiler/evaporator, it will return on heat flux, pressure and load reductions.

6.5 Customization of Base Tables to Deal with Dryout and Circulation Problems

HRSGs with horizontal tubes (Vertical Gas Path (VGP) HRSGs) (Section 6.2a) should be carefully investigated when solid alkalization is applied. Similarly, in natural circulation fossil drum boilers with horizontal or near horizontal tubing (slope tubes), the probability of local and temporary partial loss of coolant conditions is relatively high. These situations may lead to an undesired local concentration of corrosion products and alkalizing agent by partial local steaming or even dryout. Both effects may result in locally extreme high pH values which for CT may lead to a fast tube wall loss. The same wall loss may also occur if a traditional phosphate treatment (congruent phosphate treatment) is used with the addition of mono- and/or di-sodium phosphate, but will not occur with the addition of only TSP. Hydrogen damage can also occur in these regions if contaminant (chloride) is present in the cycle.

Standard monitoring and analysis of the bulk water, either online or by grab sampling, may not recognize these reactions because of the relatively small areas affected within the total boiler/HRSG. Besides fluid dynamic investigations, the only method to detect these effects is by applying a tracer method using ^{24}Na (a conveniently short-lived Beta emitter with the gamma emission easily detected outside the boiler) followed by extensive radiation measurement over the entire evaporation area [15].

Careful consideration needs to be given to using solid alkalization in boilers/HRSGs where these local concentration reactions occur on a regular or repeated basis, as lower concentrations may not minimize this issue.

6.6 Customization of Base Tables to Deal with the Addition of Chemicals into other than the Drum (e.g., economizer inlet)

The base Tables 1-4 include situations where TSP or NaOH are added to the drums. But a number of combined cycle/HRSG plants worldwide provide steam for process use such as food production or steam heating supply. These plants usually are not allowed to use volatile ammonia or amines in the feedwater. They have to rely on solid alkali treatments (PT or CT), and in these cases the drum alkali may have to be supplemented at other locations. This means that the feedwater operates without any chemical volatile addition at low pH (~7.0). The primary means of addressing this is to use chromium-containing materials for the piping (stainless steel, 1.25% Cr or 2.25% Cr). Chemically, phosphate/NaOH can be added to the economizer or preheater inlet, perhaps with another phosphate or NaOH compound being added to the drum to balance this feedwater addition. In these cases, it is of paramount importance that FAC is controlled throughout the cycle and that total iron corrosion product levels are measured at the inlet and outlet of the economizer/preheater as well as in the drum. The preheater/economizer outlet will provide an indication of

whether FAC is occurring in those circuits: a level of $<2 \mu\text{g}/\text{kg}$ total iron remains a good target [2]. When considering alternate locations for injection of phosphate or NaOH, consideration should be given to the possibility of steaming in LP economizers/preheaters.

For units with attemperators, the source of the water needs to be chosen carefully to avoid ingress of the alkali addition into the steam.

6.7 Customization of Tables 1 and 2 to Deal with Different Feedwater Heater Materials (all-ferrous and mixed-metallurgy)

Tables 1 and 2 include all-ferrous feedwater heaters as the base condition. This might involve the use of stainless steel tubing in the low pressure (LP) heaters, carbon steel tubing in the high pressure (HP) tubing, stainless steel in both, or a combination with other ferrous alloys (such as T11 tubing (2.25% Cr)). However, many fossil drum units worldwide have: i) copper alloy tubing in the LP and/or HP tubing, ii) a mixture of copper and ferrous alloys in the LP and HP, or iii) changed alloys during the life of the plant from initially copper or mixed-metallurgy to all-ferrous. As discussed in Section 6 of the IAPWS Volatile Treatment Guidance Document [2], each of these cases needs careful consideration and will require different feedwater treatments to minimize corrosion, FAC and the transport of feedwater corrosion products to the boiler. Suggested iron and copper levels are included in the Volatile Document [2]. The ramifications for the boiler water treatments included in this PT/CT Document are that there is a need to know the rate of deposition on waterwall tubes by removing samples at regular intervals. Thicker deposits have a number of serious concerns: a) for PT, phosphate hideout can be more difficult to control; b) for both PT and CT, they will act as concentrating centers for chloride, which may eventually lead to hydrogen damage; and c) for CT, they will also act as concentrating centers for NaOH, which may eventually lead to caustic gouging. The presence of large amounts of copper in these deposits will exacerbate all the mechanisms.

6.8 Customization of Base Tables to Deal with Condenser Leaks

The important item of dealing with condenser leaks has been included in Section 5.6. Tables 1-4 have been developed for situations where the cooling water was from freshwater, city water, a lake or river, but did not include seawater or brackish water containing high levels of chloride. In these cases, customization needs to include identification of early ingress of contaminant into the cycle. This has been dealt with in the IAPWS Instrumentation Technical Guidance Document [4] by including a continuous sodium analyzer at the condensate pump discharge and by ensuring that the plant is controlled by a series of CACE instruments at the condensate pump discharge, economizer inlet, drum blowdown and in steam. Added security against this important ingress can be achieved by having “fast response” sensors (sodium and CACE) in the condenser hot well. In this way, a plant operator will immediately have no uncertainty when a contaminant event occurs and should have no doubt when there is a need to reduce pressure or shut down the unit. This key level of instrumentation should be installed to reduce the time delay of an operator checking an instrument and/or contacting the chemist for assistance.

Plants that have wet cooling towers, where cycles of concentration may vary through factors of 3 to 5 or more, will also need to provide similar customization.

As discussed in Section 5, operators of fossil drum plants without condensate polishing and with seawater cooling usually consider the addition of a solid alkali (tri-sodium phosphate or NaOH) in the drum at levels which can address contaminant ingress. Operators of multi-pressure HRSGs will need to consider the same for all evaporator circuits with particular emphasis on the HP. It is most important that action or operating procedures are developed as discussed in Sections 5.4 to 5.6.

6.9 Customization of Base Tables to Deal with Deposits

It has been understood for more than 40 years that, in fossil plants (Tables 1 and 2), feedwater corrosion products need to be controlled for both PT and CT as the first step in controlling under-deposit corrosion (UDC). In multi-pressure HRSGs, a more recent relationship was developed [16] between corrosion and FAC, which occurs in the lower pressure circuits, and deposition in HP evaporator tubes. Operating with the optimum chemistry in the IAPWS Volatile Treatment Guidance Document [2] minimizes the transport and deposition. On the contrary, use of reducing agents in the condensate/feedwater, which is known to increase single-phase FAC, and/or an amine or amine blend/mixture, increases the deposition on HP evaporator tubing noticeably [16]. It also has become clear that deposition in HP evaporators is not identical to that in conventional fossil plant waterwalls. Clear signs of concentrating reactions within deposits are seen in the former much earlier. Overall development of the operating chemistry for combined cycle/HRSG plants needs to consider the low pressure circuits, the high pressure circuits, and most importantly the interaction between the two. Unless there is a good reason to use reducing agents and amines, these should be avoided in HRSG cycles.

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