

EFFECTIVE CYCLE CHEMISTRY CONTROL

ESAA POWER STATION CHEMISTRY CONFERENCE

May 15-16, 2000

Rockhampton, Queensland, Australia

Presented by:

Otakar Jonas, P.E., Ph.D.

Jonas, Inc.

1113 Faun Road, Wilmington, DE 19803

Tel: (302) 478-1375, Fax: (302) 478-8173

email: jonasinc@mindspring.com, web: www.mindspring.com/~jonasinc

Abstract:

The technical and management approach to the control of water and steam chemistry and corrosion in utility steam cycles is presented. Background on water chemistry and corrosion is given and sources of impurities, selection of water treatment, transport of chemicals around the cycle, and the selection of sample points and monitored parameters are discussed.

TABLE OF CONTENTS

- 1 INTRODUCTION
 - 1.1 Background: Basics of Water Chemistry, Basics of Corrosion
 - 1.2 Objectives and Achievable Goals
- 2 KNOW YOUR STEAM CYCLE
 - Cycle Design and Materials, Heat Balance and Mollier Diagram, Problems
- 3 UNDERSTAND CYCLE CHEMISTRY
 - Chemical Transport, Sources of Impurities, Local Processes, Layup
- 4 SELECTION OF WATER TREATMENT, SAMPLE POINTS, TARGET VALUES, AND ACTION LEVELS
 - 4.1 Background and Rationale
 - 4.2 Selection of Water Treatment: Phosphate (Plus Hydroxide) Boiler Water Treatments
 - 4.3 Sample Points, Control Parameters, Limits, and Action Levels
 - 4.4 Monitoring
- 5 MANAGEMENT AND COMMUNICATION
- 6 CONCLUSIONS AND RECOMMENDATIONS

1 INTRODUCTION

This paper is a combination of a tutorial and an update on the effective control of steam cycle water and steam chemistry. Effective control means that the cycle components reach their design life (typically 30 years) without excessive forced outage cost due to corrosion, deposition, and scale, and that there will not be deterioration of cycle efficiency and megawatt generating capacity caused by water chemistry (scale and deposits). In the marginally designed and maintained cycles, water chemistry control cannot totally eliminate corrosion and scale, it can only be optimized, i.e., units with copper in feedwater heaters.

As can be seen from the Table of Contents, this paper summarizes all aspects of water chemistry control and gives a brief background on water chemistry and corrosion. It is based on industry experience (1-14), chemical data (2-18), guidelines and standards (2-4, 18-43), and verifications of water chemistry control approaches (2, 28, 33). Electric Power Research Institute and the ASME Research and Technology Committee on Water and Steam in Thermal Power Systems have been major contributors in the related developments.

Cost of Corrosion and Deposits

With the increase of unit sizes, stresses and heat fluxes, equipment aging, unit cycling, and the high cost of replacement power and steam, corrosion protection of the steam cycle components during operation and layup and the control of water and steam chemistry are of critical importance.

The cost of corrosion, and scale and deposit buildup in the U.S. utility systems is over \$3 billion/year (1). It is even higher for the industrial steam systems. As much as 50% of the outage time has been attributed to corrosion, with the boiler tubes, condensers, turbines, feedwater heaters, deaerators, carbon steel piping, PWR steam generators, and BWR pipe welds being the main contributors. Corrosion in industrial applications is at least as frequent. The cost of replacement power can be as high as \$100/MWh or over one million dollars a day for a large utility unit (\$7000/MWh - summer 1998). The cost of reduced or lost production in an industrial plant can be equally high.

Current problems include erosion-corrosion of carbon steel piping and other components, boiler tube failures, deaerator weld cracking, stress corrosion cracking of LP turbine blade attachments, copper deposition on HP turbine blades and loss of MW, solid particle erosion, and numerous corrosion problems in nuclear units.

Significant improvements in the corrosion and water chemistry control can be achieved at all levels by better understanding of steam cycle chemical transport, local concentration of corrosive impurities on component surfaces, and by knowledge of relevant corrosion properties of the materials used. Cooperation of operators, water chemists, the mechanical and thermodynamic designers, chemical, material, and corrosion engineering, and management is needed to achieve these improvements.

1.1 BACKGROUND

The practice of cycle chemistry control consists of purification of water outside the cycle (makeup), removal of impurities within the cycle (blowdown, air removal, condensate polishing, chemical cleaning), addition of water treatment chemicals, and monitoring. Proper design, operation, and maintenance are also a part of the cycle chemistry control. By removal of impurities, addition of water treatment chemicals, and monitoring of a few points around the cycle, we are trying to control water scale and deposit chemistry on stressed cycle component surfaces at temperature.

Basics of Water Chemistry (2-4, 7-18, 25, 26)

Water has been called a universal solvent. Over two hundred chemical compounds at concentrations from part per billion (ppb) by weight, $1 \text{ ppb} = 10^{-9}$, to almost 100% have been identified in water, steam, scale, and deposit samples (2, 3, 7-9). These impurities are either dissolved in water and steam or are present as precipitates when their concentration exceeds solubility in water or steam. In liquid water, many impurities are present as ions, making the water more aggressive; causing it to be either **acidic or alkaline**. The simple way to measure approximate concentration of these impurities down to low ppb levels is by measurement of electrical conductivity, which is a measure of both cations such as Na^+ and anions such as Cl^- . Cation conductivity is a very useful measurement of potentially harmful acidic impurities (anions). It is the conductivity of water after it passes through a cation exchange column in which cations are replaced by the hydrogen cation which is a strong contributor to conductivity and makes the measurement very sensitive.

Solubility is the ability of a liquid or gas to dissolve other chemical substances. The maximum solubility (limit) usually strongly depends on temperature and for some chemical compounds it increases with temperature, for others, such as hardness salts, it decreases with temperature (Figures 1 to 4). It also depends on the chemical mixture in the solution (speciation), and pH. When a solubility limit is exceeded, chemicals precipitate forming scale and deposits, which is undesirable. Most impurities are soluble in water and, to a lesser degree, in **superheated steam** (Figure 13).

There is usually a large difference between the concentrations, conductivities, and pH, measured in a laboratory or by an instrument at room temperature and these parameters at the operating temperature on a surface. Figure 5 shows a change of pH of typical solutions of water treatment chemicals with temperature. It shows that pH of pure water and of weak bases, such as ammonia, is reduced significantly, while the pH of strong bases such as sodium phosphate or sodium hydroxide is reduced much less, as the temperature increases.

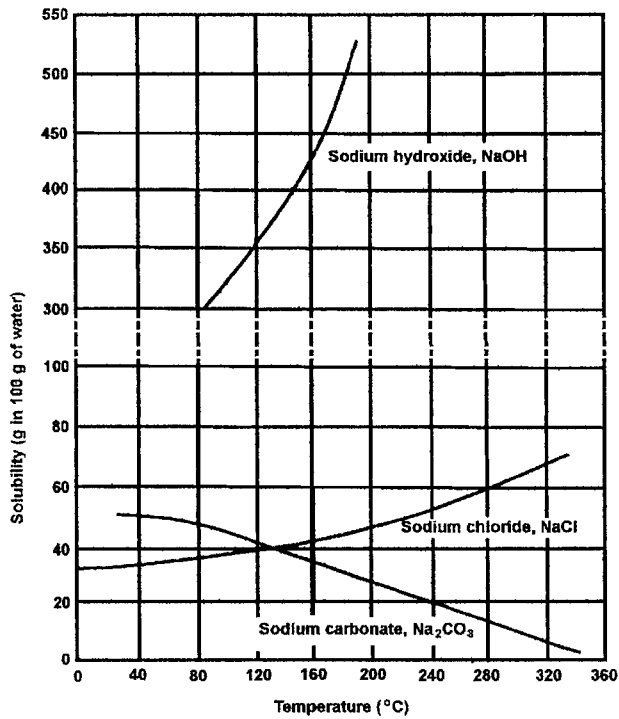


Figure 1. Solubility of sodium compounds in water

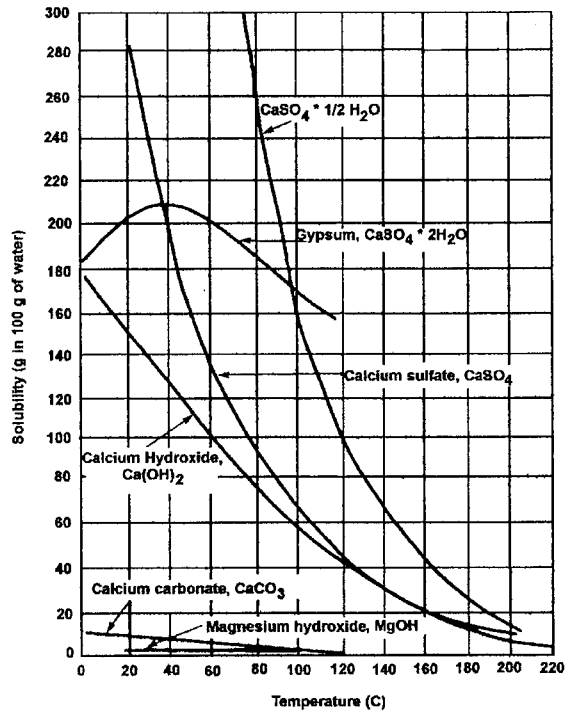


Figure 2. Solubility of calcium and magnesium compounds in water

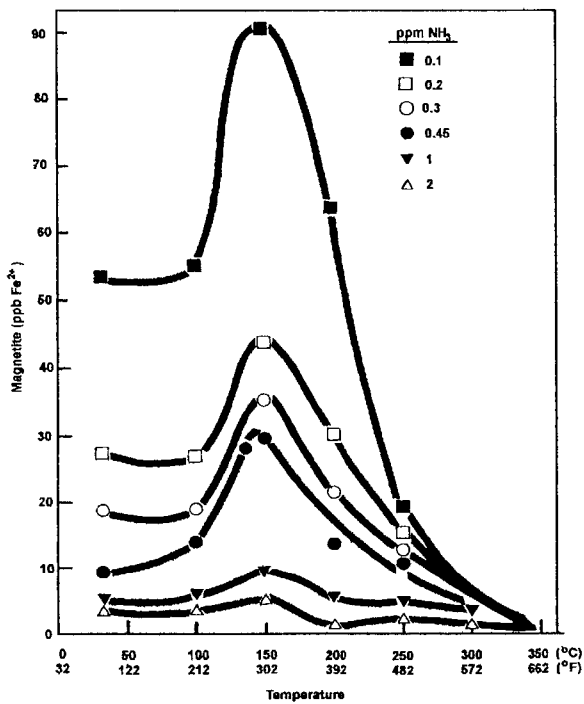


Figure 3. Solubility of magnetite in water with ammonia

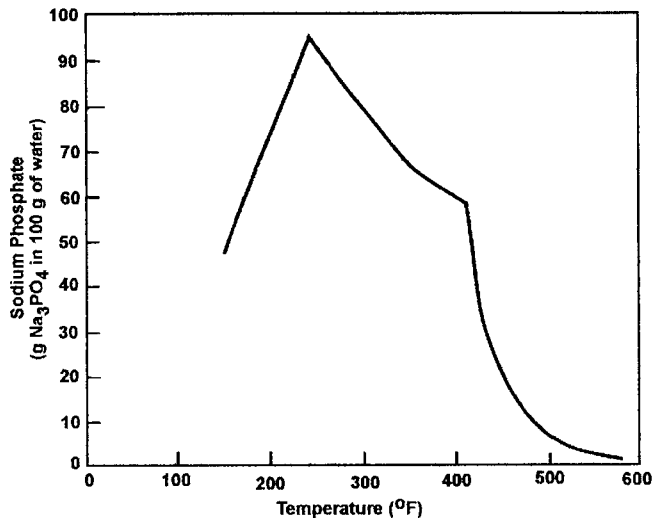


Figure 4. Solubility of trisodium phosphate in water

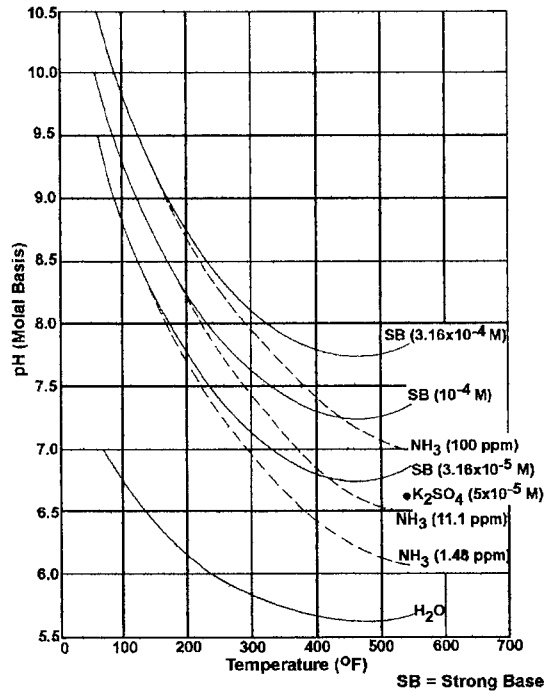


Figure 5. Change of pH with temperature

Basics of Corrosion (2, 4, 18, 25)

Corrosion is an electro-chemical process which strongly depends on temperature, chemical species and their concentration, pH, and the material exposed to water and steam. Corrosion in steam cycles has many forms, see Figure 6. In steam cycles, corrosion cracking, such as stress corrosion and corrosion fatigue, pitting, erosion-corrosion (flow accelerated corrosion), and localized fast general corrosion (usually in boiler tubes) due to concentrated salts, acids, or sodium hydroxide are the biggest concern.

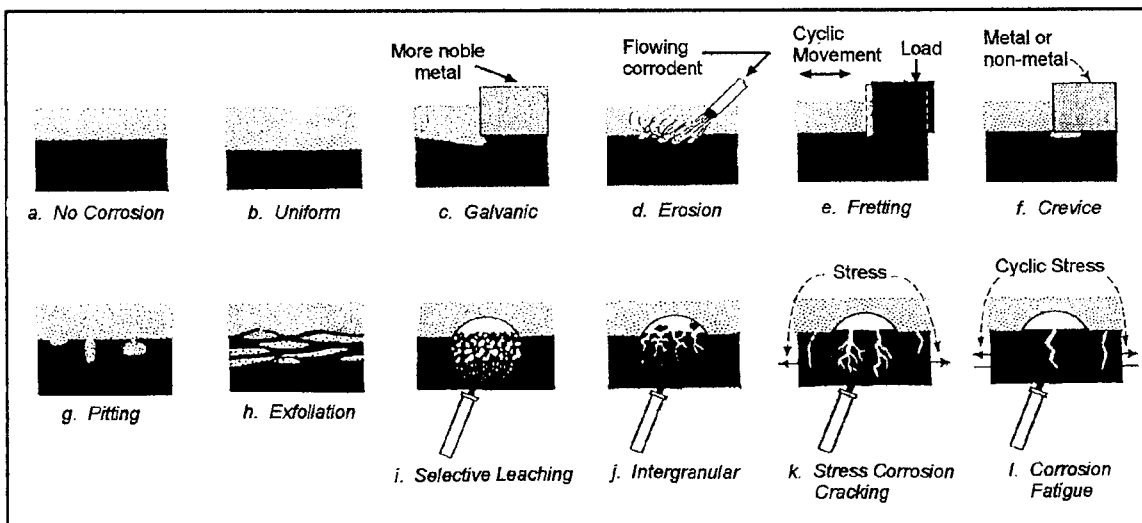


Figure 6. Corrosion mechanisms acting in steam cycles

The relationship between at-temperature pH and corrosion rate of carbon steel is shown in Figure 7. Note the increase of the corrosion rate at low pH and an even higher increase at highly alkaline pH.

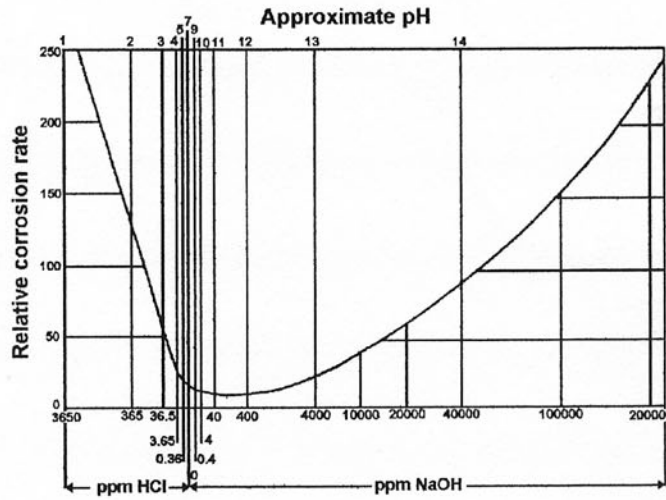


Figure 7. Effect of pH on general corrosion of carbon steel at 310°C

The relationship between water chemistry and corrosion is best illustrated in the pH-corrosion potential (Pourbaix) diagram in Figure 8. The corrosion potential is proportional to the concentration of oxygen. In this diagram for carbon steel, regions of immunity, passivity, and corrosion are outlined. The passivity can be accomplished both by magnetite and hematite on the steel surface. As can be seen from Figures 7 and 8, pH and corrosion potential link chemistry and corrosion.

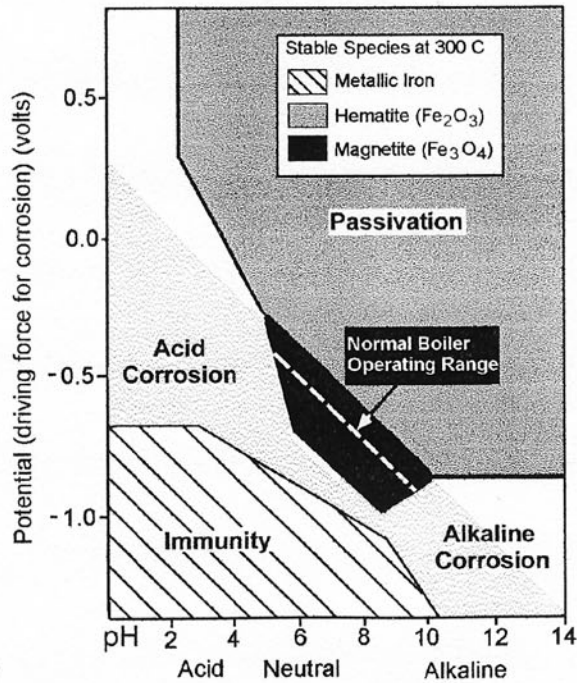


Figure 8. pH-corrosion potential diagram for carbon steel

1.2 OBJECTIVES AND ACHIEVABLE GOALS

The objectives of water chemistry control are:

- **prevention of corrosion and scale and deposit formation**
- **reducing corrodent concentrations**
- **minimizing the ingress of impurities**
- **reducing the generation and transport of corrosion products**

The goals which can be achieved by effective cycle chemistry control combined with proper design, material selection, operation, and maintenance are shown in Table 1. Generally, there should not be any water chemistry related corrosion failures and the scale and deposits should be such that only infrequent chemical and mechanical cleaning would be required. The latest developments are: turbine inspection intervals extended up to 10 years, no boiler chemical cleaning, or about every 10 years for high pressure units, and equipment guarantees extending up to 20 years.

Table 1. Achievable goals

- Equivalent availability loss due to boiler tube failures of 1.5%
 - No cycle chemistry related BTF
- No turbine steam chemistry related problems
 - LP blade pitting and corrosion fatigue
 - Turbine disk stress corrosion cracking
 - Megawatt and efficiency loss due to deposit buildup
- Turbine inspection and cleaning interval of 10 years
- Elimination of chemical cleaning
- Shorter startup period
 - Optimization of shutdown, layup, and startup
- Boiler layup without extra chemicals
- Simple, reliable instrumentation
 - Standards for instrumentation
 - QA/QC
 - Direct on-line in-situ instruments
- Representative sampling
- Automatic control of chemical additions and blowdown
- Optimum managerial approach to cycle chemistry
- Operational guidelines for all operational conditions and cycle designs

2 KNOW YOUR STEAM CYCLE

To be able to contribute to the effective cycle chemistry control, each participating personnel, such as the chemists and operators, need to be familiar with and have documentation describing the cycle design and materials, heat balance (pressures, temperatures, and flows) and local PVT conditions (Mollier diagram) for critical components. It is useful to collect all pertinent information on design, materials, water chemistry control, and experience in one document, such as a Water Treatment Questionnaire.

Cycle Design and Materials

Cycle design is described in various specifications and drawings and for the main cycle components, there are usually detailed descriptions in the control room; such as for the boiler, turbine, boiler feedpumps, and feedwater heaters. Piping and instrumentation diagrams which include chemical injection and sampling points and the makeup system are also very useful.

Heat Balance and Mollier Diagram

Figure 9 is an example of a heat balance diagram for a fossil drum boiler unit. As can be seen, it gives pressures, temperatures, enthalpies, and mass flows, and shows most major cycle components. These diagrams are usually developed for several loads, including MCR (maximum continuous rating) and the minimum load. The Mollier entropy - enthalpy diagram shown in Figure 11 is a thermodynamic map originally developed for PVT properties into which we have added key information on behavior of chemical impurities in water and steam and corrosion of critical cycle components. In troubleshooting and other analyses, heat balance and Mollier diagrams give a quick reference about what corrosion and deposition mechanisms are possible in different parts of the cycle. For example, in the superheater and reheater, only sodium hydroxide is an active corrodent during operation, which could explain stress corrosion cracking. Other impurities such as salts and acids are corrosive only in a very narrow section (salt zone) in the superheater and reheater.

Problems

Table 2 lists typical problems which can be encountered in various steam cycles. Whether or not these problems are likely needs to be determined during commissioning and early in the unit life. There are engineering solutions for all cycle chemistry and corrosion problems.

Table 2. Typical system corrosion and chemistry problems

- Condenser leaks
- Poor deaeration and high air inleakage
- Erosion-corrosion and cavitation
- High iron (and copper, nickel, zinc) in feedwater and boiler water due to erosion-corrosion and the use of improper water treatment chemicals; high iron due to exfoliation in the superheater and reheater

- Incompatibility of water treatment with copper and iron alloy combination resulting in corrosion and high iron and copper concentrations in feedwater
- Copper and phosphate deposits in the HP turbine reducing MWs and efficiency
- Poor pH control on surfaces in wet steam regions due to ammonia/amine volatility, poor buffering and acid neutralization
- Poor impurity removal (metal oxides, organics, salts and acids)
- Organic acids produced by decomposition of water treatment chemicals
- Water and steam chemistry control in peaking units
- Contaminated return condensate
- Use of wrong, even harmful, water treatment chemicals
- Insufficient monitoring of cycle chemistry and sampling errors
- Interference of high ammonia or amine concentration with good operation of condensate polishers
- Sticking turbine valves due to deposits
- Insufficient layup protection
- Cycle contamination during maintenance
- Damage of new units due to the lack of corrosion protection during storage and erection and poor or no commissioning

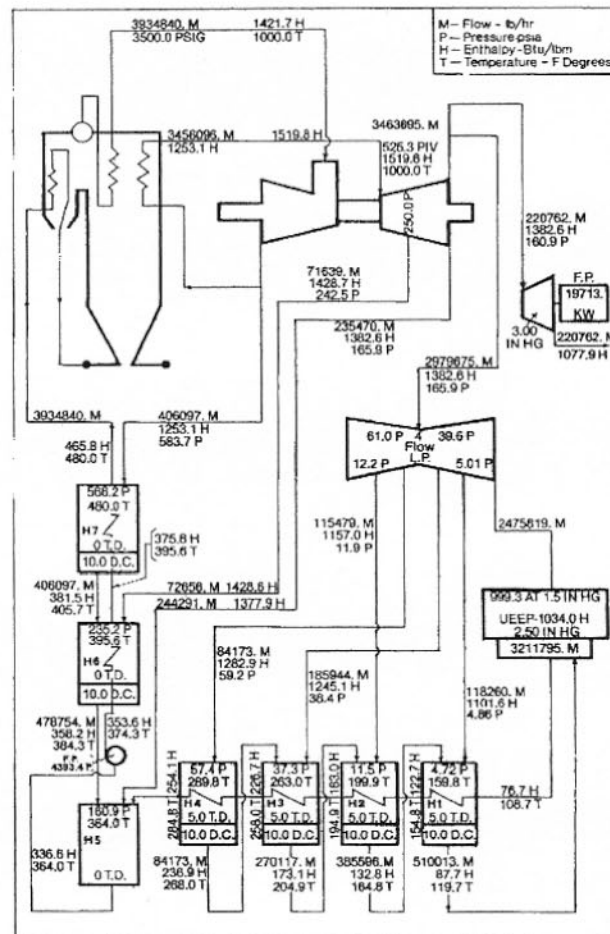


Figure 9. An example of heat balance diagram for a fossil drum boiler unit

3 UNDERSTAND CYCLE CHEMISTRY

To understand cycle chemistry for a specific steam cycle, there needs to be understanding of the transport processes and chemical reactions, sources of impurities, and the local impurity concentration processes (such as on the hot side in boiler tubes or in the turbine), local highly stressed areas where stress corrosion or corrosion fatigue can occur, and locally high flow velocity and turbulence where erosion-corrosion can be active; all this for operation, startups, and layup.

Chemical Transport (2, 7, 8, 12, 18)

Knowledge of cycle chemical transport characteristics 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. In particular, drum boiler carry-over vs. load, deaerating capabilities of the condenser and deaerator vs. load, kinetics of chemical reactions of oxygen scavengers, performance of the makeup and condensate polishers, effectiveness of blowdown in removing oxides, aeration of the makeup and condensate in the storage tanks, and quantitative effects of condenser leaks and air inleakage should be known. Figure 10 illustrates chemical transport for a drum boiler cycle.

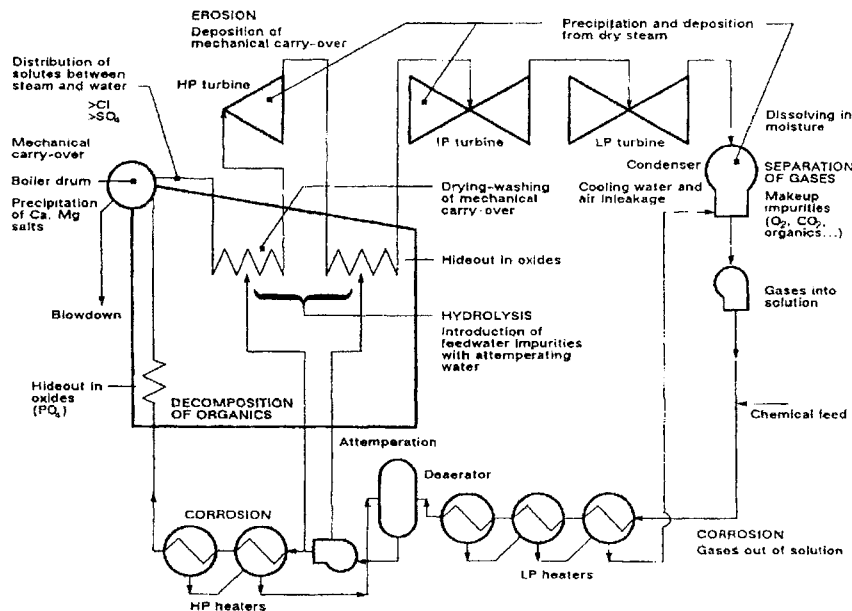
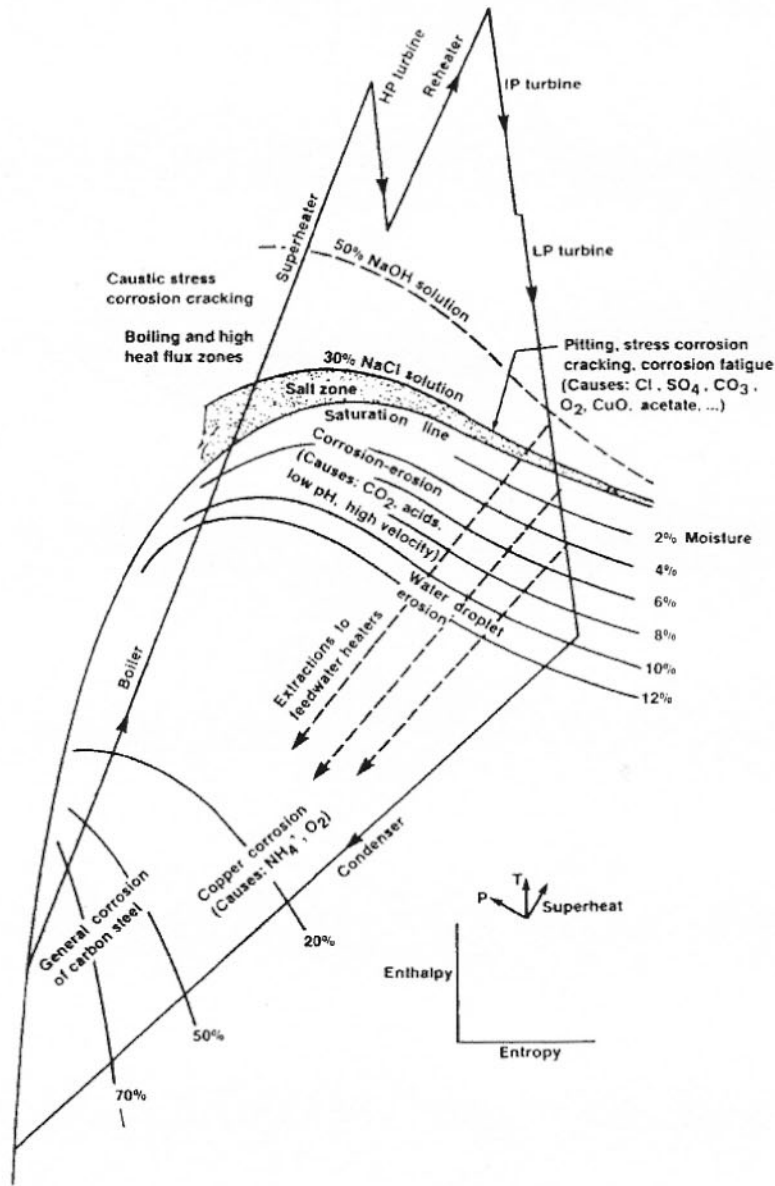


Figure 10. Chemical transport in the conventional drum boiler cycle

The relationships between thermodynamics and corrosion throughout the cycle are illustrated in Figure 11, which is a Mollier (enthalpy - entropy) diagram showing the cycle parameters, including the steam expansion line for a typical fossil utility plant. The regions where impurities can concentrate and promote corrosion are given for NaCl and NaOH. The boundaries of the region of the thermodynamic stability for liquid solutions of sodium chloride (salt zone) are shown. Sodium chloride deposition and associated corrosion are likely to occur across this

narrow region in the last stages of the low-pressure 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.



Note:
 This diagram illustrates regions where impurities will concentrate and promote corrosion. Points in the diagram should relate to actual conditions at component surfaces, not to the theoretical average flow path conditions. Heat transfer, surface cleanliness, crevices, and surface-flow stagnation conditions determine the actual surface temperatures and pressures.

Figure 11. Mollier diagram for a drum boiler cycle with regions of impurity concentration and corrosion

Sources of Impurities (2, 7, 8, 12-14, 18)

In order 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 quickly prevent impurity ingress and to remove the impurities from the cycle. Figure 12 shows major sources of impurities which need to be controlled. The impurity control requires early detection and elimination of condenser tube leaks, air leakage, malfunction of makeup and condensate polishing systems, control of purity of water treatment chemicals, and control of solvents, preservatives, and cleaning agents used during manufacture and maintenance of cycle components. For the early detection of impurity ingress during operation, proper chemical sampling and monitoring must be implemented.

Removal of impurities is mostly by boiler blowdown, condensate polishing and filtration (when used), and deaeration. Mechanical deaeration occurs in the condenser and in the deaerator. Oxygen is also removed chemically by oxygen scavenging. By controlling the ingress and generation of impurities, their removal in a few points around the cycle, and through chemical additives, local deposition and corrosion processes on component surfaces, such as boiler tubes and turbine blades, can be controlled.

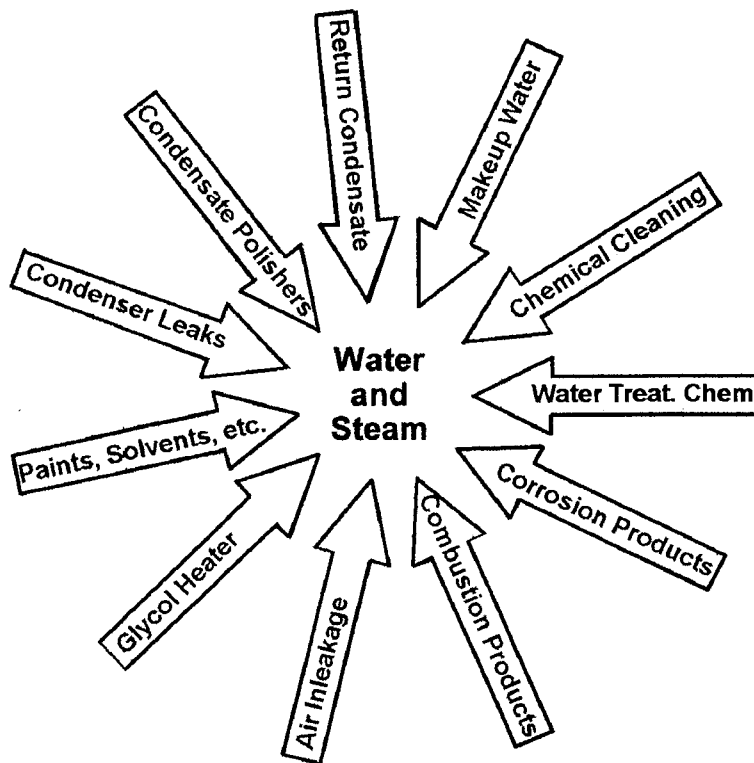


Figure 12. Sources of impurities

A great reduction of cycle corrosion and generation of corrosion products during startups is achieved by filling the system with deaerated water. Therefore, the condensate and makeup storage tanks which are used to fill the boiler, deaerator, and other cycle components during

startup should be nitrogen sparged and blanketed to prevent air ingress into the system. Transport of these corrosion products can be prevented by condensate filtration or polishing.

Water Purification

High purity makeup and feedwater are easily achievable with the standard water purification equipment (2, 14-23, 25, 26). The costs for production of high purity water are quickly compensated by the lower cost of water treatment and chemical cleaning, higher cycle efficiency, and a lower forced outage rate due to corrosion failures. The cost differential between production of good makeup and a mediocre one is small and negligible compared to the value of the produced steam and electricity. This is even true for cycles where large amounts of return condensate need to be purified before returning into the cycle.

Use of Copper Alloys (2, 8, 16, 17, 23)

The 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 different pH and other water chemistry parameters than used in control of corrosion of carbon and other steels. It is often impossible to achieve good control of both types of these materials. For this reason, it is best if the use of copper alloys is avoided. Avoidance of copper is further supported by the strict limits for copper in aqueous discharges.

Local Processes (2-4, 8-10, 18)

The local processes which concentrate impurities on surfaces include:

- concentration due to a temperature gradient in water, i.e., boiler tubes; boiling point elevation of solutions
- evaporation of water on hot surfaces, i.e., film boiling and steam blanketing in boiler tubes, evaporation of moisture in turbine and feedwater heaters
- sorption and ion exchange on the surface oxides
- local deposition of precipitates/suspended solids in water and steam

Localized corrosion can be caused by:

- local stress concentration and/or defects - stress corrosion and corrosion fatigue
- local variation in material composition or scale on surfaces - pitting or cracking
- locally high turbulence or droplet impingement - erosion-corrosion and cavitation

Layup

Understanding of the layup conditions in major cycle components is necessary to avoid general corrosion, particularly of carbon steel in boilers, heaters, and condensers. Corrosive deposits on turbine blades and disks can cause severe pitting during an unprotected layup when moisture and oxygen are present. Aerated layup water in boilers and elsewhere corrodes carbon steels and the corrosion products re-distribute during startup.

4 SELECTION OF WATER TREATMENT, SAMPLE POINTS, TARGET VALUES, AND ACTION LEVELS (2-3, 8 to 14, 18 to 25)

This Section gives the basic information and a rationale for selection of water treatment and water and steam chemistry **control parameters**. The outlined methodology is also used for determination of the **Target Values (limits)** for the water and steam chemistry control parameters.

4.1 BACKGROUND AND RATIONALE

The following factors are used to establish limits that will control the environment at component surfaces to prevent deposition and corrosion:

- relationships between the chemical compositions of major cycle streams (mechanical and chemical transport)
- relationships between the analyzed species (mostly elements and ions) and actual molecular species
- effects of heat transfer, boiling, condensation, volatility, chemical reactions, ionization, e.g., chemical thermodynamics and kinetics

There should be Target Values and Action Levels for significant contaminants at critical sampling points. In addition to the aforementioned considerations, the criteria for establishing the Target Values include:

- the optimal steam and water chemistry for protecting cycle components (boiler, turbine and preboiler components) from deposition and corrosion
- achievability with current operating and water treatment practices
- practicality, based on causing overall economic benefits without imposing undue burdens on operations

Limiting the concentrations of contaminants throughout the cycle to levels consistent with the levels in the steam tolerable by the turbine adequately protect the boiler and other cycle components. Thus, the rationale for fossil cycle water and steam chemistry control requires that overall cycle chemistry must satisfy the turbine requirements for steam purity. The tolerance of low-pressure turbines to very low concentrations of salts and hydroxides in superheated steam is illustrated in Figure 13 by the solubility lines. Solubility in superheated steam decreases exponentially as the steam expands (with specific volume) (2, 3, 9, 30)

Starting with turbine steam composition, which is ruled by salt and hydroxide solubility at the saturation line (Figure 13), and considering mechanical and vaporous carry-over, the allowable impurity concentrations in boiler water can be determined. Both mechanical (Figure 14) and vaporous (Figure 15) carry-over are pressure dependent, therefore, the Target Values for boiler water contaminants are also pressure dependent. Units having sliding pressure control can benefit from relaxed boiler water chemistry limits at reduced pressure.

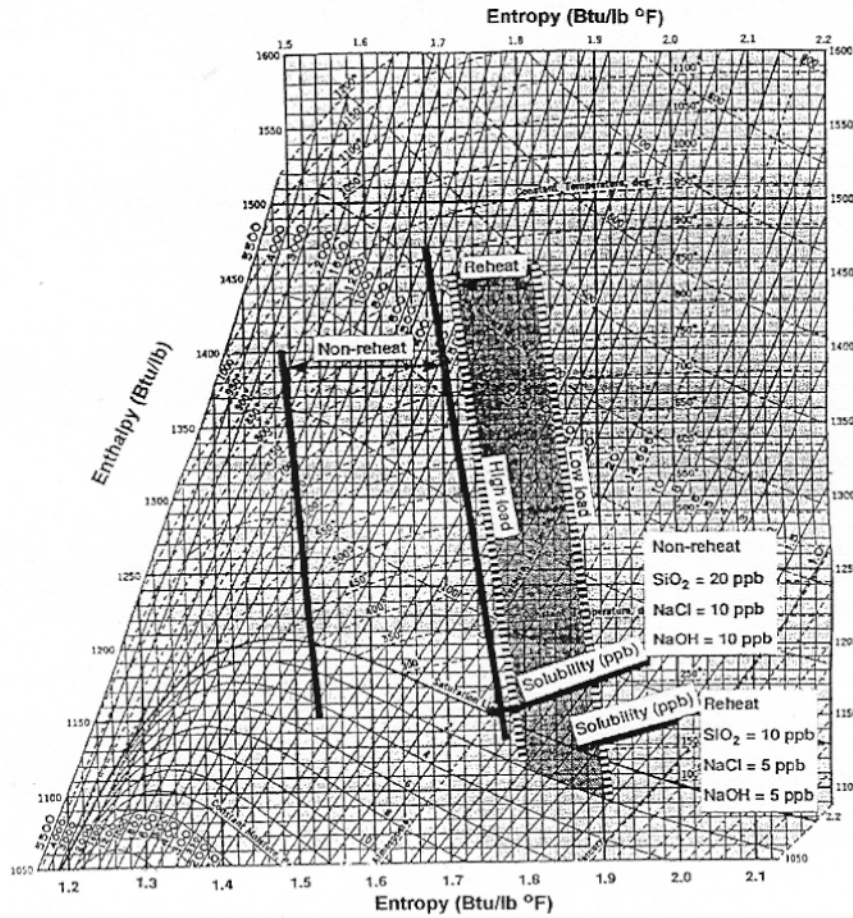


Figure 13. Mollier diagram for reheat and non-reheat turbine steam expansion with solubilities for three steam impurities

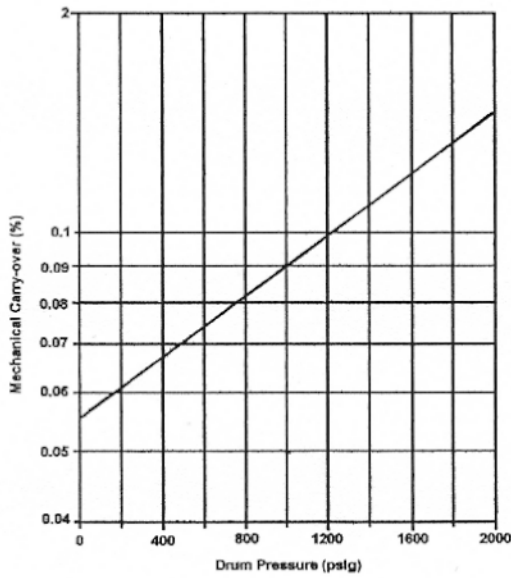


Figure 14. Representative drum boiler mechanical carry-over

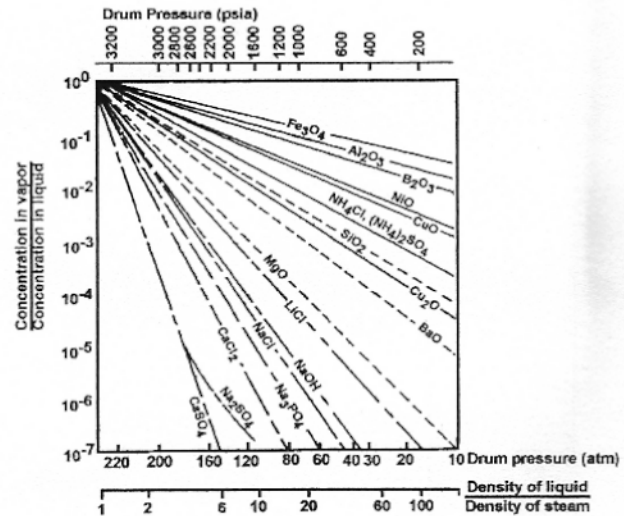


Figure 15. Distribution ratios (volatility) for common boiler water contaminants

For drum boiler cycles, the sequence for derivation of boiler water, feedwater, and makeup water limits is shown in Figure 16. To derive boiler water limits, steam purity limits are divided by the total carry-over of the individual major impurities. From the boiler water limits, which should also be checked for deposition behavior and corrosion in the boiler tubes, feedwater limits can be 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 cannot be achieved (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.

The makeup water limits for all cycles should be similar to the steam purity limits and feedwater limits because the makeup water should not be contaminating the feedwater.

The solubilities of a variety of chemical compounds in boiler water (Figures 1 to 4) are considered, in addition to the steam purity considerations, to avoid deposition on boiler tube surfaces. The most significant of these compounds are magnetite (Figure 4) and trisodium phosphate (Figure 5), both of which have retrograde (decreasing with temperature) solubilities.

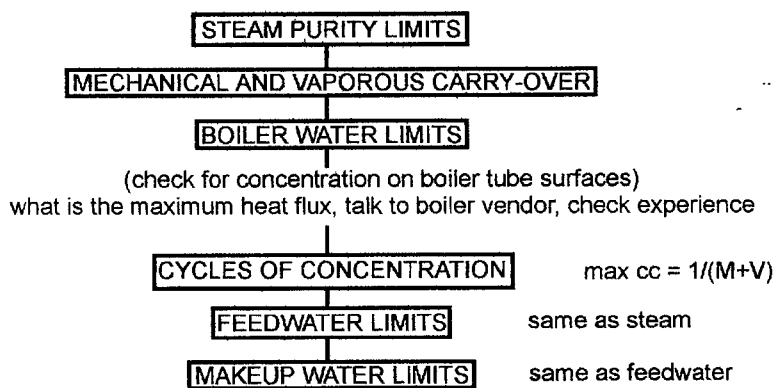


Figure 16. Derivation of water chemistry limits for drum boiler cycles where cc = cycles of concentration, M = mechanical carry-over, V = vaporous carryover

4.2 SELECTION OF WATER TREATMENT

Ideally, selection of boiler water and feedwater treatment should be a part of unit design and material selection. There are six basic water treatments used for utility units worldwide:

- Congruent Phosphate (Na/PO₄ molar ratios 2.2 to 2.8)
- Coordinated Phosphate, Na₃PO₄
- Phosphate plus Hydroxide/Equilibrium Phosphate
- Sodium Hydroxide
- All-volatile Treatment (AVT)
- Oxygenated Treatments (OT) (CWT-combined, NWT-neutral)

In addition, there are many combinations of polymeric dispersants and chelating agents with other chemicals. These two organic treatments are used to prevent deposition of hardness chemicals

(calcium and magnesium salts) in boilers. They are not needed in cycles with good makeup water and good return condensate. A description of the water treatments is given in Table 3. A guide for selection of water treatments is in Table 4.

For the sodium phosphate and hydroxide boiler water treatments, water treatment chemicals are added into the boiler drum. All-volatile and oxygenated treatments are feedwater treatments - no chemicals are added into the boilers, the boiler water has no buffers, and its at-temperature pH is close to neutral.

Feedwater Treatment - Control of feedwater, steam, and condensate pH is achieved by injection of ammonia or amines into feedwater. To protect carbon and low alloy steels, the pH needs to be within the range of 9.2 to 9.6. Depending on their volatility, these chemicals also alkalize the moisture droplets and films in the wet steam regions of the cycle.

Which of these treatments should be selected depends on:

- purity of makeup water and of return condensate
- type of boiler
- 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

Boilers operating with high heat flux and experiencing phosphate hideout may require the use of equilibrium phosphate boiler water treatment (EPT) or, for cycles with high purity water, AVT or OT can be used.

Changing Water Treatment - When chemical upsets occur during operation of cycles on AVT, sodium phosphate or sodium hydroxide can be injected into the boiler water to neutralize acids and maintain pH within the normal limits. When a permanent water treatment change is contemplated, it is recommended to inspect and possibly chemically clean the boilers before the new water treatment is started. When a change is made, it may take several weeks of transient water chemistry before the system stabilizes.

Phosphate (Plus Hydroxide) Boiler Water Treatments (2, 10, 11, 18, 19, 22, 33)

Four basic phosphate boiler water treatments are used today (see Table 3 and Figure 17): conventional phosphate, equilibrium phosphate, coordinated phosphate, and congruent phosphate.

In boilers where phosphate hideout and maintaining of boiler water pH is a problem, phosphate plus hydroxide, also called equilibrium phosphate boiler water treatment, may be beneficial (10, 11, 22). There is a divided opinion about the dangers of phosphate hideout. Many actual phosphate boiler water treatments are operated with a small excess of free hydroxide alkalinity in the range of 0.2 to 1 ppm. In England, where most of the utility units use sea water for condensate cooling, boilers are operated with only sodium hydroxide. CEGB guidelines state that the sodium hydroxide concentration should be 2.5 times that of NaCl.

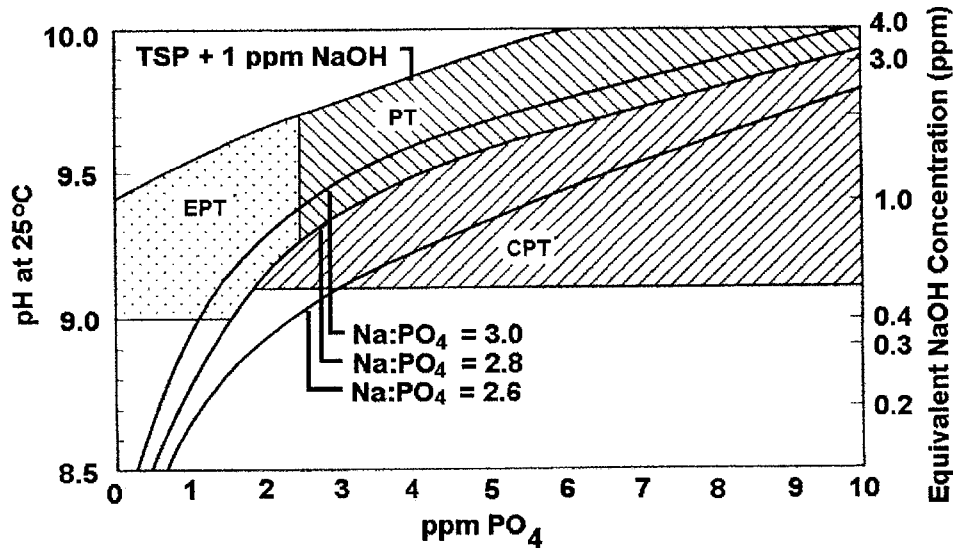


Figure 17. Schematic of operating ranges of boiler water on equilibrium phosphate treatment (EPT), congruent phosphate treatment (CPT), and phosphate treatment (PT)

Before using a boiler water treatment with free hydroxide, boiler and cycle materials need to be evaluated for possible hydroxide corrosion and steam blanketing in the horizontal and slanted boiler tubes. In units with austenitic stainless steel reheaters and superheaters, there is a danger of intergranular cracking when hydroxide carry-over occurs.

Equilibrium Phosphate Concentration

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) which the boiler can tolerate without forming solid phases on the heat transfer surfaces. These solid phases are usually first formed in boiler tubes with the highest heat flux and inadequate mass flow where the departure from nucleate boiling, DNB, occurs. Horizontal and slanted tubes can also accumulate solid deposits because of steam blanketing.

The equilibrium phosphate concentration can be experimentally determined by increasing the phosphate feed to the point when there is no more increase in PO_4 concentration in the boiler water. This is the equilibrium PO_4 concentration. The normal PO_4 limit should be about one-half of the equilibrium concentration. This experimental determination should be periodically repeated (about once a year) because the equilibrium concentration changes with the boiler cleanliness.

Table 3. Characteristics of the leading boiler water and feedwater chemical treatment programs (3, 23)

Program	Favorable	Unfavorable
Conventional phosphate, Na_3PO_4 (+NaOH)	Hardness salts are converted to a form readily removed by bottom blowdown; relatively high levels of suspended solids are successfully controlled; acids neutralized; surface passivation by PO_4	High pressure boilers cannot tolerate intentional formation of boiler sludge; required alkalinity levels are too high for operation above 10.4 MPa (1500 psig); oil or organic contamination produces highly adherent deposits; possible "underdeposit" corrosion by concentrated NaOH
Equilibrium phosphate	No hideout effects due to reactions on waterwall tubes; some acid neutralization in boiler	Requires very low concentration of impurities; frequent revisions of limits
Coordinated phosphate, molar ratio $\text{Na}:\text{PO}_4 \sim 3$	Caustic corrosion may be eliminated; deposit form makes for easy removal; produces low solids levels and high steam purity; acids neutralized; surface passivation by PO_4	In boilers containing deposits, chemical interaction of iron and phosphate can lead to caustic corrosion; phosphate hideout
Congruent phosphate, molar ratio $2.2 \leq \text{Na}:\text{PO}_4 \leq 2.8$	Caustic and acid corrosion eliminated; deposit form makes for easy removal; produces low solids levels and high steam purity; acids neutralized; surface passivation by PO_4	Control of the $\text{Na}:\text{PO}_4$ molar ratio may be difficult; continuous feed and blowdown may be required; phosphate hideout; at very low $\text{Na}:\text{PO}_4$ molar ratios (2.1) corrosion by phosphoric acid is possible
Sodium or lithium hydroxide	Acid neutralization in boiler, no hideout of phosphates	Can cause rapid corrosion when concentrated in high quality regions or underdeposits; vaporous carry-over in steam at higher pressures; difficult to analyze
Chelates, ethylenediamine-tetraacetic acid (EDTA), nitrilotri-acetic acid (NTA)	Optimum heat transfer and boiler efficiency obtained under good feedwater parity conditions; allows boiler operation with some hardness; elimination of boiler sludge prevents formation of adherent deposits involving oil/organics	Inability to accurately test/control free chelant residual can lead to overfeed and subsequent corrosion (heightened when treatment is applied to deposit-bearing boiler); will not complex iron or copper under normal boiler water pH conditions; presence of oxygen in boiler water can cause dechelation and corrosion; decomposition at higher temperature

Polymeric dispersants	Disperse iron; complex hardness	Testing/control; decomposition at higher temperatures; can be overloaded with hardness and form organic deposits; expensive
All-volatile (AVT) (ammonia, morpholine, cyclohexylamine, ETA, AMP, etc.)	“Near-zero solids” in boiler water and high purity steam realized under ideal feedwater conditions, with some corrosion protection; no carry-over of solids; condenser leakage detection by sodium measurement; boiler deposition of corrosion products easy to remove by chemical cleaning	Feedwater contamination may exceed inhibiting ability of volatile feed, leading to boiler corrosion; introduction of contaminants into feedwater produces deposits that may be hard to remove; marginal acid neutralization in feedwater and steam (ammonia in wet steam regions), none in boiler; corrosion of copper alloys by NH ₄ OH and oxygen; decomposition of organic amines
Neutral, ~200 ppb, oxygen added (mostly for once-through boiler units)	No interference of additives with condensate polishing, high purity effluent, less regeneration (discharges); low corrosion rates of ferritic steels; less friction in boiler tubes (no ripples)	Requires very low concentrations of impurities in water; no corrosion protection in a case of an upset; corrosion of copper alloys; precise control required; corrosion of some stellite valve seats
Combined water treatment (CWT) 50-200 ppb O ₂ ; 200 ppb NH ₃ (mostly for once-through boiler units)		

Condensate Polishing and/or Filtration (2, 18, 23)

As can be seen in Table 4, condensate polishing is recommended for units using seawater, brackish water, and cooling towers for condenser cooling and for high pressure units and units with once-through boilers. This is to prevent the effects of condenser leaks and provide additional operating flexibility when operating with small leaks. In the cogenerating units where 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 need to be considered in designing the filtration system. Sintered metal filter elements are recommended.

Table 4. Guide for selection of water treatments

Boiler	Pressure (psi)	Cooling Water	Water Treatment
Drum	<2400	Fresh	PO ₄ , PO ₄ +OH, NaOH, AVT
		Salty, Cooling Tower	PO ₄ , PO ₄ +OH, NaOH, AVT + Cond. Polishing
	>2400	All	Equil. 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 or volatile amines, oxygen scavenging, when needed, is by hydrazine or possibly by 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 carry-over.
3. For phosphate boiler water treatments, phosphate hideout and equilibrium concentration need to be experimentally determined.

Organic Chemicals (12-14, 23)

During the past 20 years, many new organic boiler water treatment chemicals and oxygen scavengers have been introduced. They all decompose, forming organic acids and CO₂. 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, similarly as during commissioning.

If proprietary treatments are to be used, the vendor should supply the user with useful test methods for monitoring the program. The validity and sensitivity of such methods should be established. Generally, on-line analyzers are not available to monitor proprietary treatments. However, there has been a recent effort to develop on-line analyzers for some hydrazine substitutes.

The industrial and utility users of water treatment chemicals need to know the pressure and temperature range of their application 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 (Table 5).

Table 5. Data needed for all 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.)

4.3 SAMPLE POINTS, CONTROL PARAMETERS, LIMITS, AND ACTION LEVELS

Water and steam samples should be close to the main sources of impurities and they should represent the environment in main cycle components. The sample points for a typical drum boiler cycle are: makeup, condensate, condensate polisher effluent (total and individual polishers), deaerator outlet, final feedwater (economizer inlet), boiler blowdown or a downcomer, saturated steam (multiple samples), and hot reheat (see Figure 18) (19).

The **chemical control parameters** for individual sample points should include the parameters responsible for equipment corrosion (pH, oxygen, major corrosive impurities), parameters which indicate that the corrosion is present (iron, copper, corrosion hydrogen), and the parameters which indicate ingress of impurities (cation conductivity of condensate).

For routine monitoring, 10 to 15 **Core Parameters** (Figure 18) need to be monitored. Except for iron and copper, all these 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 **commissioning and troubleshooting**.

Normal Limits for these parameters are derived, per the rationale described in Section 4.1. These conservative limits assure that there is no corrosion and scale and deposit formation beyond the conditions for reliable operation and life expectancy. To allow temporary exceedance of the normal limits, up to 3 **Action Levels** are provided, together with the recommended cumulative hours. There is usually only one condition for **Immediate Shutdown** - boiler water pH.

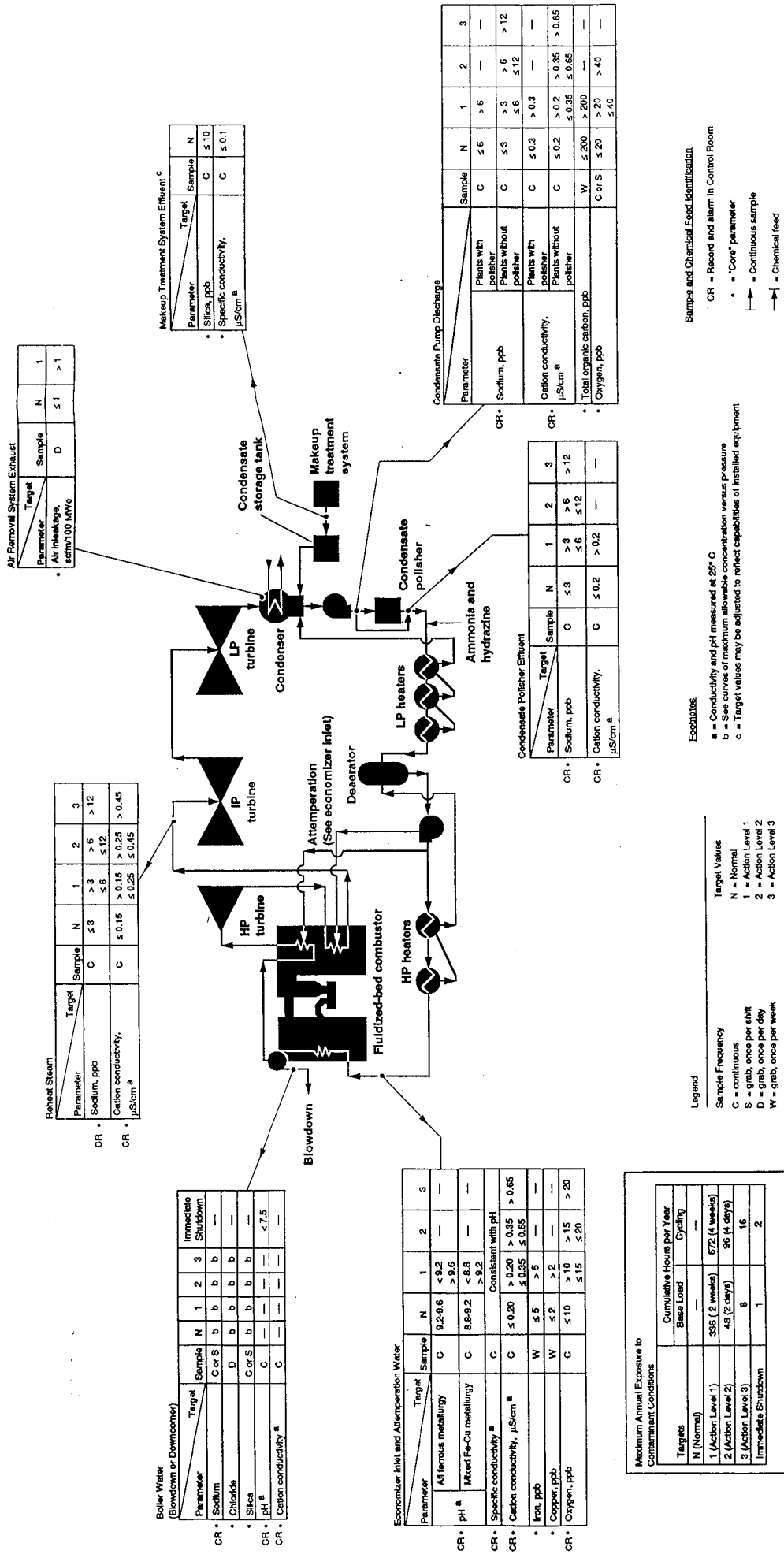


Figure 18. Water and steam chemistry control for a drum boiler unit on phosphate treatment - Core Parameters

4.4 MONITORING (2, 18-25, 31-45)

It is imperative that the cycle chemistry be **monitored around the clock**, preferentially by on-line continuous instrumentation. Around-the-clock monitoring is typically most efficiently done by the control room operators with the chemists helping with interpretation and verification of data and many other tasks. Interpretive monitoring and rapid reactions to chemical upsets (as quick as 15 min.) should be provided for all types of operation and layup.

EPRI ChemExpert software (25), based on artificial intelligence and expert system principles, has recently been successfully developed. It is aimed at the control room operators and can be incorporated into the DCS (digital control systems). It performs on-line validation of instrumental data and results of grab sample analysis, quickly identifies chemical upsets, gives instructions for corrective actions (including the time interval), has a training and maintenance module, and performs automatic reporting and data storage for the life of the unit.

Diagnostic monitoring (44) of corrosion, leaks, and many other parameters can also prevent forced outages and equipment deterioration. For the turbine, several monitoring tools have recently been developed to aid in troubleshooting of deposition and corrosion problems and monitoring of exfoliated oxides gives input to the related reduction of iron transport (45).

Sampling

Representative sampling helps provide accurate information on the composition of water and steam (2, 18, 24, 34, 35, 38, 39). **Isokinetic sampling** is recommended for sampling two-phase flows and the streams with suspended solids, such as steam and feedwater (35). The sample lines should be short with the liquid sample flow velocity about 6 ft/sec to assure turbulent flow and avoid buildup of deposits.

Quality Assurance and Quality Control (36-38, 41-43)

It is recommended to institute an **Analytical QA/QC Program** (41-43) to assure that the sampling and analytical errors are minimized and that the, often expensive, corrective actions are not based on erroneous data. Sampling errors could be as high as several hundred percent and analytical errors up to 100% are not uncommon.

5 MANAGEMENT AND COMMUNICATION (2, 18, 25)

Management leadership and a clearly stated policy on water chemistry and corrosion control are essential components for efficient operation of every steam cycle (18). The following items should be covered:

- water chemistry and corrosion control considerations in cycle and component design
- commissioning of related hardware and practices
- operator and chemist training
- round-the-clock monitoring and timely response to upsets
- recordkeeping for the life of the unit
- periodic review of records and periodic audits
- QA/QC of sampling, analysis, and maintenance practices

- water chemistry consideration in failure and root cause analysis
- cost evaluation - water chemistry control vs. corrosion and scale

It is suggested that each utility or operator develop a Cycle Chemistry Program consisting of a set of guidelines and procedures. The following are typical contributions by the **Chemical Staff**:

- optimization of cycle chemistry, instrumentation, and control
- quality control of sampling, analytical procedures, water treatment chemicals, ion exchange resins, etc.
- prevention of contaminant ingress into the cycle, including maintenance procedures
- prevention of corrodent/corrosion product generation and transport
- prevention of corrodent/corrosion product deposition and cleaning of cycle components
- evaluation of new water treatment chemicals and processes
- use of "expert systems" and record keeping
- daily water chemistry control
- participation in the root cause analysis of related problems
- training

Communication within the power station, utility, and with outside organizations should be an integral part of the job of the System and Station Chemists. They should transfer important information to management, technicians, and operators.

Training

Training of chemists and operators, together with selected maintenance and engineering staff, should be an integral part of the cycle chemistry control activities. Every control room operator needs to be trained and be able to interpret basic water chemistry data and quickly select corrective actions to chemical upsets.

MANY EQUIPMENT PROBLEMS RESULT FROM THE DIMINISHED ROLE OF THE WATER CHEMIST COMBINED WITH A LACK OF TRAINING OF OPERATORS.

Reporting

It is recommended to produce daily, monthly, and yearly water chemistry reports and to develop a quantitative measure of the quality of control. Typical measures are percent of time out-of limit for individual core parameters or for a combined parameter. It is important to explain, in the daily reports, what the cause was of the off-limit chemistry.

Water chemistry, outage, and maintenance records should be kept for the life of the equipment to aid in possible future root cause analyses of corrosion and deposit problems. There should be a yearly report on the cost of water chemistry control and related outages.

Audits

As a part of unit commissioning, after the water chemistry is changed, and about every five years, water chemistry control practices should be audited by a group of in-house experts or by an outside consultant. Such an audit typically takes two days per unit plus one day to prepare final conclusions and recommendations. In our experience with over 100 audits, there have always been recommendations which resulted in cost savings and a contribution to reliability and safety.

Life Extension

In managing water chemistry and corrosion control, equipment life exhaustion due to corrosion needs to be considered as a part of the life extension activity. The rate of damage and the effects of water and steam chemistry on erosion-corrosion, boiler tube corrosion, turbine blade pitting and cracking, feedwater heater and condenser tube corrosion, etc., should be known and lead to planned outages and equipment repairs or replacement. For analytical instrumentation, the useful life on analyzers (which is typically ten years) should be considered.

6 CONCLUSIONS AND RECOMMENDATIONS

1. The achievable goals of the effective cycle chemistry control include: no boiler tube corrosion and overheat failures, boiler chemical cleaning interval over 15 years, no turbine blade and disk corrosion failures, ten-year intervals between turbine overhauls, no significant loss of turbine generating capacity and efficiency due to deposits, boiler wet layup without special chemical additions, no chemical hold during startups, and no turbine solid particle erosion.

2. The old problems which are improving include boiler tube corrosion and overheat failures, turbine deposit buildup, and erosion-corrosion of wet steam and feedwater piping. Newly emerging problems include: erosion-corrosion in piping and combined cycle HRSGs, stress corrosion cracking of LP turbine blade attachments, and the problems caused by some new organic water treatment chemicals (formation of organic acids, scale).

3. The safety-related issues include pipe perforation due to erosion-corrosion and cavitation, corrosion cracking of carbon steel welds in pipes, deaerators, and boiler flash tanks, and cracking of economizer and superheater headers.

4. Dollar savings are achievable by avoiding forced outages, reducing startup time, improving steam purity and reducing of turbine deposition, reducing the cost of chemicals (no need for expensive organic chemicals), by quick and appropriate corrective actions in cases of chemical upsets, and by preventive maintenance (condenser leaks, air leakage, ion exchange resins, ...).

5. Effective cycle chemistry control is enhanced by periodic audits (in-house specialists or an outside expert), QA/QC of sampling and instrumentation, operator and chemist training, cooperation and communication between operators, maintenance, engineering, and chemists, and a clear management mandate and assignment of responsibilities.

6. The best cycle chemistry can be achieved through its consideration in the cycle design and material selection, commissioning, and periodic (about every 5 years) determination of the cycle chemical characteristics (boiler carry-over, performance of makeup and condensate polishing, deaeration, and layup protection).

7. Near-future trends in cycle chemistry and corrosion control are likely to include the use of expert systems, automatic control of chemical feed and blowdown, in-line instrumentation (pH, corrosion potential, particulates), and an enhanced role of control room operators with the chemists in an advisory role and as analysts.

8. The current competitive business environment is forcing efficient and reliable operation with less frequent overhauls and inspections and long-term equipment guarantees. The cost of forced outages escalated during the summer of 1998 to up to \$10,000 per MWh as compared to the cost of generation, as low as \$2 per MWh.

REFERENCES

1. O. Jonas. "Cost of Corrosion and Scale in U.S. Utilities." *Proc. of Fossil Plant Water Chemistry Symposium*, Electric Power Research Institute, Palo Alto, CA, CS-4950, 1985.
2. *ASME Handbook on Water Technology for Thermal Power Systems*. ASME/EPRI 1989.
3. O. Jonas. "Steam." *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 21, 3rd Ed. John Wiley and Sons, 1983, pp. 507-551.
4. *Modern Power Station Practice Vol. 5: Chem. and Metallurgy*. CEGB/Pergamon Press, 1971.
5. *Combustion - Fossil Power Systems*. Combustion Eng. Inc., now ABB.
6. *Steam: Its Generation and Use*. Babcock and Wilcox Co.
7. O. Jonas. "Transport of Ionic Impurities in Fossil and PWR Cycles - New Observations." *42nd Intl. Water Conf.*, Pittsburgh, 1981, Paper No. IWC81-40.
8. O. Jonas. "Transport of Chemicals in Steam Cycles." Paper No. 245, Corrosion/85, NACE, March 25, 1985, Boston.
9. O. Jonas and A. Pebler. *Characterization of Operational Environment for Steam Turbine Blading Alloys*. Electric Power Research Institute, Palo Alto, CA, August 1984. EPRI CS-2931.
10. O. Jonas and R. Layton. "Phosphate Boiler Water Treatment for High Pressure Boilers." *Proc. 2nd Fossil Plant Cycle Chemistry Conference*, GS-6166, Electric Power Research Institute, Palo Alto, CA, January 1989.
11. J. Stodola. "Review of Boiler Water Alkalinity Control." *Proceedings 47th Intl. Water Conf.*, Pittsburgh, 1986, pp. 234-243.
12. O. Jonas. "Beware of Organic Impurities in Steam Power Systems." *Power*, Sept. 1982, pp. 103-107.
13. O. Jonas. "Use of Organic Water Treatment Chemicals." *VGB Conference, Organische Konditionierungs-und Sauerstoffbindemittel*, Lahnstein, Germany, March 1994.
14. O. Jonas. "Controlling Oxygen in Steam Generating Systems." *Power*, May 1990.
15. W.L. Pearl, et al. "Deoxygenation in Cycling Fossil Plants." *Proc. Int'l Conf. on Fossil Plant Cycle Chemistry*, TR-100195, Electric Power Research Institute, Palo Alto, CA, Dec. 1991.
16. N.I. Dickinson, D.N. Felgar and E.A. Pirsh. "An Experimental Investigation of Hydrazine-Oxygen Reaction Rates in Boiler Feedwater." *Proc. of the Am. Power Conf.*, Vol. 47, 1985.
17. *Effects of Hydrazine and pH on the Corrosion of Copper-Alloy Materials in AVT Environments with Oxygen*. Electric Power Research Institute, Palo Alto, CA, December 1982. NP-2654.
18. *Interim Consensus Guidelines on Fossil Plant Cycle Chemistry*. Electric Power Research Institute, Palo Alto, CA, June 1986. CS-4629.
19. *Guidelines on Cycle Chemistry for Fluidized-Bed Combustion Plants*. Electric Power Research Institute, Palo Alto, CA, Sept. 1993. TR-102976. Also, Int'l Water Conf. Paper IWC-93-50, 1993.
20. *Cycle Chemistry Guidelines for Fossil Plants: All-Volatile Treatment*. Electric Power Research Institute, Palo Alto, CA, April 1996. TR-105041.
21. *Cycle Chemistry Guidelines for Fossil Plants: Oxygenated Treatment*. Electric Power Research Institute, Palo Alto, CA, December 1994. TR-102285.
22. *Cycle Chemistry Guidelines for Fossil Plants: Phosphate Treatment for Drum Units*. Electric Power Research Institute, Palo Alto, CA, December 1994. TR-103665.
23. *Selection and Optimization of Boiler Water and Feedwater Treatments for Fossil Plants*. Electric Power Research Institute, Palo Alto, CA, April 1996. TR-10540.

24. *Cycling, Startup, Shutdown, and Layup Fossil Plant Cycle Chemistry Guidelines for Operators and Chemists*. Electric Power Research Institute, Palo Alto, CA, August 1998. TR-107754.
25. O. Jonas and L. Machemer. *EPRI ChemExpert, Cycle Chemistry Advisor for Fossil Power Plants*. Electric Power Research Institute, Palo Alto, CA, December 1998. CM-112136.
26. *Guidelines for Makeup Water Treatment*. Electric Power Research Institute, Palo Alto, CA, March 1990. GS-6699. New Guidelines to be published in 1999.
27. *Guidelines for Chemical Cleaning of Fossil-Fueled Steam Generating Equipment*. Electric Power Research Institute, Palo Alto, CA, June 1993. TR-102401.
28. *Consensus on Operating Practices for the Control of Feedwater and Boiler Water Chemistry in Modern Industrial Boiler*. ASME, 1994.
29. *Boiler Water Limits and Steam Purity Recommendations for Water Tube Boilers*. American Boiler Manufacturers Association, Third Edition, 1982.
30. O. Jonas. "Determination of Steam Purity Limits for Industrial Turbines." *Proc. Intl. Water Conference*, Pittsburgh, 1988, pp. 137-147.
31. "VGB Guidelines for Boiler Feedwater, Boiler Water and Steam for Water Tube Boilers with Pressure of 64 Bar and Higher." *VGB Kraftwerkstechnik* 60, No. 10, Oct. 1980, pp. 714-721.
32. *Chemical Control of the Steam Water Circuit of Drum-Type and Once-Through Boilers*. CEGB, Generation Operation Memorandum 72-Part 1, April 1983.
33. O. Jonas and B. Dooley. "International Water Treatment Practices and Experience." *Proc. of the International Water Conf. 51st Annual Meeting*, Pittsburgh, 1990, pp. 396-403.
34. *Guideline Manual on Instrumentation and Control for Fossil Plant Cycle Chemistry*. Electric Power Research Institute, Palo Alto, CA, April 1987. CS-5164.
35. O. Jonas. *Development of a Steam Sampling System*. Electric Power Research Institute, Palo Alto, CA, Dec. 1991. TR-100196.
36. J. Rice. "Industrial Water Quality Measurement: A Retrospective/Prospective View." *Proceedings 50th Intl. Water Conference*, Pittsburgh, PA, 1989, pp. 150-170.
37. 1990 International Conference on Measuring Waterborne Trace Substances. Electric Power Research Inst. and Natl. Inst. of Standards and Technology, August 1990, Baltimore, MD.
38. O. Jonas. "A Critical Overview of Power Station Sampling and Analysis of Water and Steam." *ASTM & ASME Symposium on Power Plant Instrumentation for Measurement of High Purity Water Quality*, Milwaukee, June 9-10, 1980. ASTM STP 742 (1981) pp.11-23.
39. O. Jonas, et al. "In-Line Monitoring of Flow of Exfoliated Oxides." *Solid Particle Erosion of Utility Steam Turbines: 1985 Workshop*, EPRI CS-4683, August 1986.
40. *Reference Manual for On-Line Monitoring of Water Chemistry and Corrosion*. Electric Power Research Institute, Palo Alto, CA, March 1995. TR-104928.
41. S. P. Hall. *Quality Control in Power Plant Laboratories*. Illinois Power Co., 1983.
42. "Standard Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water." ASTM Standard D2777-96.
43. O. Jonas. "QA/QC of Sampling and Analytical Procedures." Report by Jonas, Inc. Sept. 1997.
44. O. Jonas. "Diagnostic Monitoring - An Overview." *Power*, January 1992.
45. O. Jonas. "On-line Diagnosis of Turbine Deposits and First Condensate." *55th Annual Intl. Water Conf.*, Pittsburgh, PA, Oct. 31-Nov. 1-2, 1994.