

# Understanding steam-cycle chemistry

For steam plants, there is perhaps no more important O&M fundamental than the production and maintenance of high-purity water—whether you're running a 30-yr-old coal-fired plant, a nuclear station, or an advanced combined cycle. While proper water treatment will not guarantee the prevention of corrosion, deposits, scale, and carryover, improper treatment will most certainly guarantee their progression

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**T**oday, over 90% of the water treatment knowledge needed for reliable operation of steam plants is available, thus corrosion and excessive scale or deposit buildup can be prevented. However, numerous problems continue to plague powerplants, including:

- Erosion/corrosion of carbon steel piping and other components.

- Boiler-tube failures.

- Deaerator weld cracking.

- Pitting, corrosion fatigue, and stress corrosion cracking of low-pressure (l-p) turbine blades and blade attachments.

- Copper deposition on high-pressure (h-p) turbine blades, causing loss of megawatts.

- Solid particle erosion.

To understand steam-cycle chemistry, you

protecting cooling-water systems threatened by poor-quality, recycled waste streams.

## Outsourcing fills out

And all of these advanced technologies are more affordable, thanks to expanded outsourced offerings from water treatment specialists. These days, power producers rely on vendors to do more than just peddle chemicals—such as independently test water samples at least weekly, participate in boiler and cooling-tower inspections, and provide quarterly reports on a plant's overall water treatment program.

## Power is knowledge

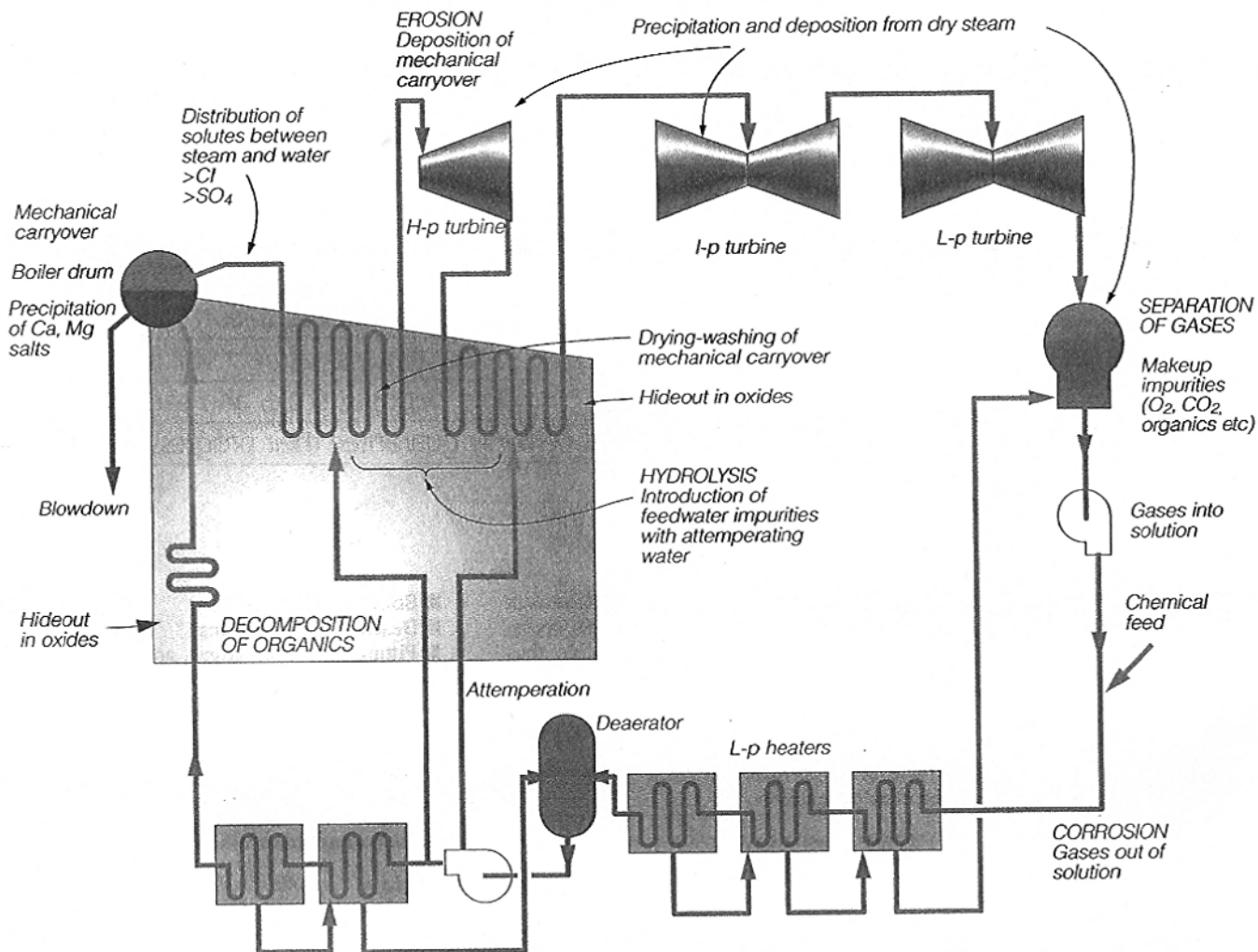
Regardless of what level of outsourcing you choose or which technologies you apply, one thing is clear: Successful water treatment requires well-run fixed systems—referred to as “external treatment”—in conjunction with a meticulous chemical treatment program—or “internal treatment.” In this Special Section, *POWER* magazine brings you up to date on both subjects, with articles authored by some of the most respected specialists in the industry.

To further enhance your knowledge of

water treatment, *POWER* has teamed up with the industry's premier water treatment conference: *The 61st Annual International Water Conference*. This year's event, slated for Oct 22-26 at the Westin William Penn Hotel, Pittsburgh, Pa, includes sessions on: steam generation; cooling and process water; wastewater recycling/discharge; and business/management trends.

For details on the conference, check out [www.eswp.com/water.html](http://www.eswp.com/water.html).

**Robert Swanekamp, PE,**  
Editor-in-Chief



1. Water treatment chemicals, and their decomposition/reaction products, can be transported throughout the steam cycle. So too can corrosion products, and inorganic and organic impurities that leak into the system

need to combine a knowledge of cycle design, operation, and materials with an awareness of chemical and corrosion processes. These include intended and unintended chemical reactions of treatment chemicals, the undesirable reactions of impurities, and the concentration of these impurities in particular areas of the cycle—such as on the hot side of boiler tubes or in the turbine.

In addition to the purely chemical reactions, combinations of chemical and physical phenomena, such as locally high flow velocity and turbulence together with low pH, can cause erosion/corrosion. These conditions must be understood as they change during lay-up, startup, and operation. Many of the chemical requirements of a steam cycle are determined by its most chemically sensitive component: the steam turbine.

### Chemical transport

Chemical-transport characteristics are important in selecting a water treatment program, establishing chemistry control limits, managing the ingress and removal of impurities, and troubleshooting water

treatment problems (Fig 1). Chemical transport is affected by:

- Steam-drum carryover (mechanical and volatile vs pressure).
- Deaerating capabilities of the condenser and deaerator.
- Boiler heat flux, load, and the rate and magnitude of load changes.
- Kinetics of chemical reactions of oxygen scavengers, amines, chelants, and polymeric dispersants.
- Performance of makeup and condensate polishers.
- Effectiveness of blowdown in removing oxides.
- Aeration of makeup water and condensate in storage tanks.
- Effects of condenser leaks and air leakage.

The relationships among cycle thermodynamics, chemistry, and corrosion are useful in identifying trouble spots. They can be illustrated in a Mollier (enthalpy vs entropy) diagram that shows the cycle parameters, including the steam expansion line for a typical fossil-fuel-fired powerplant (Fig 2). The regions where impurities

can concentrate and promote corrosion are depicted for sodium chloride (NaCl) and sodium hydroxide (NaOH). Also, the boundaries of the region of thermodynamic stability for liquid solutions of NaCl—referred to as the “salt zone”—can be shown. Deposition of NaCl and associated corrosion are likely to occur across this narrow region in the last stages of the I-p turbine. The location of the region where contaminant deposition will occur is related to the actual conditions at component surfaces rather than the theoretical average turbine flow-path conditions. Heat transfer, surface cleanliness, crevices, and surface-flow stagnation determine the actual surface temperatures and pressures which, in turn, govern the behavior of chemical impurities and corrosion.

### Sources of impurities

In order to maintain the lowest practical concentrations of impurities (both dissolved and suspended) throughout the cycle, there must be provisions to quickly prevent impurity ingress and to remove the impurities from the cycle. Fig 3 shows

major sources of impurities that need to be controlled. Early detection of impurity ingress during operation requires proper chemical sampling; real-time, round-the-clock monitoring; and clear instructions on actions to be taken when contamination occurs.

Impurities are removed predominately by boiler blowdown, condensate polishing and filtration (when used), and periodic cleaning. Oxygen is removed through mechanical deaeration in the condenser and in the deaerator, as well as through addition of oxygen scavenging compounds.

Several local conditions can concentrate impurities in specific areas of the steam cycle. These include:

- Temperature gradients in water—such as those occurring at the inner diameter of boiler tubes.
- Evaporation of water on hot surfaces—for example, film boiling and steam blanketing in boiler tubes, or evaporation of moisture in turbines and feedwater heaters.
- Local deposition of precipitates/suspended solids in water and steam circuits.
- Oxide scale—

sorption, ion exchange, and capillary boiling.

## Water purification

High-purity makeup water and feedwater can be achieved with commercially available equipment. Production costs of high-purity water are quickly recovered by the lower cost of chemical cleaning, higher cycle efficiency, and a lower forced-outage rate from corrosion and deposition prevention. This is even true for cycles where large amounts of return condensate need to be purified before returning into the cycle. Using the wrong materials in a steam plant can increase the potential for corrosion, scaling, and deposition. For example, water and steam chemistry control is much simpler and more efficient when copper alloys are avoided throughout the cycle. Control of copper-alloy corrosion requires

reducing conditions and a lower pH compared to control of corrosion of carbon and other steels. Poor materials selection may also create conditions that are prone to failure. For example, local stress concentration and/or defects can result in stress

boiler, feedwater, and condensate treatment chemicals.

- Selection and verification of control parameters and chemistry limits.
- Selection of monitoring and analytical methods.
- Training of chemists and operators.
- Management support.

■ Short- and long-term verification that the program works through audits, use of corrosion coupons, internal inspections, failure-rate and root-cause analysis, and so on.

## Feedwater

Control of pH in the boiler typically is achieved by injection of ammonia or amines into the feedwater. Depending on their volatility, these chemicals also alkalinize the moisture droplets and films in the wet steam regions of the cycle. To protect carbon and low-alloy steels, feedwater pH should be maintained between 9.2 to 9.6, as measured at room temperature. A lower pH control range of 8.8 to 9.2 is required for mixed metallurgy systems—where copper and carbon steel are present in the feedwater system.

Note: The pH at operating temperature at surfaces is often much lower than the pH measured in a room-temperature sample. Ammonia and amines are “weak bases” which have little benefit under high-temperature conditions, such as in the boiler. A pH reading of 9.5 at room temperature has no meaning for boiler water control unless strong bases (phosphate or hydroxide) are present.

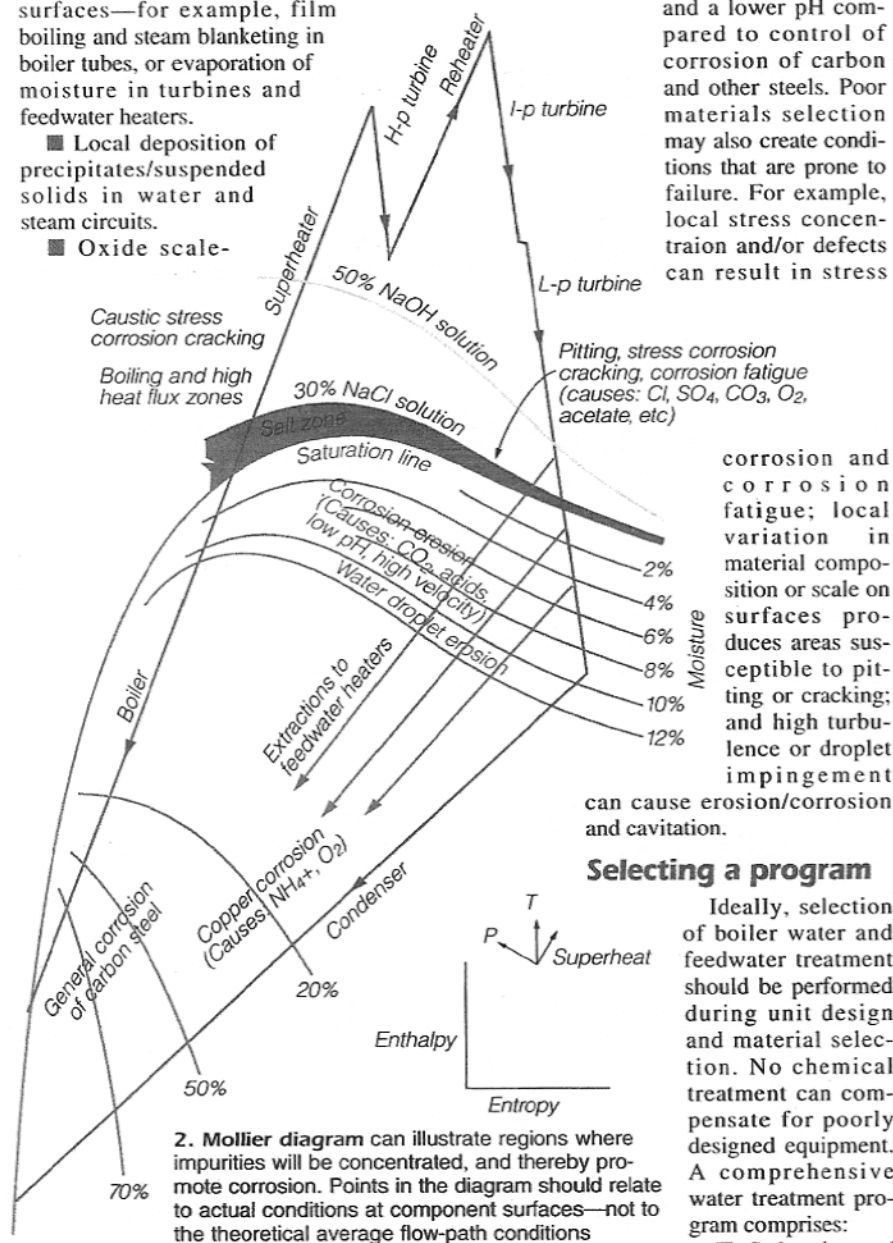
## Boiler water

There are six basic water treatment programs in use today (table, next page):

- Congruent phosphate ( $\text{Na}/\text{PO}_4$  molar ratio equals 2.2 to 2.8).
- Coordinated phosphate (using trisodium phosphate,  $\text{Na}_3\text{PO}_4$ ).
- Equilibrium phosphate (phosphate plus hydroxide).
- Sodium hydroxide.
- All-volatile treatment (AVT)—feedwater treatment only.
- Oxygenated treatments (OT).

In addition, organic polymeric dispersants and chelating agents—either EDTA or NTA—can be combined with phosphate or hydroxide programs for lower-pressure, industrial boilers. These two organic chemicals help to prevent the deposition of hardness chemicals—principally calcium and magnesium salts—and iron in boilers. They are not needed in cycles with good makeup water and good return condensate and are limited by temperature and other factors.

Condensate polishing is recommended for units using seawater, brackish water, or cooling towers for condenser cooling, and for high-pressure drum boiler units or once-through boilers. Reason: To minimize the effects of condenser leaks and



can cause erosion/corrosion and cavitation.

## Selecting a program

Ideally, selection of boiler water and feedwater treatment should be performed during unit design and material selection. No chemical treatment can compensate for poorly designed equipment. A comprehensive water treatment program comprises:

- Selection of



provide additional operating flexibility when operating with small leaks. In cogeneration units where the purity of return condensate often cannot be guaranteed, condensate polishing also should be considered. New sintered stainless steel filter elements are useful at any condensate temperature.

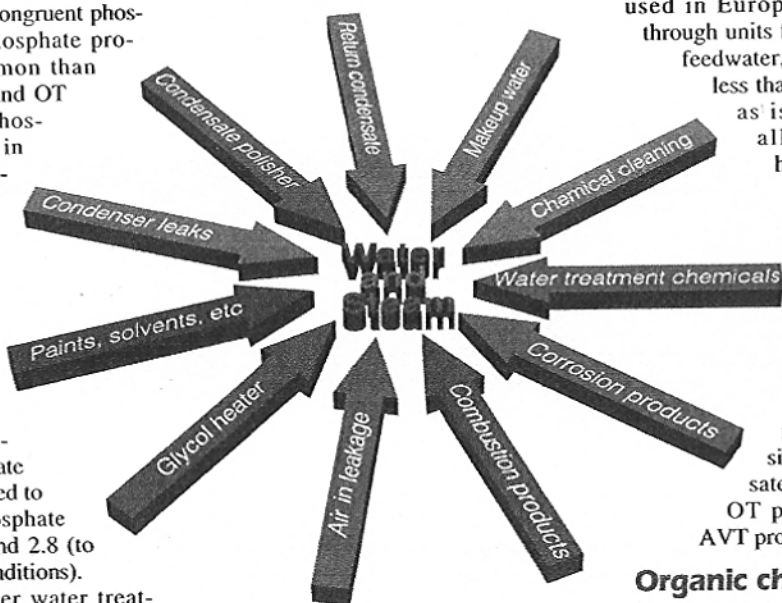
## Phosphate programs

Coordinated phosphate, congruent phosphate, and equilibrium phosphate programs are far more common than sodium hydroxide, AVT, and OT programs. Coordinated phosphate is used extensively in industrial boilers and combined cycles. This treatment—which uses trisodium phosphate and, under certain boiler conditions, also produces hydroxide—was thought to have caused caustic gouging in higher-pressure units. Therefore, congruent phosphate treatment was developed where pH and phosphate concentration are coordinated to maintain a sodium-to-phosphate molar ratio between 2.2 and 2.8 (to avoid caustic and acidic conditions).

For all phosphate boiler water treatments, but particularly for higher-pressure, high heat-flux units, the maximum phosphate concentration should not exceed the “equilibrium concentration”—defined as the maximum concentration of phosphate in the boiler water at maximum load which the boiler can tolerate without forming solid phases on heat-transfer surfaces. Burner condition, fuel changes, firing rates, and boiler cleanliness all play a role in the amount of phosphate that a boiler can tolerate.

Feeding phosphate in excess of the equilibrium concentration can cause a condition known as “phosphate hideout,” which causes boiler pH and phosphate concentrations to swing out of the control

limits. Equilibrium phosphate treatment has been used successfully since the 1980s in h-p utility boilers. However, it requires excellent feedwater purity, a clean boiler, and good control of the maximum heat flux because the alkaline buffer concentration is usually very low and the boiler water pH is mostly controlled by NaOH.



3. Impurities can invade a steam cycle from many places and at any time. Early detection will minimize the damage they cause

## Other boiler programs

The sodium hydroxide program is used in many lower-pressure industrial boilers, particularly in units with softened makeup water, and in utility drum boilers for neutralization of acid ingress with seawater in-leakage.

AVT was used first in supercritical boilers. The weak bases used in the program—ammonia or volatile amines—control feed-

water pH, but have little or no effect on boiler water pH. Chemical oxygen scavenging is typically done with hydrazine or possibly by alternative scavengers. Since the boiler water in an AVT program contains no phosphate or buffering salts, it cannot tolerate any contamination. Thus, full-flow condensate polishers are required.

Oxygenated treatment is the newest program in the US, though it has been used in Europe and Russia on once-through units for many years. Ultra-pure feedwater, with cation conductivity less than 0.15  $\mu\text{S}/\text{cm}$ , is required, as is an absence of copper alloys in the feedwater heaters.  $\text{O}_2$  in the form of oxygen gas or hydrogen peroxide is injected into the feedwater at a controlled rate. The result is formation of a dense protective iron-oxide film—magnetite plus hematite—in the boiler and in feedwater piping resulting in very low corrosion rates. Full-flow condensate polishers are required in OT programs, as they are in AVT programs.

## Organic chemicals

During the past 20 years, many new organic boiler-water treatment chemicals and oxygen scavengers have been introduced. As they decompose, starting at approximately 300F, organic acids and  $\text{CO}_2$  are formed. Some can even polymerize, forming harmful deposits.

Industrial and utility users need to know the pressure and temperature range of their applications and 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.

Edited by David Daniels

(WATER TREATMENT continues on p 68)

## Program selection guide

Type of boiler/cycle	Boiler pressure (psi)	Cooling water	Possible programs
Drum, softened water makeup, marginal return condensate	<1200	All	Congruent phosphate, sodium hydroxide (possibly with chelant and/or dispersant)
Drum, demineralized makeup, good or polished return condensate	<2400	Fresh water	Coordinated, congruent, and equilibrium phosphate, sodium hydroxide, AVT
		Seawater or cooling tower	Coordinated, congruent, and equilibrium phosphate, sodium hydroxide, AVT (with condensate polishing)
	>2400	All	Equilibrium phosphate, AVT, OT (all with condensate polishing)
Once-through and high heat-flux drum	All	All	AVT, OT (all with condensate polishing)

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