

Current Water Treatment Practices—Utility and Industrial Steam Systems

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This article gives the technical basis for selection of water treatment programs and summarizes the common water treatments used in utility and industrial steam systems. It is based on surveys of U.S. and international water treatment practices and on reviews and audits of water and steam chemistry of more than 400 fossil fuel utility and industrial power plants, including combined cycle units.

With the increase in unit sizes, stresses, and heat fluxes, as well as equipment aging, unit cycling, and the high cost of replacement power and lost industrial production, corrosion protection of steam cycle components during operation and layup and the control of water and steam chemistry are of critical importance. The cost of corrosion and of scale and deposit buildup in U.S. utility systems is more than \$3 billion/year.

It is even higher for industrial steam systems. As much as 50% of outage time has been attributed to corrosion, with damaged boiler tubes, condensers, turbines, feedwater heaters, carbon steel (CS) piping, pressurized water reactor (PWR) steam generators, and boiling-water reactor (BWR) pipe welds being the main contributors. The cost of replacement power can be as high as \$100/MWh, or more than \$1 million/day for a large utility unit. (The cost reached \$7,000/MWh at one utility in summer 1998.) The cost of reduced or lost production in an industrial plant can be equally high. It is now projected that 1,000 new power plants will be needed in the U.S. in the near future.

Current Water Treatment Status

Current corrosion and erosion problems include erosion-corrosion of CS piping and other components, boiler tube failures, deaerator weld cracking, corrosion fatigue, and stress corrosion cracking of low-pressure turbine blades and blade attachments. In addition, copper deposition on high-pressure turbine blades is responsible for MW losses. Solid particle erosion in turbines; erosion-corrosion; pitting of condenser, heater, and economizer tubes; and numerous corrosion problems in nuclear units also occur.

The developments changing water chemistry control include:

- Diminishing role of the plant water chemist, together with limited training and experience of the operators and outside chemists who now are often in charge of water treatment.
- Proliferation of the use of organic water treatment chemicals and their improper use, leading to generation of organic acids; and lack of knowledge and analysis of their behavior.
- Better water purification equipment and use of demineralized high-purity makeup—no need for expensive organic water treatments.

TABLE 1

ACHIEVABLE GOALS

- Oxygenated treatment for utility (and possibly industrial) units with high-purity feedwater.

In light of current trends, water treatment specialists see the following as their primary objectives:

- Preventing cycle component corrosion and the resulting forced outages and repairs.
- Operating at the maximum thermodynamic efficiency (minimum heat rate) and generating capacity by control of scale and deposits.

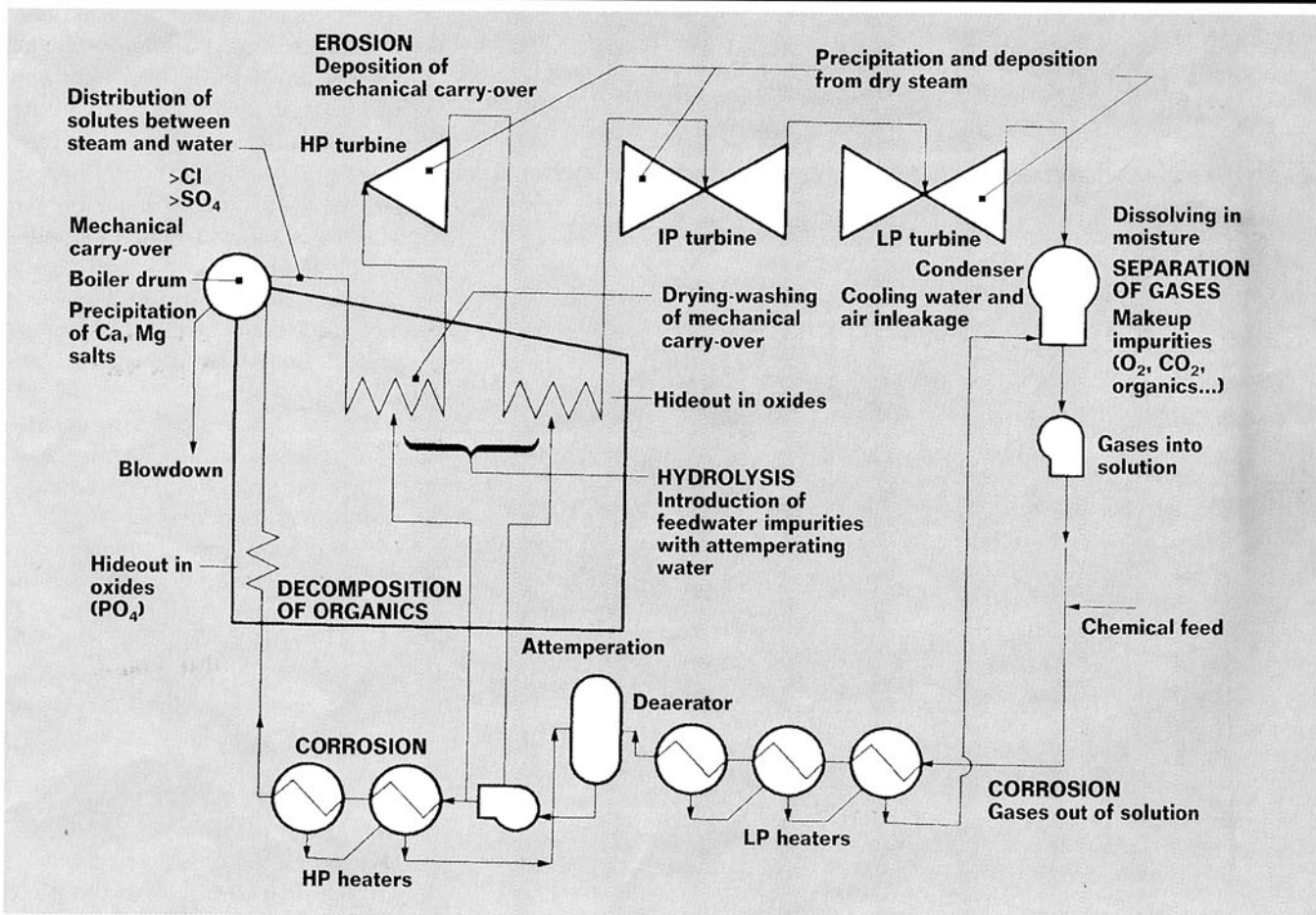
Table 1 shows the goals that can be achieved by effective cycle chemistry control combined with proper design, material selection, operation, and maintenance. Generally, there should not be any water chemistry-related corrosion failures. Also, the scale and de-

- Equivalent availability loss caused by boiler tube failures <1.5%—none cycle chemistry-related.
- No turbine steam chemistry-related problems—LP blade pitting and corrosion fatigue, disk stress corrosion cracking, MW and efficiency loss because of deposit buildup.
- Turbine inspection and cleaning interval of 10 years.
- Elimination of boiler chemical cleaning.
- Shorter startup—optimization of shutdown, layup, and startup.
- Boiler layup without extra chemicals.
- Simple, reliable instrumentation—quality assurance/quality control, direct on-line instruments.
- Representative sampling.
- Automatic control of chemical additions and blowdown.
- Optimum managerial approach to cycle chemistry.
- Operational guidelines for all operational conditions and types of steam cycles.

posits should require only infrequent chemical and mechanical cleaning. The latest developments are promising: turbine inspection intervals extended up to 10 years, no boiler chemi-

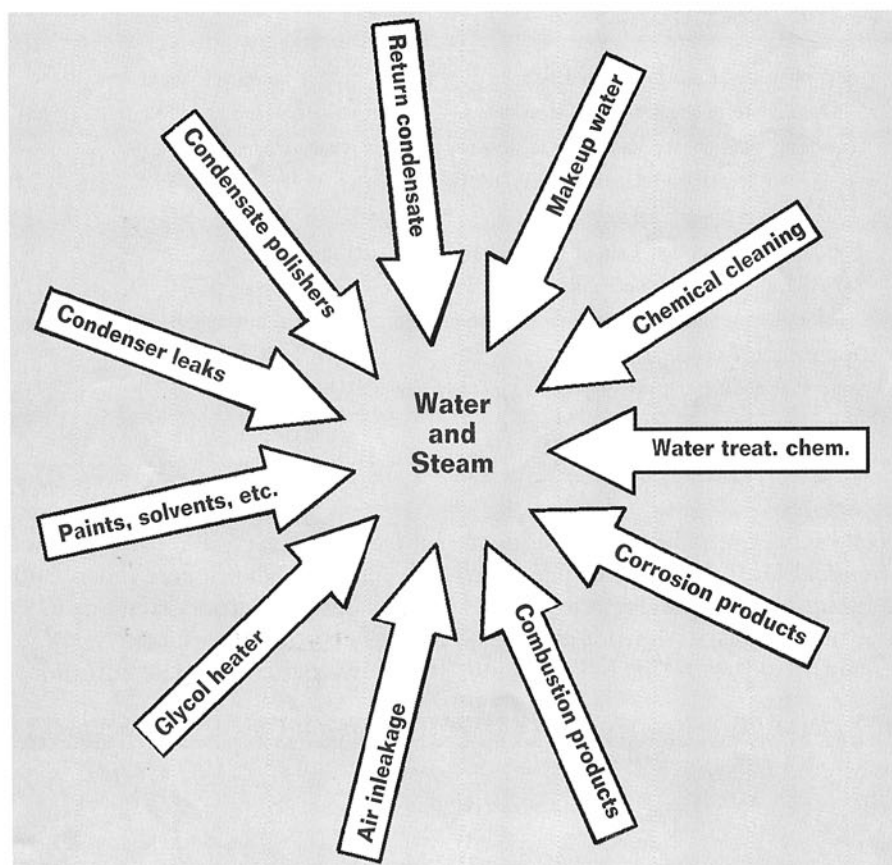
cal cleaning (or cleaning about every 10 years for high-pressure units), and equipment guarantees extending to as long as 20 years. An estimated 90% of the knowledge and technology needed

FIGURE 1



Chemical transport in the conventional drum boiler cycle.

FIGURE 2



Sources of impurities.

TABLE 2
GUIDE FOR SELECTION OF WATER TREATMENT

Boiler/Cycle	Pressure [psi (MPa)]	Cooling Water	Water Treatment
Drum, softened water makeup, marginal return condensate	<1,200 (8.3)	All	PO ₄ (+OH +chelant and/or dispersant)
Drum, demineralized makeup, good or polished return condensate	<2,400 (16)	Fresh	PO ₄ , PO ₄ + OH, NaOH, AVT
		Salty, cooling tower	PO ₄ , PO ₄ + OH, NaOH, AVT + cond. polishing
	>2,400	All	Equilibrium PO ₄ , AVT, or CWT + cond. polishing
Once-through and high heat flux drum	All	All	AVT, CWT, NWT—all with cond. polishing

Notes:

1. Feedwater pH is adjusted with ammonia (NH₃) or volatile amines. Oxygen scavenging, when needed, is by hydrazine or alternate scavengers. When using organic water treatment chemicals, special evaluation of their decomposition, toxicity, and analytical interferences, etc., is needed!
2. Operation with free OH should be evaluated with respect to boiler (including superheater and reheater), turbine, and other cycle component materials and boiler carryover.
3. For phosphate boiler water treatments, phosphate hideout and equilibrium concentration need to be experimentally determined.

for troubleshooting steam systems is available.¹⁻¹⁴ Operators just need to find and apply it.

Cycle Chemistry

Controlling chemistry for a specific steam cycle requires an understanding of the transport processes and chemical reactions involved. This would also include sources of impurities, local impurity concentration processes, such as on the hot side in boiler tubes or in the turbine, and local highly stressed areas where stress corrosion or corrosion fatigue can occur. Locally high-flow velocity and turbulence, where erosion-corrosion can be active, also must be considered. All of these factors apply to operation, startup, and layup.

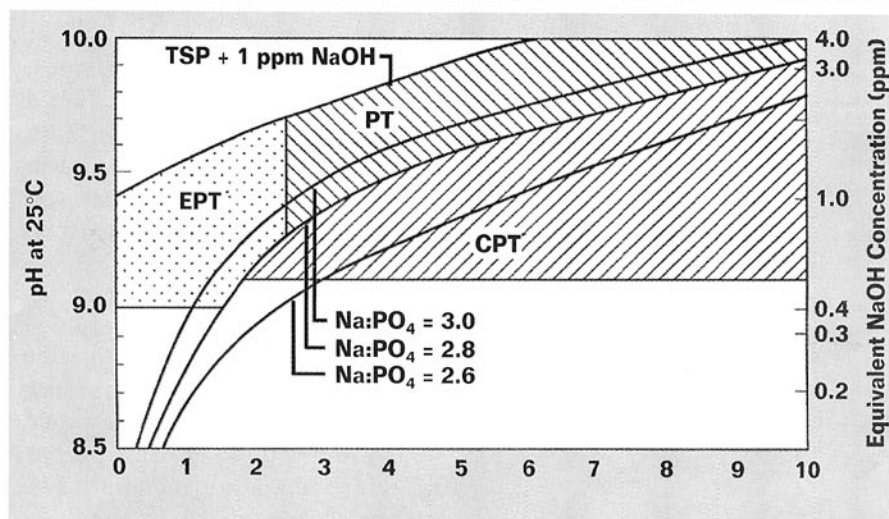
CHEMICAL TRANSPORT

Knowledge of cycle chemical transport characteristics¹⁻⁶ is important in the selection of water treatment and water chemistry control limits, in the control of ingress and removal of impurities, and in troubleshooting water chemistry and corrosion problems. Specific issues that arise include influence of load on drum boiler carry-over (mechanical and volatile) and on capabilities of the condenser and deaerator. Chemical reaction kinetics and decomposition of oxygen scavengers, amines, chelants, and polymeric dispersants also must be taken into account. Performance of the makeup and condensate polishers, effectiveness of boiler blowdown in removing oxides, aeration of the makeup and condensate in the storage tanks, and quantitative effects of condenser leaks and air in-leakage should be known. Figure 1 illustrates chemical transport for a drum boiler cycle.

SOURCES OF IMPURITIES

To maintain the lowest practical concentrations of impurities (dissolved and suspended) throughout the cycle and specifically in the boiler and the turbine, there must be provisions to

FIGURE 3



Schematic of operating ranges of boiler water on equilibrium phosphate treatment (EPT), congruent phosphate treatment (CPT), and coordinated phosphate treatment (PT). Na:PO_4 = molar ratios.

TABLE 3

DATA NEEDED FOR ALL WATER TREATMENT CHEMICALS

- Hydrothermal stability in the cycle.
- Kinetics of reactions.
- Decomposition products and their effects.
- Analytical interferences.
- How to monitor/analyze.
- Toxicity of the product, its decomposition products, deposits, etc.
- Measured effects on pH, conductivity, cation conductivity, and iron and copper concentrations.
- Stability in chemical addition tanks and storage containers.
- Solubility and volatility of the chemical and its decomposition products.
- Behavior of dried-out solutions (deposits in reheaters, superheaters, turbines, valve "gluing").
- Behavior under short- and long-term layup conditions and during startup (decomposition—acid formation, scale formation, disposal, etc.).

prevent impurity ingress and to remove impurities from the cycle. Figure 2 shows major sources of impurities that operators should control. Impurity control requires early detection and elimination of condenser tube leaks, air inleakage, and malfunction of makeup and condensate polishing systems. Operators must control water treatment chemical purity and control solvents, preservatives, and cleaning agents used during manufacture and maintenance of cycle components. For the early detection of im-

purity ingress during operation, proper chemical sampling and monitoring must be implemented.

Removal of impurities is accomplished mainly through boiler blowdown, condensate polishing and filtration (when used), and deaeration. Mechanical deaeration occurs in the condenser and in the deaerator. Oxygen also is removed chemically by oxygen scavenging. If operators control ingress and generation of impurities and their removal at a few points around the cycle and use chemical ad-

ditives, they can control local deposition and corrosion processes on component surfaces (such as boiler tubes and turbine blades).

WATER PURIFICATION

High-purity makeup and feedwater are easily achievable with the standard water purification equipment.^{1,7} The costs for production of high-purity water are quickly compensated for by the lower cost of water treatment and chemical cleaning, higher cycle efficiency, and a lower forced outage rate from corrosion failures. The cost differential between a good makeup and a mediocre one is negligible compared to the value of the produced steam and electricity. This is true even for cycles in which large amounts of return condensate need to be purified before returning into the cycle.

SELECTION OF WATER TREATMENT

Ideally, selection of boiler water and feedwater treatment should be a part of unit design and material selection.^{1,2,5,6,8-14}

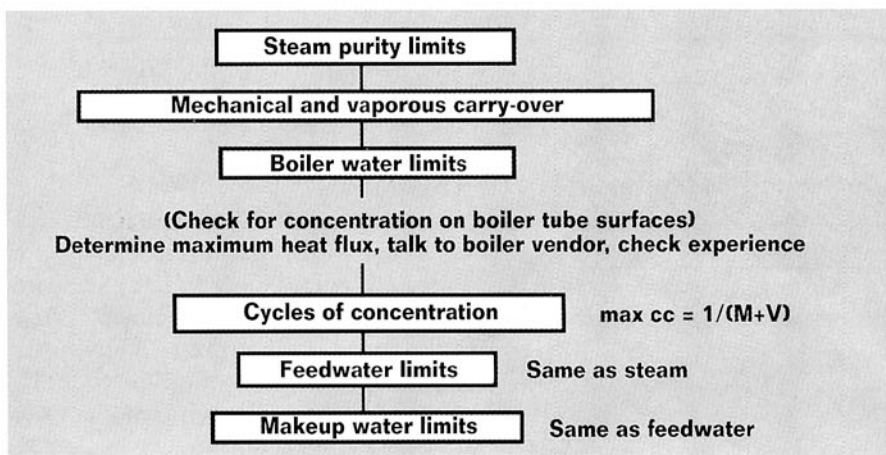
There are six basic water treatments used for utility units worldwide:

- Congruent phosphate (Na:PO_4 molar ratios 2.2 to 2.8).
- Coordinated phosphate, using trisodium phosphate (Na_3PO_4).
- Phosphate plus hydroxide/equilibrium phosphate.
- Sodium hydroxide (NaOH).
- All-volatile treatment (AVT).
- Oxygenated treatments (OT) (combined water treatment [CWT], neutral water treatment [NWT]).

The first four treatments are boiler water treatments, and the last two are feedwater treatments that only affect the boiler water by keeping feedwater corrosion products under control.

In addition, there are many combinations of polymeric dispersants and chelating agents with other chemicals. These are used mostly in lower-pressure industrial units. These two organic treatments prevent deposition of hard-

FIGURE 4



Derivation of water chemistry limits for drum boiler cycles where cc = cycles of concentration, M = mechanical carry-over, V = vaporous carry-over.

ness compounds (calcium and magnesium salts) and iron oxides in boilers. They are not needed in cycles with good makeup water and good return condensate. Table 2 provides a guide for selecting water treatments.

Control of feedwater, steam, and condensate pH is achieved by injecting NH_3 or volatile amines and an oxygen scavenger into feedwater. To protect carbon and low-alloy steels, the pH should be within the range of 9.2 to 9.6. Depending on their volatility and ionization at temperature, these chemicals also alkalize the moisture droplets and films in the wet steam regions of the cycle.

Which of these treatments should be used depends on several factors:

- Purity of makeup water and return condensate.
- Boiler design.
- Boiler pressure and maximum heat flux.
- Chemistry of cooling water (fresh, salt, brackish, cooling tower).
- Use of copper alloys (condenser, feedwater heaters).
- Use of condensate polishers.

Phosphate (plus hydroxide) boiler water treatments, combined in lower-pressure industrial boilers with chelants and polymeric dispersants, are the most common. Adherence to the selected phosphate treatment can be

checked using the pH - PO_4 diagram (Figure 3).

For all phosphate boiler water treatments, the maximum phosphate concentration should not exceed the equilibrium concentration. This is the concentration of PO_4 in the boiler water under the maximum heat flux conditions (maximum load) that the boiler can tolerate without forming solid phases on the heat transfer surfaces.

As shown in Table 2, condensate polishing is recommended for units using seawater, brackish water, and cooling towers for condenser cooling, and for high-pressure drum boiler units and units with once-through boilers. This technique prevents the effects of condenser leaks and provides additional flexibility when operating with small leaks. In the cogeneration units in which return condensate purity cannot be maintained, condensate or return condensate polishing is also beneficial. Filtration of condensate, return condensate, or feedwater is useful in removing suspended iron and copper oxides. Water temperature and pressure drop across the filter should be considered in designing the filtration system.

During the past 20 years, many new organic boiler water treatment chemicals and oxygen scavengers have been

introduced.^{5,13-14} They all decompose, forming organic acids and carbon dioxide (CO_2). Some polymerize, forming harmful deposits. Before applying these chemicals in a steam cycle, their properties should be determined, the experience should be verified, and within a few weeks of the first application, the cycle chemistry should be analyzed in much more detail than during normal operation. If proprietary treatments are to be used, the vendor should supply the user with appropriate test methods for monitoring the program.

The users of water treatment chemicals must know the allowable pressure and temperature range for their application as well as the nature and behavior of the decomposition products. To evaluate the effects of any water treatment chemical, data pertinent to its chemical transport, decomposition, cycle material corrosion, deposit and scale buildup, toxicity, and analytical interferences should be known (Table 3).

If concentrations of contaminants throughout the cycle do not exceed levels in the steam that are tolerable to the turbine, the boiler and other cycle components will be adequately protected. Thus, the rationale for fossil cycle water and steam chemistry control requires that overall cycle chemistry satisfy the turbine requirements for steam purity.

Figure 4 shows the sequence for derivation of boiler water, feedwater, and makeup water limits for drum boiler cycles. To derive boiler water limits, divide steam purity limits by the total carry-over of the individual major impurities. From the boiler water limits, which should be checked for deposition behavior and corrosion in the boiler tubes, feedwater limits are derived by dividing the boiler water limits by the cycles of concentration. In a modern drum boiler unit, the blowdown should be as low as possible and feedwater limits should be similar to the steam purity limits. If this

is not achievable (because of a marginal purity makeup or return condensate), the boiler will have to operate with higher blowdown, and the feedwater limits can be higher.

For routine control, 10 to 15 core parameters should be monitored.⁵ Except for iron and copper, all parameters can be monitored continuously with instruments. It is recommended that the core parameters be monitored and alarmed in the control room. Additional parameters are recommended for the audit, commissioning, and troubleshooting.

Future Developments

The future is already here in many well-run utility units operated by a handful of operators. These include units with no aqueous discharge and units using few chemicals. We believe that these trends will spread.

Many helpful tools include

- Guidelines for all types of units and water treatments.
- Reliable instrumentation including diagnostic monitors.
- Better design and commissioning.
- Operator training in water chemistry and corrosion control.
- Preventive maintenance.
- Expert systems and automatic control.

Competitive pressures are forcing reductions in operating personnel. For a reliable operation, this can be compensated only by better instrumentation, better water purification, and better control of impurity ingress.

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