CHEMISTRY - 224

THE CONDENSATE, FEEDWATER AND BOILER SYSTEM

Note: For Conventional General Authorization Training the candidate is required to memorize:

(a) the desired boiler water pH numerical values, and

(b) that all other desired values are ALARA.

OBJECTIVES

On completion of this lesson the trainee will be able to:

General

2.1 State and briefly explain two major objectives of chemical control of the Condensate, Feedwater and Boiler System.

2.2 (a) Name two types of sludge and scale deposit-forming substances and state their sources.

(b) State three adverse effects of sludge and scale.

(c) Define blowdown and briefly describe its purpose.

2.3 Define carryover, as it applies to boiler steam.

2.4 Briefly explain why, apart from sodium and silica, only conductivity measurements are used to assess the quality of makeup water before it is admitted to the feedwater system.

Standard Operation

2.5 State the desired operating conditions (numerical values required where indicated) and describe the method(s) regularly used to maintain these conditions for the following Condensate, Feedwater and Boiler System parameters:

(a) Boiler water pH (numerical values required)
(b) Boiler water cation conductivity
(c) Dissolved oxygen
(d) Hydrazine
(e) Sodium, chloride, sulphate, silica
(f) Iron and Copper

Non-standard Operation

2.6 For each of the following Condensate, Feedwater and Boiler System parameters state:

(a) The possible cause(s) or source(s), where applicable, of the non-standard condition

(b) The method(s) of control

(c) The consequence(s) if no action is taken.

The required number of each of the above is shown in the box below.

# Required (a)	(b)	(c)		
2	3	3	(i)	High boiler water pH
2	3	2	(ii)	Low boiler water pH
3	3	4	(iii)	High dissolved O_2
2	2	1	(iv)	High sodium
2	2	1	(v)	High sulphate
1	2	1	(vi)	High chloride
2	2	3	(vii)	High boiler water cation conductivity
2	2	3	(viii)	High silica
2	2	2	(ix)	Low hydrazine
1	1	1	(x)	High hydrazine
1	1	2	(xi)	Tritium

2.7 (a) Indicate which non-standard control parameters heve level 3 action limits, and
(b) Why these values are in place.

Startup and Shutdown Concerns

2.8 State the major chemistry-related concerns for the Condensate, Feedwater and Boiler System when the unit is started up and shut down.

Sources of Information

2.9 State the sources of information employed to monitor the chemical parameters of the Condensate, Feedwater and Boiler System and the makeup water.

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INTRODUCTION

The terms **steam generator** and **boiler** are used interchangeably throughout many station documents. Technically, the "steam generators" in our nuclear stations do not fit the Ontario Boilers and Pressure Vessels Act definition of a "boiler". However, in the interest of simplicity and to avoid confusion of short forms, only the word **boiler** will be used in this module. The term "Condensate, Feedwater and Boiler (C,FW,B) System" refers to the complete secondary (H_2O) side. This comprises the boiler, turbine, condenser, condensate extraction pump, LP feedheaters, deaerator, boiler feedpumps and HP feedheaters as a working unit.

Good chemical control of the C,FW,B System ensures minimum corrosion of the system hardware, the boiler tubes being the most critical. It also impacts directly on the control of other operational concerns of this system, eg, boiler tube scale, and tubesheet and tube support plate sludge and deposits.

This control commences with the use of makeup water prepared to a high purity standard in the water treatment plant (WTP). At the point of addition to the circuit and elsewhere, chemical additives are introduced to establish operational parameters best suited to the chemical control objectives of the C,FW,B System. An in-line chemical monitoring system, supported by chemical control laboratory grab sample analysis, ensures these operating conditions are optimized.

Five different names are given to the one working fluid of the C,FW,B system shown in Figure 1.

These names, which relate to the physical location of the working fluid within the cycle, are explained below:

Condensate refers to the working fluid from the point of origin in the condenser hotwell, through the condensate extraction pumps (CEP) and the low pressure heaters, to and including the deaerator.

Makeup describes the WTP product which enters the circuit at the condenser to replenish losses and maintain the proper fluid balance in the circuit.

Feedwater refers to the working fluid from its entry to the deaerator storage tank, through the boiler feed pump (BFP) and high pressure feedheating section until it enters the boiler.

Boiler Water/Steam - In the boiler, the working fluid is termed boiler water until it becomes steam and exits the boiler. It remains steam until it closes the loop as condensate in the condenser hotwell.

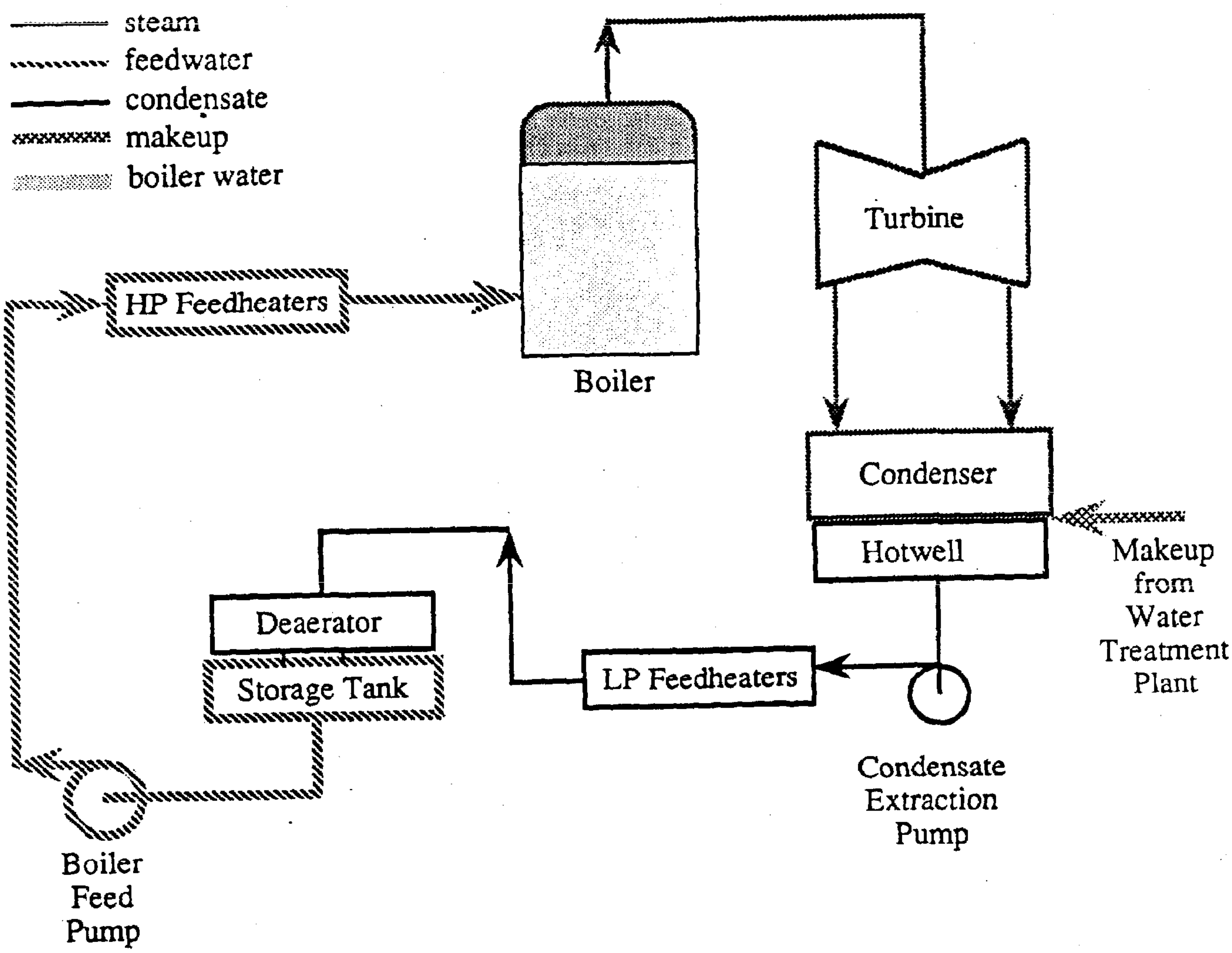

Figure 1: The Condensate, Feedwater and Boiler System

GENERAL

OBJECTIVES OF C,FW,B CHEMICAL CONTROL

The primary objective of chemical control of the condensate, feedwater and boiler system is to minimize corrosion of the entire system by controlling pH and the concentration of oxygen and dissolved ionic impurities. In addition to component wastage such corrosion is undesirable because of the resultant transport of corrosion products to the boilers.

Another major objective of chemical control of the C,FW,B system is to minimize sludge and scale formation in the boiler.

In the following, the three sub-system areas of Figure 1 are examined in regard to corrosion, scaling, and sludge buildup.

Condensate

The objective of chemistry control of the condensate system, Figure 2, is to minimize corrosion of the entire boiler steam and water system by maintaining a suitable pH and removing O_2. Oxygen enters the condensate via air in-leakage to the subatmospheric parts of the turbine/condenser, and via the makeup water.

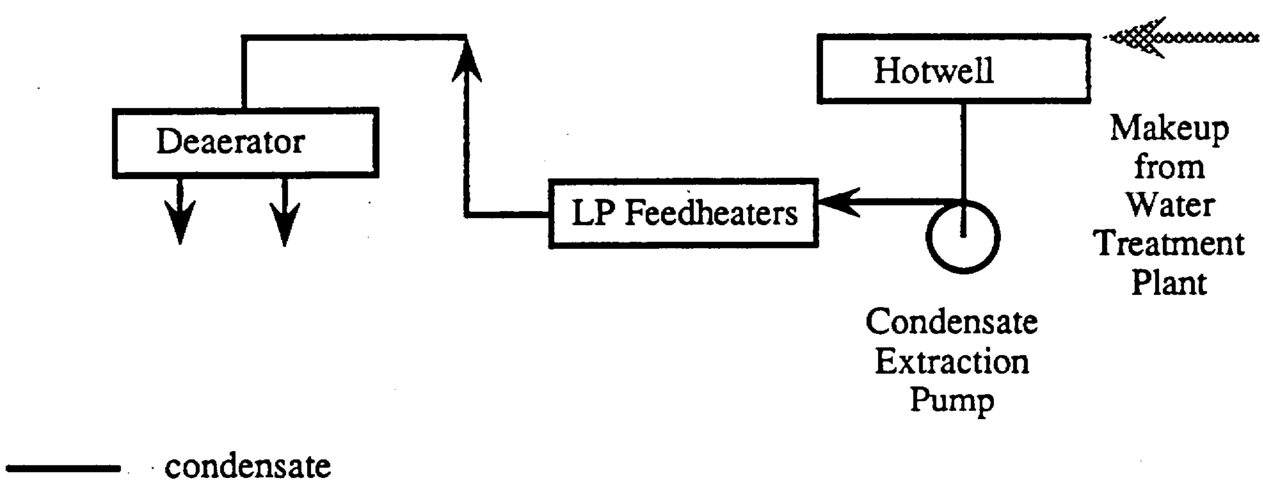

Figure 2: Condensate Section of Figure 1

Feedwater

The objective of chemistry control of the feedwater system, Figure 3, is to continue to provide protection against corrosion, particularly in the boiler, by maintaining low dissolved oxygen and low impurity levels. Minimizing corrosion reduces the quantity of corrosion products entering the boiler. This is very important, because the buildup of sludge can lead to under-deposit boiler tube corrosion at the tubesheet and tube support plates and also impairs heat transfer.

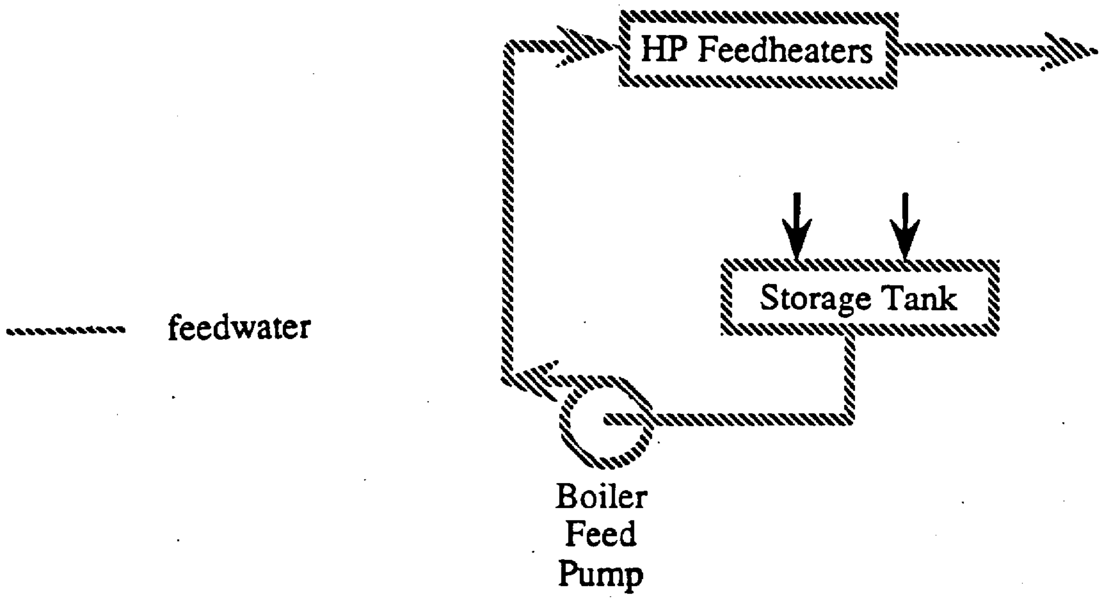

Figure 3: Feedwater Section of Figure 1

Boiler

The objective of chemistry control in the boiler system, Figure 4, is to minimize the corrosion of boiler tubing and other structural materials. To meet this objective the pH is maintained alkaline as described under Standard Operation, and impurity concentrations are kept low as described under Scale and Tubesheet Deposits.

Several problems can arise due to impurities in the boiler water;

In particular, sodium, chloride and sulphate above specification can result in tube corrosion.

Silica is kept at low concentrations to minimize contribution to scale and sludge in the boiler.

Ca^{++} and Mg^{++} ions (which can enter the condensate from the condenser cooling system if condenser tube leaks occur) are another prime contributor to scale and sludge.

The buildup of sludge and corrosion products on boiler tubesheets is also of particular concern, and especially so in the event of condenser in-leakage or WTP upsets. This is because ions such as OH^-, Cl^-, Na^+ and $SO_4^{=}$ can concentrate in the sludge pile or any crevice, by factors of 10^4 to 10^5, thereby further increasing the risk of corrosion of the boiler tubes.

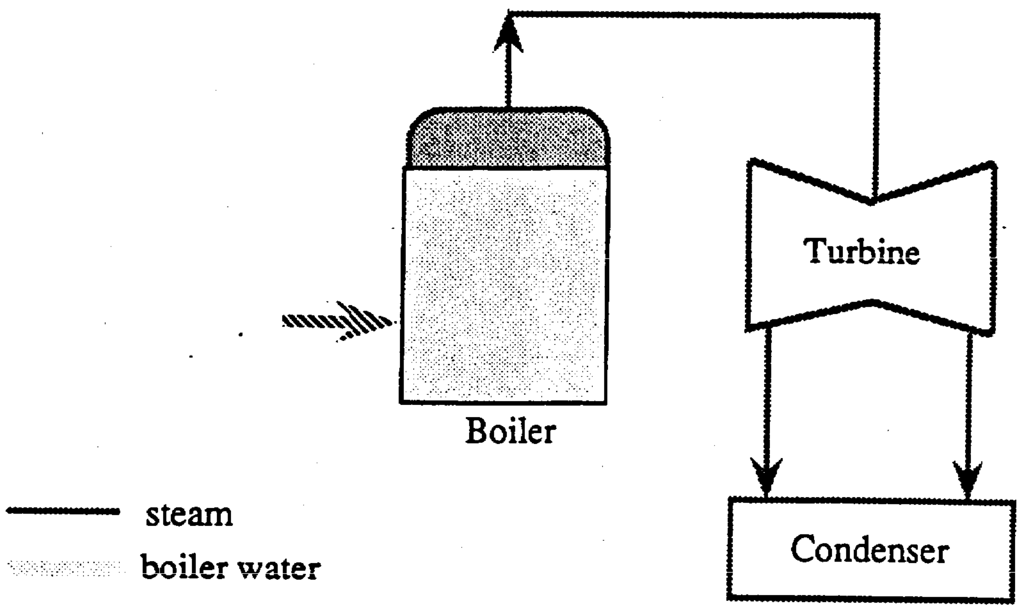

Figure 4: Boiler Section of Figure 1

Summary

- Corrosion within the entire C,FW,B system and hence transport of corrosion products to the boiler are minimized by controlling pH, oxygen concentration and dissolved impurities.
- Corrosion control also minimizes deposit formation in the boilers.

SLUDGE AND SCALE

The problem due to the presence of sludge and scale is closely associated with the concern for corrosion in boiler water chemical control . As shown in Figure 5, boiler scale is the layer of foreign material adhering to the outside of the boiler tubes.

Deposits comprise the particulate material which generally settles in low flow areas of the boiler such as the tubesheet or tube support plate surfaces. Often what was initially scale flakes off boiler tubes to add to these deposits. Deposits and corrosion are closely interrelated, since much of this material originates as corrosion products elsewhere in the feedwater train.

Sludge and Scale Forming Substances

There are two general types of sludge and scale forming substances:

(a) Suspended Inorganic Solids (Particulates)
(b) Dissolved Inorganic Material

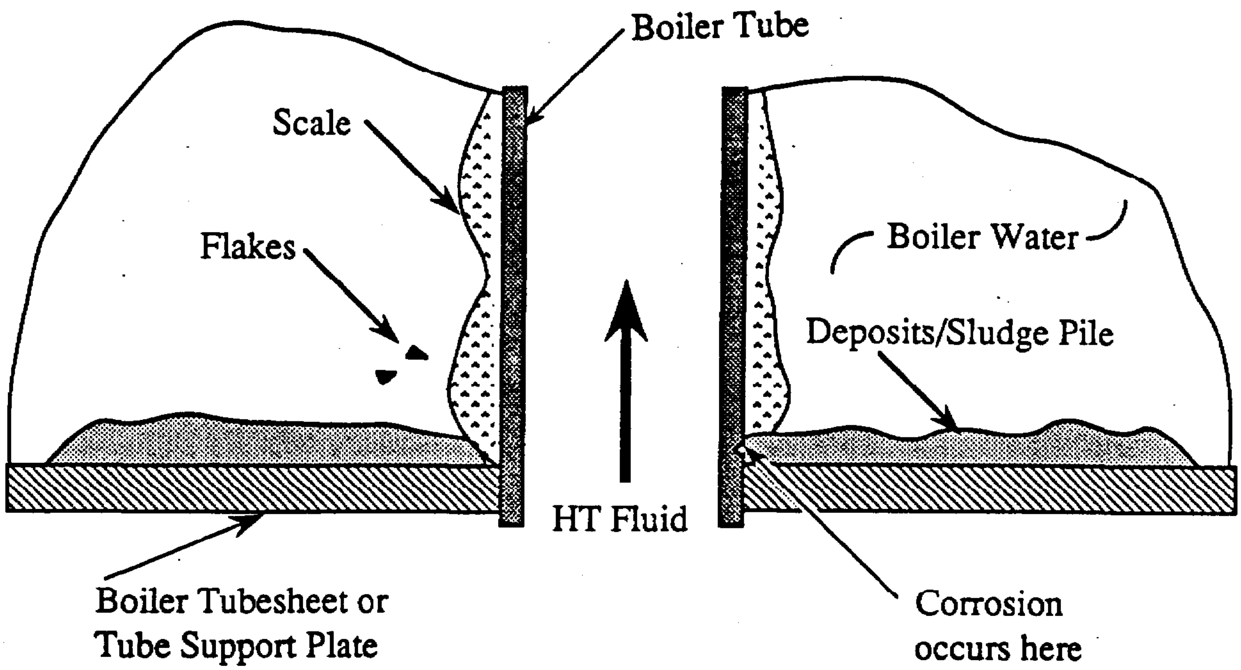

Figure 5: Boiler Tube Scale and Tubesheet Deposits

(a) **Suspended Inorganic Solids (Particulates)**

A major source of this material are the particulates that develop throughout the boiler steam and feedwater circuit from various corrosion processes. Much smaller quantities enter the circuit in fresh makeup, but they do become significant if allowed to accumulate in the boiler. Finally, an acute source of suspended solids is raw water ingress from main condenser tube failures. These are mainly silicates of calcium and magnesium.

The makeup water is normally very pure. Therefore, a high percentage of suspended boiler solids consist of corrosion products, mostly iron oxides and copper metal, transported from pre-boiler locations into the boiler. The copper corrosion products originate from the copper alloy tubes used in the condensers and feedheaters in early CANDU stations only (BNGS-A and PNGS).

(b) **Dissolved Inorganic Materials**

Four general categories of dissolved solids found in boiler water are:

(i) Calcium and Magnesium Salts (water hardness)
(ii) Silica
(iii) Sodium, Chloride and Sulphate ions
(iv) Corrosion Products (mostly iron and copper compounds)

(i) **Calcium and Magnesium Salts** (Water Hardness)

If there are no condenser tube leaks there should be no calcium or magnesium salts entering the boiler. However, if there are condenser tube leaks, raw water containing these salts, which are primarily bicarbonates of calcium and magnesium, will be drawn into the condensate stream. They will tend to concentrate in the boiler water. Calcium sulphate and magnesium carbonate demonstrate inverse solubility (solubility decreases as temperature increases) and eventually may precipitate. They will collect in the sludge pile or bake onto the boiler tubes. Other calcium and magnesium species, particularly silicates, also occur.

One reaction for this scale formation occurs in the boundary layer surrounding the tubes where the hotter environment promotes bicarbonate decomposition and subsequent deposition of calcium and magnesium carbonate on the tube walls. The following equation is an example of this reaction; an analogous reaction occurs for magnesium bicarbonate:

$$\underset{\text{Calcium Bicarbonate}}{Ca(HCO_3)_2} \xrightarrow{\text{Heat}} \underset{\text{Scale}}{CaCO_3} + H_2O + CO_2$$

(ii) **Silica**

Silica is present in trace quantities in makeup water. On rare occasions, it may also be present as a result of a WTP IX breakthrough or a condenser tube leak. Silica contributes to tubesheet deposits and boiler scale. The special role played by silica in carryover in high-pressure fossil fuel stations is not a factor in NGD boilers because of lower temperature.

(iii) **Sodium, Chloride and Sulphate Ions**

These ions enter the system as trace contaminants in the makeup water or as a result of a condenser tube leak. On rare occasions, Na^+ may also be present because of a WTP IX breakthrough. Sulphate ions form scale, and all three concentrate in the sludge pile creating a corrosive environment for the boiler tubes.

(iv) **Corrosion Products**

Dissolved corrosion product species comprise mostly iron and copper compounds, reflecting the materials of construction. Some come out of solution to contribute to sludge piles and scale. Also, oxidizing species such as Cu^{++} and Fe^{+++} can aggravate corrosion by elevating galvanic cell voltages.

If main condenser tube leaks develop and raw water enters the system, all categories of dissolved solids become acute, significant contaminants.

Dissolved and Suspended Organic Material

A malfunctioning turbine gland seal can permit turbine lubricating oil to enter the condensate, feedwater and boiler system. Raw water entering the system via condenser tube leaks may contain organics. Bacteria growth in the demineralized water system can also contribute organics to the makeup water. Organics may cause corrosion by breaking down into acids such as formic and acetic.

Water Treatment Plant Malfunction

Although the occurrence of WTP failures is not high, poor makeup water purity is a potential source of boiler water impurities. A serious WTP excursion or malfunction could admit out-of-specification makeup water and/or resin regenerant solutions high in dissolved impurities content to the system. This may require a unit or station outage, to cleanse the contaminated system with clean makeup water.

Adverse Effects of Sludge and Scale

If deposits, sludge, scale or entrained particles accumulate in particular areas of the boiler, the probability of further problems due to higher concentrations of certain ions is increased.

One example is under-deposit corrosion (ie, corrosion occurring under the sludge or any deposit) where a localized high concentration of chloride at the base of boiler tubes leads to pitting of the tubes. Similarly, hydroxyl (eg, NaOH) buildup can promote caustic attack of the boiler tubes.

Any scale on boiler tubes reduces heat transfer efficiency and therefore forces heat transport system temperature upwards. Large deposits on the tube support plates of the boilers may also cause problems with boiler level control.

Particles entrained in the boiler water contribute to erosion of components and can also settle out and form deposits that present sites for under-deposit corrosion. Over time, deposits of sludge become very hard - in fact like concrete. Removal becomes extremely difficult. High pressure water lancing or chemical cleaning are methods. currently used.

Any of the above forms of corrosion or erosion can cause shortened boiler tube life, leading to heat transport leaks into the boiler if through wall corrosion occurs.

Blowdown

Blowdown is the method employed to maintain boiler water impurity levels within chemical specification. In this procedure, a portion of the boiler water is discharged to the CCW outfall, and the fluid level in the system is restored using high purity makeup. Although this process also removes some suspended solids, it is not an efficient method for reducing the suspended solids content of the boiler.

The use of blowdown reduces scaling on boiler tubes and the concentration of undesirable ions in tubesheet deposits by removing dissolved solids, and at the same time helps reduce tubesheet deposit buildup by removing some suspended solids.

Types of Blowdown

There are two types of boiler water blowdown, intermittent manual and continuous.

In continuous blowdown, as the term implies, water is withdrawn continuously from the boiler. Rate adjustments are made according to control test results. Continuous blowdown provides the advantage of maintaining close control of boiler water concentrations at all times.

The intermittent manual blowdown is necessary regardless of whether or not continuous blowdown is also used. The blowdown take-off point is located in the lower area of the boiler, so that in addition to lowering dissolved and suspended solids concentration, it will also aid removal of non-hardened sludge that tends to concentrate in the lower portion of the boiler and on the tubesheet. The water turnover rate is substantially greater than with continuous blowdown.

Summary

- Two types of sludge and scale-forming substances and their sources are:

TYPE		SOURCES
Suspended Inorganic Solids (Particulates)		Corrosion in boiler steam and feed water system. Ingress of raw water via condenser tube leaks.
Dissolved Inorganics Materials	Ca & Mg Bicarbonates	Raw water via condenser tube leaks.
	Silica	Traces in makeup. WTP IX breakthrough. Condenser tube leaks.
	Na^+, Cl^-, SO_4^{--} Ions	Traces in makeup. Condenser tube leaks. Na^+ from WTP IX breakthrough.
	Corrosion Products	Feed train corrosion.

- Adverse Effects of Sludge and Scale:
  - Soluble impurities concentrate in sludge by factors of 10,000 to 100,000, creating a very hostile enviroment with respect to corrosion
  - Under-deposit corrosion of tubes beneath the sludge pile via pitting and/or caustic attack
  - Sludge, over time, becomes extremely difficult to remove (like concrete)
  - Reduced heat transfer through boiler tube walls, unit efficiency drops
  - Possible shorter tube life resulting in a heat transport leak into the boiler, if through wall corrosion occurs
  - Production concerns
  - Deposits on tube support plates may lead to level control problems

- Blowdown is the continuous or intermittent removal of water from the boiler and its replacement with clean makeup water, in order to remove both dissolved impurities and suspended solids from the boiler.

- The purpose of blowdown is to reduce corrosion by minimizing the concentration of undesirable ions in deposits and by maintaining impurity levels at or below specification. It also helps to reduce the buildup of sludge and scale.

CARRYOVER

Carryover is the entrainment of impurities such as boiler water, solids and gases in steam exiting the boiler, and in simple terms may be viewed as steam contamination. Two mechanisms of carryover are mechanical and vaporous carryover. In mechanical carryover, water carried over in the steam contains soluble impurities such as sodium. Vaporous carryover is a function of the solubility of substances in the steam eg, silica.

Chemically, the problem of carryover centres on the soluble and insoluble solids contained in the water, (especially silica). These can lead to deposit formation on steam system components such as valve stems and plugs and turbine blading. However, owing to the low operating temperature and pressure in CANDU nuclear station boilers, vaporous carryover of silica has not been a problem to date. A detailed description of carryover is provided in 234, lesson 2.

Summary

- Carryover is the entrainment of impurities in steam leaving the boiler.

MAKEUP WATER QUALITY MONITORING

The traces of non-volatile impurities, eg, Ca^{++}, Cl^-, SO_4^{--}, in makeup water are almost all ionic. Therefore conductivity measurements, which reflect total dissolved ion content, provide an accurate indication of overall purity, except for sodium and silica which are monitored by on-line analysis.

Direct pH measurement of the very low conductivity makeup water is not used because of its inherent inaccuracy in the essentially nonionized water. Recall that pH measurements respond only to $[H^+]$ ions.

Sodium and silica have individual specifications because:

- They are the most likely species to break through IX columns.
- The sodium specification is so low that it can be exceeded without causing the conductivity specification to be exceeded.
- Silica is ionized only slightly, thus imparting very little conductivity to the water.

STANDARD OPERATION

Control and Monitoring of the C,FW,B System Operating Conditions

Figure 6 provides an overview of the control and monitoring of the C,FW,B system, and shows that:

- dissolved oxygen is reduced by the deaerator and by the addition of hydrazine,
- pH is controlled by adding ammonia or morpholine downstream from the CEP discharge,
- dissolved and suspended solids are reduced by blowdown,
- cation conductivity, oxygen, hydrazine, pH and sodium analyzers provide on-line monitoring information that is also verified by the analysis of periodic grab samples.

(a) **Boiler Water pH Control**

The pH of the water in the C,FW,B system is controlled via chemical additions downstream of the CEP discharge. On-line pH measurements are made in this area, prior to the LP feedheaters. Thus boiler water pH is controlled by maintaining the feedwater at the correct pH. Although the value of the desired operating pH for the C,FW,B system depends on the materials used in the vessels and piping, it is always alkaline.

In the newer CANDU stations, eg, BNGS-B and DNGS-A, the condenser and feedheater tubes are made of stainless steel, and the piping and most other components are of carbon steel. Thus the C,FW,B system is essentially "all-ferrous". In the older stations, eg, PNGS and BNGS-A, copper alloy tubing is used in the condensers and feedheaters, while carbon steel piping and components are used elsewhere in the C,FW,B system. This mix of materials creates a chemical control problem in that the **optimum pH** for copper alloys is 6-9, whereas for carbon steel it is 10-12. Therefore the chemical control of copper/ferrous systems differs from that of all-ferrous systems.

Copper/Ferrous Systems

For those stations with mixed copper/ferrous materials, a compromise is required and the desired condensate pH is 9.1. The pH is controlled using the amine morpholine (C_4H_9NO). This pH is the best compromise for protection of both metals in the system. While more alkaline conditions would be better for both the iron and the magnetite on the ferrous piping, the higher alkalinity would be harmful to the copper alloy condenser and feedheater tubes. Maintaining the above desired condensate pH keeps the **boiler water pH at the desired value of 9.1**.

The use of ammonia is undesirable because it promotes the oxidation of copper and zinc when oxygen is present.

All-Ferrous Systems

The desired condensate pH is 9.8. The pH is maintained at stations with all-ferrous feed trains by the addition of ammonia. The use of morpholine has been demonstrated to result in reduced corrosion product transport in the feedwater, and reduced erosion/corrosion in two phase (wet steam) regions. For this reason morpholine use is also specified at the stations with all-ferrous feed trains. It is not intended that morpholine will be used to maintain the pH, although it will certainly contribute. Both additives are volatile and thus impart alkalinity to the condensate. Maintaining the above desired condensate pH keeps the **boiler water pH at the desired value of 9.6**.

Volatility is important because all of the water which cycles through the boiler eventually vaporizes. If the added chemicals did not boil off with the water, they would tend to concentrate in sludge deposits in the steam generator, creating corrosion-promoting conditions. As an example, sodium phosphate is a base of the right strength, but its lack of volatility makes it unsuitable for this application. The use of these volatile bases (morpholine and ammonia) is often referred to as "AVT", ie all-volatile treatment.

Desired Boiler Water pH	Copper/Ferrous Systems 9.1	All-Ferrous Systems 9.6

Boiler tube composition is also station-dependent. For example:

- PNGS A&B - Monel
- BNGS A&B - Inconel 600
- DNGS - Incoloy 800

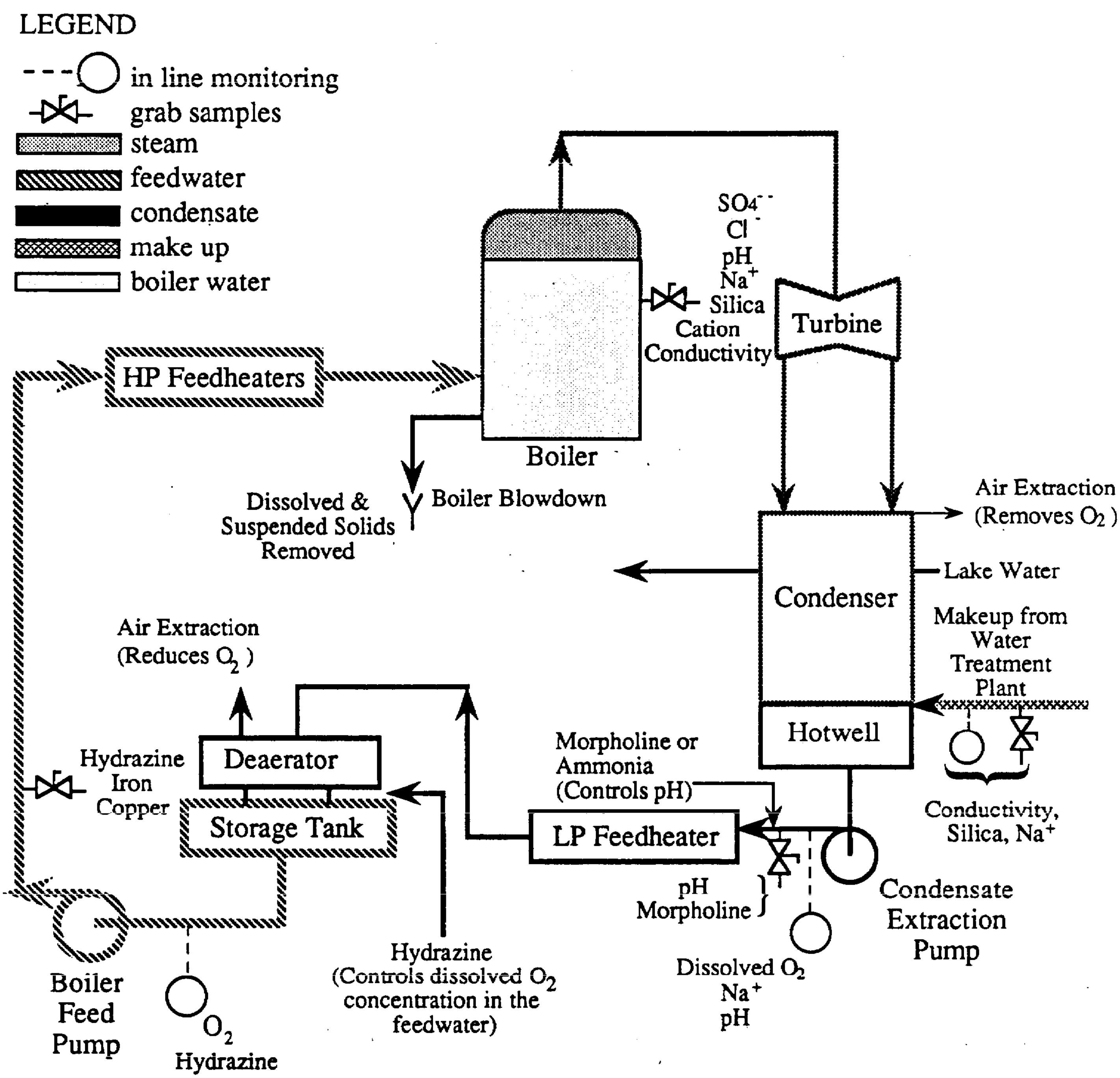

Figure 6: Condensate, Feedwater and Boiler System Chemical Control

(b) **Boiler Water Cation Conductivity**

Boiler water has a high background conductivity (K°) because of pH additives (morpholine, ammonia) and traces of lakewater salts and dissolved corrosion products. Hence, ordinary (specific) conductivity is not sensitive enough to be used as a control parameter. Therefore a sample of boiler water is passed through a cation exchange column, which replaces all cations (including those of morpholine, ammonia and hydrazine) with the much more conductive H^+ ion. Also, the conductive hydroxides formed by morpholine or ammonia have been replaced by non-conductive water. This heightens the sensitivity for the presence of anions (normally Cl^- and/or SO_4^{--}), because HCl and H_2SO_4 are more conductive than any of their salts. The conductivity of a sample thus treated is called **cation conductivity**. The desired cation conductivity for boiler water is ALARA with the specification being < 0.3 mS/m.

The use of very low conductivity makeup water from the WTP is a major factor in maintaining the conductivity of the boiler water ALARA. Continuous blowdown controls the boiler water conductivity by constantly removing impurities from the system. Cation conductivity of the boiler water is monitored by continuous analysis, with grab sample verification, and is a shutdown control parameter, ie a unit must be shut down if a specified value is exceeded. Maintaining cation conductivity ALARA protects against boiler tube corrosion.

(c) **Dissolved Oxygen**

Because oxygen is a strong oxidizer, dissolved O_2 is the most harmful impurity in the C,FW,B system.The desired concentration of dissolved O_2 in the condensate and feedwater is ALARA, while the actual specifications are ≤ 10 µg/kg for the condensate and ≤ 5 µg/kg for the feedwater.

Dissolved oxygen control is achieved in three stages following the condenser air extraction system. Since the main source of oxygen is from air leaking into sub-atmospheric parts of the turbine/condenser/extraction steam lines, a program to locate and seal air in-leakage is a major control factor.

Dissolved oxygen is removed from the condensate by the deaerator (DA) which contains sprays and cascade trays over which the hot water tumbles. The combination of heat and large surface area imparted to the water provides very efficient stripping of dissolved gases (DA operation is described in 234.). Oxygen is reduced to < 10 µg/kg (ppb) and nitrogen is also removed. This efficient stripping action reduces the consumption of hydrazine.

The final stage of dissolved oxygen removal is by the injection of hydrazine, (N_2H_4), between the deaerator and the deaerator storage tank, to chemically react with the remaining oxygen. Again, see Figure 6. It is injected at this point to:

- provide adequate temperature for reaction
- provide hold up time in the D/A storage tank
- ensure it will not be removed by the D/A

The chemical reaction is:

$$\underset{\text{Hydrazine}}{O_2 + N_2H_4} \rightarrow N_2 + 2H_2O$$

The nitrogen formed is non-corrosive.

A modest excess of hydrazine is required to control the dissolved O_2 concentration of the boiler feedwater to ≤ 5 µg/kg. This excess will gradually cause a slight pH elevation owing to ammonia (NH_3) formation from hydrazine decomposition. In ferrous-brass tubed systems the excess must be closely controlled to prevent copper dissolution.

(d) **Hydrazine**

The specification for hydrazine depends on the materials used in the system:

- Ferrous/Copper: 10 - 30 µg/kg
- Ferrous: 10 - 60 µg/kg

These hydrazine levels are selected, as noted above in (c), to control the dissolved O_2 concentration in the boiler feedwater at ≤ 5 µg/kg.

Control is achieved by adjustment of the rate of hydrazine addition in response to on-line and/or grab sample analysis.

(e) **Sodium, Chloride, Sulphate, Silica**

The desired level of these impurities throughout the C,FW,B system is ALARA.

The only two sources of these impurities are (a) raw water, via condenser tube leaks, and (b) makeup water from the WTP. Therefore, overall "control" is achieved by monitoring continuously and quickly finding and plugging any leaking condenser tubes while also maintaining high purity makeup. These impurities are removed from the boiler by blowdown.

(f) Iron and Copper

The desired level for these two impurities is also ALARA. As mentioned earlier a major objective of secondary side chemical control is to minimize the transport of corrosion products to the steam generator. Because of the structural materials in the system, in particular copper alloys and carbon steel, copper and iron species make up most of the corrosion products.

Thus maintaining feedwater iron and copper at or below specification represents the achievement of this objective.

Summary

The following table summarizes the standard conditions for the Condensate, Feedwater and Boiler Water Systems.

FLUID	CONTROL PARAMETER	DESIRED CONDITION	CONTROLLED BY
Condensate	pH (all-ferrous systems)	9.8	Adding ammonia[1].
	pH (ferrous/copper systems)	9.1	Adding morpholine[1].
	Dissolved O_2	ALARA	Minimizing air inleakage. Degassing in the condenser. Deaerator removes O_2. Adding hydrazine[2].
	Sodium (a diagnostic parameter)	ALARA	Monitoring to detect and minimize effects of condenser tube leaks.
Feedwater	Dissolved O_2	ALARA	Minimizing air inleakage. Deaerator removes O_2. Adding hydrazine[2].
	Total Iron, Total Copper	ALARA	Maintaining desired pH and low dissolved O_2. Blowdown.
	Hydrazine	Slight Excess	Addition control in response to chemical analysis.
Boiler Water	Cation Conductivity	ALARA	Using high purity makeup. Blowdown.
	pH (all-ferrous systems)	9.6	Adding ammonia[1].
	pH (ferrous/copper systems)	9.1	Adding morpholine[1].
	Chloride, Sodium, Silica, Sulphate	ALARA	Minimizing condenser tube leaks. Using high purity makeup. Blowdown.

[1]The addition point for morpholine/ammonia is downstream of the CEP discharge.

[2]The hydrazine addition point is between the deaerator and the deaerator storage tank.

NON-STANDARD OPERATION

If an upset occurs within the C,FW,B system, a variety of chemical parameters can be monitored to identify possible causes or sources of the non-standard condition. Diagnosis following chemical analysis provides direction for the action required to restore normal operation.

Table 1 summarizes the key C,FW,B chemical parameters that are used to identify the possible cause(s) or source(s) of non-standard conditions, the method(s) of control and the consequence(s) if no action is taken. The failure mechanisms, such as stress corrosion cracking or buildup of corrosives in scale and sludge, have all been discussed previously, but it is worthwhile to add some clarifications and emphasis.

The Action Level 3 parameters for the C,FW,B system are Feedwater dissolved O_2 and Boiler cation conductivity, sulphate, chloride and sodium.

Dissolved O_2

Dissolved O_2 has shutdown action levels in the feedwater system:

(i) to minimize corrosion product transport to the steam generators;
(ii) because of the contribution of dissolved oxygen to corrosion of steam generator tubes, in particular, pitting corrosion in the presence of chloride.

Dissolved O_2 is the most harmful impurity in the C,FW,B system. It converts the protective magnetite on the carbon steel components to porous rust, and also promotes general metal corrosion throughout the system. The resulting corrosion products add to tube sheet sludge deposits. Various types of corrosion are accelerated by an increase in dissolved O_2 concentration.

Dissolved O_2 increases the aggressiveness of the chloride ion, particularly under the localized anodic conditions that encourage pitting corrosion. When oxygen in the galvanic cell is reduced ($4e^- + 2H_2O + O_2 \longrightarrow 4OH^-$), the voltage of the existing galvanic cell is raised significantly, thereby enhancing corrosion by the chloride ion. The net effect is the production of an acidic chloride environment which tends to continue, raising the amount of positive charge, and causing more chloride ions to migrate to the anode.

Boiler Cation Conductivity

This parameter represents an overall indicator of anionic impurity levels in the steam generator. These impurities represent both aggressive inorganic anions such as sulphate and chloride, as well as benign organic anions. The organic anions provide a level of background cation conductivity so that at low cation conductivities, organic anions are the major contributor. At high cation conductivities, the inorganic anions will usually provide the major contribution. Shutdown actions are in place because of the adverse effects individual inorganic anions can have.

Sulphate

Boiler sulphate has shutdown action levels for three main reasons:

(i) it can cause intergranular corrosion of steam generator tubes particularly I-600;
(ii) it can cause pitting attack of steam generator tubes although usually less severe than chloride; and
(iii) acidic sulphate can cause localized corrosion of ferrous materials such as tube support plates.

Chloride

Boiler chloride has shutdown action levels because it can cause:

(i) corrosion of ferrous support plate material; and
(ii) pitting corrosion of nickel alloy boiler tubes particularly in the presence of dissolved oxygen and an acidic environment .

Sodium

The main reason why boiler sodium has shutdown action levels is the concern for intergranular corrosion or stress corrosion cracking of the boiler tubes since sodium concentrates as a hydroxide. The locations of most tube defects has been in tube to tubesheet crevices, tube to tube support plate crevices, or sections of tubing surrounded by sludge pile.

Comments Regarding Table 1

Water Treatment Plant Excursions

The specific conductivity of the WTP demineralized water used for makeup is continuously monitored before it enters the C,FW,B systems. Therefore the products of a WTP excursion can only enter the C,FW,B stream as a result of at least two of the following: operator errors, on-line instrument failure, and valve failure.

Since there are no IX columns in the C,FW,B system, blowdown and the addition of pure makeup water is the only available method of diluting any off-specification makeup water entering the C,FW,B system. Depending on the severity of the excursion, a "hot soak" using makeup water may be required to leach some of the impurities out of the sludge pile. These impurities are then removed by blowdown, draining, and refilling with clean makeup water.

Silica

Silica contributes to boiler scale and sludge, mostly in the form of silicates. Although it contributes to carryover at fossil stations, silica is not a serious problem at nuclear stations because of the much lower boiler temperatures.

Tritium

Tritium emissions via steam release or blowdown constitute a potentially unmonitored environmental hazard. Tritium above background found in the C,FW,B water indicates a boiler tube leak with the economic consequences of loss of D_2O, repair costs and the cost of replacing lost power production during the shutdown.

Table 1: Condensate, Feedwater a

(A summary of the key C,FW,B chemical parameters that are us

	NON-STANDARD PARAMETER	POSSIBLE CAUSE/SOURCE
(i)	High pH (Condensate, Boiler)	WTP "base" excursion allows NaOH to enter makeup stream.
		Excess amine/ammonia injection.
(ii)	Low pH (Condensate, Boiler)	WTP "acid" excursion allows H_2SO_4 to enter makeup stream.
		Insufficient amine/ammonia.
(iii)	High Dissolved O_2 (Condensate, Feedwater)	Air in-leakage to sub-atmospheric sections of turbine/condenser. Malfunction of degassing equipment. Insufficient hydrazine.
(iv)	High Boiler Water Sodium	WTP "base" excursion allows regenerant to enter makeup stream.
		Condenser tube leaks are letting raw water into C,FW,B system.
(v)	High Boiler Water Sulphate	SO_4^{--} may be from WTP.
(vi)	High Boiler Water Chloride	
(vii)	High Boiler Water Cation Conductivity	WTP "acid" excursion allows SO_4^{--} to enter makeup stream.
		Condenser tube leaks are letting raw water into C,FW,B system.
(viii)	High Silica in Boiler	Poor makeup quality.
(ix)	Low Hydrazine	Increased O_2 in feedwater.
		Inadequate hydrazine injection.
(x)	High Hydrazine	Injection rate too high.
(xi)	Tritium	Boiler tube failures.

ıd Steam Generator System - Non-Standard Operation

ιo identify the causes and control of non-standard conditions and the consequences if no action is taken)

METHOD OF CONTROL	CONSEQUENCE IF NO ACTION TAKEN
Additional boiler blowdown and replenish with pure makeup (no IX columns). Hot soak if necessary.	Boiler tube corrosion due to high OH^-, especially under sludge pile.
Correct injection dosage of amine/ammonia.	Corrosion of copper alloys, especially in the presence of O_2 and NH_3. eg, condenser and feedwater tubes at PNGS and BNGS-A. Discharge of ammonia to environment via blowdown.
Additional boiler blowdown and replenish with pure makeup. Hot soak if needed.	Concentration of H_2SO_4 in sludge pile accelerates corrosion of boiler tubes. Loss of protective magnetite layer on carbon steel surfaces permits general corrosion.
Correct injection dosage.	
Locate and seal air leaks. Increase rate of hydrazine injection. Check air extraction system. Check deaerator operation.	General magnetite breakdown and metal corrosion throughout the C,FW,B system. Corrosion products add to sludge deposits. Dissolved oxygen increases the aggressiveness of the chloride ion.
Additional boiler blowdown and replenish with pure makeup. Hot soak if needed. (Shutdown required.)	Boiler tube corrosion and possible failure.
Additional boiler blowdown and replenish with pure makeup. Shutdown if required. Plug leaking condenser tubes.	
Additional boiler blowdown and replenish with pure ▸ makeup.	Boiler tube scale formation. Boiler tube corrosion and failure. Loss of protective magnetite layer on carbon steel surfaces permits general corrosion.
Plug leaking condenser tubes. ▸	
Additional boiler blowdown and replenish with pure ▸ makeup.	Boiler tube scale formation. Increased tubesheet deposits. Possibility of carryover.
Locate and seal air leaks into system.	General magnetite breakdown and metal corrosion through the C,FW,B system. Also, corrosion products add to tubesheet sludge deposits.
Increase hydrazine injection rate.	
Decrease hydrazine flow.	Ammonia formation: NH_3 corrodes copper alloys.
Shutdown, repair, observing environmental and economic limits.	Potential for unmonitored emission of tritium to the environment. Economic penalty with respect to D_2O losses and down-time.

STARTUP AND SHUTDOWN CONCERNS

Minimizing corrosion continues to be the focus in **shutdown** chemistry control in the C,FW,B system. Alkalinity and hydrazine levels are therefore maintained at operational values in the short term.

Minimal sodium, chloride and sulphate concentrations are desirable. Elevated concentrations due to hideout return will occur on shutdown. These species concentrate beneath deposits and within crevices to concentrations much higher than the bulk water during normal operation. When heat flux and temperature are reduced, species diffuse back into the bulk water from confined regions. This phenomenon has led to implementing hot and cold soak procedures whereby accumulation of sodium, chloride and sulphate are reduced in boiler crevices and the sludge pile. Drain and refill of the boiler may be necessary to reduce contaminant levels.

When a shutdown will exceed seven days, "boiler layup", which means increasing the hydrazine concentration in the boiler water, is implemented. Boiler water homogeneity is maintained by recirculating the boiler water. Amine additions are continued to maintain pH alkaline. The alkalinity contribution from the additional hydrazine reflects in a slightly higher pH level. Close attention is paid to any increased ammonia concentration from hydrazine decomposition. Although not normally expected at lay-up temperatures, any such ammonia must be controlled because:

(a) Releases to the environment must be minimized,
(b) Copper alloys in the system would be at risk.

Nitrogen blanketing may also be used to exclude air from the system during boiler layups.

During **startup**, the main boiler chemistry concern is high corrosion product particulate levels, which result in deposit buildup. The counteraction to this is to perform intermittent manual blowdown to whatever extent is practicable with respect to the availability of makeup water.

Every effort should be made to ensure chemistry is within specification as soon as possible after startup. Operating specifications apply at and above 30% full power. Tests indicate that relatively small quantities of impurities hide out at this power level compared to full power. This chemical specification point ensures that when power is raised, the available quantity of species to hide out is at a minimum.

Operational specifications are only applied at 30% power because condensate and feedwater oxygen specifications are difficult to achieve at lower power levels because more components are draining to the condenser. Lower deaerator steam flows at low power levels are also not as effective in oxygen scrubbing.

SOURCES OF INFORMATION

On-Line Monitoring

On-line monitoring, indication and annunciation provide current information, trending and alarms for the operator with respect to pH, Cation Conductivity, Specific Conductivity, Dissolved Oxygen, Sodium and Hydrazine.

Grab Sample Analyses

Grab sample analyses are done routinely by the chemical unit. All of the above on-line variables are verified by this technique and any need for instrument calibration and repair is confirmed. Additional grab sample analysis covers a number of parameters, either impractical or impossible to monitor on-line. These grab sample analyses comprise Silica, Amine/Ammonia, Sulphate, Chloride, Iron, Copper, pH and Tritium, along with verification of the above on-line parameters. The data is also used for historical records.

Summary

The following table summarizes the sources of information used to monitor the chemistry of the makeup water and the C,FW,B systems:

SYSTEM	ON-LINE MONITORING	GRAB SAMPLE ANALYSES
WTP (Product)	Conductivity Na^+, Silica	
C,FW,B - Condensate	Dissolved O_2, Na^+, pH	Morpholine, Ammonia
C,FW,B - Feedwater	Dissolved O_2, Hydrazine	Iron, Copper
C,FW,B - Boiler Water		Cation Conductivity, Tritium, Silica, Na^+, Cl^-, SO_4^{--}, pH

ASSIGNMENT

You should ensure that you can answer the objectives if they are presented as questions. Also answer the following questions:

1. (a) State the two reasons why deposits in boilers are undesirable.
   (b) State three methods used to minimize the buildup of sludge pile deposits.

2. State two reasons why boiler blowdowns are required during normal operation, even when the makeup water is within specification and there are no condenser tube leaks.

3. In a few sentences, describe the importance of maintaining alkaline pH in the C,FW,B system.

4. (a) Identify the most harmful of all impurities in the C,FW,B system, under standard operating conditions.
   (b) State four problems created or aggravated by this impurity.
   (c) State briefly how this impurity is controlled.

5. Briefly explain how under-deposit corrosion may be minimized in the C,FW,B system.

6. In a few sentences describe why it is important to maintain very high makeup water purity.

7. A condenser tube starts to leak. Explain its effects on the following C,FW,B parameters:
   - pH
   - Cation Conductivity
   - Sodium
   - Silica
   - Sulphate
   - Chloride
   - Dissolved Oxygen
   - Iron
   - Copper

8. (a) State which C,FW,B chemistry parameters have Action Level 3 values.
   (b) Explain why these parameters have Action Level 3 values.
   (c) State the response required if these Action Level 3 values are exceeded.

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