# 5

# CYCLES WITH ONCE-THROUGH BOILERS ON ALL-VOLATILE TREATMENT (AVT)

## 5.1 INTRODUCTION

The operating philosophy for once-through steam generating units recognizes that all soluble feedwater contaminants have to dissolve in the superheated exiting steam and be within the allowable turbine inlet steam purity limits. The corrosion products transported to the steam, generator from the pre-boiler system that would be available for deposition in the lower radiant furnace, have to be maintained at a concentration level low enough to avoid any necessity for, or to provide economical operating periods between, chemical cleans to remove these deposits before they cause equipment damage.

Therefore, the feedwater treatment has to be volatile, either AVT (these guidelines) or OT.(9) The alkalizing agent used has to meet the requirement of being completely volatile and not being thermally decomposed at exiting superheated steam temperatures in excess of 538 °C (1000 °F) at both subcritical and supercritical pressures. The only volatile chemical found to meet these requirements is ammonia ($NH_3$) that is applied as ammonium hydroxide ($NH_4OH$).

In selecting the optimum cycle chemistry, the materials used for condenser tubing and in feedwater systems have to be respected. Application of copper or copper alloys for condenser or feedwater heater tubing requires particular consideration (copper species transport into the steam generator and have solubility in steam). To optimize control and transport of feedwater contaminants, feedwater systems should be constructed of iron-based materials.

Full flow condensate polishing systems utilizing either "deep-bed" and/or "powdered-resin" systems are utilized at the condenser discharge or in the low pressure feedwater system at temperatures below the decomposition point of anion exchange resins (140°F, 60°C). Some systems are designed with pre-coat or cartridge filters ahead of the condensate polishers.

### *5.1.1 All-ferrous metallurgy systems*

Feedwater systems having carbon steel heaters and piping are required to operate at a pH of 9.2-9.6 (at 25°C or 77°F) to minimize flow-accelerated corrosion. In absence of carbon dioxide, adjusting this pH requires the addition of 500-2200 ppb of ammonium hydroxide as $NH_3$ (Figure 5-1). Additional application of a reducing agent such as hydrazine is not advised for units with all-ferrous metallurgy. The oxidizing-reducing potential, ORP, will be just above 0 mV when operating without any reducing agent, and in this way will minimize flow-accelerated corrosion.(1,2)

There are still a few organizations operating units with once-through boilers and all-ferrous metallurgy using a reducing agent such as hydrazine (or an alternative). This type of AVT does not represent the state-of-the-art treatment and should be converted to oxidizing AVT (AVT(O)) or OT.

In units with copper alloys employed for condenser tubing (arsenical copper, aluminum bronze, brass, 90-10 and 70-30 copper-nickel alloys) copper corrosion in the air removal section of the condenser or in crevices between the tube and the tube support plate may require a reduction of the upper boundary of the pH operating range (e.g., from 9.6 to 9.4).

When the cycle pH is relatively high, the polishers—for economic and regenerant waste disposal reasons—should, if possible be operated normally in the ammonium form and/or beyond the ammonia breakthrough for the deep bed cation resins. Many utilities maintain stand•by resin beds in the hydrogen form to use during periods of condenser leakage. Powdered resins (having low ion exchange capacity) are normally operated in the ammonium form. Ammonium form operation reduces the efficiency of mixed bed ion exchangers especially for sodium removal from the condensate, although continuing to efficiently remove both iron and copper corrosion products from the condenser (if copper containing condensers are utilized).

This guideline does not address oxygenated treatment, which solves many of these problems and is covered by a separate Oxygenated Treatment Guideline,(3) which will be revised in 2004.

### 5.1.2 Mixed-metallurgy systems

Cycles with once-through boilers and mixed-metallurgy in the feedwater system are not very common. Nevertheless, some information dealing with this untypical configuration is appropriate.

Feedwater systems with feedwater heater tubing made of copper or copper alloys are required to operate at a pH of 9.0-9.3 (at 25°C or 77°F) and under reducing conditions (the optimum ORP should be between –300 and –350 mV) to minimize the copper corrosion and transport of copper oxides into the boiler.(4)

Adjusting this pH requires the addition of 250-700 ppb of ammonium hydroxide as $NH_3$ (Figure 5-1). Controlling air in-leakage and the feed of aqueous solution of a reducing agent such as hydrazine in front of the feedwater systems is required for ensuring the required reducing conditions in the entire feedwater system.(4) The reader is referenced to Section 4 in this Guideline where mixed-metallurgy systems are extensively covered.

The cycle pH is lower than in cycles with all-ferrous metallurgy. This makes polisher operation in the H/OH cycle more practical.

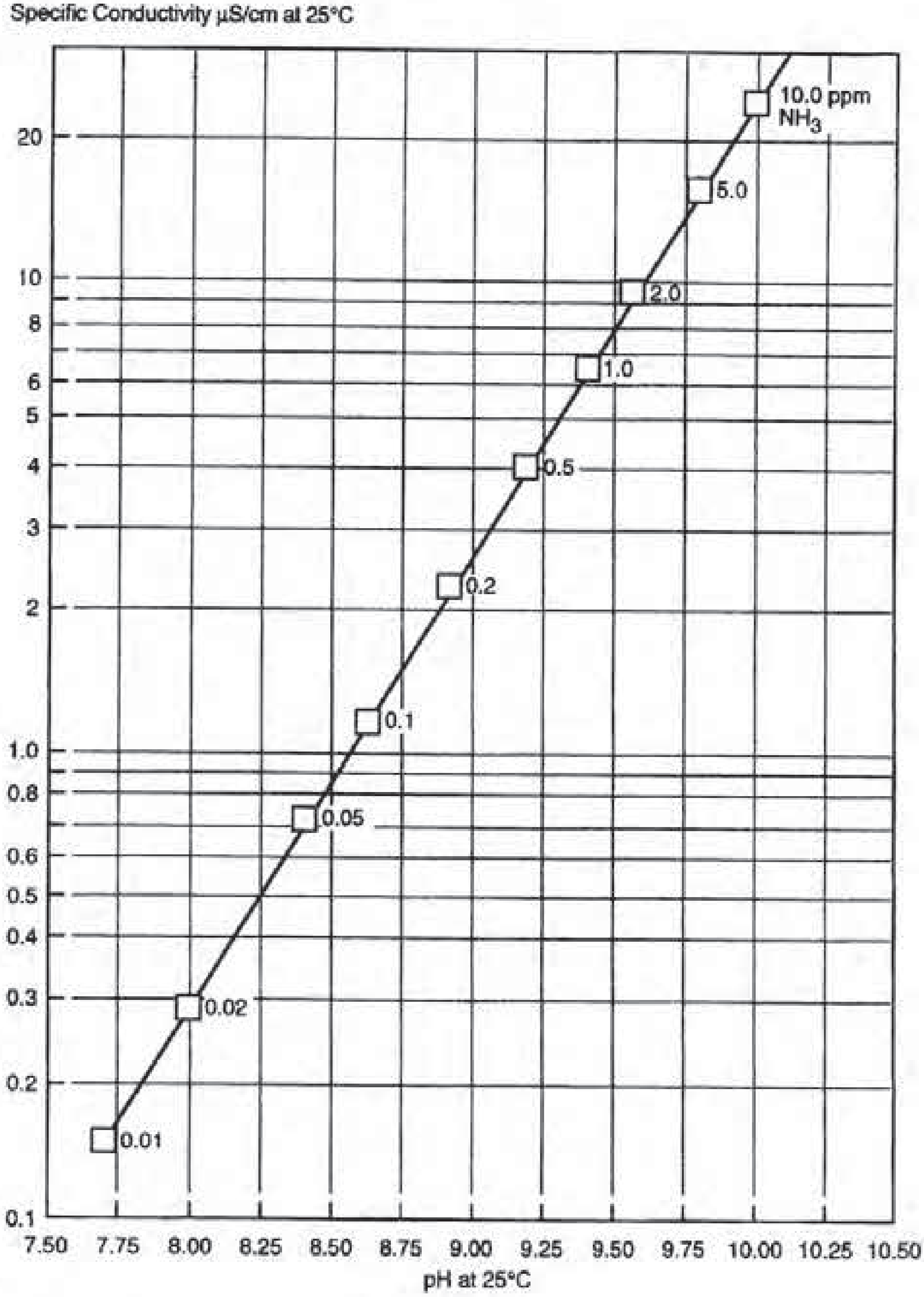


**Figure 5-1**
**Theoretical Relationship Between Specific Conductivity and pH for Ammonia Solutions**

## 5.2 AVT GUIDANCE

Cycle chemistry target values and action levels are presented in this section for each monitoring point for units with once-through boilers on all-volatile treatment. A target or normal value and as many as three action levels are given for each parameter at each monitoring point. This section is intended to be used by operating staff and management personnel.

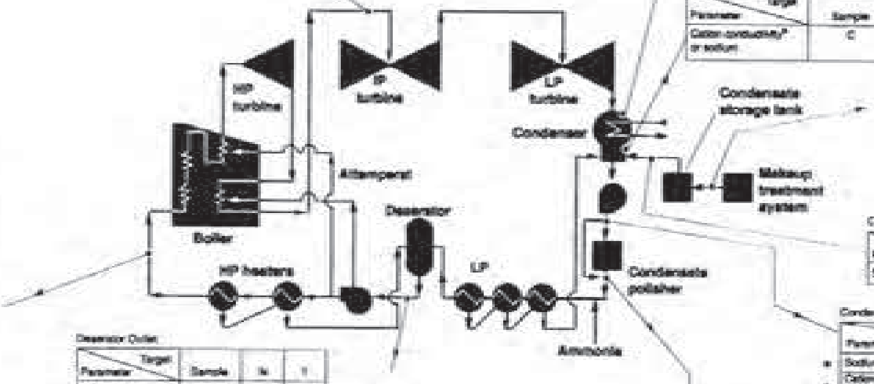
Similarly designed once-through boilers may behave differently in response to impurity ingress and feedwater corrosion product ingress because of differences in pre-boiler systems, balance-of-plant designs and materials choices, differences in makeup system design and operation, variable effectiveness of air-removal equipment, and variable avoidance of cooling water in-leakage control.

Minimizing deposition of pre-boiler corrosion product oxides in the waterwalls of once-through boilers is critical and it plays a key part in a number of boiler tube failure (BTF)(5) mechanisms especially in overheating and for circumferential cracking mechanisms. In the long term, the accumulated deposits must be removed by "timely" chemical cleaning to avoid and/or reduce the incidence of these boiler tube failures.(6) This should be the basis of the optimization of AVT and is, of course, one of the reasons to consider conversion of the unit to oxygenated treatment (OT). The first step is to use the road map approach described in Section 2 to optimize the feedwater treatment for all possible operating circumstances.

## 5.3 TARGET VALUES

The sample points, monitoring parameters, target values, and action levels were established for those plants having once-through boilers. The following figures show the target values and action levels for each sample point and monitoring parameter:

- Cycle chemistry diagram (Figure 5-2) for all-ferrous systems operating with oxidizing conditions, AVT(O).
- Cycle chemistry diagram (Figure 5-3) for mixed-metallurgy systems operating with reducing conditions, AVT(R).
- pH versus ammonia at different carbon dioxide levels (Figure 5-4).



Reheat Steam

| Parameter \ Target | Sample | N | 1 | 2 | 3 |
|---|---|---|---|---|---|
| • Sodium, ppb | C | ≤ 2 | ≤ 4 | ≤ 8 | > 8 |
| • Cation conductivity, µS/cm^a | C | ≤ 0.2 | ≤ 0.4 | ≤ 0.8 | > 0.8 |
| Silica, ppb | T | ≤ 10 | ≤ 20 | ≤ 40 | > 40 |
| Chloride, ppb | T | ≤ 2 | ≤ 4 | ≤ 8 | > 8 |
| Sulfate, ppb | T | ≤ 2 | ≤ 4 | ≤ 8 | > 8 |
| Total organic carbon, ppb | T | ≤ 100 | > 100 | — | — |
| Specific conductivity^a | T | — | — | — | — |

Air Removal System Exhaust

| Parameter \ Target | Sample |
|---|---|
| + Air inleakage, scfm | C or S |

Condenser Leak Detection Trays or Hotwell Zones (if applicable)

| Parameter \ Target | Sample |
|---|---|
| Cation conductivity^a or sodium | C |

Makeup Treatment System Effluent

| Parameter \ Target | Sample | N |
|---|---|---|
| Sodium, ppb | C | ≤ 2 |
| Chloride, ppb | T | ≤ 3 |
| Sulfate, ppb | T | ≤ 3 |
| Silica, ppb | C | ≤ 10 |
| • Specific conductivity, µS/cm^a | C | ≤ 0.1 |
| Total organic carbon, ppb | T or W | ≤ 300 |

Economizer Inlet (EI) and Attemperation Water

| Parameter \ Target | | Sample | N | 1 | 2 | 3 |
|---|---|---|---|---|---|---|
| pH^a | All-ferrous metallurgy | C | 9.2-9.6 | < 9.2<br>> 9.6 | — | — |
| Ammonia | | D | Consistent with pH | | | |
| Specific conductivity^a | | C | | | | |
| • Cation conductivity, µS/cm^a | | C | ≤ 0.2 | ≤ 0.4 | ≤ 0.8 | > 0.8 |
| Iron, ppb | | T | ≤ 2 | > 2 | — | — |
| Copper, ppb | | T | ≤ 2 | > 2 | — | — |
| • Oxygen, ppb | | C | ≤ 10 | > 10 | — | — |

Condensate Storage Tank Effluent

| Parameter \ Target | Sample | N (aluminum tanks only) |
|---|---|---|
| Sodium, ppb | W | ≤ 10 |

Deaerator Outlet

| Parameter \ Target | Sample | N | 1 |
|---|---|---|---|
| Oxygen, ppb | T | ≤ 20 | ≤ 40 |

Condensate Polisher Effluent (CPE)

| Parameter \ Target | Sample | N | 1 | 2 | 3 |
|---|---|---|---|---|---|
| • Sodium, ppb | C | ≤ 3 | ≤ 6 | ≤ 12 | > 12 |
| • Cation conductivity, µS/cm^a | C | ≤ 0.2 | ≤ 0.4 | ≤ 0.8 | > 0.8 |
| Silica, ppb | C | ≤ 10 | > 10 | — | — |

Condensate Pump Discharge (CPD)

| Parameter \ Target | Sample | N | 1 |
|---|---|---|---|
| • Sodium, ppb | C | ≤ 3 | > 3 |
| • Cation conductivity, µS/cm^a | C | ≤ 0.3 | > 0.3 |
| Total organic carbon, ppb | T | ≤ 200 | > 200 |
| • Oxygen, ppb | C | ≤ 10 | ≤ 20 |

Maximum Annual Exposure to Contaminant Conditions

| Targets | Cumulative Hours per Year | |
|---|---|---|
| | Base Load | Cycling |
| N (Normal) | — | — |
| 1 (Action Level 1) | 336 (2 weeks) | 672 (4 weeks) |
| 2 (Action Level 2) | 48 (2 days) | 96 (4 days) |
| 3 (Action Level 3) | 8 | 16 |
| Immediate Shutdown | 1 | 2 |

Legend

Sample Frequency
C = continuous
S = grab, once per shift
D = grab, once per day
W = grab, once per week
T = troubleshooting and commissioning

Target Values
N = Normal
1 = Action Level 1
2 = Action Level 2
3 = Action Level 3

Footnotes

a = Conductivity and pH measured at 25° C

Sample and Chemical Feed Identification
• = "Core" parameter alarmed in Control Room
+ = "Core" parameter
⊢ = Continuous sample
⊣ = Chemical feed

Figure 5-2
Cycle Chemistry Diagram for a Once-Through Unit on All-VolatileTreatment. All-ferrous metallurgy in feedwater system. Operating with an oxidizing environment (no reducing agent).

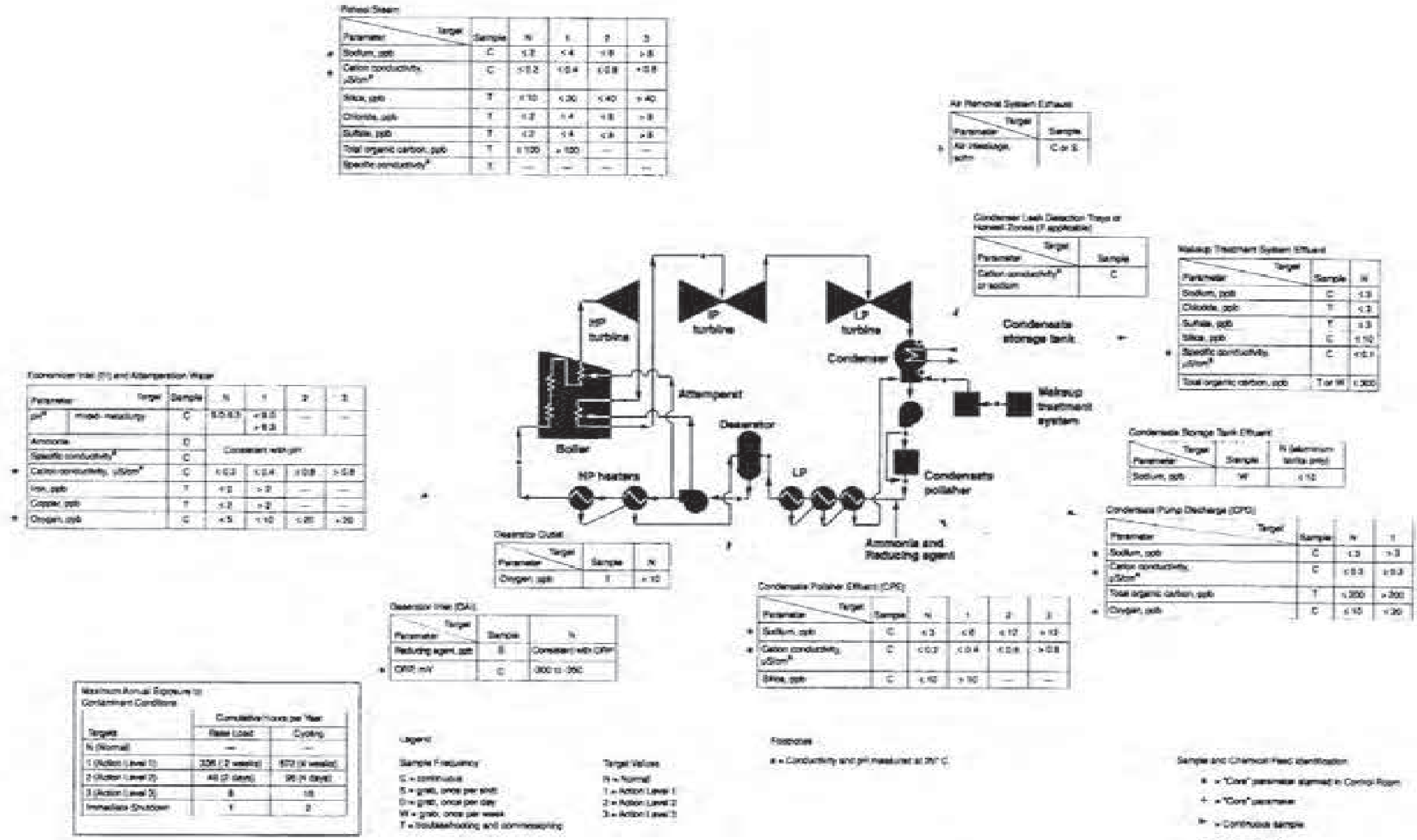


Figure 5-3
Cycle Chemistry Diagram for a Once-Through Unit on All-Volatile Treatment. Mixed-metallurgy feedwater systems. Operating with a reducing environment (reducing agent added)

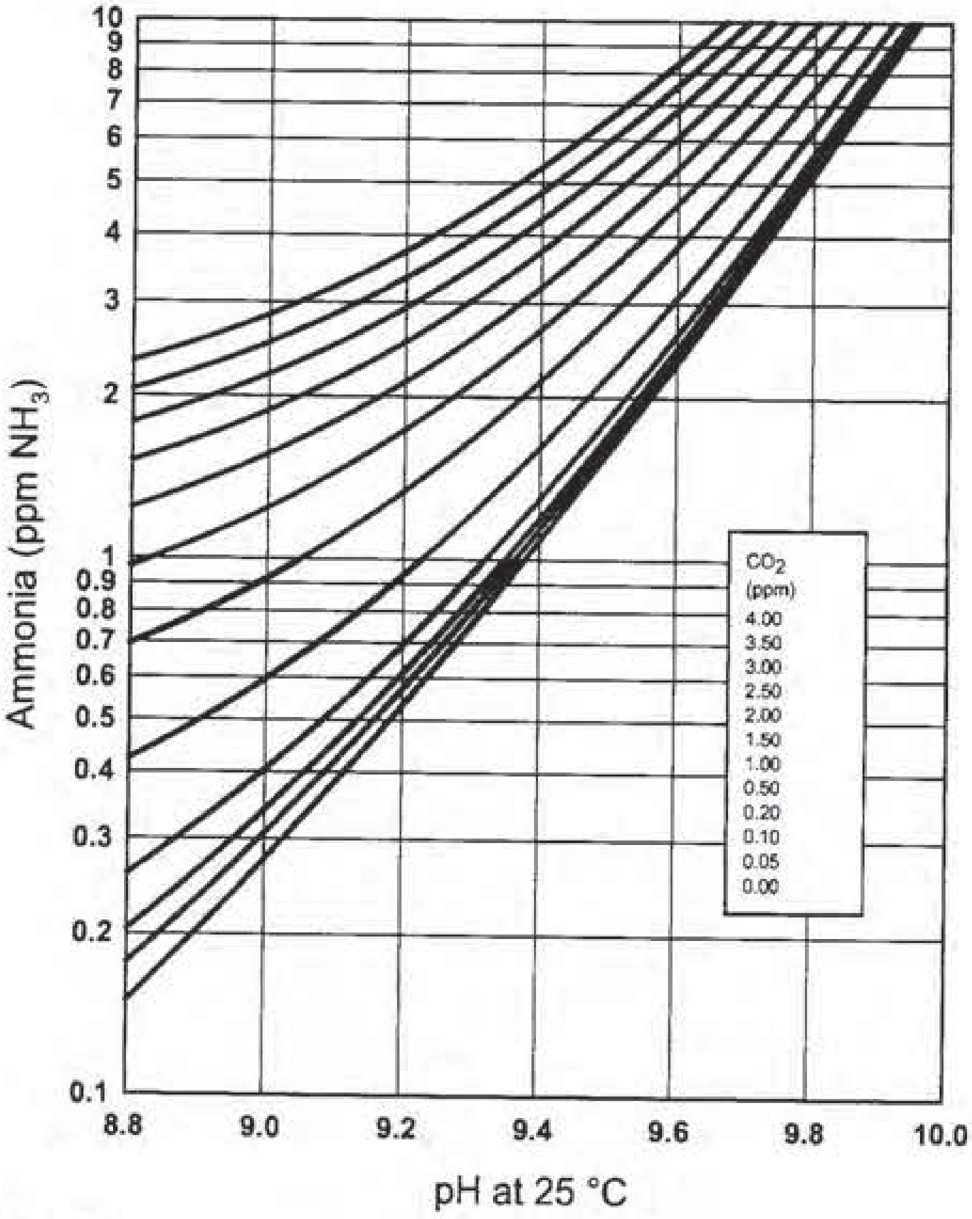


**Figure 5-4**
**Ammonia Concentration vs. pH for Various Carbon Dioxide Concentrations. Note: the top curve represents 4 ppm $CO_2$ and the bottom curve represents zero $CO_2$. Source: from unpublished data derived from volatility code discussed in Section 3.3.1**

There are a number of features to keep in mind when adapting Figures 5-2 and 5-3 to an individual plant. Particular emphasis has been placed in the development of these new guideline cycle diagrams to make control of a unit as simple as possible, and to minimize repetitive grab sampling.

- The Core Parameters (Table 3-1) are indicated by an asterisk (*). These instruments should be monitored continuously and on-line. These have a "C" for "continuous" in the sample column.
- There are a number of other parameters, which have also been designated by a "C" as they provide useful confirmation of unit condition, but are not regarded as "Core" instruments. These parameters are: silica and sodium in makeup, and specific conductivity at the economizer inlet.
- There are a number of other parameters on these diagrams, which have been newly designated in this guideline as "T" for troubleshooting. It is only necessary to monitor these if one of the continuous "Core" instruments provides an indication that the parameter is out of its "normal" guideline value. In most cases, this will be accomplished by grab sample; however, in some cases an organization might have decided to install a continuous analyzer. In the case of iron and copper at the economizer inlet, it should be recognized that in a well operated plant it should not be necessary to monitor these parameters more frequently than once or twice a year; and then only to confirm the feedwater regime remains optimized.

A copy of Figure 5-2, modified if necessary to reflect specific unit characteristics and/or experience, could be included in the plant operating procedures and prominently displayed in the control room, water and steam sample room, and chemistry laboratory. Copies could also be displayed at the makeup treatment system control panel and the condensate polisher control panel (if applicable).

## 5.4 NORMAL OPERATION FOR ONCE•THROUGH UNITS ON AVT

### *5.4.1 All-ferrous feedwater systems*

Normal AVT(O) chemistry control includes the injection of ammonium hydroxide (NH4OH) for pH control. The pH control range for systems utilizing carbon steel is 9.2•9.6 (77°F, 25°C). This requires 500•2200 ppb of ammonia as NH3 (see Figure 5•1) in the absence of carbon dioxide. Reagent grade chemicals are recommended to avoid any unknown contamination from chemical additions.

### *5.4.2 Mixed-metallurgy systems*

Normal AVT(R) chemistry control includes the injection of ammonium hydroxide ($NH_4OH$) for pH control and of a reducing agent such as hydrazine for ORP control. The pH control range for mixed-metallurgy systems is 9.0-9.3 (77°F, 25°C). This requires 250-700 ppb of ammonia as $NH_3$ (see Figure 5-1) in the absence of carbon dioxide. Dosing of hydrazine into the condensate upstream of feedwater heaters in association with good air in-leakage control and less than 10 ppb of oxygen at the condensate pump ensures a reducing ORP in the range of –300 to –350 mV at the deaerator inlet. Here, too, reagent grade chemicals are recommended to avoid any unknown contamination from chemical additions.

### 5.4.3 Monitoring and Corrective Actions

A comprehensive monitoring program should be established, based upon the use of continuous monitors where available, supplemented by grab samples, only if necessary as outlined in Section 5.3. Comprehensive monitoring protocols are given in several EPRI Guidelines such as the *Cycling, Startup, Shutdown and Layup Fossil Plant Cycle Chemistry Guidelines for Operators and Chemists.*(7)

An important new parameter for copper control in mixed-metallurgy cycles in this revision of the AVT Guidelines is ORP. The ORP must be in the reducing range to control copper adequately, as previously described. It is especially important that ORP is monitored in the LP feedwater at the deaerator inlet, and not just at the economizer inlet. Conditions could be reducing in the HP feedwater (at the economizer inlet), but oxidizing in the LP feedwater due to excessive air in-leakage or oxygen saturated makeup additions.

Some organizations have reported problems with the use of ORP sensors and variable ORP readings. It is important that these instruments are calibrated and subjected to frequent QA. Please see Appendix B for comprehensive details.

Deviations from established target values must be vigorously investigated and brought rapidly under control if copper and iron are to be minimized in the cycle. This is covered in Section 6 of these guidelines.

## 5.5 REACTIONS TO CONTAMINANTS IN THE CYCLE

Air in-leakage is a concern as it can affect condensate polisher anion capacity due to carbon dioxide removal and, of course, affects condensate pump discharge dissolved oxygen concentrations. This is particularly important in cycles with mixed-metallurgy because operating with oxygen levels greater than 10 ppb at the condensate pump discharge will jeopardize the ability to have reducing conditions in the LP feedwater system. Air in-leakage is also important for units operating with oxidizing AVT(O) and OT.

Condenser cooling water in-leakage, makeup water contamination, condensate storage tank contamination and improper condensate polisher regeneration can also be sources of contaminants. Three typical examples are:

- chloride or sulfate excursions due to condenser in-leakage
- caustic or acid contamination from makeup (or condensate polisher) regenerant or
- silica from extraneous sources

Satisfactory operation of once-through steam generators and the associated turbines requires that the cation conductivity of condensate (downstream polishers), feedwater, and steam is less than 0.2 μS/cm.

This revision of the AVT Guideline suggests that maximum normal operation levels for final feedwater in cycles with all-ferrous metallurgy should be: iron <2 ppb, copper <2, oxygen 1-10 ppb, sodium <2 ppb, and cation conductivity <0.2 µS/cm.

For cycles with mixed metallurgy, maximum normal operation levels in the final feedwater should be: iron <2 ppb, copper <2, oxygen <5 ppb (ORP –300 to –350 mV), sodium <2 ppb, and cation conductivity <0.2 µS/cm.

During a contamination period, firing of the boiler should be stopped if

- feedwater cation conductivity exceeds 2.0 µS/cm for 5 minutes and remains constant or is still increasing;
- feedwater cation conductivity exceeds 5.0 µS/cm for 2 minutes and does not show an evident decreasing tendency;
- the sodium content detected at the condensate polisher effluent exceeds 20 ppb for 5 minutes and remains constant or is still increasing;
- the sodium content detected at the condensate polisher effluent exceeds 50 ppb for 2 minutes and does not show an evident decreasing tendency.

## 5.6 REFERENCES

1. B. Chexal, J. Horowitz, B. Dooley et al., *Flow-Accelerated Corrosion in Power Plants.* EPRI, Palo Alto, CA: 1998. TR-106611-R1.
2. Guidelines for Controlling Flow-Accelerated Corrosion in Fossil Power Plants. EPRI, Palo Alto, CA: 1997. TR-1088859.
3. Cycle Chemistry Guidelines for Fossil Plants: Oxygenated Treatment. EPRI, Palo Alto, CA: 1994. TR-102285.
4. Guidelines for Copper in Fossil Plants. EPRI, Palo Alto, CA: 2000. 1000457.
5. R. B. Dooley and W. P. McNaughton, Boiler Tube Failures: Theory and Practice. EPRI, Palo Alto, CA: 1996. TR-105261, V1-3.
6. Guidelines for Chemical Cleaning of Conventional Fossil Plant Equipment. EPRI, Palo Alto, CA: 2001. 1003994.
7. Cycling, Startup, Shutdown and Layup Fossil Plant Cycle Chemistry Guidelines for Operators and Chemists. EPRI, Palo Alto, CA: 1998. TR-107754.

# 6

# AVT CHEMISTRY CONTROL AND CORRECTIVE ACTIONS

## 6.1 CHEMISTRY CONTROL

The main purposes of chemistry control are to minimize the risk of deposition and corrosion in the boiler and turbine. The new EPRI approach in these revised AVT Guidelines (outlined in Section 3.3.1) involves setting limits to protect both the boiler and turbine. The boiler limits are within those required to protect the turbine. The type of boiler, whether once-through or drum-type, has important implications on chemical conditioning and control. Operating pressure, type of firing (coal, oil or gas) and whether the unit is fitted with all-ferrous or mixed-metallurgy feedwater heaters and condensate polishing, all have important bearings on feedwater and boiler water treatment.

For once-through boilers, the limits for feedwater and boiler water are the same as those for steam, since any impurities either deposit in the boiler or are carried over into the steam. Higher concentrations of impurities can be tolerated with drum-type boilers, because, within limits, these can be allowed to accumulate in the boiler water, without impacting on steam purity, and can then be removed from the system by blowdown.

As heat fluxes and operating pressures increase, so does the concentration factor between the bulk water and surfaces of the boiler tubes. Unless the concentration of impurities is reduced accordingly, increased corrosion and deposition will result. For drum-type boilers the amount of boiler water impurities and conditioning chemicals carried over into the steam depends on vaporous and mechanical carryover.

Vaporous carryover used to be calculated in previous EPRI Guidelines from the "ray" diagram, but it was recognized that this has considerable limitations. A much improved method is now available based on the EPRI sponsored work on volatility discussed in Section 3.3. Mechanical carryover is based on the graph developed by EPRI (Figure 3-2), based on information supplied by boiler manufactures. Under AVT conditions, it usually represents only a relatively small fraction of the total carryover (mechanical carryover plus vaporous carryover). It is recommended that total carryover is measured on individual drum boiler units under various operating conditions.

Traditionally, all-volatile treatment (AVT) with ammonia and a reducing agent (hydrazine), added to the feedwater to increase the pH and "remove" residual oxygen, has been used as the method of conditioning. Oxygenated treatment (OT), where a small amount of oxygen is added to the feedwater instead of a reducing agent, is now used for most once-through boilers with great success. OT is also being used for drum type boilers. Very high purity feedwater must be used for both types of boiler, and for this reason such units are equipped with condensate polishing plants.

All-volatile treatment can be used for drum type boilers with no further addition of conditioning chemicals, but being volatile, the alkalizing agent is rapidly lost from the boiler water into the steam and very little remains as a buffer against the ingress of impurities. Also, since volatile additives are hardly dissociated at boiler water temperatures, they do not provide much alkaline pH correction under these conditions.

The experience gained with OT demonstrates that the traditional strict limits of low oxygen are not required for AVT, provided that there are no copper containing alloys in the feedwater systems. Indeed, the presence of traces of oxygen in the feedwater reduces the risk of flow-accelerated corrosion in all-ferrous feedwater systems. Mixed-metallurgy feedwater systems are unsuitable for treatment with OT or AVT(O), and feedwater low oxygen concentrations must be maintained together with the use of a reducing agent in order to minimize the dissolution of copper and carryover and deposition in the superheater and HP turbine. Slightly lower feedwater pH values are also used to further reduce the attack on copper alloys.

Condenser leaks are often the main source of impurities and, therefore, their incidence and nature of the cooling water has an important bearing on the plant chemistry and corrosion. Even for apparently similar operating and water chemistry conditions, some plants are far less tolerant than others and are more susceptible to corrosion and failures. Similarly, some plants are more susceptible to carryover of impurities into steam and, thus the actual history of the plant has to be taken into consideration.

Makeup water can also be a source of contamination, as can off-site sources of condensate and contamination during storage. Condensate polishers are valuable in improving the quality of condensate and are essential for once-through boilers. Makeup plant and condensate plant malfunctions can also be sources of contamination.

Solid alkalis, such as trisodium phosphate or sodium hydroxide, can be added to the boiler water of drum type boilers to increase the buffering capacity and tolerance to the ingress of impurities. Such additions can be made under AVT operating conditions, as a temporary measure to protect the boiler during excursions in water purity, for example due to minor condenser leaks. However, great care still needs to be taken to control the buildup of impurities and alkalizing agents to prevent damage to the boiler and excessive carryover into the steam.

Target and Action Levels have been developed for makeup water quality, condensate, feedwater, boiler water and steam for once-through and drum-type boilers. Information on sampling points, frequency of sampling, core and diagnostic parameters, limits and action levels are given in earlier sections of the guidelines. These should be adhered to and used as the basis of chemical control. It is essential that a full QA/QC program is in place for recording, evaluating and storing the data (see Appendix E).

## 6.2 CORRECTIVE ACTIONS

A series of corrective actions have been developed. Although comprehensive, they are not meant to be all-inclusive or universally applicable.

Two approaches are included below, first from key sampling points around the water/steam cycle (as used in earlier versions of the guidelines) and then by looking at different types of problems, the approach which is used in EPRI ChemExpert Cycle Chemistry Advisor for Fossil Plants program.

Possible causes of chemistry excursions for key points in the condensate, feedwater, boiler water and steam circuit are described in Table 6-1. This table can be used to help identify the sources of ingress of impurities. Corrective actions for key points in the condensate system, feedwater system, boiler water (drum type boilers only) and the steam circuit are given in Tables 6-2 to 6-5.

Advice on cycle chemistry problems, diagnosis, actions to be taken and the consequences of not taking the actions have been developed within the EPRI ChemExpert program. Information on the most common problems—makeup system malfunctions, condenser leaks, condensate polisher malfunction, excessive or insufficient reducing agent, corrosion and flow-accelerated corrosion in the feedwater system, boiler carryover (drum type boilers only), the introduction of impurities by attemperation spray, air in-leakage to the hotwell, colloidal silica and iron through the makeup systems, and boiler layup problems—has been abstracted from ChemExpert and is given in Tables 6-6 to 6-12. Further examples of problems, diagnosis, actions to be taken and the consequences of not taking action are contained within the ChemExpert program.

**Table 6-1**
**Possible Causes of Chemistry Excursions**

| Parameter | Insufficient Boiler Blowdown | Condenser Leakage | Condensate Polisher | Makeup Demineralizer | Ammonia Feed System | Reducing Agent Feed System | Air-In-leakage | Deaerator | Feedwater Dissolved Oxygen | Feedwater pH | Polisher Resin Leakage |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. Sodium | X | X | X | X | | | | | | | |
| 2. Chloride | X | X | X | X | | | | | | | |
| 3. Sulfate | X | X | X | X | | | | | | | X |
| 4. Silica | X | X | X | X | | | | | | | |
| 5. pH | X | X | X | X | X | | | | | | |
| 6. Cation/specific conductivity | X | X | X | X | X | | X | | | | X |
| 7. Dissolved oxygen | | | | x | | X | X | X | | | |
| 8. Total organic carbon | X | X | X | X | | | | | | X | X |
| 9. Free hydroxide | X | X | X | X | | | | | | | |
| 10. Ammonia | | | | | X | | | | | | |
| 11. Iron | | | | | | | X | | X | X | |
| 12. Copper | | | | | | X | X | | X | X | |
| 13. ORP | | | | | | X | X | X | X | | |

**Table 6-2**
**Condensate System – Corrective Actions**

| Parameter | Corrective Action |
|---|---|
| **Condenser Leak Detection Trays** | |
| Sodium | Locate and repair:<br>1. Leaking tube or joint.<br>2. Waterbox flange to shell leaks |
| **Condensate Pump Discharge** | |
| Sodium*<br>Cation conductivity* | 1. Identify source of contaminant by checking – makeup treatment system effluent; condenser tube leak. |
| **Condensate Polisher Effluent** | |
| Sodium*<br>Cation conductivity*<br>Silica | 1. Identify source of contaminant by checking - condenser tube leak; makeup treatment system effluent; exhausted polisher resins; fouled resins.<br>2. Regenerate polishers.<br>3. Clean or replace resins. |

* Core parameters

**Table 6-3**
**Feedwater System – Corrective Actions**

| Parameter | Corrective Action |
|---|---|
| | **Deaerator Inlet** |
| Dissolved oxygen<br>Reducing agent<br>ORP | 1. Identify source of dissolved oxygen by checking – condenser for inefficient deaeration in hotwell; condenser and feedwater train for air in-leakage.<br>2. If reducing agent dosing reduced, it may be necessary to increase.<br>3. If increasing reducing agent feed, check for excessive increase of ammonia and pH. |
| | **Deaerator Outlet** |
| Dissolved oxygen | 1. Check deaerator performance.<br>2. Check deaerator vent control.<br>3. Check deaerator inlet oxygen. |
| | **Economizer Inlet** |
| pH | 1. Check ammonia and adjust feed, as necessary.<br>2. Identify source of contaminants by checking – condensate polisher quality; condenser for tube and air leakage. |
| Ammonia | 1. Check pH and adjust chemical feed, as necessary. |
| Specific conductivity<br>Cation conductivity* | 1. Check ammonia in feedwater (specific conductivity)<br>2. Identify source of contaminants by checking – makeup treatment system effluent quality; condensate polisher effluent quality; condenser for tube and air in-leakage. |
| Iron<br>Copper | 1. Identify cause by checking – pH of feedwater; dissolved oxygen in condensate; reducing agent dose; condenser for air in-leakage; FAC, iron and copper pickup. |
| Reducing agent<br>Dissolved oxygen* | 1. Identify source of oxygen, optimize in condensate and feedwater.<br>2. If reducing agent dose reduced, increase to control oxygen.<br>3. If increasing reducing agent feed, check ammonia and pH increase. |

* Core parameters

**Table 6-4**
**Boiler Water - Corrective Actions (Drum Boilers only)**

| Parameter | Corrective Actions |
|---|---|
| **Boiler Water or Blowdown** | |
| Sodium, Chloride<br>Sulfate, Silica<br>Cation conductivity* | 1. Increase blowdown.<br>2. Reduce operating pressure.<br>3. Identify source of contamination by checking - makeup treatment system effluent quality; condensate polisher effluent quality; condenser tube leakage. |
| pH* | 1. Identify source of contamination by checking – makeup treatment system effluent quality; condensate polisher effluent quality; condenser tube leakage.<br>2. Increase blowdown.<br>3. Convert to equilibrium phosphate or caustic treatment.<br>4. Shut down if pH drops below limits. |

* Core parameters

**Table 6-5**
**Steam Circuit - Corrective Actions**

| Parameter | Corrective Actions |
|---|---|
| **Saturated, Superheated and Reheated Steam** | |
| Sodium*, Chloride<br>Sulfate,<br>Total organic carbon (TOC) | 1. Increase blowdown.<br>2. Identify source of contaminants by checking – makeup treatment system effluent quality; condensate polisher effluent quality; condenser tube leakage; attemperation; boiler drum internals. TOC useful for troubleshooting. |
| Cation conductivity* | 1. Increase blowdown.<br>2. Identify contributing parameters by checking; individual anions and total organic carbon in steam. |

* Core parameter

**Table 6-6a**
**Makeup System Malfunction**

| Diagnosis | Actions to be Taken | Consequences* |
|---|---|---|
| 1. Check specific conductivity* and silica of the makeup treatment system effluent.<br>2. Check condensate pump discharge sodium* and cation conductivity*; if the increase coincides with the makeup addition, it confirms problem.<br>3. Check condensate storage tank conductivity, sodium and sulfate.<br>4. If no condensate polishers: check relationship pH - $NH_3$ - conductivity in feedwater.<br>5. Check sodium, cation conductivity* and pH* in boiler water.<br>6. Check chemical feed for impurities. | 1. For Action Levels 1 and 2, use regenerated makeup train, drain condensate storage tank, as needed.<br>2. Reduce load immediately, do not increase boiler blowdown until ingress of impurity is stopped.<br>3. If Action Level 3 of any parameter occurs: orderly shutdown, drain condensate storage tank, deaerator tank and boiler, as needed.<br>4. Check contamination of the superheater, reheater and turbine. Chemically clean and water wash, as needed.<br>5. Find root cause and correct the situation. | 1. Increased boiler corrosion.<br>2. Buildup of silica and other deposits in the turbine and possibly other cycle components. |

* Consequences if not corrected
* Core parameter

**Table 6-6b**
**Makeup Regenerant - NaOH, $H_2SO_4$ or HCl Leaking Into the Cycle**

| Diagnosis | Actions to be Taken | Consequences˙ |
|---|---|---|
| **Sodium Hydroxide Leaking Into the Cycle** | | |
| 1. Check specific conductivity* & pH of makeup plant effluent.<br>2. Check condensate pump discharge sodium* and cation conductivity*. If the increase coincides with the makeup addition to the condenser, it is a contamination problem.<br>3. Check condensate storage tank conductivity, sodium and sulfate or chloride.<br>4. Units without condensate polishers: check the relationship of feedwater conductivity – pH – $NH_3$.<br>5. Check sodium, cation conductivity* and pH* in boiler water blowdown. | 1. Action Level 3: reduce load immediately, do not increase blowdown; switch to regenerated makeup train and drain condensate storage tank, as needed.<br>2. Action 2 level: reduce load immediately.<br>3. For orderly shutdown, drain condensate storage tank, deaerator storage tank and boiler, as needed.<br>4. Check contamination of the superheater, reheater and turbine. Chemically clean and water wash, as needed.<br>5. Find root cause and correct the situation. | 1. Possible stress corrosion cracking in the turbine and austenitic stainless steel sections of the superheater and reheater.<br>2. Possible caustic gouging in the boiler generating tubes.<br>3. Possible stress corrosion of cracking of stainless steel feedwater heater tubes. |
| **Sulfuric or Hydrochloric Acid Leaking into the Cycle** | | |
| As 1, 2, 3, 4 and 5 above. 6 Check status of regeneration of ion exchange system in makeup plant. | As 2, 3, 4 and 5 above. | 1. Cycle corrosion and contamination.<br>2. General corrosion and FAC of carbon steel in the preboiler cycle.<br>3. Hydrogen damage of boiler tubes.<br>4. Pitting of boiler steam generating tubes, superheater and reheater lower bends.<br>5. Pitting and corrosion fatigue in turbine. |

˙Consequences if not corrected
* Core parameter

**Table 6-7**
**Condenser Tube Leak**

| Diagnosis | Actions to be Taken | Consequences' |
|---|---|---|
| 1. Compare sodium* and cation conductivity* of condensate pump discharge and hotwell. All increased is confirmation.<br>2. Polisher effluent conductivity drifting up is confirmation.<br>3. Blowdown Na, cation conductivity drifting up, pH drifts down (up in some cases) = confirmation. Check chemical feeds for impurities. | 1. Boiler water at Action Level 3 - immediate shutdown, drain & flush boiler, check deaerator storage tank, and condenser hotwell water, drain and flush.<br>2. Parameters within Action Level 2 – immediately reduce load, isolate one condenser water box, find leaks and plug. Feed emergency $Na_3PO_4$ or NaOH to control boiler pH.<br>3. Maintain lower load and keep condensate polisher effluent within limits.<br>4. Increase boiler blowdown. | 1. Increased corrosion of the preboiler cycle.<br>2. Scale formation and hydrogen damage of the boiler generating tubes.<br>3. Stress corrosion cracking of austenitic stainless steel superheater, reheater and turbine components.<br>4. Turbine deposits, pitting and corrosion cracking, if problem persists. |

' Consequences if not Corrected
* Core parameter

**Table 6-8a**
**Condensate Polisher Malfunction/Exhausted**

| Diagnosis | Actions to be Taken | Consequences' |
|---|---|---|
| 1. Compare condensate pump discharge conductivity*, sodium*, condensate polisher effluent cation conductivity* and silica to these parameters in the effluent.<br>2. Compare the in and out ratio for iron.<br>3. Analyze effluent samples from individual polishers for resin fines.<br>4. Check chemical feeds for impurities | 1. Take malfunctioning polishers out of service and regenerate.<br>2. Determine whether problem is ammonia back washing of acid regenerant, resin leakage or polisher exhaustion.<br>3. Take resin sample and restore or replace the resin, as required.<br>4. Check the regeneration procedure and correct, as required.<br>5. Check condensate polisher strainers and fix. Check condensate polisher strainers, elements and precoat pump check valve and fix.<br>6. Powdered systems check for element and precoat pump leak and fix. | 1. Caustic or acid corrosion of boiler steam generating tubes and turbine.<br>2. Pitting in reheater due to acid sulfate deposition.<br>3. Silica and other deposits in the turbine. |

' Consequences if not corrected
* Core parameter

**Table 6-8b**
**Condensate Polisher – Caustic or Acid Regenerant Leakage**

| Diagnosis | Actions to be Taken | Consequences' |
|---|---|---|
| | **Leakage of Caustic Regenerant** | |
| 1. Compare feedwater sodium to condensate and makeup.<br>2. Check sodium* in the combined and individual polisher effluents & in steam.<br>3. Increasing trend in boiler & feedwater pH shows problem.<br>4. Check feedwater pH - $NH_3$-conductivity relationship; high pH indicates problem.<br>5. Check chemical feeds for impurities. | 1. Reduce load and boiler pressure.<br>2. Check boiler carryover and steam sodium: if high, wash the turbine within two days.<br>3. Fix the polisher regeneration system. | 1. Caustic cracking of austenitic stainless steels in heaters, superheater, reheater and turbine.<br>2. Caustic gouging in the boiler in the high heat flux zones |
| | **Leakage of Sulfuric or Hydrochloric Acid Regenerant** | |
| 1. Compare feedwater, condensate, makeup and steam cation conductivities.*<br>2. Analyze feedwater, blowdown, condensate and polisher effluent samples for sulfate or chloride.<br>3. Analyze the conductivity – pH – $NH_3$ relationships.<br>4. Monitor $SO_4$ or Cl in steam and monitor pH* in boiler.<br>5. Check chemical feeds for impurities. | 1. Reduce boiler pressure and unit load.<br>2. If boiler water sulfate, chloride or cation conductivity reached Action Level 2, go to orderly shutdown, drain the boiler, fill with ammoniated deaerated water with reducing agent, analyze after 3 hours, repeat if necessary.<br>3. If the cation conductivity and sulfate or chloride in the boiler water was only Action Level 1, feed emergency trisodium phosphate.<br>4. Take boiler tube samples, clean boiler as needed. | 1. Increased corrosion and FAC of the preboiler cycle and economizer.<br>2. Pitting and hydrogen damage in boiler generating tubes.<br>3. Pitting, corrosion fatigue and stress corrosion cracking in the turbine.<br>4. Generation of large quantities of corrosion products and their deposition, dirty boiler. |

' Consequences if not corrected
* Core parameter

**Table 6-9**
**Excessive or Insufficient Concentration of Reducing Agent**

| Diagnosis | Actions to be Taken | Consequences* |
|---|---|---|
| **Excess Reducing Agent leading to High Iron in Feedwater** | | |
| 1. Check historical data for feedwater iron and copper concentration vs reducing agent.<br>2. Analyze grab samples for iron and copper in feedwater. | 1. Optimize the concentration of reducing agent in relation to iron and copper concentration in final feedwater. 2. Minimize air in-leakage.<br>3. Use condensate polishers as much as possible. | 1. Increased rate of corrosion and FAC in the preboiler cycle and economizer.<br>2. Scale buildup in boiler steam generating tubes.<br>3. Scale buildup on boiler orifices (assisted circulation boilers) and on feedwater control valves.<br>4. Reduced output.<br>5. If orifice plugging: danger of long or even short-term overheat and high pumping costs for circulating pumps |
| **Insufficient Reducing Agent leading to High Copper in Feedwater** | | |
| 1. Check reducing agent and oxygen concentrations around the cycle.<br>2. Check the reducing agent addition system (day tank, pump, etc). | 1. Increase reducing agent addition rate to achieve the optimum concentration in feedwater as determined by ORP being reducing (-300 to 350mV).<br>2. If air in-leakage rate is higher than recommended, reduce to the normal level. Confirm by ensuring oxygen at CPD is < 10 ppb | 1. Increased rate of corrosion of the copper alloys in the feedwater<br>2. Deposit buildup on the boiler waterwall tubes<br>3. Buildup on boiler orifices<br>4. Possible deposition on HP turbine and reduced output |

* Consequences if not corrected

**Table 6-10**
**Corrosion and/or Flow-Accelerated Corrosion in the Feedwater**

| Diagnosis | Actions to be Taken | Consequences* |
|---|---|---|
| | **Carbon Steel** | |
| 1. Analyze iron in feedwater during normal operation and startups: high during cold startups indicates layup corrosion.<br>2. Inspect shell condenser, shell and tube sides of feedwater heaters (particularly tube inlets), FAC audit of feedwater & wet steam systems<br>3. Check the concentrations of oxygen, reducing agent and pH, and their latest changes in condensate and final feedwater. Increased concentration of reducing agent and reduced pH can be the cause of the problem. | 1. Optimize reducing agent concentration, oxygen and pH.<br>2. Operate condensate polishers as much as possible.<br>3. Check the condensate polishers resins for iron fouling and clean the fouling, if needed.<br>4. Assure preboiler system cleanliness and proper preoperational cleaning of feedwater during cold starts.<br>5. Fill the deaerator storage tank and boiler with deaerated water, install condensate storage tank nitrogen sparging and blanketing or other deaeration, if needed | 1. Scale formation in the boiler generating tubes.<br>2. Increased boiler carryover due to suspended solids, possibly leading to deposit buildup in the turbine.<br>3. Reduced life and possible safety issue of corroding components.<br>4. Possibility of perforation and rupture of piping or feedwater tubing<br>5. Plant safety issue |
| | **Copper Alloys** | |
| As 1 above for Cu, Ni and Zn.<br>2. Inspect copper alloy tubing used in condensers and feedwater heaters.<br>3. Check with maintenance for use of copper-bearing thread lubricants.<br>4. Verify the concentration of reducing agent, oxygen, ammonia and pH in condensate and final feedwater. 5. Check air in-leakage and its recent trends. | As 1 above.<br>2. Minimize air in-leakage by eliminating sources. 3. Optimize layup procedures for copper bearing components, e.g. condenser & feedwater heaters.<br>4. Find root cause of copper alloy corrosion and plan actions.<br>5. Replace copper alloys in high pressure feed heaters asap.<br>6. Operate with reduced boiler pressure when Cu concentration in boiler water is above 50 ppb. (See Appendix Section F.3) | As 1 above, plus superheater.<br>As 2 above.<br>3. Copper deposits in the HP turbine and reduced MW generating capacity and efficiency.<br>4. Acceleration of boiler tube corrosion due to nickel deposits. |

* Consequences if not corrected

**Table 6-11**
**High Boiler Carryover (Drum Boilers only)**

| Diagnosis | Actions to be Taken | Consequences* |
|---|---|---|
| 1. Check with operators about drum level, boiler pressure, megawatts and changes of boiler pressure and load.<br>2. Analyze samples of feedwater and boiler water for alkalinity, total organic carbon and suspended solids<br>3. Check the makeup system and polisher sodium.<br>4. Compare current carryover with the commissioning measurements at same load.<br>5. If the problem persists, inspect the turbine.<br>6. Check % carryover (mechanical) and compare with baseline. | 1. Reduce load and boiler pressure.<br>2. Eliminate sources of high hydroxide alkalinity, suspended solids and organics, as needed.<br>3. Verify correct operation of condensate polishers and the regeneration.<br>4. Inspect superheater and reheater for deposits.<br>5. Wash turbine as need (without disassembly at reduced speed).<br>6. Inspect boiler drum internals and level control.<br>7. May need to repeat carryover tests. | 1. Deposition and corrosion in the turbine.<br>2. Possibility of scale formation in the superheater and reheater and short or longterm failures.<br>3. Sticking turbine valves. |

* Consequences if not corrected

**Table 6-12**
**Impurity Introduction into Turbine by Attemperating Sprays**

| Diagnosis | Actions to be Taken | Consequences* |
|---|---|---|
| 1 Analyze steam before and after attemperation.<br>2 Discuss with Operations the use of attemperating sprays.<br>3 Check feedwater sodium, cation conductivity and copper, and the latest trends. | 1 Stop ingress of impurities into feedwater (condensate polishers, condenser leaks, makeup).<br>2 Minimize the use of attemperation, if the problem persists<br>3 Measure metal temperatures | 1 Deposit buildup and corrosion in the turbine.<br>2 Deposition of salts in the superheater and reheater leading to tube failures from pitting during shutdown.<br>3 High copper in feedwater could lead to deposits in superheater and HP turbine. |

* Consequences if not corrected

**Table 6-13**
**Air In-leakage to Hotwell**

| Diagnosis | Actions to be Taken | Consequences* |
|---|---|---|
| | **Air In-leakage above the Hotwell Line** | |
| 1. Check air eject of vacuum exhaust air flow and its history.<br>2. Check condensate pump discharge oxygen and cation conductivity and their trends for different recent loads.<br>3. Where air in-leakage is high and oxygen is low, it is an indication of air in-leakage above the water line. | 1. Using helium leak detector, find locations of air in-leakage and fix.<br>2. Activate additional air ejectors or vacuum pumps, as needed, to keep condensate oxygen & cation conductivity within normal values.<br>3. Typical air in-leakage locations are LP turbine glands, condenser/ LP turbine base joint, LP turbine rupture disks, and the two lowest pressure feedwater heater safety valves and sight glasses. | 1. Fast exhaustion and release of impurities from condensate polishers, if in operation.<br>2. FAC and increased corrosion of copper based alloys in feedwater.<br>3. Increased iron and copper scale buildup in the boiler steam generating tubes.<br>4. FAC in the economizer and LP turbine.<br>5. Increased propensity for oxygen pitting of carbon steel components during shutdown. |
| | **Air In-leakage below the Hotwell Line** | |
| As 1. and 2. as above.<br>3. Where air in-leakage is high and oxygen is high, it is an indication of air in-leakage below the water line.<br>4. Condensate pump discharge oxygen and cation conductivity increased or drifting up is confirmation. | As 1 and 2 above.<br>3. Frequent air in-leakage locations are suction of condensate pump, various hotwell connections, improperly designed makeup addition, pits and holes at the bottom of the condenser hotwell. | As 1, 2, 3, 4 and 5 above. |

* Consequences if not corrected

**Table 6-14**
**Colloidal Silica and Iron through the Makeup System**

| Diagnosis | Actions to be Taken | Consequences* |
|---|---|---|
| | **Colloidal Silica** | |
| 1. Compare silica (iron) in makeup effluent, condensate storage tank, condensate polisher in and out, blowdown & saturated or hot reheat steam. Feedwater silica (iron) higher than polisher effluent or condensate pump discharge indicates colloidal silica (iron).<br>2. Analyze grab samples for total organic carbon at the makeup system effluent and condensate storage tank. High TOC may be due to presence of organic colloids containing silica (iron).<br>3. Filter makeup system and condensate storage tank samples through 0.5 micron Millipore and analyze filtrates.<br>4. Audit the pre-treatment and makeup treatment system and measure variation of the source water iron, silica and organics. | 1. Correct the situation leading to the pickup of colloids at the influent to makeup system (raw water).<br>2. Check and correct the pre-treatment system.<br>3. Modify the makeup system.<br>4. Operate with increased blowdown as needed. | 1. Scale buildup in the boiler and turbine, lower turbine output and efficiency |
| | **Colloidal Iron** | |
| As 1, 2, 3 and 4 as above. | As 1, 2, 3 and 4 as above. | 1. Increased rate of scale buildup in the boiler.<br>2. Condensate polisher resin fouling.<br>3. Foaming, increased boiler carryover and turbine deposits. |

* Consequences if not corrected

**Table 6-15**
**Boiler Layup Problems**

| Diagnosis | Actions to be Taken | Consequences* |
|---|---|---|
| | **Lost Nitrogen Blanket** | |
| 1. Check nitrogen pressure and supply system. | 1. Restore nitrogen supply.<br>2. Fix nitrogen leaks as needed. | 1. Boiler corrosion.<br>2. Corrosion-generated iron and copper oxides will precipitate and redeposit in the boiler. Some will be carried into the superheater and turbine during startup.<br>3. Possible effects on turbine MW generating capacity and efficiency.<br>4. Iron and copper fouling of condensate polishers. |
| | **Low Boiler Water pH** | |
| 1. Take duplicate sample of boiler water, measure pH and conductivity. | 1. Restore pH by injecting ammonia and circulating boiler water.<br>2. If there is a high concentration of suspended oxides in the boiler water, drain and refill the boiler. | 1. Dissolution and subsequent redeposition of iron and copper oxides in the boiler.<br>2. Carryover of oxides into the superheater and turbine during startup.<br>As 3. and 4. above. |
| | **High Boiler Water Oxygen** | |
| 1. Check nitrogen pressure and supply system | 1. Restore nitrogen supply.<br>2. Fix nitrogen leaks as needed. | As 1, 2, 3 and 4 above (for lost nitrogen blanket). |

* Consequences if not corrected

## 6.3 INFLUENCE OF TREATMENT CHEMICAL PURITY ON CYCLE CHEMISTRY

It should be clearly understood that the EPRI AVT Chemistry Guidelines and the tables on chemistry excursion troubleshooting and corrective actions assume that the treatment chemicals applied to the cycle are not a significant source of impurities that would influence parameters such as cation conductivity, sodium, chloride, sulfate, silica and total organic carbon. However, this is not always the case.

Fortunately, the frequency of cycle chemistry excursions traceable to variations in chemical purity is low. Only very rarely do chemical purity deviations result in significant and apparent excursions from normal chemistry in the steam-water cycle. In most cases, only very minor changes in cation conductivity and perhaps pH will be observed. Such changes are often and usually correctly associated with variations in other unit-specific conditions such as condenser air in-leakage rates, makeup water consumption rates, makeup water organics content, or contamination attributed to minute (and sometimes intermittent) condenser leaks. Therefore, additional cases may exist where treatment chemical purity contributes to the cycle chemistry problem but is not even considered as a possible cause of the out of specification readings.

Whenever an investigation of a water chemistry excursion using the tables presented earlier in this section (or, preferably, versions of these generic response guidelines customized to individual units in the fleet) fails to conclusively identify the responsible root cause of the excursion, the purity of the treatment chemicals should be evaluated. This may be accomplished in a number of ways. Theses include:

- Collection of a sample of each treatment chemical in use for laboratory analysis-this approach is obviously effective but may require an unacceptable amount of time, depending on the analytical capabilities of the organization.
- Analysis of condensate (or feedwater) samples collected on each side of the chemical injection point(s)-this approach is not likely to be beneficial except in cases of fairly significant excursions that have no other apparent cause.
- Isolation of the suspect chemical feed system(s) for a brief period and observing the impact on cycle chemistry-this approach is most effective when the unit has satisfactory levels of reliable on-line instrumentation, however, other chemistry parameters such as pH and ORP will also be effected by this action.
- Isolation of the suspect chemical feed system(s) and simultaneous startup of backup feed system(s) with treatment chemicals of satisfactory purity-this is clearly a preferred practice in units that provide redundant feed systems.

In cases where sampling of the treatment chemical for analysis is desired, consideration should also be given to dilution water purity. This means that in units where the treatment chemicals are diluted on-site prior to injection to the cycle, samples of diluted and undiluted chemical solution should be collected. The last approach indicated can most easily be followed if a new supply of the chemical is applied to the unit before all of the existing supply has been consumed.

As stated previously, cycle chemistry deviations caused by impurities in the treatment chemicals are generally infrequent events of very minor magnitude. Therefore, the possibility exists that extended and undetected unit operation with low levels of impurities present in the treatment chemicals applied could ultimately result in or contribute to chemistry related damage in the boiler and turbine. Traditionally, organizations have avoided such concerns through development of chemical purchase specifications and through testing of chemicals received from suppliers to verify compliance with specifications. However, in today's competitive business climate, this approach is all too commonly minimized or eliminated. In those organizations that purchase treatment chemicals on the open market and emphasize price rather than purity, the importance of operating a unit with a new chemical supply and evaluating the chemistry prior to consuming all of the previous supply should be readily apparent.

Ultimate responsibility for development of optimum treatment chemical specifications applicable to individual fossil plants must remain with the organization. One reason for this is that there are differences in chemical manufacturing, processing, dilution, packaging and labeling practices around the world and there is no single chemical purity specification that can adequately encompass the variety of product strengths and grades that may be available at any given location. Also, the organization's chemical purity specification usually becomes part of a legal agreement between the organization and the chemical supplier. Again, there are clearly no general product specifications that will be universally applicable to all conceivable business arrangements for provision of the needed chemical treatments.

In developing individual treatment product specifications, the ultimate goal is to ensure that normal usage of the treatment chemical will not result in deviations from any of the plant specific chemistry limits for normal operating conditions as well as chemistry limits for any other operating conditions, such as wet layup, for which the chemical is to be used. This goal is, in general, readily attainable providing that only fully deionized water is used to dilute the active chemical. However, it is most reliably attained when ammonia is used for feedwater pH control and hydrazine (when not prohibited and for reducing AVT in cycles with copper) is used as the reducing agent. Use of neutralizing amines for pH control and of alternative reducing agents, whether due to site prohibitions on hydrazine usage or for other reasons, makes it more difficult to attain guideline chemistry values, particularly cation conductivity, by virtue of the fact that these treatment chemicals are subject to thermal degradation, resulting in formation of carbon dioxide and/or organic acids. Special care must therefore be taken when establishing customized chemistry limits and action levels for fossil units that are treated with these chemicals. Also, it should be recognized that the effects these treatments have on the cycle chemistry tend to make it more difficult to identify the responsible cause of minor deviations from normal chemistry.

# A

# OXYGEN REMOVAL TECHNIQUES FOR TREATED MAKEUP

Previous Sections have described the importance of maintaining strict control to prevent dissolved oxygen and carbon dioxide from entering the heat cycle in order to minimize iron and copper corrosion and transport. It was noted in Section 4 that 40% of utilities surveyed by EPRI put aerated water directly into the cycle, while 66% put makeup into storage tanks which are vented to atmosphere.(1) It is obvious that these types of operating procedures are counter-productive if corrosion is to be fully controlled.

This appendix describes methods by which makeup water can be deoxygenated (and some of these methods also remove carbon dioxide) and stored in such a way as to prevent further aeration.

Another important source of ingress of oxygen and carbon dioxide is air in-leakage via negative pressure in the condenser and low end of the heat cycle. This subject is addressed in Appendix C.

## A.1 VACUUM DEAERATION

Vacuum deaeration is a process, which removes both oxygen and carbon dioxide. A typical vacuum degasifier, which accomplishes this task, is shown in Figure A-1. This equipment consists of a packed tower with a vacuum pulled from beneath the packing and with water sprayed over the top of the packing. The water trickles down through the packing, which provides a large surface area for removal of oxygen and carbon dioxide. The vacuum induces vaporization of water and produces an upward flow of water vapor together with oxygen and carbon dioxide. The water is collected in the bottom of the tower and is pumped from there to the next stage of the system.

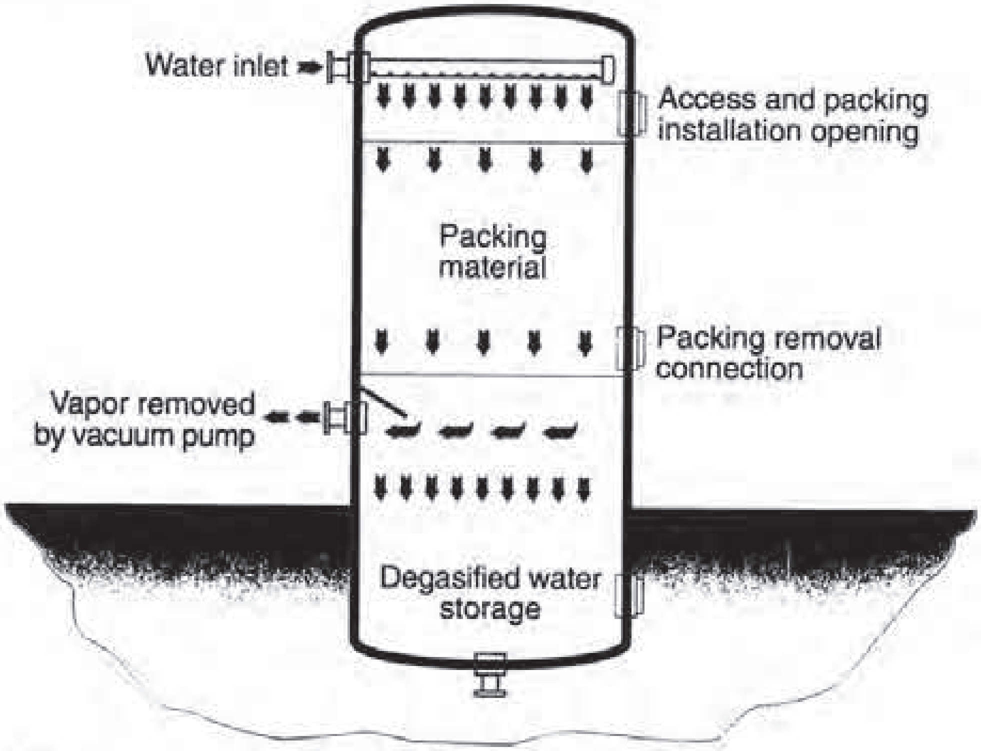


**Figure A-1**
**Vacuum Degasifier**

The process of vacuum degasification is based on Henry's Law, which states that the concentration of an ideal gas in solution is proportional to its vapor pressure (or partial pressure). Therefore, if the pressure over a solution is reduced by a vacuum, dissolved gases must leave the water and enter the vapor phase to establish a new equilibrium. Increasing the vacuum increases the degree of gas removal.

The vacuum supply to the degasifier can either be steam jet ejectors or vacuum pumps. The degasifier is typically located preceding the first anion unit of a demineralizer train in order to minimize the ionic loading to the anion unit by removing carbon dioxide. Forced draft decarbonators effectively remove carbon dioxide but saturate the water with oxygen.

Typical removal levels for a vacuum degasifier are: carbon dioxide to 5 ppb and oxygen to 10-20 ppb. Increasing the packing height in the tower and increasing vacuum will result in higher gas removal.

The vacuum degasifier is quite tall, typically in the range of 25-40 feet (7.6–12.2 m). One reason for this is to provide room for the packing material and the other is to provide sufficient suction head for the transfer pump. Because of its height, vacuum degasifiers may be difficult to backfit into an existing power plant arrangement. This equipment requires considerable maintenance in order to maintain constant vacuum conditions. In addition, the vacuum equipment is relatively energy intensive to operate.

For a typical 300 gpm vacuum degasifier unit, the following costs are estimated(2) in year 2000 dollars:

Capital Cost: $125,000

Installation Cost: $65,000 to $200,000 depending on location and complexity of installation.

Operating and Maintenance (O&M) Cost: 3 to 5% of capital cost per year for normal operations.

## A.2 CATALYTIC OXYGEN REMOVAL

The use of hydrazine or other reducing agents to remove oxygen is commonly practiced at many power plants and is usually fed at the condensate pump discharge or the outlet of the condensate polisher (if one is installed). The reaction between hydrazine and oxygen can be expressed as follows:

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$

The reaction is stoichiometric, requiring equal amounts of hydrazine and oxygen for the reaction to proceed to completion. At ambient temperatures this reaction proceeds very slowly. However, in the presence of a catalyst, such as activated carbon, the reaction proceeds rapidly. Therefore, this technology can and is being used to remove oxygen from makeup water. The equipment consists of a vessel containing activated carbon to which hydrazine is fed using a positive displacement chemical pump. The process is patented (3) and is said to achieve makeup oxygen concentrations less than 10 ppb.

Overall costs for the catalytic process are about $1.15 to $1.60 per 1000 gallons depending on system flow rates.

Another patented process (4) similar to the above makes use of strong base anion resins in the hydroxide form as a catalyst to remove oxygen from makeup water. Either hydrazine or carbohydrazide provides the active ingredient for reaction with oxygen.

These catalytic processes can treat the water either going to storage or coming from storage. However, when large quantities of water are required, such as during startups, it may be impractical to provide equipment of sufficient size to meet such demands when processing water from storage.

One disadvantage of these catalytic processes is that carbon dioxide is not removed. Therefore, when used in demineralizer systems treating waters high in bicarbonate alkalinity, operating costs can be expected to be substantially higher than when using a vacuum degasifier, for example. However, when the catalytic systems are used in conjunction with a membrane system, both carbon dioxide and oxygen can be simultaneously removed (see discussion which follows under membrane systems).

Another disadvantage associated with the carbon bed system is that an ion exchange bed is required to remove excess hydrazine and carbon leachables from the effluent stream (3) .

## A.3 MEMBRANE SYSTEMS

Membrane systems are presently utilized today for many applications, including reverse osmosis, ultrafiltration, microfiltration, and electrodeionization. Another membrane process, which is achieving popularity in water treatment applications, is the use of microporous, hydrophobic membranes for the transfer of gases to and from aqueous streams.

Gas transfer membranes (GTM's) for the removal of oxygen and carbon dioxide from makeup water are constructed of an array or bundle of hollow fiber hydrophobic polypropylene membranes which are gas permeable and water impermeable. The hollow fiber configuration, with the gas phase inside the fiber and the liquid phase outside, provides high surface area for maximum efficiency for gas removal processes. One such design encloses the hollow fiber array within a pressure vessel, which includes an internal baffle to promote turbulent flow and mass transfer. An example of this equipment is shown in Figure A-2.

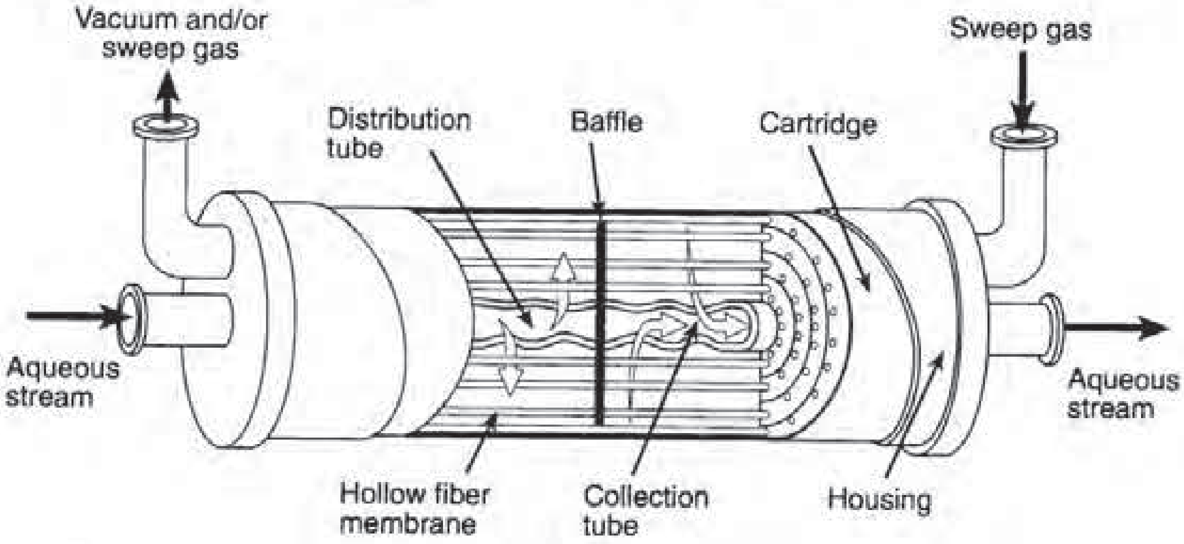


**Figure A-2**
**Components of a GTM Unit**

By altering the partial pressure of a gas at the air/water interface, a driving force is created which results in the mass transfer of a gas into or out of solution. There are three ways to alter the partial pressure of a gas in a GTM system:

- Apply a vacuum to the inside of the hollow fiber
- Use a "sweep" gas, usually nitrogen, which effectively lowers the partial pressure of other gases such as oxygen and carbon dioxide
- Use both a vacuum and a "sweep" gas

The effectiveness of this membrane technology is governed by several factors:

- Water flow through the system
- Water temperature

- Amount of vacuum applied
- Volume and purity of the sweep gas

With a suitably designed system, oxygen levels of less than 1 ppb in the effluent water stream are said to be achievable. An example of a GTM system used to remove oxygen from boiler feed water at a petroleum refinery[5] is shown in Figure A-3. In this case, two parallel trains of GTM units are provided, each having 3-10 inch (7.6–25.4 cm) membrane contactors connected in series. The nitrogen sweep gas is 99.9% pure, and flows at a rate of 1.5-2.0 scfm. Vacuum requirements are ~ 25 acfm at –28 inches of mercury. The 200 gpm (760 litres/min) of product water contains less than 15 ppb of dissolved oxygen.

An example of a hybrid system which combines both GTM's for carbon dioxide and a catalytic oxygen removal system[6] is shown in Figure A-4. This is an outsourced plant in use at a nuclear facility.

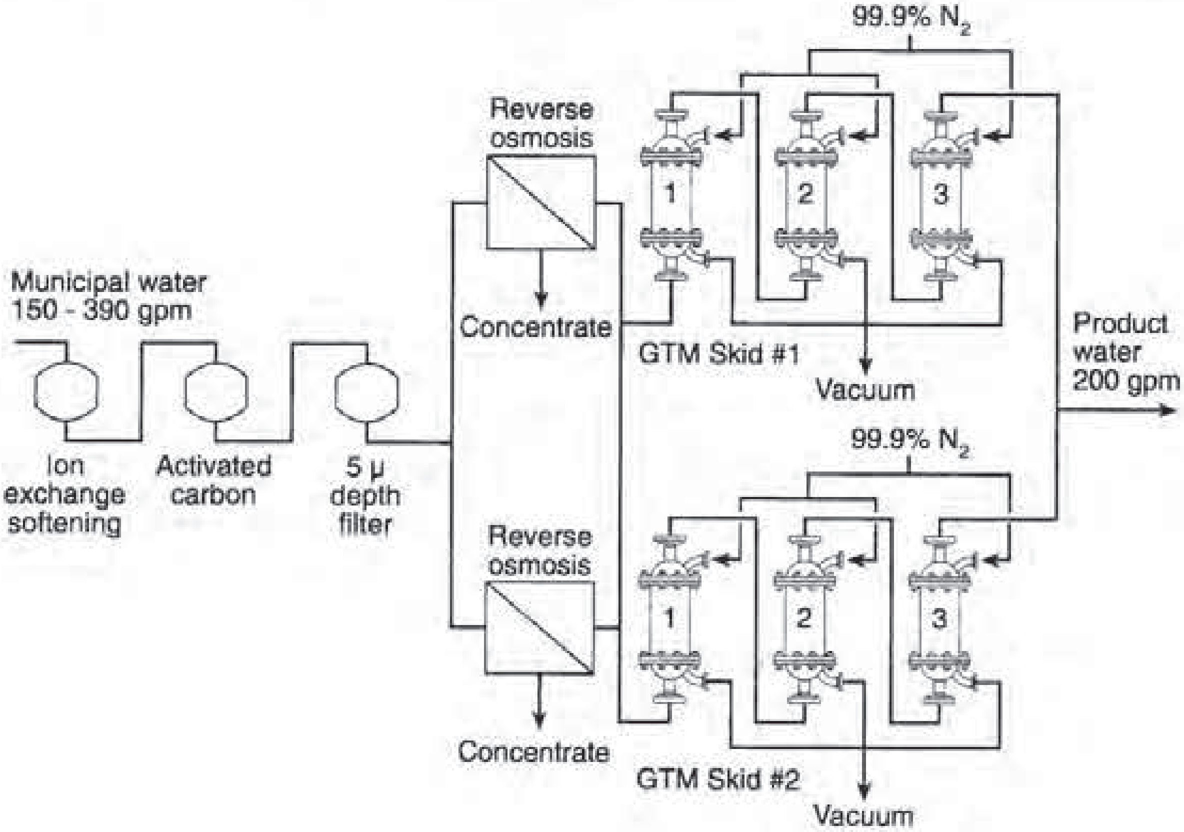


**Figure A-3**
**GTM System Process Flow Diagram (Note: 1 gal = 3.785 litres)**

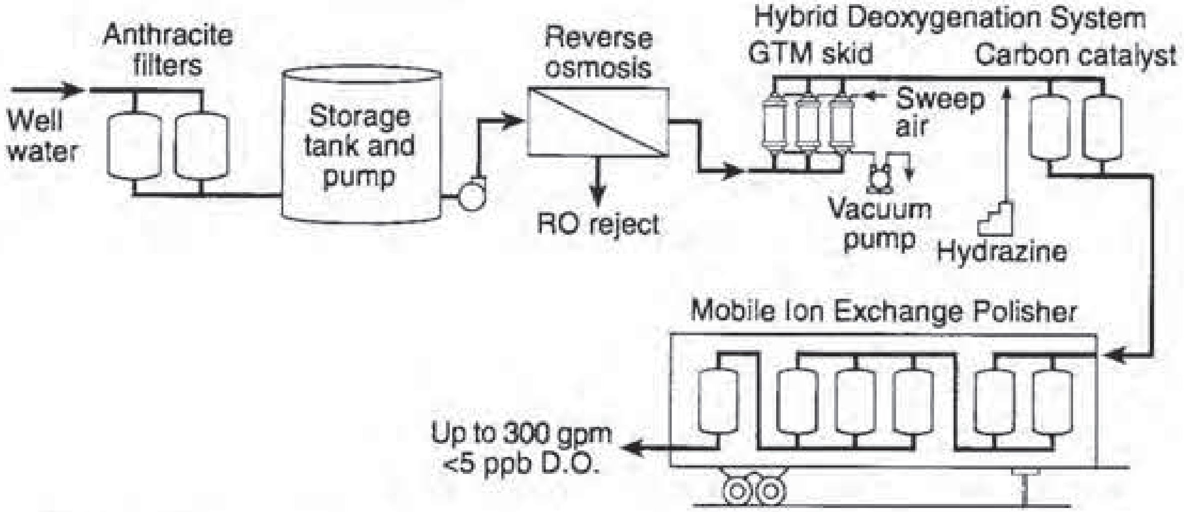


**Figure A-4**
**GTM System Process Flow Diagram (Note: 1 gal = 3.785 litres)**

This GTM system consists of three skid-mounted contactors in parallel, a vacuum pump, valving to allow an air sweep, and instrumentation to monitor vacuum level and air sweep volume. The membrane system is primarily for carbon dioxide removal, but also removes some oxygen. (The use of an air sweep rather than nitrogen probably limits the extent to which oxygen can be removed in this part of the system).

Hydrazine injection occurs at the GTM effluent using a small, diaphragm positive displacement pump. Any remaining oxygen in the RO permeate water reacts with the hydrazine as it passes through two activated carbon vessels connected in parallel. The water then enters a three-bed ion exchange system for further polishing. This system consists of a strong acid cation, strong base anion and a mixed bed unit.

This hybrid system produces up to 300 gpm of purified water at less than 5 ppb of dissolved oxygen. It is significant to note that the deoxygenated water is stored in a tank with a nitrogen blanket. The tank effluent is tested daily for dissolved oxygen, which consistently measures below 5 ppb.

Overall costs for the GTM process are about $0.60 to $1.15 per 1000 gallons (3785 litres) depending on the degree of oxygen removal required and the systems flow rate.

## A.4 MAKEUP WATER STORAGE

The results of oxygen removal by any of the above are completely negated if the makeup water is stored in tanks, which are vented to atmosphere. There are several ways that tanks can be equipped to prevent air ingress:

- Plastic or rubber diaphragms
- Floating covers

- Nitrogen positive pressure purging

The use of plastic or rubber diaphragms to protect condensate storage tanks from oxygen ingress has been very limited in the electrical generating industry. This is the result of relatively high installed costs, high maintenance costs and the fear (perhaps justly so) that the diaphragm might fail causing a major disruption in power plant operations. Also, diaphragms would be difficult, and possibly impossible to install in existing tanks.

Floating covers have been in use, especially in petroleum refinery tanks, for many years. Their purpose in this case is to prevent undue evaporation of volatile liquids. Here again, installation of floating covers has not been popular at electrical generating plants for some of the same reasons as given above for diaphragms. Backfit of floating covers on existing condensate tanks, while perhaps possible, would certainly require considerable engineering and would undoubtedly be quite expensive.

Probably the most feasible means to prevent oxygen ingress to condensate storage tanks is to provide a nitrogen blanketing system. Such a system is relatively easy to install on existing tanks and inexpensive to operate, given the low cost of nitrogen and the modest amount of nitrogen required to operate the system.

One such system(7) is shown in Figure A-5. This system has a nitrogen bottom sparger (A), inlet pipe sparger (B), nitrogen supply and controls (D), oxygen or conductivity analyzer (F), tank pressure control (C), and an overflow pipe (E). The sparging itself is through sintered stainless steel sparging elements. Two pressure regulators control the nitrogen pressure to the spargers; one for the bottom sparger and one for the inlet pipe sparger. This is followed by a passive critical orifice flow element. This element prevents the nitrogen flow from exceeding the capacity of the tank pressure control siphon, which vents the excess pressure.

By having a sparger in the inlet water supply to the tank, any residual dissolved oxygen in that water should be effectively removed. The sparger in the bottom of the tank will prevent the ingress of air.

The following costs are estimated to be associated with the system shown in Figure A-5(7) in year 2000 dollars:

Capital Cost: $20,000 to $30,000

Installation Cost: $5,000 to $10,000

Nitrogen Consumption Costs: $100 per month assuming storage tank inflows and outflows are not excessive.

The system in Figure A-5 would most probably use cylinder nitrogen, because of the relatively low consumption. The purity of cylinder (or cryogenic) nitrogen is 99.995%.

Other, simpler nitrogen blanketing systems merely provide a slight positive pressure in the storage tank by using a small continuous flow of nitrogen applied at the top of the tank. This design, as compared to the above, probably requires a larger consumption of nitrogen and lacks the obvious advantage of the purge system for incoming water to the tank.

While removal of oxygen from makeup may appear costly at first glance, it is essential to the proper control of iron and especially copper in the feedwater cycle. In the overall picture, the use of deaerated makeup water will produce savings, since iron and copper corrosion and transport will be reduced.

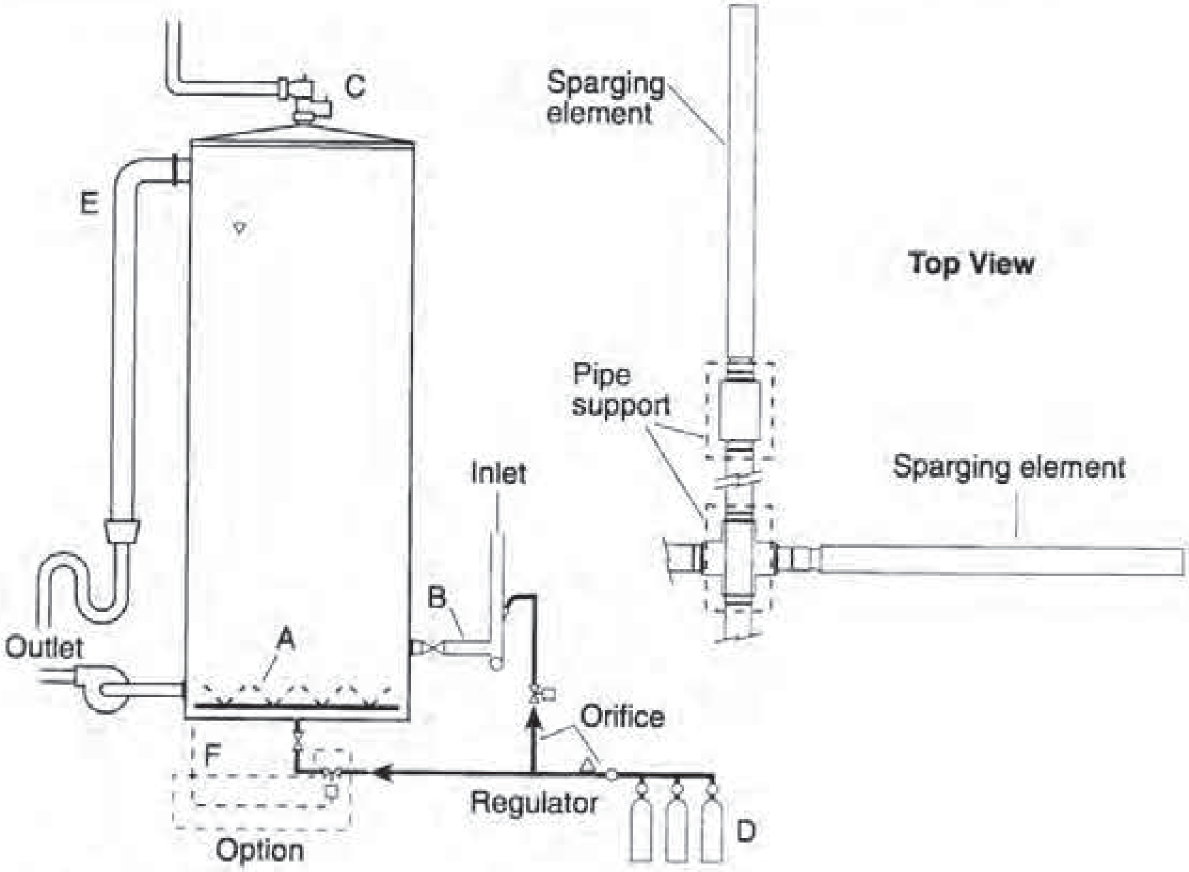


**Figure A-5**
**A Storage Tank Nitrogen System and Sparging Elements**(7)

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# B
# OXIDATION-REDUCTION POTENTIAL (ORP)

## B.1 INTRODUCTION

Research investigating the electrochemistry of copper alloys under feedwater heater conditions suggests that maintenance of a stable cuprous oxide layer requires tight control of ORP (and pH). Further, corrosion experiments have pointed out that, during unit shutdowns, elemental copper and cuprous oxide will be converted to cupric oxide in a matter of hours, unless reducing chemistry is maintained. Effective implementation of reducing AVT chemistry therefore requires that on-line surveillance of ORP be practiced and that action be taken as needed in response to deviations from target values for this parameter in the cycle.

Industry has, for many years, been interested in real time measurements of corrosion rates in operating systems and considerable effort has been devoted to development of analyzers for this purpose. Commercially available monitors are available for surveillance of either ORP or electrochemical potential (ECP). Field experience with these monitors is most extensive in the nuclear power industry, both with *in situ* and sidestream analyzers, but limited in the fossil industry to ORP analysis of conditioned samples. Most field experience in fossil plants has been with ORP surveillance of final feedwater at the economizer inlet. However, findings of EPRI's Program Copper indicate the deaerator inlet to be the preferred monitoring point for ORP due to the difficulty of maintaining reducing conditions in the low pressure heaters.

## B.2 OVERVIEW OF ORP AND CORROSION MONITORING TECHNOLOGY

Since these potentials have been measured in power plants only in recent years, it is appropriate to briefly review the terminology relating to these potentials. ORP (also known as the reduction•oxidation (redox) potential) and corrosion potential are specific types of electrochemical potential (ECP). Both types of ECP are measured as a potential difference between a metal electrode and a reference electrode immersed in the environment of interest, and the value of the measured potential is determined by the specific oxidation and reduction reactions occurring at the metal/environment interface.

In the case of a corrosion potential measurement, the metal electrode may be the power plant component itself (such as a pipe or heat exchanger tube) or it may be a separate piece of metal (a "probe") having a chemical composition similar to the component of interest and immersed in the environment of interest. When a metal, such as iron, is corroding in an environment, such as water containing dissolved oxygen, the primary oxidation reaction is irreversible and heterogenous:

$$\text{e.g., } Fe \rightarrow Fe^{2+} + 2e^- \qquad \text{(eq. B-1)}$$

This reaction, together with the primary reduction reaction,

$$\text{e. g., } H_2O + \tfrac{1}{2}O_2 + 2e^- \rightarrow 2OH^- \qquad \text{(eq. B-2)}$$

controls the corrosion potential measured. Theoretically, each corrosion product is thermodynamically stable only in a specific corrosion potential range. A change in the corrosion reaction product from $Fe^{2+}$ to $Fe_3O_4$ to $Fe_2O_3$, for instance, would be reflected in a change in the corrosion potential.

When the measuring electrode is platinum or some other noble, non-corroding metal, the potential measured can still be considered a corrosion potential of sorts but, more correctly, it is an ORP measurement. Under such circumstances, the primary oxidation reaction, occurring at the metal/environment interface is simply the reverse of the reduction reaction. For instance, the reduction reaction in Eq. B-2 would be in equilibrium with the following oxidation reaction:

$$2OH^- \rightarrow H_2O + \tfrac{1}{2}O_2 + 2e^- \qquad \text{(eq. B-3)}$$

and the rates of the forward and backward reactions are usually quite small. Here, the oxidation and reduction reactions do not involve (irreversible) corrosion; rather they are reversible, homogeneous reactions reflecting the oxidative power of the environment. The platinum (or other noble metal) electrode merely provides a surface upon which the reversible reactions can be detected and monitored as an ORP. The oxidation reaction (e.g. Eq. B-3) also occurs on corroding metals, but the corrosion reaction (e.g. Eq. B-1) normally occurs at a much higher rate and it controls the value of the corrosion potential.

In summary, while ORP and corrosion potential are measured in a similar way, the former reflects the oxidative power of the environment while the latter reflects the corrosion reaction occurring on the metal surface. The corrosion potential will be dependent on the ORP in that an increase in ORP will normally be accompanied by an increase in the corrosion potential, but ORP and corrosion potential seldom have the same value.

Two important reversible reactions that influence the ORP of a power plant environment can be written as follows:

$$H_2O + \tfrac{1}{2}O_2 + 2e^- \leftrightarrow 2OH^-, \quad E = 1.228 - 0.0591pH + 0.0148\log p_{O_2} \qquad \text{(eq. B-4)}$$

$$2H^+ + 2e^- \leftrightarrow H_2, \quad E = 0.000 - 0.0591pH - 0.0296\log p_{H_2} \qquad \text{(eq. B-5)}$$

where E is the ORP at 25°C (77°F) measured with respect to a standard hydrogen electrode (SHE); and $p_{O_2}$ and $p_{H_2}$ are respectively the partial pressures of oxygen and hydrogen in the environment. The 2-directional arrows in Eq. B-4 and Eq. B-5 indicate the reversibility of the reactions. Similar relationships can be derived for other temperatures.

From these equations, it is clear that environments containing dissolved oxygen have a higher ORP than those containing hydrogen ions (or hydronium ions) at all pH values. Furthermore, in both equations, the ORP is decreased by about 59 mV for each increase of 1 pH unit at 25°C. The ORP also decreases as the partial pressure of oxygen decreases and the partial pressure of hydrogen increases. Consequently, ORP may be used to control or monitor the oxidizing power of fossil plant feedwater on oxygenated treatment or of BWR nuclear plant reactor water on hydrogen water chemistry.

As might be expected, the ORP is also influenced by the presence of reducing agents such as hydrazine and hydrogen, and ORP measurements are often used to ensure that hydrazine levels are maintained at correct levels(1,2). Details of how and why ORP and corrosion potential measurements are made in power plants can be found elsewhere(3,4).

## B.3 HARDWARE, CALIBRATION AND MAINTENANCE

### *B. 3.1 Voltmeter Selection*

When making corrosion potential and ORP measurements, it is important to use a voltmeter with an input impedance that is sufficiently high that current does not flow through the reference electrode. Current flow would cause the reference electrode to "polarize" and give inaccurate readings. This is particularly important in test environments (such as high purity water) that have very low conductivities. An electrometer with an input impedance exceeding $10^{12}$ ohms is usually adequate in these low conductivity solutions, but higher input impedances may be necessary in some cases. The selection of a higher input impedance is often accompanied by an increased sensitivity to AC pick-up and "noisy" measurements. Where the electrometer allows selection of the input impedance, the optimum setting can be achieved by starting at a very high input impedance, then reducing the input impedance stepwise until the corrosion potential reading begins to drift or change in an unexpected fashion, indicating polarization of the electrodes. At this juncture, the input impedance should be increased immediately to a somewhat higher value so as to eliminate the polarization.

### *B.3.2 Reference Electrodes*

All ECP measurements, including corrosion potential and ORP, utilize a reference electrode that must be maintained and periodically checked for proper operation. It is common practice to check reference electrode potentials against the potentials of other nominally identical reference electrodes. All measurements should agree within one millivolt and any reference electrode not meeting this standard should be withdrawn from service. Some reference electrodes can be rejuvenated and brought back into service simply by replacing the internal electrolyte (see below), but some reference electrodes are not designed for rejuvenation and must be discarded.

Ideally, all reference electrodes should be calibrated periodically because they tend to change with time. The apparatus needed to make such a calibration using a hydrogen electrode as the standard is described in ASTM G5-87(5). The rate that a reference electrode degrades depends partly on the type of service it sees and the contaminants it picks up from the service environment . For instance, a silver/silver chloride (Ag/AgCl) electrode, commonly used for both corrosion potential and ORP measurements at temperatures up to 300°C (572°F), is susceptible to irreversible damage if contaminated with sulfide. The formation of silver sulfide on the electrode surface causes a permanent change to occur that cannot be fixed by recalibration.

Calibration may also be impossible if the silver chloride component has been reduced to silver by hydrogen that has diffused through the reference electrode internal electrolyte from the bulk environment. Dilution of the internal electrolyte (usually potassium chloride, KCl) with the bulk environment may also occur, especially at high temperatures (e.g. above 200°C or 392°F) and when there is a pressure differential between the inside and outside of the reference electrode chamber. Dilution of the KCl will cause the reference potential to drift from the initial value, so periodic replacement of this solution is recommended in electrode designs that allow this.

### B.3.3 Corrosion Potential Probe

If the reference electrode has been properly maintained and calibrated, nothing further can be done to calibrate the corrosion probe because there is no "correct value" or standard corrosion potential available for calibration purposes.

When reporting corrosion potentials, the reference electrode should always be cited. For instance, if a potential measurement, E, is made using a Ag/AgCl reference electrode that contains an internal 3.0M KCl solution, the potential would be written as E volt (Ag/AgCl, 3.0M KCl). Standard conversion tables are available that relate all reference electrode potentials to the standard hydrogen electrode (SHE) scale. Consequently, the measured potential can be converted easily by the reader to an equivalent value measured using a different reference electrode. Some conversion factors are shown in Table B-1 for reference electrodes in common use and for temperatures in the range 20-30°C (68-86°F).

For instance, an ECP of +500 mV measured at 20°C (68°F) versus an SCE can be converted to an ECP versus an SHE, by adding 247 mV:

$$\text{ECP (SCE)} = +\,500\ \text{mV} \qquad \text{(eq. B-6)}$$

$$\text{Therefore, ECP (SHE)} = +\,500\ \text{mV} + 247\ \text{mV} = +\,747\ \text{mV} \qquad \text{(eq. B-7)}$$

### B.3.4 ORP Probe

Corrosion scientists and electrochemists in the research world typically report ORP values on the SHE scale even though the measurements are rarely actually made using an SHE. In practice, a more robust, more convenient reference electrode is used and the value measured is converted to the SHE scale either by calculation or by adjustment of instrument zero during calibration. In the power industry, however, ORP values are usually reported with respect to the reference electrode contained in the ORP probe. Such a practice is potentially confusing only because the reference electrode used is not routinely mentioned when reporting the ORP value.

Fortunately, the great majority of ORP probes used in power plants use one type of reference electrode: the Ag/AgCl reference electrode. Also fortunately, the internal electrolyte in the reference electrode, which influences the electrode potential, is typically potassium chloride with a concentration ranging from 3M to a saturated solution. An increase in the chloride concentration over this range would decrease the reference electrode potential by no more than 11 mV for temperatures in the range 20°C to 30°C (68-86°F) (see Table B-1). Since errors of 11 mV would be considered small for most practical ORP measurements, knowledge of the precise KCl concentration is usually not an issue at near-ambient temperatures. Corrections for KCl concentration may be necessary if the ORP is measured at higher temperatures. Nevertheless, confusion has arisen when ORP values measured versus a Ag/AgCl reference electrode are inadvertently compared with others measured versus an SCE or SHE. Consequently, it is recommended that the reference electrode used for the measurement is always mentioned along with the measured ORP values [e.g., ORP = 0.100 V(Ag/AgCl, sat. KCl)].

**Table B-1**
**To Convert ORP or Corrosion Potential Values Measured Using Reference Electrode #1 to Values on Reference Electrode #2 Scale, Add the Indicated Conversion Factor to the Measured Potential**

| Convert From Potential (mV) Versus Reference Electrode #1* (Listed Below) | Add the Conversion Factor Below to Convert To Potential (mV) Versus Reference Electrode #2* | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | To SCE | | | To Ag/AgCl (3M KCl) | | | To Ag/AgCl (sat. KCl) | | | To SHE | | |
| | 20°C 68°F | 25°C 77°F | 30°C 86°F | 20°C 68°F | 25°C 77°F | 30°C 86°F | 20°C 68°F | 25°C 77°F | 30°C 86°F | 20°C 68°F | 25°C 77°F | 30°C 86°F |
| **From SCE** | — | — | — | +34 | +35 | +36 | +45 | +45 | +45 | +247 | +244 | +241 |
| **From Ag/AgCl (3M KCl)** | -34 | -35 | -36 | — | — | — | +11 | +10 | +9 | +213 | +209 | +205 |
| **From Ag/AgCl (sat. KCl)** | -45 | -45 | -45 | -11 | -10 | -9 | — | — | — | +202 | +199 | +196 |
| **From SHE** | -247 | -244 | -241 | -213 | -209 | -205 | -202 | -199 | -196 | — | — | — |

* Ag/AgCl = silver chloride; SCE = saturated calomel electrode; SHE = standard hydrogen electrode.
Note: the presence of liquid junction potentials may result in the listed conversion factors being in error by 1 or 2 mV.

When comparing ORP measurements, they should be referred to the same reference electrode scale. As described above, the conversion factors shown in Table B-1 can be used to convert from one reference electrode scale to another. For instance, an ORP of +100 mV measured at 25°C (77°F) versus a Ag/AgCl, sat. KCl reference electrode can be converted to an ORP versus an SHE, by adding 199 mV:

$$\text{ORP (Ag/AgCl, sat. KCl)} = 100\ \text{mV} \qquad \text{(eq. B-8)}$$

$$\text{Therefore, ORP (SHE)} = 100\ \text{mV} + 199\ \text{mV} = 299\ \text{mV} \qquad \text{(eq. B-9)}$$

The instrument used to measure ORP may be calibrated using standard solutions that have known ORP values. For instance, one possible set of standard ORP reference solutions are based on pH 4 and pH 7 buffer solutions, similar to those used for pH meter calibration. However, for ORP standards, quinhydrone is added to the buffer solutions, which forms a reversible oxidation-reduction couple when dissolved in water. Hydrogen ions participate in the reaction between the quinone and hydroquinone, creating a pH dependent equilibrium:

$$C_6H_4O_2 + 2H^+ + 2e^- \leftrightarrow C_6H_6O_2 \qquad \text{(eq. B-10)}$$

Quinone Hydroquinone

$$E = E^\circ - [2.303RT/(2F)] \times \log a_{hq}/a_q - [2.303RT/F] \times pH \qquad \text{(eq. B-11)}$$

When the activity of quinone ($a_q$) is equal to the activity of hydroquinone ($a_{hq}$), the second term on the right hand side of Eq. B-11 drops out so that the electrode potential, E, is dependent only on pH.

The quinhydrone solutions are prepared by dissolving 10 grams of quinhydrone in one liter of pH 4 or pH 7 buffer solution[8]. Quinhydrone is not very soluble, so only a small amount will dissolve in the buffer solution, changing it to an amber color. However, it is important that excess quinhydrone is used so that solid crystals are always present. The quinhydrone powder poses a moderate health risk, causing irritation of the lungs with prolonged exposure to the dust. The calibration solutions are fairly innocuous unless ingested in large amounts.

For the pH 4 and 7 quinhydrone solutions, ORP values of about 263 mV and 86 mV, respectively, can be expected at 25°C when measured against a Ag/AgCl, sat. KCl reference electrode[4,6,7]. These values are consistent with a change of 59.0 mV per pH unit, which are consistent with the calculated value of 2.303 RT/F (= 59.2 mV at 25°C or 77°F) in Eq. B-11. ORP values for the standard solutions at other temperatures and for other reference electrodes are provided in ASTM D1498-93[8] and are reproduced in Table B-2.

**Table B-2**
**Expected ORP Values for Reference Quinhydrone Solutions at pH 4 and pH 7**

| Reference Electrode* | ORP Value (mV) | | | | | |
|---|---|---|---|---|---|---|
| | pH 4 Buffer Solution | | | pH 7 Buffer Solution | | |
| | 20°C (68°F) | 25°C (77°F) | 30°C (86°F) | 20°C (68°F) | 25°C (77°F) | 30°C (86°F) |
| Ag/AgCl | 268 | 263 | 258 | 92 | 86 | 79 |
| SCE | 223 | 218 | 213 | 47 | 41 | 34 |
| SHE | 470 | 462 | 454 | 295 | 285 | 275 |

* Ag/AgCl = silver/silver chloride (sat. KCl); SCE = saturated calomel electrode; SHE = standard hydrogen electrode

The quinhydrone standards are easily made but they are stable for only about 8 hours and are not expected to yield highly reproducible ORP values. Nevertheless, ORP values in freshly prepared solutions are expected to be within 10 mV of the values listed in Table B-2, and an ORP value measured with a probe in one of these standards can usually be considered acceptable if it lies within 30 mV of the listed value. If the electrode does not respond as expected or has a slow response, it should be cleaned and the calibration procedure repeated. Removal of oily or organic deposits can be achieved with a detergent or, if necessary, methanol or isopropyl alcohol. For removal of contaminants or mineral deposits, the electrode should be soaked in 10% nitric acid for 10 minutes. Alternatively, ASTM D1498-93 suggests the use of warm (70°C or 158°F) aqua regia for about 1 minute(6). As a last resort, the platinum surface can be polished with a 600 grit wet-dry emery cloth or a 1-3 micron alumina polishing powder to remove any stubborn coatings or particulates. The electrode will need to soak in tap water or purified water for at least 30 minutes after performing any of these cleaning procedures.

A single point calibration (or "standardization") like this is often considered adequate because ORP meters, unlike pH meters, do not have "slope calibration" to allow adjustment of the response to a specified change in ORP. Nevertheless, it is usually good practice to verify that the ORP probe (platinum/reference electrode combination) is operating in a predictable fashion by measuring the ORP in a second standard solution. If the electrode potential does not change by the expected amount, the electrode should be cleaned and re-calibrated, as described above.

Other ORP calibration solutions are available based on the ferrous/ferric cyanide or ferrous/ferric sulfate equilibrium reactions, but the quinhydrone standards are more widely used. Also, it has been suggested that a saturated sodium sulfite solution could be used to verify instrument response to negative ORP readings(7).

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# C
# AIR IN-LEAKAGE MONITORING AND CONTROL

## C.1 CYCLE AIR IN-LEAKAGE

A recent EPRI publication, *Condenser In-Leakage Guideline*[6], gives comprehensive details on how to conduct a monitoring program for air in-leakage using tracer gases. This document would be a valuable reference for those contemplating the purchase and use of this technology.

Program Copper research has clearly indicated that higher levels of air in-leakage into the cycle, which cause the ORP to change from reducing to oxidizing, will change the surface oxide layers from $Cu_2O$ to non-protective CuO. Allowing the air in-leakage to continue for more than 8 hours will lead to increasing conversion to CuO and increased levels of copper in the feedwater.

Constant vigilance must be exercised to prevent air in-leakage to the cycle from those equipment elements under vacuum at any or at all times. Particular problem areas include pump seals, valve bonnets, threaded joints, and especially the expansion joint between the turbine and condenser. Monitoring the amount of air in-leakage (flow to the vacuum pumps) is essential for proper control of oxygen / carbon dioxide. Such monitoring will determine when an exhaustive effort must be made to find and fix the source of air leakage. The Heat Exchange Institute recommends that air in-leakage be restricted to no more than 1.0 scfm per 100 MW of generating capacity. This same value has been included in all EPRI Guidelines to date.

## C.2 ROTAMETERS

Excess air in-leakage not only affects iron and copper corrosion and subsequent deposition, but also increases turbine backpressure, which directly reduces electrical generating capacity. A complete analysis of the effects of air in-leakage on condenser efficiency was made[2, 3] using a "multisensor" probe. This multisensor probe and its use in measuring air in-leakage is further described later in this Section.

Typically, utilities employ a rotameter at the exhaust of the steam jet air ejector or mechanical vacuum pump to quantify air in-leakage. This was the standard approach at the time plants were designed and constructed. Manual readings were planned to be taken, normally once a day, however, current manpower often restricts this. Air in-leakage can increase and remain at potentially damaging levels for hours or possibly days before the excess in-leakage is discovered, since turbine backpressure may not have increased significantly or noticeably.

Under certain conditions, rotameters provide adequate flow rate measurements of air in-leakage. However, many factors can affect the accuracy of the readings so obtained, such as debris, exhauster pulsations, water carryover, etc. Rotameters also have limited range, generally 10:1. Therefore, most problematic air in-leakages cause the rotameter to be pegged against the high level stop. Rotameters receive essentially very little maintenance and are checked very infrequently at many plants. In these situations, the operator has no idea of the extent of the air in-leakage, given the fact that the turbine backpressure rise may appear to be rather small and insignificant.

In an attempt to mitigate these inherent problems with rotameters, a series of instruments were developed which featured continuous readouts of air in-leakage. These earlier developments had some serious drawbacks, such as not being able to distinguish between water vapor and air; and, operating under the principle that the condenser exhaust gases were always at saturation, when in fact, they were not.

## C.3 MULTISENSOR PROBE

Subsequent developments have produced instrumentation, which apparently solved these earlier limitations and is available commercially at the present time. One such instrument features a multisensor probe (MSP) which is installed in the exhaust line from the condenser. This device is depicted in Figure C-1.

This instrument has the ability to directly measure the mass properties of gas in the condenser vacuum line, as well as computed parameters based on thermodynamics. The instrument combines a gas analyzer with a total mass flow meter. The instrument utilizes a velocity-measuring device, and other facilities for measuring temperature, pressure, and relative saturation. By including the measurement of pipe diameter, the instrument can separate the effects of non-condensable gas from water vapor and to compute individual and combined properties of the gas mixture. As a result, the following parameters of the gas flowing in the exhauster suction line are either directly measured or are determinable:

- Air in-leakage
- Volumetric flow
- Total mass flow
- Water vapor mass flow
- Water vapor/air mass ratio (relative saturation)
- Water vapor density
- Air density
- Partial pressure of water
- Partial pressure of air
- Total pressure
- Temperature

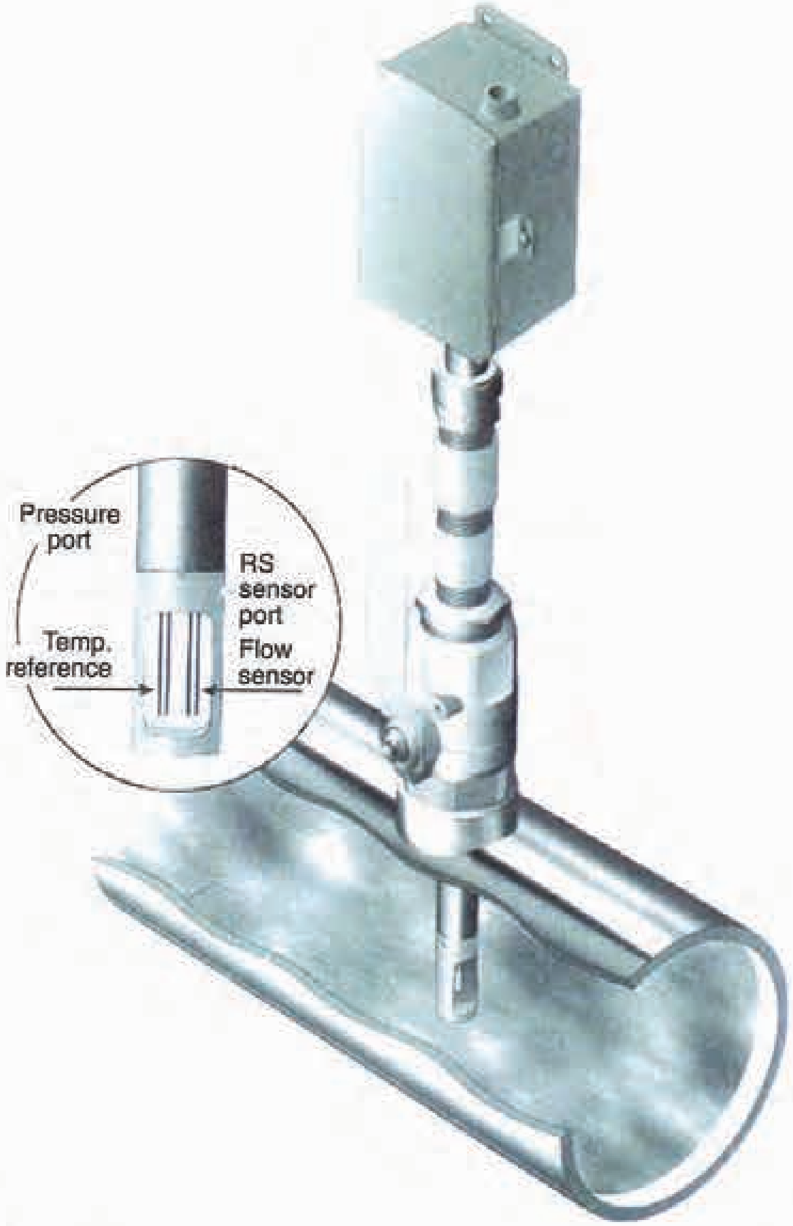

**Figure C-1**
**Multisensor Probe**

Air in-leakage, as measured by the MSP is the sum of all leak sources entering the subatmospheric pressure system and subsequently flowing through the exhauster line upstream of the sensor location. The MSP, however, does not measure air entering the low-pressure system beyond that (downstream), such as at valves, input connections, and shaft seals. The MSP does measure the exhauster capacity, which is useful to gauge the capacity of the exhausters to remove the gas mixture from the condenser.

Evaluation and analysis of condenser system performance and measurement of in-leakage is best accomplished with the use of five MSP probes as shown in Figure C-2. Each probe is identified by a number that is used to categorize performance information and to help pinpoint possible leak locations, as illustrated in Table C-1 and Table C-2.

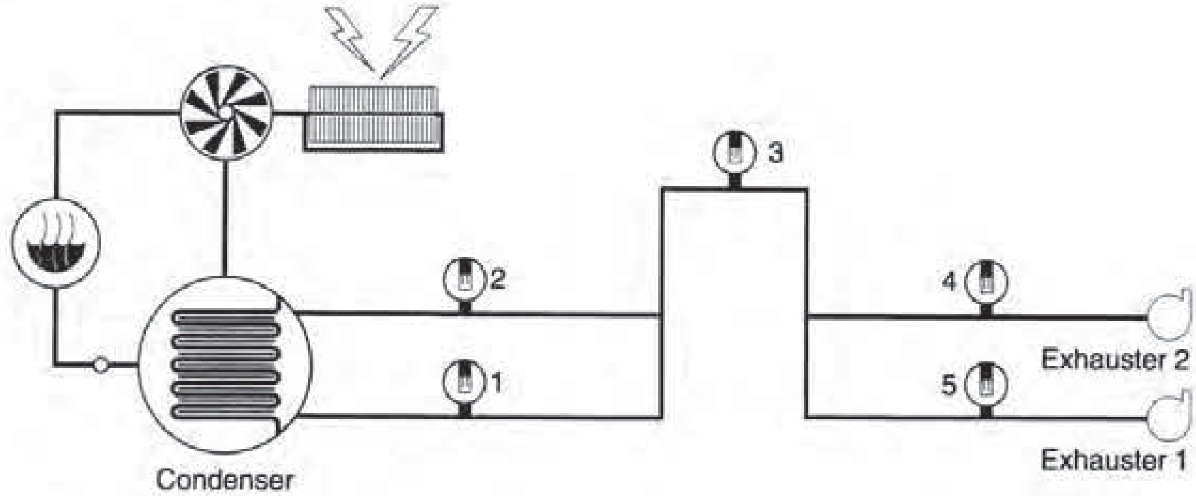

**Figure C-2**
**Multisensor Probe Instrument Schematic**

**Table C-1**
**Examples of a Five-Probe Air In-leakage Measurement System**

| Leak Location | Probe Indications of Air In-Leakage (SCFM) and Plant Dissolved Oxygen (DO) |
|---|---|
| Below water line, left side of condenser | Much higher than normal DO,<br>1 > 2<br>1 + 2 = 3 = 4 + 5,<br>4 = 5 |
| Above water line, right side of condenser | Slightly higher or normal DO,<br>2 > 1,<br>1 + 2 = 3 = 4 + 5,<br>4 = 5 |
| Small leak or faulty exhauster down stream of probe 4 | Slightly higher or normal DO,<br>1 = 2,<br>1 + 2 = 3 = 4 + 5,<br>4 < 5 |
| Large leak of failed exhauster down stream of probe 4 | Slightly higher or normal DO,<br>1 = 2,<br>1 + 2 = 3 < (4 + 5),<br>5 > 4 (back flow at 4) |
| Center joint seal, LP bearing seal, or other central location | Slightly higher or normal DO,<br>1 = 2,<br>1 + 2 = 3 = 4 + 5 |

**Table C-2**
**MSP Probe Indications for Various Probe Positions**

| Leak Location | Probe Indications of Air In-Leakage (SCFM) |
|---|---|
| Normal tight system | 1 = 2.5 SCFM<br>2 = 2.5 SCFM<br>3 = 5 SCFM<br>4 = 0 SCFM (exhauster 2 not in service)<br>5 = 5 SCFM |
| Abnormal, need to locate and fix leaks (central joint seal) | 1 = 15 SCFM<br>2 = 18 SCFM<br>3 = 33 SCFM<br>4 = 16.5 SCFM<br>5 = 16.5 SCFM |
| Abnormal, need to locate leaks and fix Nash pump shaft seal in exhauster 2 | 1 = 20 SCFM<br>2 = 20 SCFM<br>3 = 40 SCFM<br>4 = 20 SCFM (Differences due to reversed flow<br>5 = 60 SCFM through shaft seal being sensed) |

## C.4 HELIUM AND SULFUR HEXAFLOURIDE METHODS

The use of the MSP is certainly helpful in determining the extent of air in-leakage and providing guidance relative to where, generally, leaks may be occurring. After this assessment, it will be necessary to further determine the exact location of the leak(s). The two methods typically used for this purpose are helium leak detection and sulfur hexafluoride leak detection. Both use a sophisticated analyzer in conjunction with these tracer gases.

Air in-leakage testing is done by drawing a sample of condenser off-gas while releasing the tracer gas (helium or sulfur hexafluoride) at those areas within the vacuum boundary where leaks may be expected to occur. Since the condenser is under vacuum, the tracer gas migrates into the condenser shell, and from there it is removed by the air-removal system. A leak is identified when an off-gas sample containing the tracer gas passes through the analyzing equipment and is detected.

Helium was the first tracer gas to be successfully utilized in determining air leaks. The testing is accomplished by injection of helium at various locations (within the vacuum boundaries) and detection of helium in the condenser off-gases by use of helium mass spectrometry. This system is still in use today for detecting air in-leakage. There are some limitations to the use of this technique, however, particularly as regards sensitivity of response, which is particularly important in the detection and evaluation of very small leaks.

The fundamental advantage of sulfur hexafluoride ($SF_6$) is that it can be detected in very low concentrations, as low as 0.1 ppb. By contrast, the lowest detectable concentration of helium is 1 ppm. SF6 analysis is about 10-100 times more sensitive than helium detection.

The sensor technology for $SF_6$ is based on the principle of electron capture[4]. Figure C-3 is a general view of the $SF_6$ analyzer while Figure C-4 is a schematic diagram showing how the off-gas sample passes through the analyzer. To remove oxygen from the gas sample, hydrogen gas is introduced. This mixture enters a catalytic reactor in which the hydrogen and oxygen react to form water.

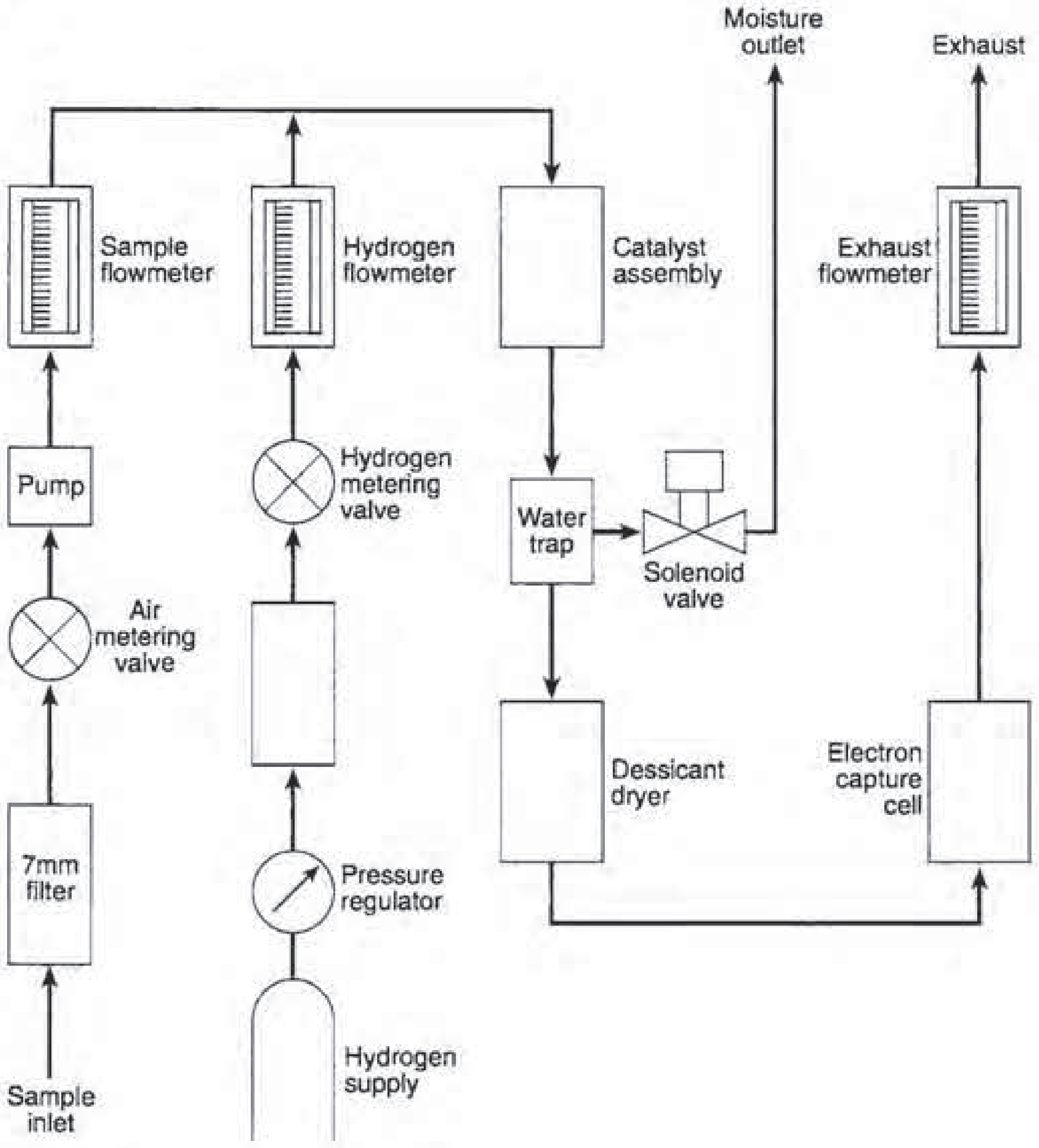

**Figure C-3**
**Flow Schematic for $SF_6$ Analyzer System**

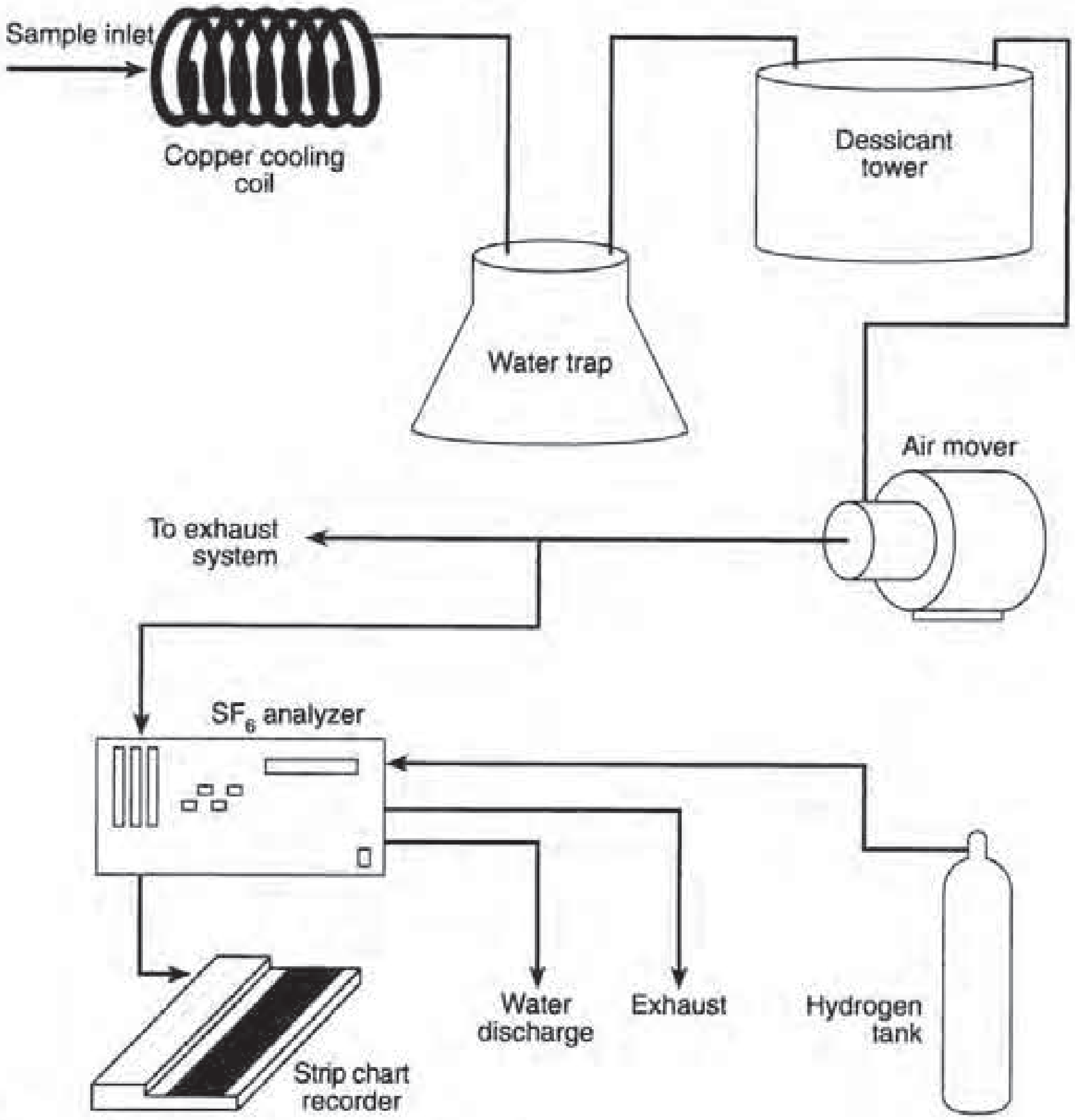

**Figure C-4**
**Schematic Diagram of $SF_6$ Sampling System**

SF6 can generally be used wherever helium can be used, although the converse may not always be true and there are situations in which use of helium is preferred. The following guidelines may be applied:

- If unit air in-leakage is in excess of 10 CFM, either gas may be used. If less, $SF_6$ is preferred.
- If the unit is running at greater than 20% turbine power, either gas may be used. If the unit has no turbine power and the leak is so bad that the unit can not be brought up to any turbine power level, standard procedure would dictate the use of helium.
- The search for the cause of air leakage below the steam space requires the use of $SF_6$ as the standard procedure.

- Inspections of units of less than 50MW capacity should always use helium.

The determination of air in-leakage using tracer gases requires a great deal of experience and a considerable outlay of capital if the necessary equipment is to be purchased. There are, however, consulting firms specializing in the evaluation of air in-leakage. These firms have their own equipment and are well versed in this technology. A typical study is estimated to cost between $3500 and $5000 in today's market(5).

## C.5 UTILITY AIR IN-LEAKAGE PROGRAM

One large utility has developed a formal program to control air in-leakage at each of their power plants (1). The program starts with a comprehensive written procedure which is continuously updated as new information is forthcoming and new experiences noted. The program and its revisions are controlled by central staff and implemented at each plant by the plant's performance engineering group. Formal training is given to each participant in the program.

The program is based on a daily monitoring and recording of air in-leakage at the vacuum pump or steam jet air ejector exhaust. The instrument presently in use for this purpose is a thermal gas mass flow meter, costing in the range of $2000 to 3000 each. Air in-leakage at the utilities' various plants is normally in the range of 5-8 scfm/ 100MW, depending upon unit size, configuration, etc. In addition, close attention is paid to unit backpressure, an increase of which could indicate increased air in-leakage. Continuous readings of dissolved oxygen at the condensate pump discharge are carefully reviewed as another indication of increased air in-leakage.

At the first indication of increased air in-leakage (scfm readings above the established base, increased backpressure, higher dissolved oxygen), a leakage test is initiated. An important part of the program is the establishment of a checklist, which delineates all of the various sampling points and their location at each plant elevation. For example, the turbine room sample points are broken down by directions- north, south, east and west relative to the turbine.

The equipment used for air in-leakage detection is a helium mass spectrometer. The detector is located at the vacuum pump or steam ejector exhaust. A unique feature of the program is the use of a wireless video camera, which constantly focuses on the readings of the air in-leakage detection unit. The results (leakage or no leakage) are transmitted to the operator via a remote wireless receiver. Thus, only one person is required to conduct a test, minimizing manpower.

The detection instrument has an internal vacuum pump and requires a dry sample for proper operation. The inlet sample tubing is passed through a cooling coil embedded in ice, followed by two water traps in series prior to entering the instrument.

Tests start at the top of the unit, working down, since helium, being lighter than air, will rise. If testing started at the bottom of the unit, the rising helium would be sucked into leaks further up, severely hampering interpretation of results.

Most tests are conducted at medium, or preferably, at full load, to maximize condenser vacuum and, subsequently, potential air in-leakage. At times, however, it is necessary to test at low loads to determine leakage at those areas of the low end of the cycle that are under pressure at high loads but under vacuum at low loads. An example would be the low pressure feedwater heaters.

Some examples of sampling points which are emphasized in the test procedure are condenser and condensate pump expansion joints, various flanges and pipe fittings, turbine horizontal shell flanges, turbine rupture diaphragms, turbine shaft seals, various turbine penetrations, pipe plugs, valve packings, etc.

Helium is sprayed at each test area at low pressure, about 10 psi, for only about 2-3 seconds to prevent too much helium from escaping, which could result in false readings and misinterpretations. It is necessary to note any extraneous air currents at a particular sampling location to prevent helium from "spreading out" and causing false leak indications.

Generally, to save time, a group of adjacent test points are sprayed with helium at the same time. If there are no leaks found, the next group of test points is sprayed. However, if leaks are recorded, further tests are required to isolate the offending location. A record of leak location is made together with the relative intensity of the leak.

Another practice, which is followed on a periodic basis, about once per year, is to flood the condenser with water to above the tube sheet and to look for water leaks from possible cracks in the condenser shell, attached piping welds or valve packings. Before performing this operation it will be necessary to determine explicitly whether the structural supports provided are sufficient to hold the extra weight of water within the condenser.

Results of all testing are submitted to the maintenance staff at the plant for necessary repairs, replacements, etc.

This program has been very effective in reducing oxygen and carbon dioxide from entering the cycle. Corrosion and corrosion transport have been reduced substantially since the program has been initiated.

## C.6 REFERENCES

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3. W. H. Stroman and J. W. Harpster "Continuous Monitoring for Condenser Air In-Leakage" Presented at the 2002 Spring Meeting, ASME Research Committee on Power Plant and Environmental Chemistry, Charleston, SC, March 11-13, 2002
4. La Porte and R. E. Putman, " The Practical Application of SF6 and Helium for Condenser Tube and Air In-leakage Detection". *Proceedings of the 19th Annual Electric Utility Chemistry Workshop*, University of Illinois, May 11-13, 1999.

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# D

# BENCHMARKING A UTILITY'S CHEMISTRY ORGANIZATION

## INTRODUCTION

Utility chemists often ask how good or bad they are in terms of their cycle chemistry operation and organization, and where do they rank with other utilities for a utility of their size. If such questions were answerable then they would be able to use the information as the first step in justifying new cycle chemistry equipment, or improvements to their current ability.

Insufficient quantitative data exist to rank utilities in terms of chemically influenced availability loss, reliability and performance degradation. For example, the NERC/GADS database has not continued to collect boiler tube failure (BTF) mechanistic data since the finish of EPRI's Boiler Tube Failure Reduction Program (BTFRP) in 1991.

An initial attempt was made with EPRI's Cycle Chemistry Improvement Program (CCIP) to measure a utility's improving cycle chemistry by monitoring a series of direct and indirect cost indices. This was very successfully used by the CCIP participating utilities.

Currently most utilities require short payback periods with associated accurate savings to justify cycle chemistry equipment and improvements.

Much thought has been given to this topic and the current assessment methodology will provide an initial assessment for rating a utility's chemistry organization. Participation and survey by a large number of utilities over the next year will solidify the rating. It could also be used by individual utilities to monitor improvements.

## ASSESSING THE CYCLE CHEMISTRY ORGANIZATION OF A UTILITY

The attached form is a self-assessment. It involves a series of "results oriented", "cycle chemistry influenced" factors. Each of the five factors is capable of being assessed quantitatively, and, as a whole, represent the key performance and availability indicators (results) by which the chemistry organization should be judged. Each factor relates to the Goals of the EPRI Cycle Chemistry Program. It is suggested that a utility make the initial assessment with data from the last five years. Improvements/changes could then be assessed on an annual basis. The methodology will work best when applied to a single unit/plant, but can be also applied to a utility system.

### A. Chemically influenced Boiler Tube Failures (BTF)

What percentage of the total numbers of BTF over the last five years, that have resulted in forced outage or unit unavailability, have been influenced by the cycle chemistry. A supplementary listing of those BTF influenced by the chemistry is provided for water-touched and steam-touched tubing. For further information on BTF Mechanisms, see "Boiler Tube Failures: Theory and Practice". B. Dooley and W. McNaughton. TR-105261.

### B. Chemically influenced turbine problems

This is in two parts. The first questions whether any LP blade/disk cracking has occurred in the last five years: this would involve either failure or identification by NDE during overhaul that cracking has occurred in the common corrosion fatigue or stress corrosion cracking areas. Has pitting been observed on LP blades

The second part involves whether copper deposition has been experienced in the HP turbine or whether excessive corrosive deposits in the LP turbine have been observed, which have required shot blasting or rinsing.

For further information on chemically influenced turbine mechanisms, see "Steam Turbine Damage: Theory and Practice". T. McCloskey, B. Dooley and W. McNaughton. TR-108943, 1999.

### C. Cycle Chemistry Instrumentation Control

This has two parts. The first involves a comparison of plant instrumentation with EPRI's core level of instruments which should be installed in every plant. A supplementary list is provided, which indicates 10 key instruments/parameters (or 11 if a polisher is installed) for drum boilers, and 9 for once-through units.

The second part involves whether these key control parameters are alarmed in the control room. A supplementary question might be whether the operators know how to react to an alarm, but this was not included as the answer would be subjective and difficult to quantify.

### D. Chemical Cleaning

This is in two parts relating to the two types of feedwater metallurgy system possible. The need to chemically clean boilers and the frequency are key indicators of whether the feedwater and boiler water treatments are optimized.

### E. High Purity Water Preparation and Use

This factor deals with the production of makeup water and its use. Because the cost of makeup production varies with supply (the range of cost is not known) and geography, an indicator based on the actual cost could not be used, although the question is asked. The addition of makeup to the cycle is dependent on the type of boiler (once-through or drum). The makeup rate is a good indicator of whether chemical control is optimized, particularly for drum boilers.

## Assessment of Cycle Chemistry Organization in a Utility

- Size of thermal plant capacity

  ☐ > 30,000 MW
  ☐ 20-30,000 MW
  ☐ 10-20,000 MW
  ☐ < 10,000 MW

| Weighting | Factor | Points | Total |
|---|---|---|---|
| 3 | A. Chemically influenced BTF (What is percentage of total number of BTF that is cycle chemistry influenced. See attached for relevant BTF) | | |
| | ☐ 0 % | 0 | |
| | ☐ < 5% | 1 | |
| | ☐ 5-15% | 2 | |
| | ☐ 15-30% | 3 | |
| | ☐ > 30% | 4 | |
| | Sub-total (Points x Weighting) | | ______ |
| 3 | B. Chemical influenced turbine problems | | |
| | ☐ LP blade/disk cracking, or pitting | 2 | |
| | ☐ No LP blade/disk cracking, or pitting | 0 | |
| | Sub-total (Points x Weighting) | | ______ |
| 2 | ☐ Copper deposition in HP reducing capacity or efficiency, or excessive deposits in LP turbine | 2 | |
| | ☐ Neither HP or LP deposition | 0 | |
| | Sub-total (Points x Weighting) | | ______ |

| Weighting | | Factor | Points | Total |
|---|---|---|---|---|
| 2 | C. | Cycle Chemistry Instrumentation and Control<br>What is percentage of EPRI core level of instruments (see attached for core level) | | |
| | | ☐ 100 % | 0 | |
| | | ☐ 90-99 % | 1 | |
| | | ☐ 70-89 % | 2 | |
| | | ☐ < 70% | 3 | |
| | | Sub-total (Points x Weighting) | | ______ |
| 2 | | Do you have these key control parameters alarmed in control room | | |
| | | ☐ Yes. All alarmed | 0 | |
| | | ☐ Yes. Some alarmed | 1 | |
| | | ☐ No. None alarmed | 2 | |
| | | Sub-total (Points x Weighting) | | ______ |
| | D. | Chemical Cleaning | | |
| 1 | | Frequency of cleaning boilers with mixed-metallurgy feedwater heaters | | |
| | | ☐ < 5 years | 3 | |
| | | ☐ 5-10 years | 2 | |
| | | ☐ > 10 years | 1 | |
| | | Sub-total (Points x Weighting) | | ______ |
| 1 | | Frequency of cleaning boilers with all-ferrous feedwater heaters | | |
| | | ☐ < 5 years | 3 | |
| | | ☐ 5-10 years | 2 | |
| | | ☐ > 10 years | 1 | |
| | | Sub-total (Points x Weighting) | | ______ |

| Weighting | Factor | Points | Total |
|---|---|---|---|
| | E. High Purity Water Preparation and Use | | |
| 1 | Do you know the cost of makeup water ($/1,000 gals) for each plant/unit | | |
| | ☐ Yes (what is it?____$/1000 gals) | 0 | |
| | ☐ No | 1 | |
| | Sub-total (Points x Weighting) | | ______ |
| | Addition of makeup to the cycle. | | |
| | For drum units, is addition generally | | |
| | ☐ <0.3 % | 0 | |
| | ☐ 0.3 – 0.5 % | 1 | |
| | ☐ >0.5 % | 2 | |
| 1 | For once-through units, is addition generally | | |
| | ☐ <0.2 % | 0 | |
| | ☐ >0.2 % | 1 | |
| | Sub-total (Points x Weighting) | | ______ |
| | **Total** | | ______ |

**Rating System**

| | |
|---|---|
| Excellent/World Class | <5 |
| Very good | 6-10 |
| Good | 11 –15 |
| Average | 16–30 |
| Below Average | >30 |

## Supplementary Information for Factor A

| **BTF Mechanisms in Water-touched Tubes that are Influenced by Cycle Chemistry** | |
|---|---|
| Mechanism | Nature of Chemistry Influence |
| Hydrogen damage | Excessive feedwater corrosion products form excessive deposits and combine with a source of acidic contamination. |
| Caustic gouging | Excessive feedwater corrosion products form deposits and combine with a source of caustic. |
| Acid phosphate corrosion | Excessive feedwater corrosion products form deposits and combine with a source of phosphate |
| Chemical cleaning damage | Excessive deposits in waterwalls lead to chemical cleaning; process errors lead to tube damage. |
| Corrosion fatigue | Poor water chemistry, shutdown or layup practices, and improper chemical cleaning worsen contribution of the environment to causing damage. |
| Supercritical waterwall cracking and overheating | Excessive internal deposits lead to increased tube metal temperatures; exacerbates mechanism. |
| Fireside corrosion | Excessive internal deposits lead to increased tube metal temperatures; exacerbates mechanism. |
| Short-term overheating | Plugging of waterwall orifices by feedwater corrosion products. |
| Erosion/corrosion of economizer inlet headers | Attack by reducing feedwater conditions. |
| Pitting (economizer) | Stagnant, oxygenated water formed during shutdown. |
| **BTF Mechanisms in Steam-Touched Tubes that are Influenced by Cycle Chemistry** | |
| Long-term overheating (creep) | If caused by restricted steam flow as a result of contaminant deposits, debris, etc. |
| Short-term overheating | Blockage from improper chemical cleaning (of SH/RH or waterwalls). |
| Stress corrosion cracking | Variety of bad environment influences, most directly related to chemistry control and practices. |
| Pitting (RH loops) | Carryover of $Na_2SO_4$ or poor shutdown practices allowing for oxygenated, stagnant condensate. |
| Chemical cleaning damage | Poor chemical cleaning practice. |

For further information on BTF Mechanisms, see "Boiler Tube Failures: Theory and Practice". B. Dooley and W. McNaughton. TR-105261.

## Supplementary Information for Factor C

**"Core" Monitoring Parameters (Minimum level of instruments for all plants/units)**

(all instruments should be on-line and continuously monitored)

| **Parameters** | **Measurement Locations** |
|---|---|
| Cation Conductivity | CP Discharge |
| Cation Conductivity | Polisher Outlet and Economizer Inlet |
| Cation Conductivity[1] | Blowdown or Downcomer |
| Cation Conductivity | Hot Reheat Steam or Main Steam |
| Dissolved Oxygen | CP Discharge<br>Economizer Inlet |
| pH (Drum Boilers) | Blowdown or Downcomer |
| Sodium | CP Discharge |
| Sodium | Polisher Outlet or Economizer Inlet |
| Sodium | Hot Reheat Steam or Main Steam |

Note 1: Drum boilers on AVT and OT.

# E
# CYCLE CHEMISTRY DATA QUALITY

## E.1 INTRODUCTION

Effective fossil plant cycle chemistry programs consist of several components. These include:

- Properly selected feedwater and boiler water treatment approaches
- Establishment of optimized and customized target values and action levels
- Provision of a suite of on-line analyzers consistent with the selected treatment approaches
- Implementation of operating practices and procedures that allow for maintaining desired chemistries under all operating conditions
- Development of operating response procedures that enable plant personnel to promptly identify deviations from normal chemistry and to initiate appropriate corrective actions

These aspects have been addressed in detail as they apply to units operating on all volatile treatment (AVT). In this section, other important aspects of cycle chemistry surveillance and control are discussed, including the following.

- Sampling and sample conditioning capabilities
- Monitoring methods
- Data acquisition, analysis and management practices
- Quality assurance and control requirements, including on-line analyzer chemistry data validation practices
- Plant staff capabilities and responsibilities

These important aspects of cycle chemistry programs are addressed in ensuing report subsections. However, it should be noted that these presentations represent summaries of best available practices in these areas. Users of these guidelines seeking additional details are strongly encouraged to consult the source documents on which these summaries are based.

## E.2 SAMPLING, SAMPLE CONDITIONING AND INSTRUMENTATION

This subsection addresses the important considerations involved with proper sampling, on-line instrumentation and analysis of grab samples. Readers should also refer to Sections 4 and 5, which delineate the types of analyzers to be used with AVT, depending on unit characteristics.

This following discussion is provided as a summary of these topics. A comprehensive discourse on these and related topics can be found in other EPRI publications.(1-6)

### E.2.1 Factors Affecting Sampling

Sampling is an important aspect of water chemistry control within the power plant. A meticulously performed analysis is of no value if a bad sample is used. Obtaining a good sample involves careful consideration of the design and operation of the sampling system.

Many factors affect how well a sample represents the medium from which it is drawn. The sample point must be selected so the sample is representative of the bulk solution, particularly when suspended material is present. Also, if chemicals are injected or other streams are introduced into the sampled medium, the sample collection point should be placed far enough downstream to ensure a completely mixed sample. Assuming turbulent flow, locating the sample collection point an equivalent length of 25 pipe diameters downstream of the chemical injection point is considered acceptable. An equivalent length of 50 pipe diameters is recommended for laminar flow.

The material and design of the sampling apparatus also play an important role in the collection of representative samples. The materials chosen for nozzles, tubing, pumps, and valves must be corrosion-resistant and compatible with the sample conditions and the analyses performed. Austenitic stainless steels (types 304, 316, and 347) are most commonly used. In addition, it is essential to select the most effective piece of equipment for carrying out a particular task. For example, needle valves have been used for reducing pressure in sample conditioning systems. However, at high temperatures, needle valves have been found to cause the thermal dissociation of water because energy is released within the small volume of the valve.

Alternate methods of pressure reduction (discussed later) for high-temperature/pressure locations are available. These methods are most effective in obtaining an unaltered and thus a more representative sample.

The sample must be rapidly cooled, preferably as close to the sampling point as possible, to preserve sample integrity.

The frequency with which a grab sample is taken is another factor affecting its representativeness. Samples should be taken at a frequency high enough to sufficiently monitor critical conditions that could reach intolerable limits. Also, the sampling frequency should be influenced by periods of load changes. For example, during startup, thermal transients release a variety of contaminants throughout the cycle that should be closely monitored. Also, the increase in the makeup requirement during these load swings introduces a greater risk of obtaining high oxygen levels unless provision is made to remove oxygen as part of the treatment (Appendix A). At such times, oxygen should be very closely monitored.

### E.2.2 Potential Problems in the Design and Operation of Sampling Systems

It is important to be aware of the potential problems in the design and operation of sampling systems. The causes of sample degradation and contamination within the tubing are numerous. One factor contributing to contamination is "crud bursts" caused by sudden increases in velocity. In addition, if the velocity of sample flow is not high enough and if suspended particles are present, deposition may occur. Chemical reactions within the tubing may also contribute to sample degradation. Some of the chemical reactions that can occur include

- decomposition of hydrazine (or proprietary reducing agents) and/or organic contaminants;
- reaction of oxygen with hydrazine (or proprietary reducing agents), corrosion products, and/or base metals;
- dissociation of water; and
- adsorption of ionic impurities onto corrosion-product (magnetite) particles and deposits.

Another consideration is that in any sample system, there is an interchange of contaminants (such as iron, nickel, and chromium) between the flowing sample and the sample line surfaces. Eventually, an equilibrium state is reached. Whenever the sample is not in equilibrium with the surface, the sample will be changed from its original state. The time needed to reach equilibrium decreases with decreased surface area and increased sample velocity. If insufficient sample velocity, less than approximately 6 feet/second (1.8 m/second) is maintained, then the equilibrium process has been known to take up to 1 month to achieve.

Sample line blockage, caused by the accumulation of deposits or large particles caught in small-diameter tubing, is another source of potential problems. Lengthy sample lines or low sample flow increase the probability of sample line blockage and can cause unacceptable time lags between sample collection and analysis.

Proper conditioning of samples is another essential consideration in the design and operation of sampling systems. Continuous analyzers require precise flow and temperature regulation to perform accurately.

Another source of potential problems in a sampling system is the sample cooling equipment. Avoiding cooling water shell-side deposits and corrosion and maintaining a constant sample flow rate through the cooling devices are important considerations.

There are also many possibilities for the degradation of a grab sample during collection and storage. Such potentials for sample degradation are especially critical for pH, conductivity, dissolved oxygen, and hydrazine analyses. Special preparation of grab samples and/or sample containers may be required, depending upon the type of analysis being performed. Chemicals are often added to the container before the sample is added to prevent sample degradation. Also, collection methods for samples to be analyzed for pH, conductivity, dissolved oxygen, ammonia, hydrazine, or organics must exclude any contact between the sample and the air. In addition, storage methods and holding times of samples from collection to analysis require special consideration to avoid degradation of samples. Applicable procedures for collection, preparation of sample containers, and sample storage and preservation are given in ASTM D 3370 "Standard

Practices for Sampling Water", and in ASTM D4453-91, "Standard Practice for Handling of Ultra-Pure Water Samples".

### E.2.3 Sample Collection

Obtaining a representative sample of superheated steam requires special sampling techniques. The goals are to avoid deposition of suspended and dissolved solids from the superheated steam, avoid effects caused by pipe surfaces, and withdraw representative amounts of all phases (steam vapor, solid particles, and water droplets).

Sampling of steam and water for on-line and grab sample chemical analysis can represent a major source of errors. Changes of up to several orders-of-magnitude in concentration of dissolved and suspended impurities have been observed when sample withdrawal, cooling, or transport are not properly performed. Recognizing this problem, EPRI established research project RP2712-8 to define priorities for sampling points and monitored parameters. By analyzing collected samples from a supercritical unit, the project team found that particulates (magnetite) in steam can transport significant amounts of contaminants. On the basis of their findings, the team designed a new isokinetic sampling nozzle, which can collect particulates in superheated steam and impurity-rich water droplets in saturated steam. The team evaluated the sampling system using the new nozzle at four utility plants.

Investigations demonstrated that the preferred sampling location for fossil cycles with reheat is the hot reheat steam pipe. This report(3) describes the following in detail:

- the optimum location of a sampling nozzle in a long vertical section of a steam pipe
- a single-port tapered nozzle, now called the "EPRI Nozzle"
- the method of nozzle attachment of a steam pipe and nondestructive inspection methods
- mechanical design requirements for vortex shedding and resonant frequency
- the location of depressurizing valves and placement of sample coolers as close to the valves a possible

In all, evaluations showed that the "EPRI Nozzle" provides a representative total sample of the impurities involved.

The nozzle extracts isokinetically a homogeneous sample from a flow region removed from the pipe inner surface and representative of the average flow velocity of the sample fluid. This arrangement results in the withdrawal of the sample with representative concentrations of dissolved, suspended, and volatile constituents. Isokinetic nozzles are equally applicable for liquid samples (condensate), especially when sampling for particulates, such as magnetite or copper oxides.

An appropriate nozzle is selected for the desired sample flow and typical conditions of the sample fluid. When the flow rate (velocity through the pipe) changes, sample flow should be adjusted to maintain isokinetic sampling.

A summary of sampling criteria is depicted in Table E-1.

**Table E-1**
**Summary of Criteria for Sampling**

| Sample | Criteria |
|---|---|
| Pressurized Condensate and Feedwater with Representative Sampling of Particulates | • Isokinetic sampling velocity<br>• Velocity of 5-6 ft/s (1.5-1.8m/sec)<br>• Primary sample cooler at the sample source<br>• Isokinetic sample probe[3] |
| Boiler Water from Blowdown Lines or Circulation Pump Manifold | • Velocity of 5-6 ft/s (1.5-1.8m/sec)<br>• Primary sample cooler at the sample source |
| Boiler Water from a Downcomer or Other Pipeline | • Isokinetic sampling velocity<br>• Velocity of 5-6 ft/s (1.5-1.8 m/sec) if consistent with isokinetic requirements<br>• Primary sample cooler at the sample source<br>• Isokinetic sample probe[3] |
| Saturated Steam | |
| *from Steam Leads* | • Isokinetic sampling velocity<br>• EPRI single port nozzle located 0.75 to 2 steam lead diameters from the steam lead inlet<br>• Sufficient nozzles should be used to provide sampling of a representative fraction of all steam leads along the drum<br>• Primary sample cooler at the sample source |
| *from Large Diameter Line* | • Isokinetic sample probe[3] |
| *from Dry Pan Sampler* | • Velocity of 5-6 ft/s (1.5-1.8 m/sec) |
| Superheated Steam | • Isokinetic EPRI sample probe[3]<br>• Primary sampler cooler at the sample source |
| Condensate at Subatmospheric Pressure (requires a special pump for this service, not available on many fossil units) | • Velocity of 5-6 ft/s (1.5-1.8 m/sec)<br>• Large diameter sample nozzles, net positive suction head actual (NPSHA), greater than net positive suction head required (NPSHR) at all conditions |

### *E.2.4 Sample Tubing*

All components of the system in contact with the sample after it leaves the boiler must be constructed of corrosion-resistant materials such as type 304, 316, or 347 austenitic stainless steels (or their low-carbon analogs). The sample tubing should be shaped so that sharp bends, dips, and low points are avoided, thus preventing crud from collecting. Routing should be planned to protect samples from exposure to extreme temperatures, and also to protect plant personnel from high-temperature sampling lines.

Steam and water velocities in the sample lines must be high enough to maintain necessary turbulence, preventing deposition in the piping and providing a well-mixed sample. A constant water velocity of more than 6 ft/s (1.8 m/sec) is desirable. In addition, line lengths must be as short as possible to reduce lag times and changes in sample composition. Tube diameters should be small enough to maintain adequate velocities without excessive conditioning or waste requirements. For the EPRI RP2712-3(2) monitoring program, 1/4-inch (6.4 mm) OD type 316 stainless steel tubing was used throughout and assembled using compression-type fittings. (Wall thickness should be compatible with pressure and temperature at the sample point.) This selection proved to be a good one, as no problems were encountered with pluggage or leakage at any of the four plants monitored and sample flow rates were consistently in the turbulent range.

#### Pumps, Valves, and Fittings

All components of the sampling system must be noncontaminating and able to withstand the mechanical and thermal stresses (pressure/temperature) involved. Both diaphragm pumps with priming devices and centrifugal pumps with high rates of recycle may be used for extracting samples from sources operated at subatmospheric pressures. Valves and fittings should be maintained leak-free.

#### Sample Water Recovery and Drains

Sample flows should be adjusted to achieve the desired sample velocity, with any excess bypassed to the drain or to the condenser hotwell, or, if appropriate, a sample collection tank. A typical sampling system handles a substantial volume of condensate-quality water each day. If this water is not reused, a significant increase in makeup requirements could result. Uncontaminated samples should be recycled where feasible, while contaminated samples should be directed to waste via the drain.

### E.2.5 Sample Conditioning

This subsection describes general requirements for sample conditioning. Specific requirements of continuous analyzers must also be satisfied.

Sample conditioning includes temperature, pressure, and flow rate regulation as well as filtration, the latter applied as required to ensure proper performance of individual analyzers.

#### Temperature Regulation

Temperature reduction should always be carried out before pressure reduction to prevent flashing, which results in deposit formation. Roughing coolers, located as close to the sample point as possible, are used to cool the sample to approximately 100°F (38°C). Isothermal baths, placed as close to the analyzers and grab sample points as possible, should be used to cool the sample and maintain it at 77°F±1°F (25°C±0.5°C). This eliminates the necessity of making temperature corrections for pH and conductivity, thus improving the accuracy of these measurements. Isothermal baths are available from several vendors specializing in the custom manufacture of sampling panels and related equipment.

### Flow Rate and Pressure Regulation

Most continuous analyzers are sensitive to sample flow rate, and the appropriate manufacturer's specifications must be followed. Usually, on-line instruments are designed to include flow regulating devices to serve as a check for those devices located upstream, but these on-line devices must not be relied upon.

A minimum recommended flow rate for grab samples is 300 mL/min (4.8 gal/hr). However, the actual flow rate should be governed by the rate required to maintain adequate and constant sample line velocities. The design velocity can be maintained by routing excess flow either to waste or the condenser hotwell, as appropriate.

Pressure regulating devices must be designed to maintain constant flow to the analyzers during normal, startup, or changing load conditions. Of the many pressure-regulating devices that exist, available types that have been used successfully are described:

- needle valves
- rod-in-capillary devices
- constant head devices and back pressure regulators

Needle valves are sufficient for reducing sample pressures from up to about 500 psig (3.45 MPa). However, at pressures nearing the critical pressure, needle valves have been found to cause the dissociation of water. This is an undesirable situation, causing a rise in the hydrogen and oxygen content of the water. Also, at higher pressures, needle valves are subject to wire-drawing.

Rod-in-capillary devices are available in two designs: the fixed rod-in-capillary device and the variable rod-in-tube capillary device. Fixed rod-in-capillary devices have a tendency to plug, and are difficult to clean. A variable rod-in-tube device is effective over a larger pressure range than a fixed rod-in-capillary device because it provides an adjustable pressure drop. In addition, the variable rod device is more easily cleaned.

Most on-line analyzers require inlet pressure to be 5-20 psig (34-138 kPag) for proper operation. The outputs from most instruments are also flow sensitive, so flow rate should be maintained as constant as possible. These flow and pressure requirements can be met by using a back pressure regulating device or a head cup. A head cup is a relatively simple device (see Figure E-1) and has been used successfully to supply pH and conductivity cells. Immediately upstream of the analyzer, a vertical leg is used to develop an 8 to 10 foot (2.4 to 3.0 meter) head. A trough for collecting overflow is placed at the top of this vertical leg. An overflow is required at all sample conditions to avoid atmospheric sample contamination. They are very reliable but they suffer a major disadvantage: they provide only a very low inlet pressure so usually they cannot be used with analyzers requiring a 5-20 psig (34-138 kPag) sample pressure. Consequently, a back pressure regulator is normally preferred over a head cup when the analyzer requires constant flow at pressure.

Use of an orifice installed in a sample flow line is not recommended for pressure and flow control because the orifice size cannot be modified easily to allow flow rate adjustments, and the orifice size changes as it wears, and therefore would have to be replaced frequently to maintain the desired flow rate and pressure, even under baseload operating conditions.

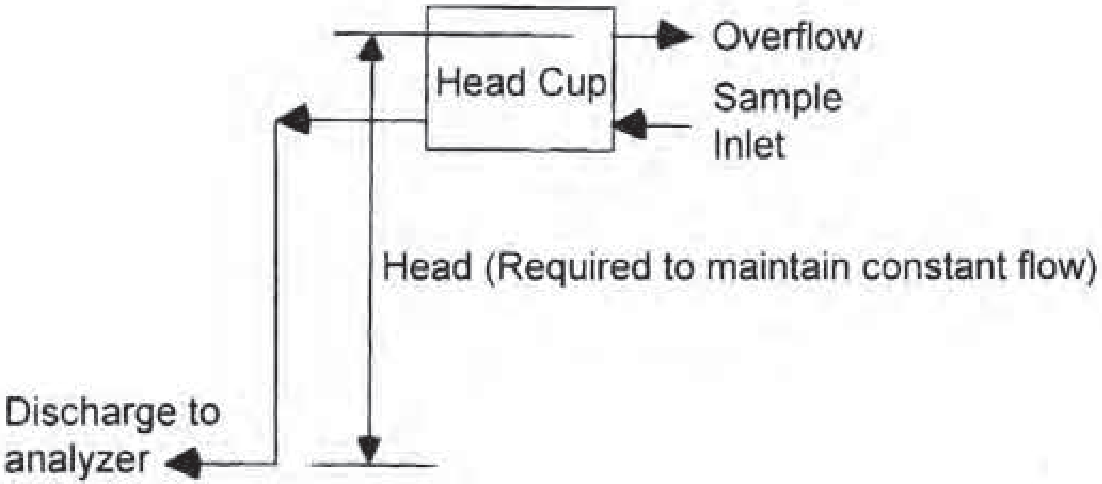


**Figure E-1**
**Head Cup for Constant Sample Flow (pressure in psi at discharge equals the head, H inches of water, divided by 27.6)**

## Sample Filters

Filters are placed before the pressure and flow regulators to prevent fouling of analyzers in those sample lines not being tested for turbidity or used as grab samples. Closer attention is needed for filters used in cycling plants: because of the heavy accumulation of scale and corrosion products, these filters require frequent maintenance. For some analyzers, filters are included in the internal design. Some analyzers also require the use of micron filters immediately upstream. Manufacturer's specifications should be checked for special requirements concerning filters. Because of the interactions of soluble impurities with suspended metal oxides(4), filtered samples may not represent total concentrations. The metal oxides retained on the filter may either adsorb or desorb trace levels of soluble impurities or change the sample composition or its properties, i.e. temperature, pH, etc.

## Sample Panels

In fossil plants, it is quite common to direct all sample lines from one or more units to a common location, often within or adjacent to the laboratory.

Most sample panels include the following components:

- pressure reducers
- relief valves
- constant temperature baths
- valves to control flow rate
- sample pressure, temperature, and flow rate indicators
- analyzer cells and elements
- sample sink for grab samples

A recorder-analyzer panel is typically provided as a separate unit. Sample panels are usually centrally located for convenience. In addition, the surrounding environment is more easily controlled when a central location is chosen for the panels.

The air in the sample room should be filtered. The room should have a positive pressure to maintain low dust levels. In addition, relative humidity should be between 50% and 70% and temperatures between 65°-78°F (18-26°C). Adequate electrical shielding is required, and refrigeration units should be located outside the sample room, whenever possible, to keep vibrations to a minimum.

Local satellite panels should be considered for new plants and for existing plants requiring supplemental instrumentation. Local sample panels provide advantages over a centrally located panel such as shorter sample lines and troubleshooting capabilities. However, these panels must have a central display. Some of the major problems concerning sample panels are the difficulties encountered during servicing and adjustment. Piping, tubing, and fittings should be arranged so instruments or devices may be removed, serviced, or calibrated without disturbing adjacent piping or tubing.

The sampling system configuration used in the RP2712-3 monitoring project is shown in

Figure E-2[2]. This configuration proved to be quite effective, and generally caused few maintenance problems during the project's four monitoring periods.

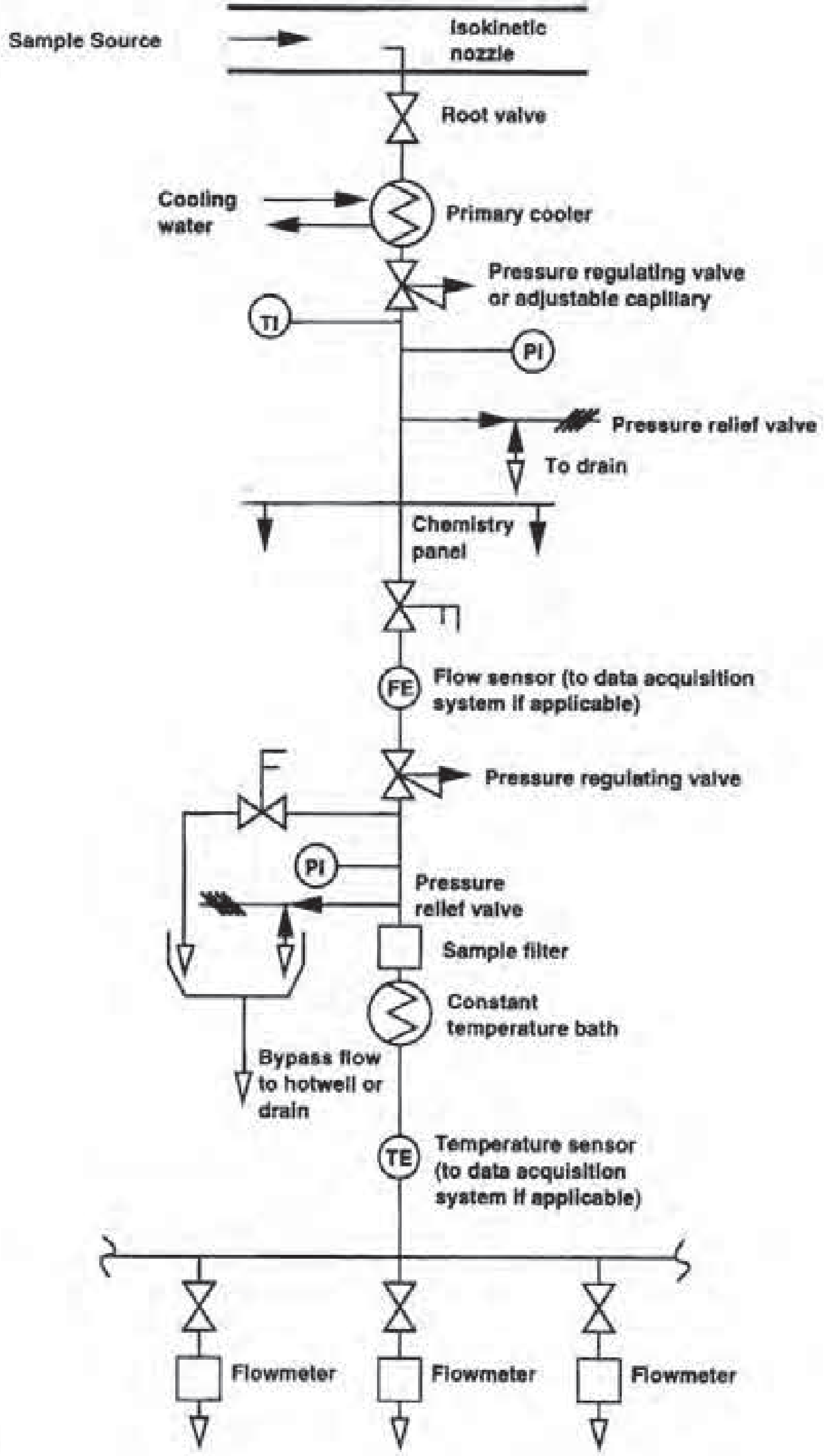


Figure E-2
Sampling System Configuration Used During RP2712-3 Project[2]

## E.2.6 Grab Sampling Procedures

This section discusses only general requirements for grab sampling procedures. Analysis methods and standards should be checked for any special requirements pertaining to grab sampling procedures.

### Grab Samples

Grab samples serve many purposes within chemical control programs, including:

- verification of results obtained from on-line monitors
- a means to measure other chemical parameters not measurable with on-line instrumentation
- troubleshooting upsets in cycle chemistry
- optimization of treatments
- determination of mechanical carryover in drum boilers

Grab samples can be taken at local sampling sites using portable conditioning units. More often, however, grab samples are taken centrally.

### Sample Containers

The selection of appropriate (noncontaminating) sample containers and closures, in addition to the container cleaning procedures, depends upon the parameter being tested and the method of analysis.

Before taking samples, the sample container should be properly labeled. This procedure helps to maintain meaningful records. A typical sample label should have the space for and include the following information:

- sample number
- date and time of sampling
- source of sample
- point of sampling
- load and mode of operation
- type and quantity of preservative added
- results of analysis performed
- name of sample collector

Provision of complete information is essential where off-site analysis of grab samples is required.

### Sample Collection and Preservation

Sample points that are regularly monitored should flow continuously. Local grab sampling points used for troubleshooting should be flushed at least four hours before collection of the sample. After the sample has been allowed to flow at a steady rate for this period, the sample containers and closures should be rinsed with the sample medium and the sample should be taken. The container should be filled completely, leaving no trapped air.

The necessary measures should be taken to ensure sample preservation. Special procedures, often involving the addition of a stabilizing chemical, are suggested in various ASTM standards and should be followed where applicable.

### *E.2.7 Corrosion Product Sampling*

Optimization of feedwater treatment involves corrosion product monitoring campaigns (Section 2). Unfortunately, centralized sampling facilities do not support collection of representative grab samples of metal oxide particulates. Lengthy sample lines have detrimental effects on any suspended corrosion products which may be present. Deposition of these materials in the line leads to either flow restriction or plugging. In some instances, deposited corrosion products may become reentrained in the flowing sample; this phenomenon is sometimes referred to as "crud bursts". Effective surveillance of corrosion products generally requires a continuously flowing sample. Temperature and pressure reductions should be performed as close to the source as practical to minimize sample line length. This approach is desirable whether the intent is to collect grab samples for laboratory analysis or to beneficially utilize integrated corrosion product sampler devices. For iron and copper transport characterizations, it is very desirable to minimize the length of the sample line and position primary coolers as close to the extraction point as possible.

As indicated earlier in Table E-1, isokinetic sampling is recommended and is especially important when monitoring metals in the steam/water cycle. Failure to maintain isokinetic conditions introduces bias, since suspended solids (and moisture in saturated steam) will not be collected in quantities consistent with their levels at the sample source.

Additional information and guidance regarding sample extraction and conditioning are available in other EPRI publications.(2,3,5,7) Also, utility personnel should consider a recent report (publication pending) from the American Society of Mechanical Engineers. This document, entitled, *Steam and Water Sampling, Conditioning and Analysis in the Power Cycle*, was prepared by the Performance Test Codes Committee (PTC 19.11).(8)

## E.3 ON-LINE MONITORING TECHNIQUES

Water chemistry monitoring is essential for all fossil units to achieve optimum performance from their chemistry programs. This section provides an overview of these topics but further information is available in other EPRI publications(2,5,7).

### E.3.1 Important Considerations for Selection of Proper Monitoring Method

Selecting the appropriate monitoring method is vital for obtaining reliable results. Method selection is based on a variety of factors; primarily, the choice must meet the required sensitivity and precision. The sensitivity, precision, and bias of some methods are not suitable for monitoring conformance with these guidelines. Variations in accuracy may mask process fluctuations and erroneously indicate conformance or nonconformance; therefore, the choice of methodology must also meet the required accuracy.

Appropriate concentration levels and compensation for possible interferences must be considered before selecting a monitoring method. The selection of a methodology also requires the evaluation of available equipment, time limitations, and the cost of analysis. The experience of the analyst and the amount of quality assurance necessary are also critical in choosing a method. If possible, there should be a trial period for analyzers, and other users' experiences with the analyzer should be investigated. In addition to using the proper procedure, proper sampling techniques must be followed to obtain reliable results.

The analyzers should be relatively simple and easy to calibrate, maintain, and check. Fewer and less complicated components increase an analyzer's dependability. Certain characteristics should be considered in analyzer selection, including the following.

- The fluid path should be simple and use a minimum amount of small-bore plastic tubing.
- Solid-state electronics should be utilized
- Auxiliary equipment, switches, and alarms should be external
- A reasonably fast response time should be provided
- The analyzer should have simple purge and flush requirements for startup and shutdown
- Maintenance and calibration should be easy and infrequently required
- The analyzer should be able to resist fouling and scaling
- The analyzer should have simple sample conditioning requirements
- A comparison of the various analyzer-specific designs available should be made
- The analyzer should be able to compensate for variations in sample flow and temperature

A very desirable feature is that the instrument sample manifold provides a means by which independently prepared standard samples may be introduced continuously, wherever desired, for the normal sample flow. Periodic checks of samples represent the surest means of determining the precision and bias of continuous instrumentation.

The monitoring and control system must furnish the laboratory with a representative sample, provide dependable feedback of measurements, and automatically protect important system constituents. The control system must also provide local grab sample lines in appropriate locations to evaluate specific pieces of equipment and to sample corrosion products.

Selection of the appropriate equipment is essential in the control of water chemistry, which is a mandatory requirements for longterm operation of all power plants.

### E.3.2 Analyzer Calibration Techniques

Calibration of monitoring equipment is essential for accurate and precise analysis. The frequency and method of calibration will vary among different types of analyzers; therefore, specific vendor instructions should be followed as closely as possible. Calibration frequency may also depend on the concentration of the particular parameter, the accuracy requirements of the analysis, and the stability of the instrument used for the measurement. All types of analyzers will lose accuracy when measuring zero or very low levels of concentrations over extended periods of time, in which case the analyzer should be calibrated more frequently. A calibration frequency should be established and rigorously followed for each individual instrument.

Another aspect of calibration accuracy is the reliability of the standards used for interlaboratory and intralaboratory comparisons. Chemical quality and the care exercised in preparation of standard solutions greatly affect chemical calibrations.

### E.3.3 Analyzer Operation and Maintenance

Sufficient priority must be given to proper operation and maintenance to ensure reliable results. The analyzer is only one part of the system and all parts must be functioning properly to guarantee reliable operation.

Manufacturers usually supply specific operating and maintenance instructions for their equipment. Failure to utilize this information will result in unsatisfactory performance and equipment downtime. A preventive maintenance schedule should be established initially and then strictly followed until sufficient performance data exist to warrant modification of the schedule. Such programs vary with respect to the type of analyzer and the nature of its environment.

## E.4 DATA COLLECTION, INTERPRETATION, AND MANAGEMENT

A data management program is essential to collect and analyze the voluminous information collected via a modern sampling and instrumentation system. Data should be recorded promptly in a format easily interpreted and retrievable. Data must be interpreted promptly by comparison to clearly established and understood criteria. The interpretation must occur in the early stages of data analysis in order to assess the need for any corrective action, which, if necessary, must be rapidly communicated to personnel who can take appropriate corrective action. Interpretation of both short-term (hours to days) and longterm (weeks to months) trends is important.

Topics covered herein include:

- data collection
- data storage and retrieval

- data analysis and interpretation
- computerized systems

### E.4.1 Data Collection

Standardized log sheets for the purpose of recordkeeping should be developed for the various sample points throughout the plant. Such log sheets should be developed to record the calibration and maintenance of laboratory equipment and continuous analyzers to ensure the regularly scheduled preventive maintenance is being performed in compliance with the maintenance schedule. These records are a necessity in identifying sources of inconsistencies in data.

Information recorded on data log sheets should include the following:

- sample point location
- date and time of sampling
- limits or action levels
- sample temperatures
- plant load
- comments

Comments should include information such as the status of the plant at the time of data collection, action levels reached, and corrective actions taken. Examples of successfully used data sheets are provided in EPRI's Cycle Chemistry Improvement Program.(4)

Data from continuous analyzers may be collected manually by periodically logging values from local indicators, or by interpreting strip charts if the plant does not have a data acquisition system. Individual values logged from local indicators will generally be more accurate than values read from strip charts; however, local indicators do not provide the thorough summary of parameter fluctuations that the strip charts do.

### E.4.2 Automatic Data Collection and Storage

Continuous analyzers can be configured to send information directly to data acquisition systems, personal computers, or control room computers. Automatic data collection provides the same information as a strip chart but with greater precision and eliminates both the time necessary to evaluate strip charts and the element of human error.

### E.4.3 Manual Storage of Chemistry Data

Manual data storage and retrieval should include accessible files of completed data sheets, daily chemistry report forms, trending plots, and action level notifications. Each data sheet should be reviewed by plant personnel responsible for chemistry to ensure the water chemistry is within normal ranges for control and that any necessary corrective actions have been taken.

A computer-based system is more efficient for storing and managing larger quantities of data. These data can be entered manually or recorded directly from a data acquisition system. Computer storage of data allows past data to be easily retrieved and, depending on the system, also provides the capability to manipulate and analyze present and past data interactively.

### E.4.4 Data Analysis and Interpretation

Data analysis and interpretation provide for the identification of adverse trends and problems in system chemistry so corrective actions can be taken. This section will introduce the means by which data analyses and interpretations are accomplished.

The "eyeball" method, as the phrase infers, is a process for viewing of data as it is being collected to detect "out-of-spec" values and inconsistencies among the data.

Graphical plotting makes use of a visual, easily interpreted format that is easy to use, low in cost, and emphasizes the order of observation with respect to time.

Putting information into graphic form is recommended for all measured parameters so slow changes can be identified in a timely manner. This procedure should be done so as to result in a simple trend graph or a control chart. A trend graph is a plot of sample parameters versus time and should have a duration of at least 30 measurements to be useful in identifying a meaningful trend. A control chart is equivalent to a trend chart, with the addition of a zero deviation point and upper/lower control points, providing specific action limits. Such capabilities, as well as generation of mass balances and histograms, are standard features of most modern, computer-based data management programs.

### E.4.5 Roles of Plant Personnel in Water Chemistry Data Collection, Interpretation and Management

Plant personnel (typically technicians or operators) are responsible for the collection and analysis of samples, completion of data sheets, construction of graphical charts, and calibration of analyzing devices. The initial responsibility for chemistry program management lies with these individuals. They must be trained to recognize not only out-of-specification conditions, but also trends that appear to be abnormal. When either of these conditions occurs, they must be instructed, by procedure and training, to notify the appropriate personnel for initiation of corrective actions.

Supervisory personnel are responsible for a more detailed review of chemistry and trends. They must be able to explain recorded occurrences and make suggestions for corrective actions to be taken and then report their findings to management.

It is the responsibility of the operating personnel to be aware of sudden changes in operating parameters and to interpret and take corrective actions when conditions needing immediate attention arise. The operators must be adequately trained so they are able to perform the described duties.

### E.4.6 Expert Systems for Water Chemistry Management

An EPRI project was initiated for the development and demonstration of an expert system to gather and analyze plant chemistry data in such a way as to result in significant conclusions relative to the need for corrective actions, as well as what those corrective actions should be. The resulting software package, known as EPRI ChemExpert, offers a variety of capabilities and features of considerable value to fossil plants(9). These include:

- Real time displays
  - Cycle arrangement
  - Sample points and chemical feed points
  - On-line analyzers (location, current readings and status)
- Management of chemistry data
  - On-line analyzer readings (direct input)
  - Grab sample data (manual input)
  - Operating parameters (via interface with plant data acquisition systems or distributed control systems)
  - Reports and graphics
  - Data storage
- Data analysis and interpretation
  - Chemistry problem identification (over 30 problems)
  - Corrective action recommendations
  - Diagnostic capabilities based on EPRI chemistry guidelines and experience of experts in the field of fossil plant water chemistry
  - Tracking of on-line analyzer performance
  - Calculation of mechanical carryover and unit specific boiler water chemistry limits (units with drum boilers)
- Personnel training
  - Definitions of chemistry terms
  - Key chemistry concepts
  - Cycle chemistry tutorials
  - Chemistry control simulation

The ChemExpert software package currently consists of four separate programs. A customization program allows the user to define unit characteristics and cycle chemistry. Either two or three action levels may be specified by the user. A diagnostic program provides verification of analytical data, warning of chemistry readings outside of limits (including problem identification and recommendation of actions that should be taken), determination of pressure and carryover dependent limits for impurities in the boiler water of drum type units, and data storage, plotting and report preparation. A cycle description and maintenance program may be used as a database of unit equipment characteristics and for planning and scheduling of operation, maintenance and calibration functions related to the chemistry program. The training program is designed for beneficial use by plant operators and technical personnel responsible for cycle chemistry.

## E.5 VALIDATION OF CHEMISTRY DATA

Verification of chemistry data is generally required prior to initiation of corrective actions, not only to determine that action is, in fact, required, but also to assure that the contemplated actions are appropriate for the chemistry conditions which exist in the unit. As many chemistry conditions require rapid recognition, evaluation and response, it is imperative that those plant personnel present at the onset of possible chemistry excursions be capable of providing the verification function. At facilities that neither have chemistry specialists on site at all times nor utilize an expert system, it is therefore crucial that operators or technicians normally present on a "24/7" basis be trained to take the steps needed to verify chemistry data and proceed with corrective actions that may be required.

Conversely, responsibility for chemistry data validation measures, as preferably outlined in the plant Quality Assurance (QA) and Quality Control (QC) program, must remain the responsibility of technical specialists. The QA/QC procedures and other data validation functions should serve to demonstrate the statistical significance of the chemistry data, thereby minimizing any doubts or concerns that actions are needed or may be inappropriate when the verification process is followed and confirms the existence of a chemistry excursion. Chemistry data validation activities should therefore, be used proactively for best results. Plant cultures which apply them reactively (only or mainly after possible chemistry excursions or after chemistry-related damage has been experienced) or have no formal data verification programs are clearly at a disadvantage. Those facilities in the latter category often operate with a false sense of security when they provide suitable levels of chemistry surveillance capabilities and data verification procedures but fail to address data verification requirements.

The needs for data validation are by no means unique to the fossil electric industry. QA/QC programs are applied in innumerable applications, many of which have far more rigorous requirements than those of fossil plants. Important and obvious examples include medical technology, the aerospace and aeronautics industry, pharmaceuticals production, computer components and communications technology, defense applications, food processing, security systems, and nuclear power generation, to name but a few. As a result, the language of QA and QC features an extensive vocabulary, which often, unfortunately, constrains its application to areas where such action is elective, rather than mandatory. Fortunately, application of effective validation techniques to fossil plants requires familiarity with a relatively small number of terms and concepts, as summarized in the working definitions of Table E-2. Recognition of the importance of cycle chemistry data validation and quality has resulted in considerable effort on the parts of utility organizations, consultants, and instrument manufacturers to evaluate requirements of fossil plants and to establish manageable programs capable of meeting these needs(10-12). Ensuing discussions provide guidance on this important subject.

**Table E-2**
**Working Definitions of QA/QC Terms for Fossil Plant Chemistry Data Validation**

| | |
|---|---|
| **Accuracy:** | The agreement between the amount of a component measured by the test method and the amount actually present. Accuracy includes both precision and bias of the method. |
| **Precision:** | The reproducibility of a method when repeated on a homogeneous sample under controlled conditions, regardless of whether or not the observed values are widely displaced from the true value as a result of systematic or constant errors (also sometimes referred to "reproducibility").<br>Note. Both accuracy and precision can vary as a function of the concentration being measured. They can also vary due to other factors such as temperature, concentrations of interferences, etc. Therefore, statements of precision and accuracy should be expressed in terms of the concentration over the range of concentrations to which they apply. If precision and accuracy are stated in percent, the range over which the relative precision or accuracy applies should be explicitly stated (e.g. "a relative accuracy of ± 10% if the amount present is achieved over a span of 0.01 to 10 mg/L").<br>$S_t$ Interinstrument precision—the standard deviation of the measured values of a specific parameter obtained by multiple continuous instruments (of the same type) at the same value in homogeneous samples of the same composition (matrix). Also, interlaboratory precision when referring to grab sample analysis by multiple laboratories on samples of the same matrix as defined by ASTM D 2777-86.<br>$S_o$ Intrainstrument precision—the pooled standard deviation of the measured values of a given parameter obtained by multiple continuous instruments (of the same type) on repeated measurement of the same specified value of the parameter in homogeneous samples of the same sample composition (matrix) when each measurement follows an interval of time where the instrument was equilibriated to a value of the parameter that was significantly different from that specified. Also, the interlaboratory or single operator precision, as defined in ASTM 2777-86, when referring to grab sample analysis by multiple laboratories on samples of the same matrix. |
| **Bias:** | The persistent positive or negative deviation of the method average value from the assumed or accepted true value.<br>Note: Both precision and bias vary as a function of the concentration being measured. They can also vary because of factors such as temperature, concentrations of interferences, etc. Therefore, statements of precision and bias should be related to the concentrations to which they apply. |
| **Sensitivity:** | The minimum observable difference in very small amounts of a component in a sample. Also, sometimes totally incorrectly referred to as "detection limit" or "detectability." |
| **Range:** | The span of amounts or concentrations over which a component can be measured monotonically in a sample. Also sometimes referred to as "span." Usually, the range covers the concentrations for which the method or instrument is actually calibrated. |
| **Response Time:** | The period of time required for an analyzer to properly measure the components in a sample from the time the sample enters the analyzer. Also known as "analyzer dead time."<br>Note: Response time should be quantified by referencing the time necessary to provide a certain percentage response to a step change in concentration. Preferably the response time for a 95% response should be provided; however, a statement of response time in terms of a somewhat lesser response (such as a 90% response) may provide sufficient information. |
| **Sampling Error:** | The deviation between the true concentration, pH, conductivity, etc. in the stream prior to sampling and the concentration in the sample presented to the analyzer; or contained, in the sample container prior to preservation or transportation for analysis. |
| **Analytical Interference:** | Analytical errors caused by interference from some chemical compounds in the mixture being analyzed. Interferences should be listed for all water treatment chemicals used and for their decomposition products. |

### *E.5.1 Precision, Accuracy, Bias and Drift*

The American Society of Testing and Materials (ASTM) defines *accuracy* as "a measure of the degree of conformity of a single test result generated by a specific procedure to the assumed or accepted true value and includes both precision and bias".(18) In other words, it is a measure of exactness or correctness of a value and is affected by both random sources of error (precision) and systematic error (bias).

ASTM defines *precision* as "the degree of agreement of repeated measurements of the same property, expressed in terms of dispersion of test results about the arithmetical mean result, obtained by repetitive testing of a homogeneous sample under specified conditions. The precision of a test method is expressed quantitatively as the standard deviation computed from the results of a series of controlled determinations".(18) In other words, precision is a measure of the reproducibility or random uncertainty of the data set. In the absence of systematic uncertainty, data should follow a random distribution pattern. This pattern is characterized by the normal distribution curve shown in Figure E-3.

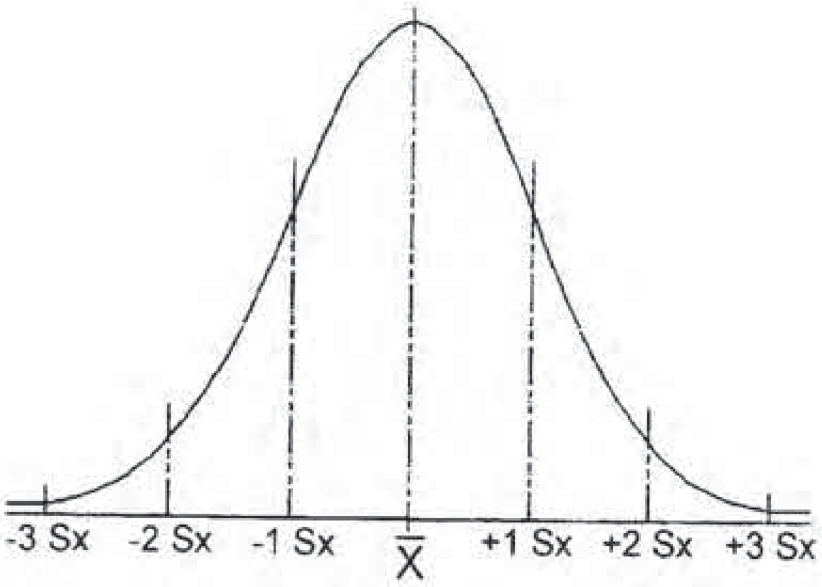


**Figure E-3**
**Normal Distribution Curve for Random Data**

A measurement of precision is given by the standard deviation ($S_x$) of the data set. Standard deviation can be used to express the distribution (or spread) of the data around the average value of the data set $(\overline{X})$. In many cases, it is convenient to express the standard deviation relative to the concentration as a relative standard deviation (RSD), sometimes expressed as the percent relative standard deviation (%RSD):

$$\text{RSD} = \left[S_X / \overline{X}\right] \qquad \text{(eq. E-1)}$$

and

$$\%\text{RSD} = \left[S_X / \overline{X}\right] \times 100\% \qquad \text{(eq. E-2)}$$

In this way, precision can be compared at varying concentrations and %RSD can be used to quantify changing precision as a function of concentration. Understanding %RSD can provide insight into instrument detection limits and instrument linearity. The %RSD tends to be very large for very low analyte concentrations. For example, for concentrations at the decision limit ($L_C$), %RSD » 60%; at the detection criteria ($L_D$), %RSD » 30%; at the determination limit ($L_Q$), %RSD » 10 (as specified by Currie(14)).

ASTM defines bias as "the persistent positive or negative deviation of the average value of a test method from the assumed or accepted true value".(5) If the data are randomly distributed, accuracy expresses the deviation from the expected value as shown in Figure E-4. Bias is called recovery when expressed as a percentage of the true value. Thus, accuracy may be expressed as a combination of recovery and relative standard deviation at a given true value.

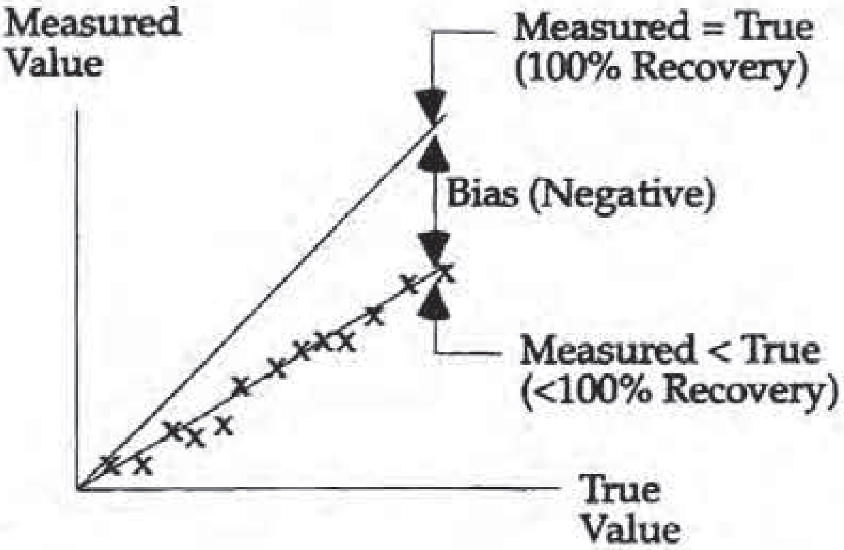


**Figure E-4**
**The Relationship Between True Value, Measured Value, and Bias. The bias in the example shown is negative, but a positive bias is also possible.**

In some cases, it is convenient to express accuracy requirements in terms of percent deviation from the target value (i.e., from the true value):

$$\%\ \text{Deviation} = \left[\overline{X} / \text{Target}\right] \times 100\% \qquad \text{(eq. E-3)}$$

Many measurement methods are more accurate at the high end of the range covered, leading to percent deviation values that change over the dynamic range of the measuring instrument. For convenience, average values may be cited for specific ranges of the parameter measured, e.g., ±20% for 1-100 ppb and ±10% for 100 ppb - 1 ppm. In some cases, a lower limit of accuracy may also be cited, e.g., ±0.5 ppb or ±10%, whichever is larger. Clearly, using percent deviation limits in this was is imperfect and does not address the overall capability of the instrument.

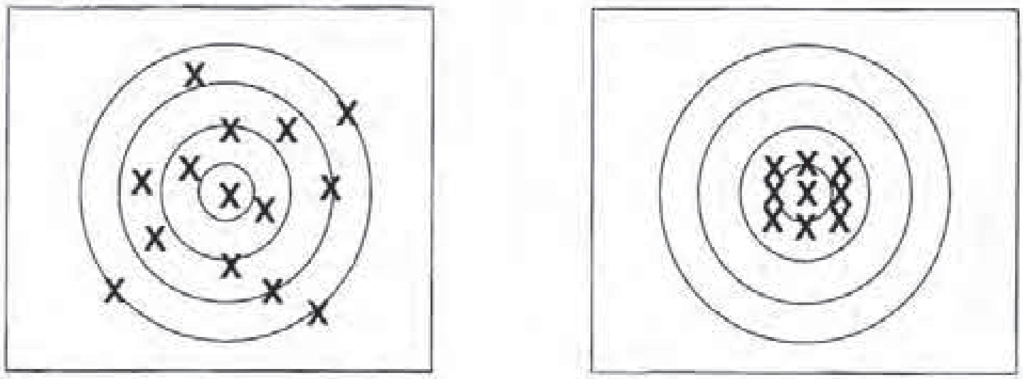
A more scientific approach utilizes the Student's "t" test(16) This approach measures accuracy as a function of the deviation from the expected value at a specified confidence coefficient, usually 95%. The test assesses the instrument's accuracy based on observed instrument behavior and is most appropriate for instruments that are used for diagnostic purposes. The Student's "t" test mathematically determines whether a statistically significant bias exists at a specified confidence coefficient. In this way it can be said conclusively that a statistically significant bias does or does not exist.

Several commercially available programs can be used to calculate statistics (such as percent deviation or the Student's "t" test), make data comparisons, and archive information. Selection of a specific program will depend upon a number of factors, including a user's data acquisition capabilities and data management needs.

Special testing can be performed to verify accuracy and precision of instrumentation or grab sample analyses over various working ranges based on the needs of the user. The precision and accuracy of a measurement may be affected by many factors, such as temperature, concentration of reagents, interferences, availability of traceable calibration standards at the concentration expected in the samples, calibration procedure, and sample size, as well as variations that develop from one instrument, operator, or laboratory to another. Consequently, accuracy and precision statements should include the range of conditions over which they apply.

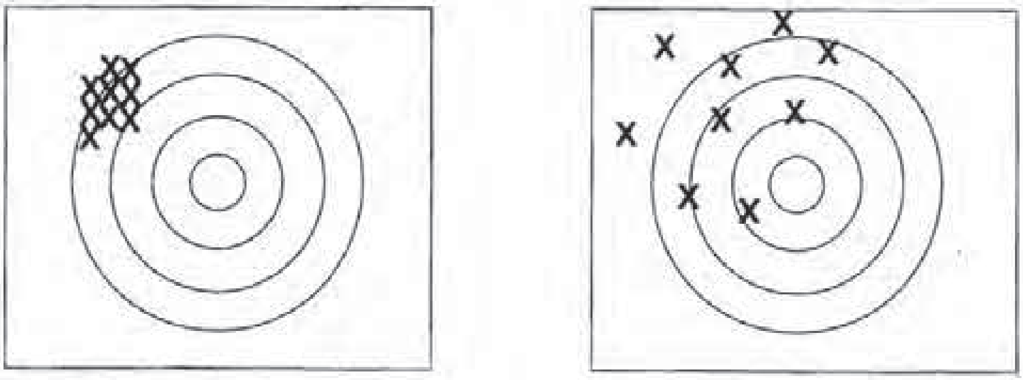
While the accuracy of an instrument can be determined immediately when it is placed into service, drift develops over time. Drift may be defined as the change in bias in a specified period caused by changes in the electronic zero of the instrumentation but, more particularly, by deterioration of the sensor. The American National Standards Institute (ANSI) defines drift in ANSI Standard C85.1-1963 as "an undesired change in output over a period of time, which change is unrelated to the input, environment, or load."(17) Drift is an important example of systematic errors (Figure E-5), which must be minimized to ensure data quality.

Instrument manufacturers do not always provide precision, accuracy, bias and drift information. Such information must therefore be determined by the user.



(a) Large random errrors, no systematic errors (large scatter of results about the true value)

(b) Small random errors, no systematic errors (small scatter of results about the true value)



(c) Small random errors, large systematic errors (small scatter of results but not about the true value)

(d) Large random errors, large systematic errors (large scatter of results but not about the true value)

Source: S.P. Hall. Quality Control in Power Plant Laboratories, Illinois Power Company, 1983.

**Figure E-5**
**Random and Systematic Errors**

## E.5.2 QA/QC for Sampling Systems

The effect of sampling errors on chemistry data are potentially significant and should be minimized through proper equipment selection. As shown in Table E-3, there are many sources of sampling errors. Total sampling error can span several orders-of-magnitude, much larger than typical analytical errors. Except for the error caused by improper withdrawal (collection) of the sample, other errors can be determined by analyzing known samples before and after the sampling system at otherwise identical sample conditions (temperature, flow, chemical species).

**Table E-3**
**Typical Sampling Errors**

- Sample Withdrawal — not representing the sampled stream
  - — not representing all phases (solid, liquid, gas)
- Deposition in sample tubing and other components
- Deposit release
- Chemical reactions in sample line or cooler
- Deposition in the pressure reducing device
- Dissociation of water in the pressure reducing device
- Leakage of cooling water into the sample in the cooler
- Corrosion of the sampling system—generation of corrosion products

Sample withdrawal error can be determined by using alternate sampling taps and nozzles or a different sampling location. Experiments have shown that for superheated and wet steam sampling, an isokinetic sampling nozzle is needed, correctly located in the steam pipe, such as described in EPRI TR-100196, *Development of a Steam Sampling System.*(3) The same type of nozzle is needed for feedwater when sampling for suspended oxides. (Also see E.2.3 and E.2.7) In sampling boiler water from the steam drum, the sample could be mixed with the incoming feedwater or separated moisture and thus be different from the water in the boiler tubes.

### *E.5.3 QA/QC for On-Line Instruments*

#### Instrument Calibration and Standardization

Establishment of effective calibration and standardization procedures are the starting point of the QA/QC program. Since manufacturer's procedures vary widely in their ability to ensure traceable accuracy, it is advisable to independently calibrate the instrument components, especially the sensing elements, after the manufacturers' procedures have been followed. Independent calibration is particularly advised for temperature sensing elements in conductivity, pH, and other instruments where automatic temperature compensation is an integral part of the instrument measurement process. For high-purity water, conductivity instrument cell calibration by comparison with a standard reference conductivity cell and measurement bridge (without temperature compensation and on the same sample flow) is recommended initially and possibly at various later intervals, depending on the fouling characteristics of the particular sample stream. For pH, calibration is best accomplished with flowing standards using two concentrations, as discussed below, one above and one below the desired measurement range, following completion of the manufacturers' initial procedures.

## Validation of On-Line Monitoring Instruments

At least four approaches to validation of on-line monitoring instruments are available: the reference sample procedure, the line sample procedure, instrument comparison, and the standard injection method. The first two approaches are described in ASTM D3764(18), a standard practice that was developed for validation of process stream analyzers in petroleum or petrochemical product steams, but which is equally applicable to power plant water streams. The last two methods are perhaps better suited to calibration of instruments but they have been used on occasion for validation purposes.

The reference sample procedure involves introduction of reference standard samples into the analyzer and subsequent comparison of the measured values with the reference values. For instance, to validate a pH monitoring device, the plant water stream could be diverted and replaced with a standard buffer solution flowing for a period long enough to allow the pH measurement. This approach is particularly useful for validating new and replacement analyzers to ensure they have been installed and commissioned in accordance with the manufacturer's recommendations.

The line sample procedure makes use of a plant water stream of interest and involves taking at least seven grab samples for laboratory analyses and comparing these results with those obtained from the on-line analyzer at the times of sampling. The data are evaluated statistically (Student's "t" test) to validate the analyzer. Suitable statistical software packages are available from some instrument suppliers to help perform this task. The line sample procedure is used more as an operational check on an analyzer that has been previously validated, and is useful in establishing the ongoing precision and bias of an analyzer in service.

The third approach involves comparing the results obtained from the on-line analyzer (A) with those obtained from a second on-line analyzer (B) exposed simultaneously to the same water stream. The latter may be a high quality, portable unit that is first validated and calibrated in the laboratory, then attached to the plant water stream system when needed to validate or calibrate analyzer A. Measurements on analyzer B are assumed to be correct and the accuracy of analyzer A can be assessed by comparing measurements on the two instruments. This method is useful for validating and verifying analyzers that measure very low analyte concentrations where the grab sampling process may introduce significant error. However, in such cases, analyzer B must first be calibrated using waters having concentrations near those needing measurement in the plant water stream. Clearly, the value of this method is very dependent on the precision and lack of drift in instrument B during the validation period.

The standard injection method can be considered a variation of the reference sample procedure in that it involves the introduction of standard solutions into the analyzer. However, the standard injection method does this by injecting the standard solution at a controlled rate into the plant water stream, also flowing at a known rate, such that the concentration of the resulting diluted standard solution can be calculated accurately. The method is otherwise similar to the reference sample procedure. In high-purity water systems, it has the great advantage of presenting the standard sample without contamination and permitting measurement with similar matrix and flow.

A general protocol for establishing the validity of on-line water analysis instruments is provided in ASTM D3864.(19) More specific protocols, detailed in EPRI Report GS-7556(20), were followed in a collaborative validation program at four power plant sites. As with the grab sample methods, on-line instruments must be validated by collecting a minimum of six data sets at each concentration level. For the four-plant collaborative study, this minimum requirement was satisfied for all of the methods except three: on-line ion chromatography, total organic carbon, and dissolved oxygen. Nevertheless, these latter three methods should be considered for use, although treated with appropriate caution.

The successful validation of on-line instrumentation requires proper installation of water and steam sample lines; close control of sample temperature, pressure, and flow rate; preparation of standard samples; and accurate analysis of grab samples. These requirements are discussed in more detail below.

## Synthesizing Standard Samples

Validation of the measurement methods can be accomplished using standard solutions (samples), over a range of well defined concentrations, produced in a continuous flow. Grab samples can be taken from this flow or the flowing standard solution can be directed to the on-line monitoring equipment under test. A method of synthesizing flowing standard solutions was described in EPRI Report GS-7556 Volume 1.(2) It involves the continuous production of very high quality reagent water, flowing at a constant, continuously measured rate, into which one or more concentrated standard solutions are injected continuously with metering pumps.

The very high quality reagent water is prepared from steam condensate which is passed through a de-oxygenation exchange bed, a carbon bed, a mixed bed and a 0.2-micron micropore filter. If source water of lower quality than steam condensate (e.g. makeup storage tank water) is used, additional purification steps may be needed. To avoid precipitation of the chemicals in the concentrated standards, Cl, $SO_4$, and organic acids are prepared in an acid solution, and Na, $HCO_3$, $N_2H_4$, $NH_3$, and $SiO_2$ are prepared in an alkaline solution; oxygen is injected as air-saturated (STP) pure water. Standard concentrations are calculated from the continuously logged standard solution flow, the metering pump flow, and the assayed concentration of the concentrated standard solutions. The metering pump flow is calculated from calibration curves, established from the rate of change of weight of the vessels containing the concentrated standards, as measured by an electronic analytical balance.

Sample synthesizers that are capable of delivering sample streams of known chemical composition to several analyzers are also commercially available.

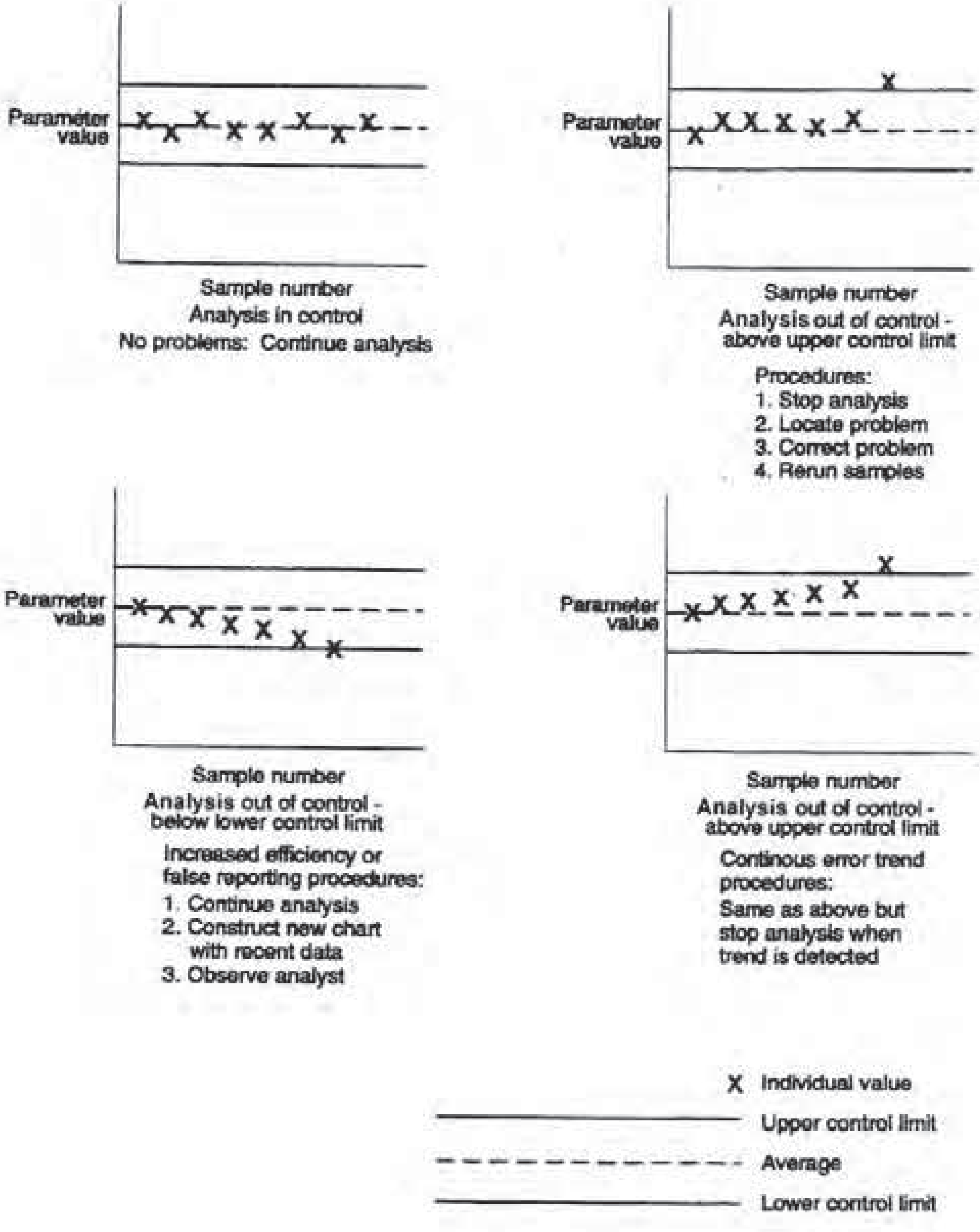
## Potential Problems in Preparation of Standards

Standards containing ammonia and organic acids (acetate, formate, etc.) may decompose or change in concentration before use unless care is taken to avoid this. Changes in composition can be prevented or minimized by using the standards immediately after preparation, or refrigerating them to 4°C during storage. The refrigerated samples should be allowed to come to room temperature just before use not only to avoid effects of temperature on the accuracy of the metering pump calibration curves, but also to avoid condensation on the outside of the standard solution tanks which, during creation of the calibration curves, would cause a weighing error.

### E.5.4 Charting of Chemistry Data to Track Instrument Performance

Whatever the interval and concentration selected for the QC tests on each instrument, including those used for analysis of grab samples, the results should be recorded on a control chart. General examples are presented in Figure E-6. As an example using data from an on-line cation conductivity instrument, charts such as those show in Figures E-7 and E-8 record the RRs and $RSD_o$s obtained from each month's QC test. The upper and lower acceptance limits for RR and $RSD_o$ are shown along with the past test results and the most recent results from the example QC test, those for month 12. Again, the use of relative recovery and relative standard deviation simplifies charting as well as the necessary calculations since it is likely there will be small differences in the true concentration used in each QC test episode.

The most useful feature of control charts is for the detection of trends in instrument performance that may required alternation of the test frequency or the instrument maintenance and calibration procedures. A trend of decreasing cation conductivity RR, as in Figure E-7, suggests a greater degree of exhaustion of the resin cartridge at the time of the tests. The latter could be the result of increased sample flow rate, increased amine level in the sample, decreasing quality of the fresh cartridge, or change in the conductivity cell constant. A review of the record of specific conductivity and pH indicates amine level to be relatively unchanged over the last several QC tests. Thus, the RR trend, when coupled with the observed increase in RSDo, noted in Figure E-8, suggests that the first priority for potential corrective action would be the careful review of the resin cartridge maintenance procedures.



Analysis in control
No problems: Continue analysis

Analysis out of control - above upper control limit

Procedures:
1. Stop analysis
2. Locate problem
3. Correct problem
4. Rerun samples

Analysis out of control - below lower control limit

Increased efficiency or false reporting procedures:
1. Continue analysis
2. Construct new chart with recent data
3. Observe analyst

Analysis out of control - above upper control limit

Continous error trend procedures:
Same as above but stop analysis when trend is detected

Source: S.P. Hall. Quality Control in Power Plant Laboratories, Illinois Power Company, 1983.

Figure E-6
Laboratory Quality Control Charts

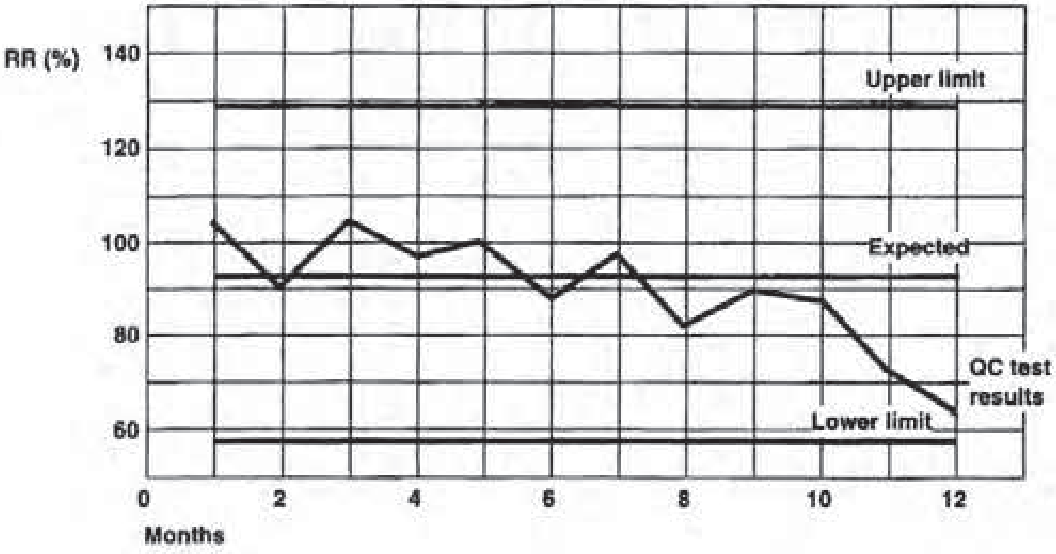


Figure E-7
Cation Conductivity Control Chart, RR%, CC = 0.5 μS/cm

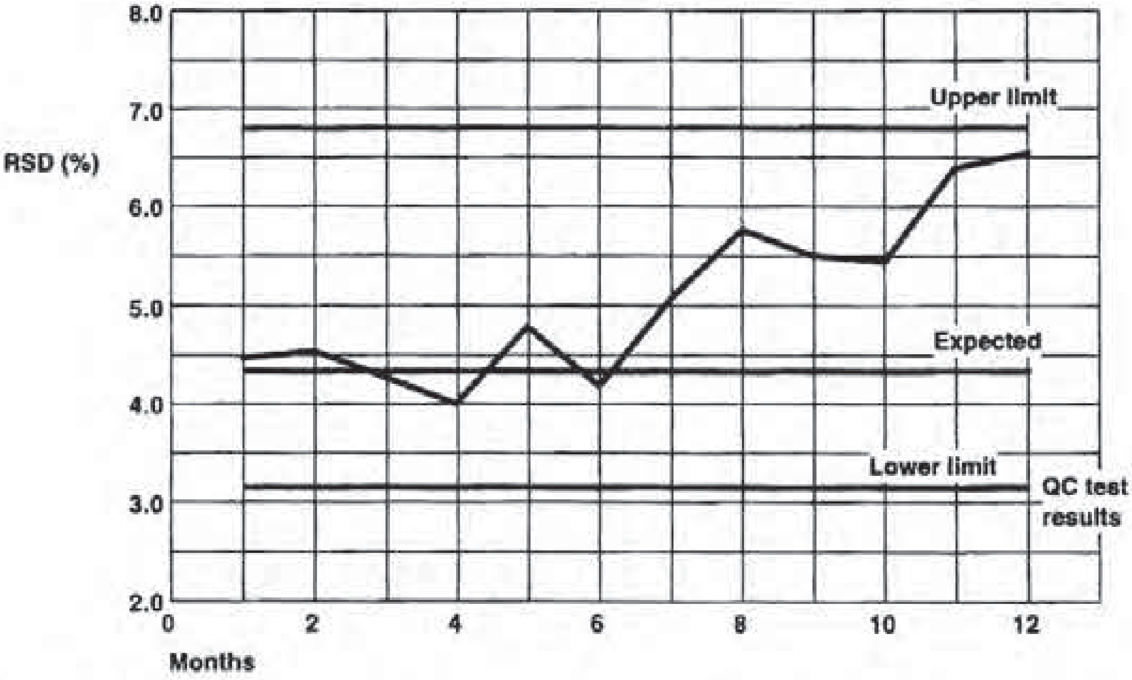


Figure E-8
Cation Conductivity Control Chart, RSD%, CC = 0.5 μS/cm

### E.5.5 Interlaboratory Assessment of Grab Sample Analysis Methods

For individual plants, the requirements for grab sample analysis include use of appropriate sample withdrawal and conditioning equipment, use of appropriate sample collection techniques and preservation methods and charting of data. As these requirements have been covered previously, results of interlaboratory assessment of available grab analysis methods are summarized.

Five methods of analyzing grab samples for trace substances in high purity water were validated in an inter-laboratory program, designed in accordance with ASTM D2777-85.(21) Up to 20 participating laboratories developed precision and recovery estimates, limits of detection, and limits of quantification for the following methods:

- Proposed Method of Test for Low-Level **Sodium** in High Purity Water by Graphite Furnace Atomic Absorption Spectrophotometry (ASTM Draft 3)
- Proposed Method of Test for Low-Level **Calcium** in High Purity Water by Graphite Furnace Atomic Absorption Spectrophotometry (ASTM Draft 1)
- Proposed Method of Test for low-Level **Magnesium** in High Purity Water by Graphite Furnace Atomic Absorption Spectrophotometry (ASTM Draft 1)
- Standard Test Methods for Trace Anions in High Purity Water by Ion Chromatography (ASTM D5542(22), Method A: **Chloride, Phosphate, and Sulfate**)
- Standard Test Methods for Trace Anions in High Purity Water by Ion Chromatography (ASTM D5542(22), Method B: **Fluoride, Acetate**, and **Formate**)

ASTM practice calls for a minimum of six data sets at each concentration level in order to derive valid estimates of performance. Because insufficient data were generated in the study for the following grab sample methods, they could *not* be properly validated but, with appropriate caution, they should be considered for future use:

- Proposed Method of Test for Trace **Cations** in High Purity Water by Ion Chromatography (ASTM Draft 1)
- Standard Test Method for Low-Level **Total Silica** in High Purity Water by Flameless Atomic Absorption Spectroscopy (ASTM D4517-85(23))
- Standard Test Method for Low-Level **Total, Organic, and Inorganic Carbon** in High Purity Water by Ultraviolet (UV) or Persulfate Oxidation, or Both, and Infrared Detection (ASTM D4779(24))

The results of this validation study were reported in 1988(25) and presented in detail in Appendix E of EPRI Report GS-7556 Volume 1. In this program, grab samples were collected in special sample bottles from flowing synthetic standards (prepared as described above), then refrigerated until they were analyzed.

### E.5.6 EPRI Experience With Chemistry Data Validation

The EPRI RP2712-3 project provided many useful insights with respect to validation of chemistry data collected from operating fossil plants.[2.20]

For all continuous instruments, a satisfactory QC program must include the periodic use of a flowing standard sample that is presented to the instrument under the same conditions that exist for the samples from the cycle. This procedure is especially important for instruments on high-purity sample streams where grab samples are easily contaminated. Continuous pH instruments on high-purity water are best calibrated, as well as validated, by passing through the flow cell, standards of composition similar to those of the samples to be measured, as described in ASTM D 5128.

For power plant operation where ammonia is used for pH control in the feedwater and steam, high-purity water with 100-500 µg/L $NH^3$ makes suitable standards. Where the use of a flowing standard is not feasible, a neutral ionic buffer should be added to the grab sample before measurement of the sample pH with an independent reference instrument. In neither case, use of flowing standards or grab sample comparison, should the pH cell be standardized with concentrated buffer solutions at any time other than the initial installation of new electrodes.

Where grab samples collected in parallel with the continuous instrument must be used for quality control, a minimum of seven replicate samples must be collected and analyzed under steady-state conditions, one for each of the seven required separate instrument datapoints, at a concentration of interest (see following section). The methods of analysis of the grab samples also must have appropriate quality control, preferably using traceable standards run "blind" by the analysts, on the basis of one standard per day or one per 10 samples analyzed, whichever is greater.

During the EPRI RP2712-3 project[2.20], no determination was made of the optimum frequency at which each type of continuous instrument should be validated. However, the two validation runs at each site during RP2712-3 were separated by an approximately two-week interval, which was sufficient for some instruments to show substantial change in bias (measured concentration minus true). The bias for the continuous $SiO_2$ analyzer, for example, increased from 8 to 12 µg/L over that time. Specific conductance, the most stable and precise of the continuous instruments, showed at a level of 2.0 µS/cm, an increase in bias from 0.14 µS/cm to 0.42 µ/S/cm. Therefore, a conclusion can be drawn that the frequency of validation at a plant should be initially set at no less than once per month. This validation should be performed at a single concentration selected to be in the middle of the normally encountered operation range, until sufficient validation data is gathered for each instrument to warrant changing the frequency. More test levels as well as more frequent tests may be required in some circumstances and with certain instruments.

#### Performance Determination

Seven replicate presentations at the same desired test level are necessary to develop a satisfactory estimate of intrainstrument (single instrument) standard deviation ($S_o$) for comparison with established precision standards for a particular instrument at that level. The presentation of each of the seven flowing standard replicates must be preceded by a reasonably short period of stable instrument reading on the regular sample source (or other source) where the concentration is different from that of the flowing standard. This interlude should be of such length that >90% of the expected reading is attained.

Seven replicates are required at a particular concentration in order to develop meaningful acceptance limits by which to determine if the instrument measurements are in control—that they perform with the expected precision and accuracy. The large number of replicates required for statistically useful limits led to the above recommendation that only one test level be selected for the initial QC program for each instrument. When using only one test concentration for the QC test for each instrument, it is important that the same test level be employed for the QC test each month, or other chosen interval, since the acceptance limits vary considerably with test concentration for some instruments while remaining nearly constant for others.

### Acceptance Limits

The standard deviation and mean of the seven replicate instrument measurements can be compared to the expected precision and mean previously determined for the particular instrument being evaluated. Since the flowing standard method may not produce exactly the same numerical results when performed at different times, (whether at the same plant or at different plants), a useful procedure is to express both the standard deviation and the mean in terms relative to the true value of the standard used. Thus, the relative recovery (RR) is the measured mean concentration of the seven replicates divided by the true concentration (T) expressed in percent, X/T x 100. Similarly, the intrainstrument relative standard deviation ($RSD_o$) is the standard deviation of the seven replicates divided by the mean concentration expressed in percent, $S_o/X$ x 100. Both the RR and $RSD_o$ determined from the QC test can then be compared with values shown in Table E-4 for the nearest true concentration, since both RR and $RSD_o$ can be considered constant for a reasonable range on either side of the selected value. The calculated value of RR actually obtained for a validation should not be greater than the upper value nor less than the lower shown in Table E-4 for RR at the selected true value. Similarly, the calculated $RSD_o$ should not exceed the upper nor be less than the lower value shown for $RSD_o$ in Table E-4.

### Use of Acceptance Limits in QC

A QC test of a particular cation conductivity (cc) instrument, for example, would start with presenting the instrument with a flowing standard sample, with a desired target cc of say 0.5 µS/cm. The standard would be presented seven times in alternate succession with a nonstandard sample with a different cc, say 0.25 or 1.0 µS/cm. Sufficient time would be allowed for the reading to stabilize. The true conductance of the flowing standard was found to be say 0.55 µS/cm based on the analysis of the concentrate, and the dilution ratio used to produce the flowing standard. If the mean of the seven replicate cc results, X, was 0.34 µS/cm, the RR would be X/T x 100, or 62%. Reference to Table E-4 shows cc = 0.5 µS/cm is the closest to the 0.55 µS/cm standard. The corresponding RR shows an upper acceptance limit of 130% and a lower limit of 59%. Therefore, it was concluded the instrument bias was within control.

**Table E-4**
**Continuous Instrument Acceptance Limits, 95% Confidence Interval (Based on Seven Replicates)**

| | True Concentration | Relative Recovery (1%) | | Intrainstrument Relative Standard Deviation (%) | |
|---|---|---|---|---|---|
| | | Lower | Upper | Lower | Upper |
| Specific cond. (µS/cm) | 1 | 79 | 119 | 3.7 | 7.4 |
| | 2 | 89 | 109 | 3.6 | 7.4 |
| | 5 | 93 | 105 | 3.6 | 7.4 |
| | 10 | 94 | 104 | 3.6 | 7.4 |
| Cation cond. (µS/cm) | 0.1 | 79 | 115 | 6.5 | 14.3 |
| | 0.2 | 70 | 121 | 4.4 | 9.7 |
| | 0.5 | 59 | 130 | 3.1 | 6.8 |
| | 1.0 | 53 | 135 | 2.6 | 5.8 |
| Na (µg/L) | 1 | 5 | 372 | 5.8 | 11.2 |
| | 2 | 1 | 243 | 4.7 | 9.0 |
| | 5 | 57 | 153 | 3.7 | 7.1 |
| | 10 | 74 | 124 | 3.3 | 6.4 |
| $NH_3$ (µg/L) | 100 | 61 | 145 | 7.5 | 18.7 |
| | 200 | 86 | 110 | 7.6 | 18.8 |
| | 500 | 92 | 97 | 7.6 | 18.9 |
| | 1000 | 93 | 94 | 7.6 | 18.9 |

Likewise, assume the seven replicate cc's yield a $S_o$ of 0.22, and an $RSD_o$ of 6.5% ((0.22/0.34) x 100). Examination of Table E-4 for cc = 0.5 µS/cm shows that the $RSD_o$ should not be less than 3.1% nor greater than 6.8% for the instrument to qualify as producing acceptable results. Since both the RR and the $RSD_o$ are within the acceptance limits, the instrument is operating in control.

Where continuous water quality instruments of a given type can be supplied simultaneously with an alternative high-quality water supply, useful information can be gained on multiple-instrument precision. Multiple-instrument precision has been shown to be generally smaller than true interinstrument precision but greater than instrainstrument precision. Thus, the RSDs obtained from alternative water supply tests normally can be expected to exceed slightly the range of acceptance limits in Table E-4, which are based on intrainstrument precision. No information can be obtained from alternative water supply tests, however, on relative recovery unless the composition of the alternative water supply can be established independently and with sufficient accuracy.

## E.6 SUMMARY

A quality assurance (QA) program for cycle chemistry data is essential if comparisons are to be made between measurements at different points within the cycle, between the same point in the cycle in different plants, and between specific points in the cycle and the plant's operating chemistry limits and action levels. The QA program must include quality control (QC) procedures for both grab sample and continuous instrument measurements. To follow the instrument manufacturers' calibration procedures is generally not sufficient, as these procedures seldom employ traceable standards. More importantly, they do not determine reproducibility (intra-instrument standard deviation) nor recovery so that instrument performance may be documented and trends in performance readily observed. Periodic validation of measurement procedures, especially continuous instrument performance may be documented and trends in performance readily observed. Periodic validation of measurement procedures, especially continuous instrument procedures, by making replicate measurements on a continuously flowing standard generates a record than can be compared readily with suggested acceptance limits as derived from the EPRI RP2712-3 program. Charting the record of validation results allows early detection and correction of problems with instrument accuracy. Close control of cycle chemistry requires accurate chemistry measurements.

Analytical quality control must be incorporated into laboratory procedures if reliable results are to be obtained. A quality control program provides for the detection/correction of problems and statistical verification of performance. The objective of such a program is to reduce measurement errors to a minimum so data can be used reliably to monitor and control cycle chemistry.

Unacceptable analytical variability arises from many sources. These include:

- incorrect analytical procedures
- calibration errors
- poor technique in following analytical procedures
- degradation of reagents utilized in analyses
- improper sampling procedures, contamination of the sample during collection and storage, reaction of the sample with the sample container
- chemical reactions during sample storage
- organic growth of bacteria and algae in the sample container

Quality control programs must provide guidelines for calibration and standardization of all laboratory equipment and reagents; and, they must establish procedures for estimating precision, bias, and sensitivity for the analytical methods performed. Limitations in the availability of equipment, number of samples, or time and experience of personnel can affect the reliability of the data obtained. Therefore, quality assurance procedures must be developed specifically in consideration of each plant's needs and abilities.

Systematic and random errors must be controlled to the maximum practical extent before evaluating precision and accuracy. Random error is present in any set of analyses in which repeated measurements are taken on the same sample. Random errors are the scatter of measurements about the true value. Systematic errors are referred to as bias and result from a tendency for the data to be greater or smaller than the true value.

Reduction in systematic errors can be accomplished through proper analytical procedures, traceable calculations, optimum personnel performance, and proper purity of reagents used in all analyses. Reagent water is a major source of systematic error; therefore, care should be used in its preparation to avoid contamination.

Various methods of evaluation of performance are available. A convenient way of monitoring the precision and accuracy of a method is to construct control charts. Control charts are used to evaluate the quality of the measurement process. Individual, multiple sample, and X-R control charts can be generated. Individual and multiple control charts operate similarly; however, multiple control charts span a range of concentrations, which avoids potential bias. The X-R control chart incorporates changes in the mean, X, and changes in the standard deviation, S, thereby making it the most useful of the three charts available.

Confidence in measurements in strengthened by inter-laboratory as well as intra-laboratory comparisons. Inter-laboratory programs should be used to establish agreed-upon requirements and laboratory procedures necessary to achieve desired quality standards. An independent facility should then inspect laboratory equipment and evaluate performance. Intra-laboratory programs identify the variability of measurement obtained when a single laboratory measures a sample repeatedly. System audits also provide valuable quality assurance information. A system audit is an investigation of the interaction of all laboratory procedures. The audit should be performed at appropriate intervals to guarantee that each aspect of the QC program is operating efficiently. A performance audit of an individual instrument is based on the outcome of the analyses of a "blind" standard sample, either on an inter-laboratory or intra-laboratory level.

A quality control program must be implemented for all analyses and must be evaluated on a regular basis to be effective. A formal quality assurance program, with written instructions and formal documentation of its implementation, is required. Plant chemistry manuals should also reflect quality control provisions. Analytical procedures and analytical evaluation methods must be established to detect quality control problems early and correct them as soon as possible. When properly executed, a quality assurance program will provide measurements of the desired precision and bias, together with the associated documentation.

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# F

# UNIT SHUTDOWN, LAYUP, STARTUP, CYCLING AND PEAKING

Initial efforts by EPRI to establish cycle chemistry guidelines for fossil units emphasized normal unit operations, including baseload operation, load cycling, and peaking service. Implementation of these guidelines in fossil plants around the world led to significant improvements for many organizations. At the same time, however, it also became apparent that the chemistry must be properly monitored and controlled during shutdown and layup, and that doing so was the only way in which organizations applying the guidelines could attain all of the cycle chemistry program goals (Section 1). EPRI benchmarking activities further reflect the relationship between effective shutdown, layup and startup procedures and the ranking of individual cycle chemistry programs.

In the absence of proper shutdown and layup procedures, the cycle is vulnerable to contamination and corrosion activity.

For example, during off-load conditions, deposited impurities may have been released into the circuit or have entered from outside, e.g. condenser leaks, carbon dioxide ($CO_2$) with air in-leakage. Therefore, it is important to consider the effects on the feedwater and steam cation conductivity, silica, sodium, chloride and sulfate concentrations during startup. If there is a leak in the reheaters, $CO_2$ and, more importantly, flyash and sulfur dioxide, ($SO_2$), may be drawn in, resulting in acidic condensed steam in the reheaters. There is some evidence that silica is washed off turbines during shutdown and startup. Oxygen concentrations in the feedwater require special consideration. Restriction will need to be applied to this parameter, but some relaxation from the normal EPRI guideline values should be possible until steady state operating conditions are achieved.

During unit startup, the effect of chemistry control impacts on the potential for fluid-side deposits, corrosion and impeding of heat transfer (furnace tube metal overheating). Focus should be directed towards the identification and correction of the root cause of the chemical control problem.

## F.1 SHUTDOWN

The shutdown periods should be viewed as a continuum of the good practices used during normal operation. For mixed-metallurgy systems, it is necessary to maintain reducing conditions in the condensate and feedwater. Having a negative ORP near the optimum value of -300 to -350 mV best ensures this and will maintain the protective cuprous oxide ($Cu_2O$) layer on the surface of copper-based feedwater heater tubes.

The shutdown period is a prelude to the layup of the unit. Layup procedures are determined by the duration of the layup, whether short or longer term. The use of nitrogen blanketing the shell side of feedwater heaters to protect feedwater heaters is presently practiced by only 13% of the recently surveyed utilities[1]. Nitrogen blanketing serves an essential purpose in preventing oxygen ingress during short or longer-term layups.

Nitrogen blanketing is an especially significant topic, since it plays an important role in the control of copper in fossil fired power plants. In order to produce an effective nitrogen blanket for oxygen exclusion from electricity generating units, comprising boilers, turbines, heaters, and all interconnecting systems, both the appropriate nitrogen supply/delivery system and the appropriate application procedures are required. The final key to success is to follow the established procedures implicitly at the time the application is needed.

Nitrogen supply systems need to be large enough to sufficiently supply nitrogen to steam systems while pressure is collapsing during cooling in order to prevent any sub-atmospheric condition from occurring; and, to preclude any air ingress into the systems being blanketed.

If cryogenic storage systems are used, they should be of about twice to three times the gaseous volume of all the equipment that is being protected per application. The vaporizing equipment must be sized to keep pace with the evacuating demand produced by the cooling and draining of the various pieces of equipment.

Membrane systems are also commercially available to generate nitrogen on-site. These units are typically skid-mounted and can easily be moved from place to place on the site. These units are available in a wide variety of sizes to accommodate most requirements of nitrogen blanketing. The units use compressed air as an inlet stream. Nitrogen purity ranges to 99.9%, and is a function of the air pressure to the unit. As the purity requirements increase, the capacity to generate nitrogen decreases. The nitrogen which is produced is very dry, with a dew point of –90 F. The units are simple to operate with no moving parts. Membrane systems may be feasible at a cost savings over cryogenic systems. However, due consideration must be given to final purity of the product gas, volume of gas production and the operating power requirements and associated auxiliary power costs.

There is little information in the literature relative to the required purity of nitrogen gas to be used for blanketing. Oxygen is the largest impurity in commercial or on-site generated nitrogen. This oxygen has a great propensity for dissolving in water, particularly deoxygenated water, which will enhance corrosion to metal surfaces. Based upon considerable experience with nitrogen blanketing systems, the suggested minimum purity for nitrogen used for blanketing purposes is 99.5%. This agrees well with the practice of feedwater heater manufacturers which use 99.6% purity nitrogen when shipping their heaters.

Nitrogen supply piping must be connected separately to all circuits and components that are normally isolated by shut-off, stop or stop/check valves during normal shutdown. Exception to this can be made if non-routine valve positioning is explicitly stated in the blanketing procedures and is accomplished during the application process. This is to ensure that all parts of all circuits can be blanketed with nitrogen.

All nitrogen piping connections must be per code requirements of the component or circuit involved. Connections can be made permanently, with welded connections and appropriate isolation and check valves; or, using the quick connect type that can be disconnected to prevent blanketing by accident if the unit is going to be inspected instead of blanketed.

The valves on the permanent type connections can be of the manual type or (preferably) can be motor-operated in order to automate the blanketing process. These valves can be wired into the control system so as to admit nitrogen as soon as the specified pressure set point for that component or circuit is reached. If the system is manual, care must be taken to monitor the pressures and to valve-in the nitrogen supply to that component at the appropriate time in order to prevent sub-atmospheric pressure from occurring, which would nullify the effectiveness of the nitrogen blanket.

Shutdown procedures that previously had been established for the unit will need to be reviewed and revised as necessary to facilitate application of the nitrogen blanket. The objective is always to replace the collapsing steam with nitrogen to prevent air ingress into the system, including the condenser.

As the turbine comes off line, the condenser and reheater need to be flooded with nitrogen to achieve positive pressure as fast as possible before shutting down the air removal system. Care must be taken not to violate any turbine cooling requirements and to not over-pressure the condenser, which may cause the rupture discs to blow.

The extraction system, which is frequently neglected, needs as much attention as any other system. The heater shells and drains need appropriate blanketing. The deaerating heater and its associated storage tank can be pegged with nitrogen as the steam pressure collapses. The superheater vents and drains should be open and nitrogen admitted at such pressure as necessary to effect a purge prior to isolation.

The boiler should be drained under nitrogen pressure if draining is desired; or, capped under a continuous nitrogen pressure if it is to remain full. The boiler can be "flash drained" (drained while above boiling temperature) to produce a dry condition, all the while under nitrogen pressure, if such a condition is desired.

If the condensate, feedwater and associated heaters are to be drained, this should be accomplished under positive nitrogen pressure. A slight positive pressure should be maintained on the isolated system once the drain is accomplished. If these systems are to remain full of condensate, a positive nitrogen pressure must exist at all times to prevent any air ingress and to replace any water that may have leaked from seals, flanges, etc.

If the unit being blanketed contains any non-drainable components or circuits, these must be identified and an appropriate nitrogen supply made available to them in order to have an effective nitrogen blanket.

Once all systems are drained and blanketed, all vents and drains should be closed. Then, a slightly positive nitrogen pressure of 2-5 psig (13.8–34.5 kPa) should be maintained on all components.

In the case of the main condenser, once the steam seals are off and the air removal systems are stopped, a positive flow of nitrogen should continue to the condenser. If a slight pressure can be maintained without excessive nitrogen consumption, this procedure is feasible. Again, care must be taken not to blow the rupture disks. A continuous small flow through the condenser and out the turbine seals is totally sufficient to keep air out of that area in almost any situation.

Cost effective and physically effective nitrogen blanketing of steam electric generating systems can be accomplished. There are certain prerequisites that cannot be circumvented if effective blanketing is to be the desired result. The nitrogen supply system has to be capable of delivering the appropriate volume and purity in the required time frame. The nitrogen application points must be located in all necessary components and circuits. The nitrogen blanket application procedures, as well as unit shutdown procedures must address all of the necessary conditions and situations. Finally, the performance of the process must be exacting in order to be successful to accomplish the ultimate objective, which is to exclude oxygen from the equipment during downtime and lay-up.

## F.2 LAYUP

The following guidelines will give desirable results for iron and copper control during short and longer-term layups. Additional information can be found in EPRI's Startup, Shutdown and Layup Guidelines.(3)

### *F.2.1 Influence of Cycle Metallurgy on Layup*

All-ferrous metallurgy systems

Adequate layup practices for layup of idle equipment fall into two general categories: the wet and the dry procedures. Wet layup requires filling of most of the system with an alkaline solution (ammonia) and preventing air ingress by pressurization with nitrogen. In units operated with a feedwater ORP of >0, reducing agents (hydrazine or alternates) should not be used for wet layup.

Dry layup requires drainage while hot, and removal of all water followed by pressurization with a moisture-free inert gas or by use of dehumidified air to maintain a low-moisture environment.

Use of wet layup solutions in units with all-ferrous feedwater systems on AVT(O) or OT should generally be restricted to short term protection. Extended wet layup without a reducing agent (as is optimum in these cycles for short term protection) could lead to pitting attack unless the equipment is reliably nitrogen capped at all times and there is a means of circulating the solution. In view of these concerns, dry layup methods are clearly preferred for units with all-ferrous feedwater metallurgy and AVT(O) or OT feedwater chemistry. Conversely, if the normal feedwater chemistry is AVT(R) extended wet layup solutions containing a suitable reducing agent can be used effectively.

### Mixed metallurgy systems

Adequate layup practices for layup of idle equipment fall into two general categories: the wet and the dry procedures. Wet layup requires filling of most of the system with an alkaline reducing solution (ammonia and hydrazine) and preventing air ingress by pressurization with nitrogen. It is emphasized that the reducing conditions have to be maintained not only during normal operation but also in all other situations (shutdown, layup, startup).

Dry layup requires drainage while hot, and removal of all water following by pressurization with a moisture-free inert gas or by use of dehumidified air to maintain a low-moisture environment.

### *F.2.2 Short-term Layup*

Short-term layup presumes that the unit will be required to operate again within a relatively short time frame. Therefore, no major changes are required from normal operating conditions, with the exception being that the unit must be protected from air ingress. The condenser vacuum and turbine seals should be maintained. The deaerator and heater shells are inerted with nitrogen, and the feedwater chemistry is maintained as before shutdown.

### *F.2.3 Intermediate and Longterm Layup*

The two methods, which are available for intermediate and longterm layup, are the wet and the dry procedures.

In the dry procedure, all components of the condensate and feedwater systems must be drained hot. Dry air or nitrogen is circulated through the equipment to remove residual moisture and to prevent subsequent corrosion of the components of the cycle.

The preferred wet procedure, only suitable for units on AVT(R), involves filling the various components with deoxygenated demineralized water containing ammonia and hydrazine. Reducing agents should not be used for layup of units on AVT(O) or OT. For units containing copper alloys, the pH of the feedwater should be limited to 9.0 to 9.3; for all-ferrous systems 9.2 to 9.6. Hydrazine is held to 40 to 50 ppm. The pH in mixed-metallurgy systems should not be allowed to rise, because increasing pH increases the solubility of copper oxides. A separate chemical purging system may be required for this purpose. Wet layup methods generally should not be used for intermediate or longterm layup of units on AVT(O) or OT feedwater treatment. Dry layup is preferred. Nitrogen blanketing is preferred for all wet layups (Figure F-4).

As the turbine spins down on shutdown, nitrogen is added to the condenser, which also purges the reheater system. A continuous purge of nitrogen is necessary to account for leakage through the turbine steam seals. Nitrogen is added to the deaerator and storage tank while the system is still hot. A small flow of nitrogen is provided to purge this system. A nitrogen cap is maintained on the shell side of the feedwater heaters.

### *F.2.4 Maintenance Outage*

Only equipment requiring maintenance should be drained (wet storage only), and nitrogen (if used) purged with air to provide an environment suitable for entry of personnel. Since nitrogen does not support human life, it is extremely important that it be completely displaced by air. The atmosphere within the equipment to be maintained should be tested with suitable test equipment to ensure the equipment is safe for personnel entry.

## F.3 STARTUP

Again it is necessary to prevent oxygen ingress, if iron and copper are to be controlled to acceptable levels. The use of deaerated makeup will appreciably reduce oxygen levels during startup (see Appendix A). Air in-leakage must be controlled, as additional parts of the heat cycle are under vacuum during low load operation (see Appendix C). The use of auxiliary steam to peg the deaerator (if available) will enhance oxygen removal at this point in the cycle.

Detection and repair of condenser leaks during startup is critical to prevent ingress of harmful contaminants such as chlorides and sulfates.

The use of a cleanup loop, in conjunction with condensate polishers and/or filters (if available) was considered in the 1980s to be helpful in reducing contaminants during startup, however they are quite expensive to back-fit; and, therefore are not in widespread usage today. There have been some back-fit installations made for those units which have been converted from base loaded to cyclic operation, and, therefore are expected to have frequent startups. Even without cleanup loops, condensate polishers and/or condensate filters can markedly decrease startup times.

### *F.3.1 Corrosion Product Filters*

A recent development, condensate filters for copper(2) shows promise for markedly reducing copper in feedwater. Results from the application of such a unit are shown in Figure F-1. Field testing of this copper-reducing filter, as reported, indicates that copper can be reduced in feedwater by more than 95%, from 600 ppb to less than 20 ppb. Iron concentrations are also said to be reduced.

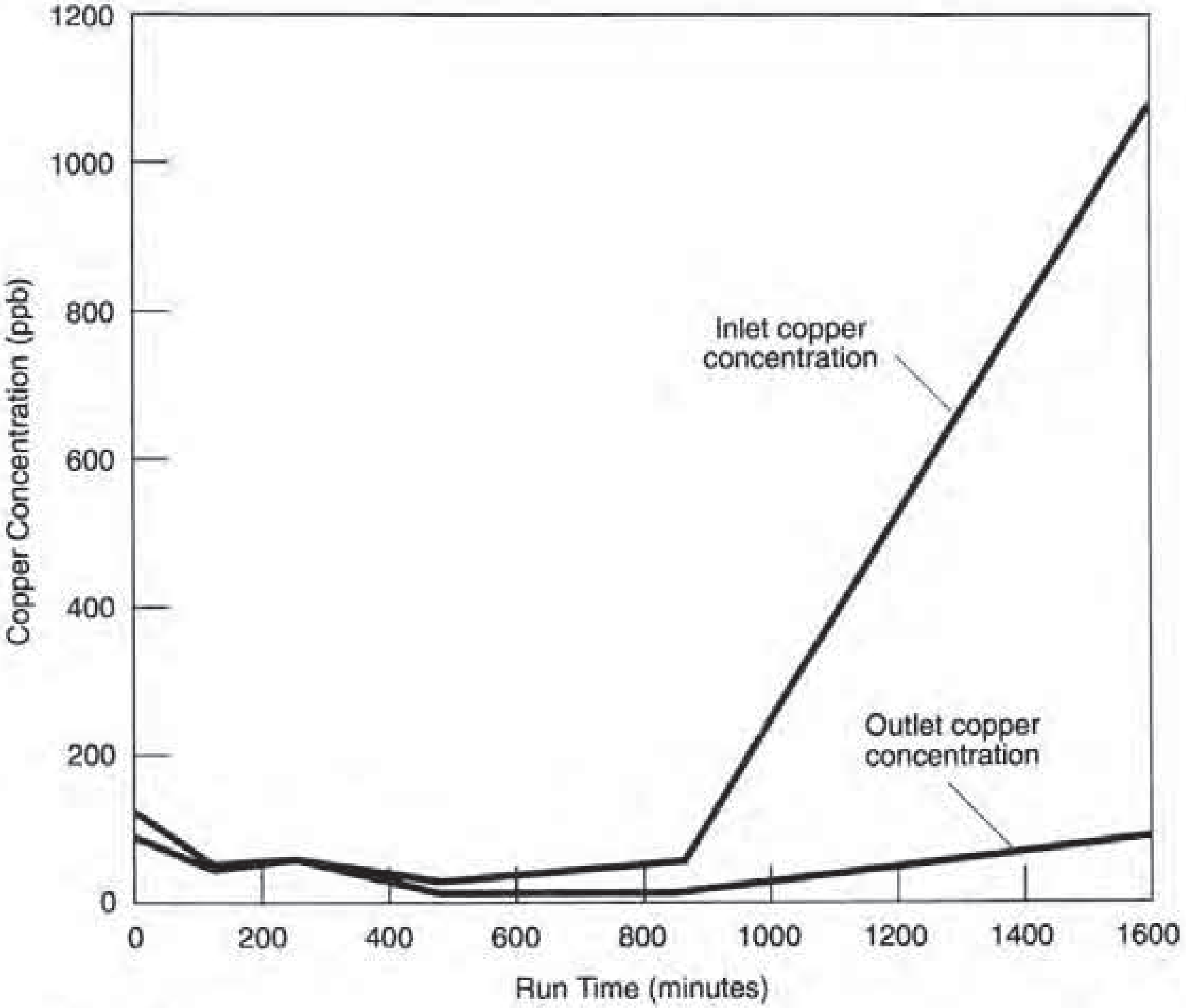

**Figure F-1**
**Copper Concentration at Virginia Power's Chesterfield Unit 6 Before and After a Filter(2)**

The copper filter is a design derived from filters already being applied in condensate filtration for particulate iron removal. The filter is a cartridge type utilizing a proprietary melt blown filter media that has a unique affinity for copper. It has no leachables, different from other plastic filter media of similar construction. Maximum operating temperature is 180°F (82°C), and maximum differential pressure is 50 psi. Other design features are shown in Table F-1(4).

After the initial tests at Chesterfield Station, the copper filter was fitted with an improved cartridge design, and retested at Chesterfield with improved results(5). Additional tests were performed at Pacificorp's Naughton Plant using the improved cartridge design. As a result of the satisfactory test results, a full set of copper reducing elements were ordered for installation at Naughton(7).

A primary limitation of condensate filters is that they cannot remove iron and copper which enter the feedwater. (Condensate polishers exhibit comparable filtration capabilities and limitations.) Development of filter elements capable of working in the feedwater environment would increase the usefulness of their devices. However, it should also be kept in mind that the need for corrosion product removal is minimized when the chemistry is controlled to minimize corrosion of materials in the cycle.

### *F.3.2 Units With Drum Boilers*

In general and to the extent practiced, it may be desirable to discard heater drains during initial startup operations (first 2-4 hours after turbine synchronization) to reduce the amount of iron and copper entering the boiler.

Initial startup depends on the layup procedures followed prior to startup. If the layup was short-term, and the unit filled with water treated for typical normal operations, startup can proceed without delay. If the feedwater system was full of water treated for longer-term layup (pH 9.0 to 9.6, hydrazine 40-50ppm) some water may have to be dumped to reduce hydrazine and ammonia to more appropriate values.

If the unit was laid up dry, the feedwater system for mixed-metallurgy systems must be filled with deaerated water from the makeup system treated with ammonia to pH 9.0-9.3, and hydrazine to achieve an ORP in the range -300 to -350mV, prior to startup. For all-ferrous systems, pH would be 9.2 to 9.6.

During startup, the boiler feedwater should be closely monitored. The following limits for the boiler feedwater have been used prior to firing the boiler:

- Oxygen < 100 ppb
- Iron < 100 ppb
- Copper < 10 ppb

By following the guidelines and procedures in Sections 4 and 5 of this document, it is expected that these limits can (and should) be reduced.

Attainment of these prefiring limits will be more difficult in units not equipped with condensate polishers and / or filtration equipment. Best control will require close compliance with the guidelines for unit shutdown and layup. However, for mixed-metallurgy systems the Program Copper research(6) has indicated that transition of protective cuprous oxide will occur to non-protective cupric oxide in a matter of hours in oxygenated water. Thus it is important to quickly reach ORP levels between –350 and –300 mV for these systems.

**Table F-1**
**Design features of copper filter[4]**

| Sizes | | |
|---|---|---|
| **Filter Diameter (in/mm)** | **Filter Length (in/mm)** | **Max. Flow (gpm/lpm)** |
| 6 / 152.4 | 40 / 1016 | 83 / 321 |
| 6 / 152.4 | 60 / 1524 | 130 / 492 |

| Housings | |
|---|---|
| **Number of Filters** | **Aqueous Rated Flow (gpm/lpm)** |
| 1 | 130 |
| 2 | 260 |
| 3 | 390 |
| 4 | 520 |
| 7 | 910 |
| 12 | 1560 |
| 19 | 2470 |

After firing the boiler, monitoring of the condensate and feedwater must be continued, both for chemistry parameters and to ensure that temperature ramps are maintained according to equipment manufacturer's specifications.

Boiler water chemistry concentration levels vs. pressure curves (see Section 4) can be utilized to control sodium, silica, chlorides and sulfates to provide protection to the steam turbine. Boiler pressure should remain at reduced levels such that these contaminant values, as shown on the curves, are not exceeded before pressure can be increased to the next level. Maximum use of blowdown and condensate polishing (if available) will minimize startup times.

Several organizations with mixed-metallurgy systems have established boiler water "holds" for copper during startups, similar to the philosophy established very much earlier for "holds" on silica boiler water levels during startups. One such startup curve is shown in Figure F-2 [7]. The first version was established in 1987, but was modified in 1993 in an effort to shorten unit startup times. The revised curve for 1993 reduced startup times from 48-60 hours (1987) to about 12 hours.

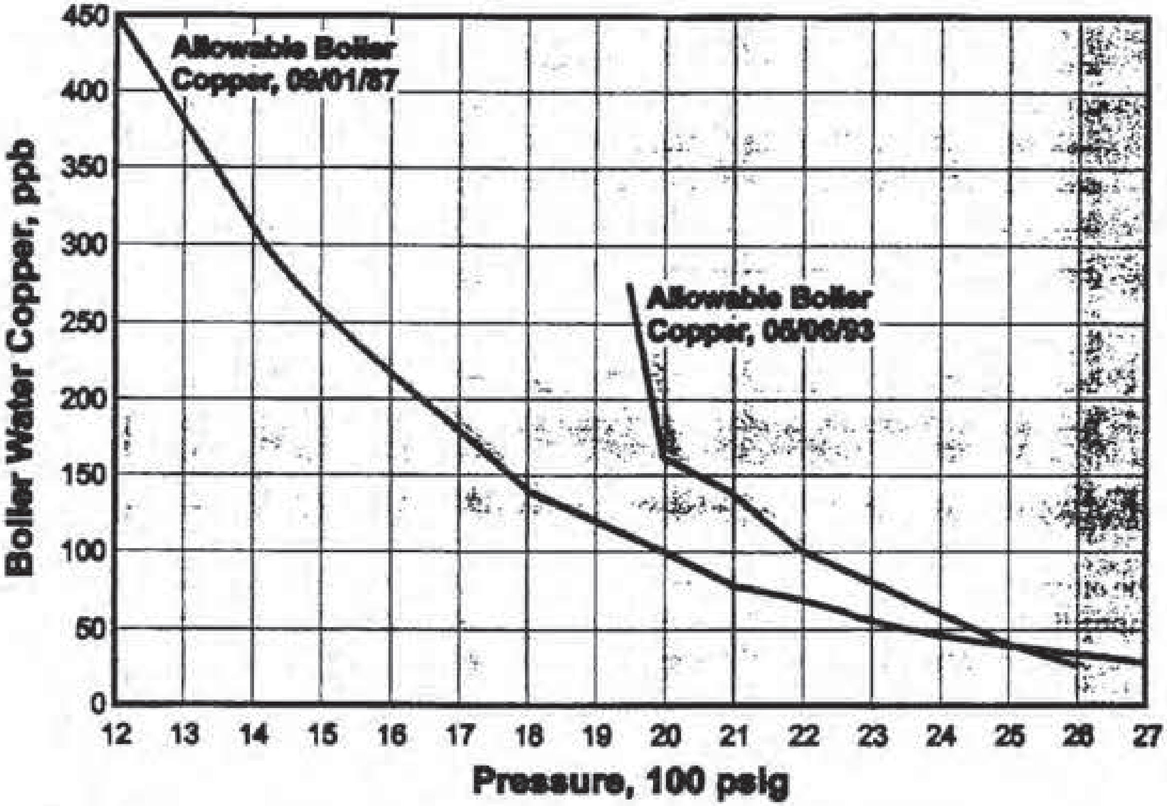

**Figure F-2**
**Boiler Water Copper Concentration/Drum Boiler Pressure Control Curves Developed at Miami Fort Station**[7]

Figure F-3 shows a boiler water copper control curve derived for a 2 ppb copper limit in steam, which was developed for the EPRI Copper Guidelines.[m] Since it is difficult to quantify analytically the individual species (cupric or cuprous) in the boiler water, it was suggested that total copper be used for control purposes. The curve shown in Figure F-3 is based on the volatility of cuprous oxide, and could be used to provide an approximation of the total copper level in the boiler water which should minimize the copper in steam.

The startup curves in Figure F-2 are similar to the total copper curve of Figure F-3 in the higher operating pressure ranges, as shown in Table F-2.

Of course it should be recognized that use of a curve, such as indicated in Figure 4-7, implies that the good control philosophies for boiler water, which ensure reducing conditions are maintained during a shutdown, have not been adopted. A key example may include a maintenance outage to work or internally inspect the boiler. On the other hand, if reducing conditions are rigorously maintained then such a figure should not be needed. In this regard, it can not be emphasized more strongly that, according to the Program Copper research (Sections 1.2.4 and 3.3.1), the copper oxides will partition into steam from boiler water at high levels even during the early startup.[m] Applying these guidelines to control the chemistry under all conditions is the best approach to avoidance of copper transport problems.

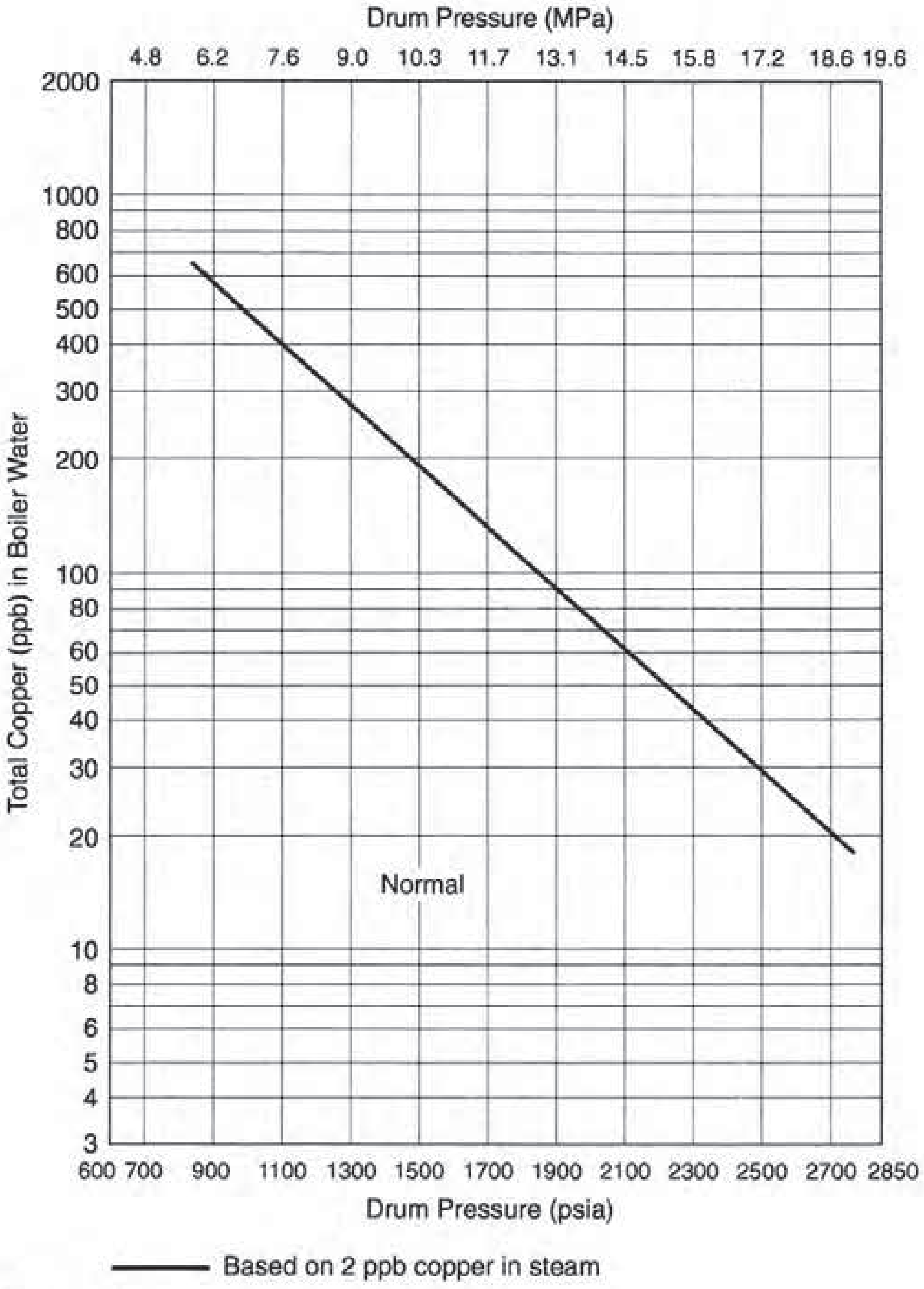

**Figure F-3**
**Drum Boiler Water Copper vs. Operating Pressure**

**Table F-2**
**Comparison Of Copper Values In Blowdown (Figures F-2 and F-3)**

| PRESSURE psi (MPa) | FIGURE F-2 (ppb) | | FIGURE F-3 (ppb) |
|---|---|---|---|
| | 1993 DATA(1) | 1987 DATA | |
| 1950 (13.4) | 275 | 110 | 85 |
| 2000 (13.8) | 160 | 100 | 75 |
| 2100 (14.5) | 140 | 75 | 65 |
| 2200 (15.1) | 100 | 70 | 50 |
| 2300 (15.8) | 75 | 50 | 45 |
| 2400 (16.5) | 60 | 45 | 35 |
| 2500 (17.2) | 40 | 40 | 30 |
| 2600 (37.7) | 25 | 25 | 25 |

During startup, any chemical excursions must be dealt with quickly and effectively to return the unit expeditiously to normal operating values. Target values at the deaerator inlet and the economizer inlet are given in Figures 4-1 and 4-2.

### F.3.3 Units With Once Through Boilers

Firing must be stopped during any startup if contamination is present.

#### Cold Startup

A key requirement for the startup system is to maintain adequate flow in the furnace walls (25% for most supercritical units and 33% for most subcritical units) to protect them from overheating during both startup and low-load operation. In early systems, any excess flow not required for turbine power operation was simply bypassed from the furnace to the condenser. Later units added a steam-water separation device sometimes called a flash tank.

It is suggested that temperature should not exceed 550°F (288°C) at the convection pass outlet until the iron levels are less than 50 ppb at the economizer inlet.

In units with mixed-metallurgy, particular attention should be given to filling the system with almost oxygen-free alkalized (ammonia and hydrazine) condensate or feedwater. The presence of oxygen and the absence of reducing conditions during startup is the main cause of the copper transport round the circuit.

Depending on the plant, and the shutdown and layup conditions adopted, several steps may be required for startup (in addition to filling the boiler following a long shutdown and safely venting nitrogen, if used). The steps used during startup are plant-specific;(3) Examples include:

- Circulation via deaerator
- Circulation via economizer
- Circulation via the boiler
- Allow firing
- Allow steam to turbine
- Turbine on one third load
- Increasing to full load.

As a rule, units meeting the normal target values specified in Figure 5-2 during normal operation and applying adequate layup techniques do not need extended cleanup steps even during a cold start. It is recommended to monitor some cold starts in detail(3), particularly with respect to pH, cation conductivity, and oxygen in corresponding cycle streams, and tailoring a unit-specific startup control procedure. The assumption is that some of the steps listed above can be markedly curtailed in comparison to the former practice or even completely omitted.

### Hot Startup

Units meeting the normal target values specified in Figure 5-2 (all-ferrous metallurgy units) or in Figure 5-5 (mixed-metallurgy units) during normal operation and stored under pressure do not require extended chemistry-related checks for hot startup. It is suggested that efforts should be made to meet a cation conductivity of <1.0 μS/cm for two minutes and the iron level should be <50 ppb before load is raised on the unit.

## F.4 ROAD MAP FOR SHUTDOWN AND LAYUP

A road map to develop shutdown and layup procedures is shown in Figure F-4(3). Because of variations in design, some generating units may require deviations to Figure F-4, or may require customization to adapt to a particular utility's needs.

Figure F-4 is divided into nine steps, which are further described as follows:

### *Step 1 - Short-Term Layup*

Short-term layup presumes that the unit will be required to operate within a relatively short timeframe. In consideration of this, no major changes are required from normal operating conditions, with the exception being that the unit must be protected from air ingress. The condenser vacuum and turbine seals are maintained; the deaerator, heater shells and boiler are inerted with nitrogen or steam; and, the feedwater chemistry is maintained according to the requirements of the treatment philosophy employed.

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KLOTZ REBUTTAL, SCHEDULE 1
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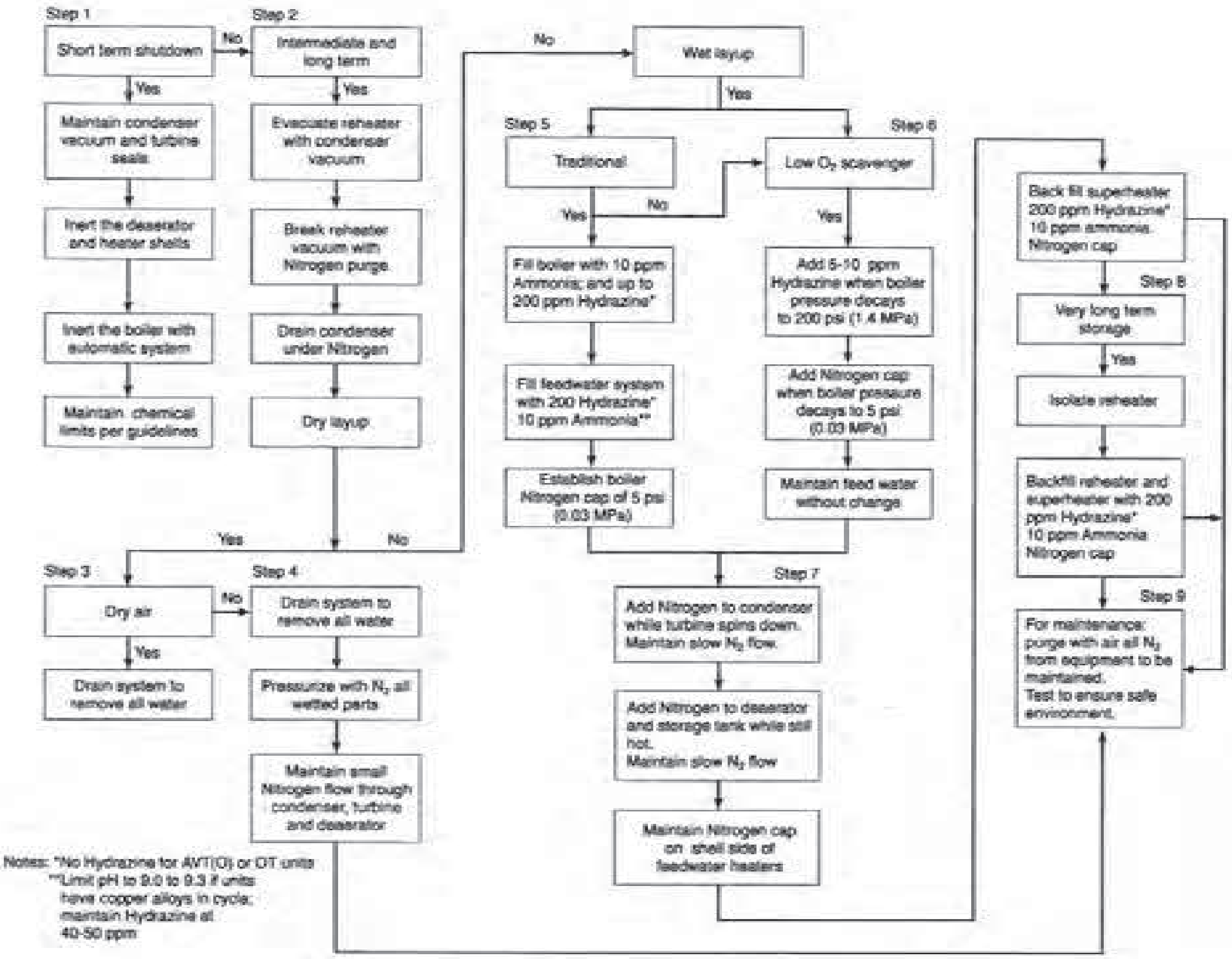

Notes: *No Hydrazine for AVT(O) or OT units
**Limit pH to 9.0 to 9.3 if units have copper alloys in cycle; maintain Hydrazine at 40-50 ppm

Figure F-4
Road Map to Develop Shutdown and Layup Guidelines Common to Most Units

### *Step 2 - Intermediate and Longterm Layup Common to Dry and Wet Layup*

Intermediate and longterm layup require additional steps to be taken to prevent corrosion during intermediate periods of layup, such as for maintenance and indeterminate cycling or peaking requirements; and during longterm layup for indefinite periods of time. Certain procedures are common regardless of whether the units are to be laid up dry or wet. There is a danger of off-load corrosion (pitting) if there are salts present. Consideration needs to be given to whether the reheater supports can take the weight if the reheater is to be filled with water.

During shutdown, the turbine, condenser (steam side) and reheater are generally considered together because, unless special facilities are incorporated, there is no practical way to isolate them. With special facilities incorporated, the reheater can be isolated from the turbine and may be stored wet (see Step 8). The turbine, however, can only be laid up dry. The condenser may be flooded and laid up wet, but several factors limit the feasibility of this procedure:

- The condenser must be supported from the bottom to handle the extra weight of a flooded condenser.
- The expansion joints between the turbine and condenser are not designed to support the weight of a flooded condenser.
- A flooded condenser tends to pull the turbine bearings out of alignment.
- Water in the condenser may cause moisture vapor to enter the turbine causing corrosion.

For these reasons, the steam side of the condenser is normally laid up dry.

For Step 2, during shutdown, the reheater is evacuated by utilizing the vacuum in the condenser. The vacuum is then broken using nitrogen pressure. The condenser is drained under nitrogen.

If the turbine steam is supplied from a header system, all valves must be tight to prevent moisture entrance into the turbine.

### *Step 3 - Dry Air Layup*

The dry air layup procedure requires that all components of the system be drained. There are several methods of maintaining dry air flow through the equipment. The advantages and disadvantages of dry air layup and the equipment required have been previously described in other EPRI documents[3,6].

### *Step 4 - Dry Layup with Nitrogen*

Nitrogen can be used for blanketing equipment, which is drained but not completely dry, or for blanketing equipment either filled with water or not, to prevent air ingress.

Step 4 is similar to Step 3, except nitrogen is used for a positive pressure on all components rather than a dry air purge. A small continuous purge of nitrogen is required, however, to protect the turbine, deaerator storage tank.

### *Step 5 - Wet Layup: Traditional Method (Boiler and Feedwater Heaters)*

For those units having copper alloy condenser tubes and/or feedwater heaters, feedwater pH should be limited to 9.0 to 9.3 by reducing ammonia. Hydrazine is held at 40-50 ppm. For these units, it is most important to maintain reducing conditions (ORP $< 0$ mV and preferably to -350 mV) to prevent increased attack of the copper alloys associated with a change of the surface oxide layers from cuprous to cupric oxide.

A nitrogen cap of 5 psi (0.03 MPa) is maintained on the boiler.

### *Step 6 - Wet Layup: Low Oxygen Scavenger Method (Boiler and Feedwater Heaters)*

Many alternatives to the traditional wet layup method have been used successfully by markedly reducing the level of hydrazine. These procedures may not require boiler draining prior to startup, thereby protecting the environment and not requiring special disposal techniques or permits. In one procedure, 5 to 10 ppm of hydrazine equivalent is injected into the boiler when the boiler pressure decays to 200 psi (1.4 MPa) (typically 3 days). The chemical injection is made using the normal chemical feed system. Natural boiler circulation at 200 psi (1.4 MPa) is sufficient to mix adequately the chemicals in the boiler water. No other changes need be made to the boiler or to the feedwater chemistry. When the boiler pressure decays to 5 psi (0.03 MPa) (typically 7 days) a nitrogen cap is applied to the boiler.

Upon return to service, the boiler may be fired without draining the layup solution. Also, since it typically take 3 days before the boiler pressure decays to 200 psi (1.4 MPa), weekend outages normally do not require a chemical injection treatment.

### *Step 7 - Wet Layup (Balance of Cycle)*

As the turbine spins down, nitrogen is added to the condenser, which also purges the reheater system. A continuous purge of nitrogen is necessary to account for leakage through the turbine steam seals.

Nitrogen is added to the deaerator and storage tank while this system is still hot. A small flow of nitrogen is provided to purge this system.

A nitrogen cap is maintained on the shell side of the feedwater heaters. The superheater is back filled with a solution of up to 200 ppm of hydrazine and 10 ppm ammonia and a nitrogen cap maintained.

### Step 8 - Very Long Storage

For very long storage periods, the reheater is isolated from the turbine, and back filled with a solution of up to 200 ppm hydrazine and 10 ppm ammonia, and capped with nitrogen. The superheater is treated similarly.

### *Step 9 - Maintenance*

Only equipment requiring maintenance should be drained (wet storage only), and nitrogen (if used) purged with air to provide an environment suitable for entry of personnel. Since nitrogen does not support human life, it is extremely important that nitrogen is completely displaced by air. The atmosphere within the equipment to be maintained should be tested with suitable test equipment to ensure the equipment is safe for personnel entry.

Experience indicates that for mixed-metallurgy systems unit startups in the past have been a major source of copper transport to the boiler, with concentrations as high as 10 ppm during cold starts. By following the preceding startup guidelines, especially for oxygen control and air in-leakage, copper transport can be minimized during these periods.

## F.5 CYCLING AND PEAKING

Cycling is a load following operation. The unit load fluctuates with system demand, with the unit synchronized at very low loads during low-demand periods. A typical load variation for cycling units might range from 30% to 100% of design capacity.

Peaking is a form of cycling in which the unit is operated only during peak power demand periods. At off-peak hours the unit is on hot standby, depending upon the estimated time between restarts. Two-shift operation is typical of peaking units, which generally furnish power for the morning and evening high demand hours.

For guidance, Table F-3 gives suggested cumulative hours per year of exposure to contaminant conditions for cycling operations.

**Table F-3**
**Maximum Annual Exposure to Contaminant Conditions for Cycling and Peaking Operation**

| TARGETS | HOURS PER YEAR |
|---|---|
| NORMAL | - |
| ACTION LEVEL 1 | 672 (28 days) |
| ACTION LEVEL 2 | 96 (4 days) |
| ACTION LEVEL 3 | 16 |
| IMMEDIATE SHUTDOWN | 2 |

Organizations attempting to apply the criteria to peaking units are challenged by the chemistry variations associated with shutdown and startup periods, especially if no provision is made for equipment layup. For "chemistry accounting" purposes, it is generally accepted that accrued times in action level conditions should only be counted while the unit is in service at or above minimum load at which the unit is normally operated to supply power to the system. However, this approach does not lessen the value and importance of optimizing cycle chemistry under all operating conditions.

Some concerns relative to cycling and operation are given below. An * indicates the items affected by water and steam chemistry:

- increased boiler component cyclic stress with loss of unit life*
- increased turbine rotor cyclic stress with loss of rotor life*
- increased thermal stress on turbine rotor, steam chests, valves, and inner casing,* leading to corrosion fatigue
- increased solid particle erosion of HP and IP turbine blading from superheater and reheater tube exfoliation
- turbine vibration during startup/shutdown*
- possibility of furnace implosion/explosion during startup/shutdown
- steam requirements for maintaining condenser vacuum
- the need for improved boiler control to minimize unit restart and reloading times*
- acid dew point condensation- corrosion and plugging of air preheaters and back end ductwork
- flame scanner monitoring problems requiring much attention
- burner turndown ratio/flame stability at low loads- feeder turndown and mill response times during load ramps too slow
- increased frequency of chemical cleaning and more monitoring and control of steam and water chemistry needed*
- poor back end equipment performance at low load conditions
- increased possibility of mill fires and explosions during frequent starting and stopping of a unit
- distortion and internal rubbing of the boiler feed pump, if pump is not fully warmed up at startup

Some of the possible solutions to these problems are given below. Many of these solutions require considerable expenditures. An * denotes possible effects on cycle water chemistry:

- incorporate steam bypass systems*
- incorporate full arc admission
- add additional controls and monitoring equipment*

- incorporate variable pressure operation*
- use two half-sized boilers
- install turning gears on ID fans
- incorporate a condensate polishing system*
- incorporate better turbine seals
- install smaller coal mills for low load operation

Additional detailed information on this topic can be found in the EPRI's *Cycling, Startup, and Layup Guidelines*.(6)

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