Chemistry - PI 24

CHEMICAL ADDITIVES AND BLOWDOWN

In Module 21-1, we discussed the sources and effects of various impurities which may be present in the secondary system. Recall that the major problems centered on:

- deposition.
- corrosion.
- erosion.

In order to minimize these effects **chemical additives** may be injected into the system.

"What chemicals are added to the secondary system, where, and why?" (If you want to take a quick look at a secondary system schematic, see Module 70-0).

Morpholine

Morpholine is a volatile organic chemical which is in-
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pholine is a pH controller and is injected, in a modern station, automatically and continually as required on a signal from a pH monitor.

Hydrazine

Hydrazine is injected just after the deaerator. It is an oxygen scavenger and is used to pick up any oxygen which passes the deaerator.

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

Secondarily, hydrazine helps raise the feed system pH to optimum level.

Both morpholine and hydrazine are volatile liquids and do not contribute to system solids. Furthermore, they travel with the steam and help protect the steam system.

Cyclohexylamine

For those plants where only ferrous components are present (eg, Bruce B and Darlington), the use of cyclohexylamine which is a slightly stronger base than morpholine may be advantageous to achieve the higher pH required at a lower injection rate. Cyclohexylamine would be injected at the Condensate Extraction Pump discharge just the same as morpholine. Note that cyclohexylamine is also a volatile organic liquid.

Phosphates

Until quite recently, it was the practice to inject one form or other of Sodium Phosphate into the steam generator. The benefits were that phosphate would stay in the water of the steam generator and provide optimum pH conditions. Furthermore, any calcium or magnesium salts entering due to condenser leakage, would be precipitated into a soft non adherent sludge by the phosphate. (You have seen this when detergent powder consisting mainly of phosphates is added to laundry.)

Recent data (1975-1980) now points to the use of phosphates as a contributory factor in the thinning of Inconel tubes. Therefore, the use of phosphates in NGD has been discontinued. Note that for conventional ferrous boilers, "phosphate" is the treatment of choice.

Blowdown

Throughout our discussion of Secondary side impurities, it has become evident that solids will accumulate in the steam generator. These solids are: corrosion products, slight contamination of feedwater, "dirt" in systems. For the most part, these solids are not volatile and if allowed to accumulate in the steam generator, will contribute to deposition and carryover.

Another point to remember is that silica, for which there is no effective chemical treatment, accumulates in the steam generator and if its concentration is allowed to rise, it will ""boil off" and travel with the steam. Modern power plant practice sets the limit of 0.02 parts per million of silica in steam. This limit can be achieved by limiting silica in the steam generator.

"How are "inert" solids and silica controlled in the steam generator?"

Blowdown is the method used to remove part of the boiler water and replace it with makeup water. The makeup water contains a much lower impurity concentration than the boiler water and so the amount of impurity in the boiler is reduced.In addition, the boiler water is removed from the bottom of the boiler where the solids have collected. When the valves are opened, the water surges out under the high boiler pressure and the solids are carried along in slurry form.

The purpose of blowdown depends on the condition which has made it necessary. Blowdown is used to avoid scale formation due to excessive amounts of suspended solids and to prevent carryover of solids in the steam. It is also used to control high dissolved solids concentrations. For high pressure boilers (> 4000 kPa), blowdown is based upon limiting the silica content of the boiler water so as to minimize the amount of silica that goes over with the steam. Contamination of steam with silica is usually not a big problem where boiler pressures are maintained below 2800 kPa.

Types of Blowdown

a) Intermittent Manual Blowdown

There are two types of boiler water blowdown - intermittent manual blowdown and continuous blowdown. Manual blowdown (or sludge blowdown) is necessary for operation of a boiler regardless as to whether or not continuous blowdown is also used. The blowdown takeoff is usually located in the lowest part of the boiler so that in addition to lowering the dissolved solids concentration of the boiler water, it will also remove a portion of the sludge which tends to concentrate in the lower part of the boiler.

When continuous blowdown is also installed, the primary purpose of manual blowdown is to aid in the removal of suspended solids which may have accumulatd in the lower boiler. However, in instances where the boiler feedwater is exceptionally pure, blowdown can be employed infrequently (eg, at Pickering).

When continuous blowdown is not installed, it is necessary to use manual blowdown to control concentrations in the boiler water (eg, at NPD). Whenever the dissolved solids or suspended solids approach or exceed predetermined limits, it is necessary to use manual blowdown to lower these concentrations. In practice, the valve for bottom blowdown is opened periodically in accordance with an operating schedule and/or chemical control tests. From the standpoint of control and results, frequent short blows are preferred to infrequent lengthy blows. This is particularly true when the suspended solids content of the water is appreciable. Examine the records of short, frequent blows versus long, infrequent blows in Figure 1. The curves show that with the use of frequent, short blows, a more uniform concentration of solids is maintained and in general, a smaller quantity of water is blown down because of better control. However, from an operating standpoint, it is sometimes undesirable to use manual blowdown frequently enough to properly control concentrations - particularly where the feedwater solids content is high.

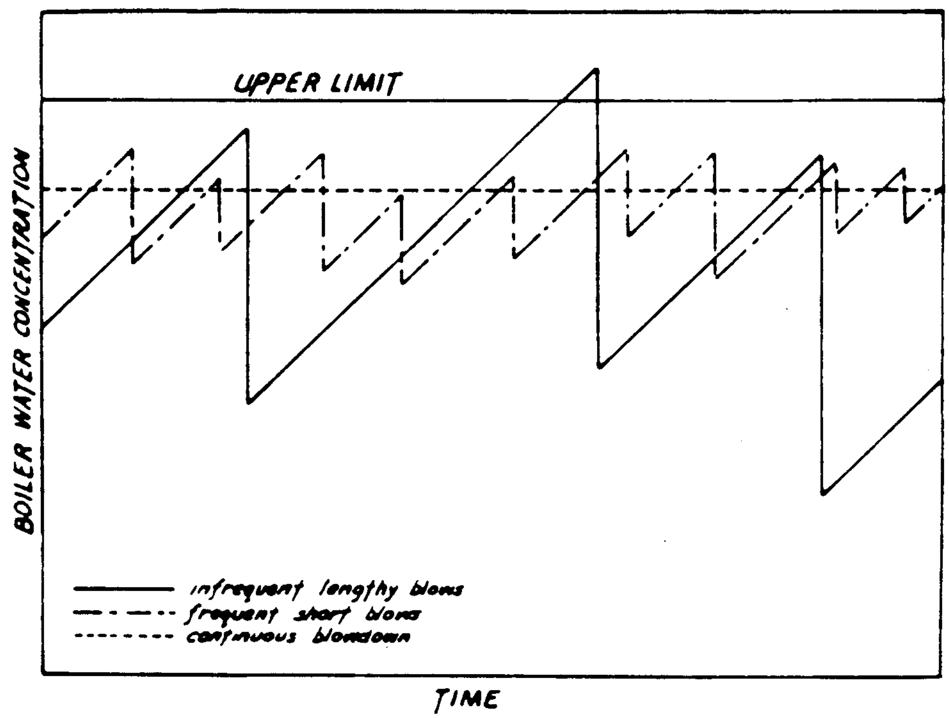

Figure 1

Effect of Different Types of Blowdown on Boiler Water Concentration

b) Continuous Blowdown

Continuous blowdown may be viewed as an extension of the practice of frequent, short blows. Blowdown water is withdrawn from the boiler continuously. Periodically, adjustments are made to the rate of withdrawal in accordance with control test results.

Continuous blowdown has two advantages. First, it is possible to maintain close control of boiler water concentrations at all times. Second, the heat content of the blowdown water can be recovered. If an efficient heat exchanger is used, the only heat loss is the terminal difference between the incoming feedwater and the blowdown water to the sewer; usually about 10°C.

Further savings can be realized by flashing a portion of the boiler water into steam at a lower pressure (a process similar to the use of dashboxes on the extraction steam lines from the turbines) and using the resulting low pressure steam for process or feedwater heating. The use of a flash tank in conjunction with a heat exchanger makes it possible to use a smaller heat exchanger as a large portion of the recoverable blowdown water heat is contained in the steam. Thus a savings can be made on capital equipment cost.

Practice Exercises

1. Fill in the following table:

Item	Added at:	for the purpose of:
Morpholine		
Hydrazine		
Cyclohexylamine		

2. Cyclohexylamine would be used if -----.

3. The purpose of blowdown is to -----.

4. Write a brief description or draw a diagram to explain the difference between continuous and intermittent blowdown.

Check your answers to these with a colleague.

Putting Things Together:

The AECB has a question which they are fond of posing which covers the material in modules 21-1 and 21-2. Perhaps you would like to draft out an answer, then compare it to the sample answer provided.

Question:

With respect to boiler feed water discuss:

(a) pH
(b) conductivity
(c) dissolved gas content
(d) organic matter

In terms of: (a) Why they are controlled.
(b) How they are controlled.
(c) Consequences of not controlling.

Answer:

(a) pH is controlled to prevent corrosion of steels and brasses in the system.

It is controlled at 8.6 - 9.2 by adding MORPHOLINE, a pH controller at the Condensate Extraction Pump discharge. MORPHOLINE is a volatile (thus will not form deposits) amine and the addition of a small amount will raise the pH to the required range. At the deaerator outlet, HYDRAZINE is added to scavenge OXYGEN. It should be noted that hyrazine is also a volatile amine and a slight excess will help maintain the pH in the desired range.

If pH is not controlled, too low a pH, ie, below 8.6 will lead to acidic attack on the mild steel in the system leading to loose corrosion products which will be transported to the steam drum. (Not to mention the damage to system components as well). Too high a pH will result in two problems:

(i) Brasses in the systems, eg, L.P. Heater tubes, will tend to dissolve.

(ii) Any protective magnetite layer on steels will tend to be removed.

The range of 8.6 - 9.2 is chosen in the first place as a compromise between the optimum pH of 10.0 for steels and a neutral pH (7.0 - 8.0) for brasses.

(b) Conductivity is a measure of dissolved ionized substances. If not controlled, these substances may accumulate as scale in the steam generator; may be carried over with steam to form turbine deposits, or may be corrosive or agents leading to stress corrosion cracking (eg, Cl^-).

Low conductivity is maintaned by adding only pure make-up water, and by ensuring integrity of the unit main condenser and by blowdown. If conductivity is not controlled, the potential hazards are:

- scaling in the steam generator
- boiler solids carryover
- corrosion of system components
- if chlorides are involed stress corrosion cracking of stainless steels and zircalloys may occur.

(c) The dissolved gases that are normally considered are

Nitrogen and Oxygen from air

Ammonia from breakdown of hydrazine and morpholine

Carbon Dioxide from breakdown of morpholine and tramp organics

Oxygen and CO_2 are corrosive to steels. Ammonia, and CO_2 are corrosive to brasses and N_2 is a nuisance as it may lead to carryover in the steam generator and adds to the non-condensibles loading of the condenser.

Gases are removed mechanically by the deaerator and by the air ejector from the air removal section of the condenser.

More specific treatments of a particular gas are:

Oxygen: Residual oxygen after the deaerator is removed by the addition of Hydrazine

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

Ammonia: Air ejector drains may be run to sewer as this is where the majority of ammonia collects.

Carbon Dioxide: Most likely neutralized at pH of 8.6 - 9.2.

The consequenes of not controlling these gases are:

- corrosion by OXIDATION (O_2)
- gouging of steels by CO_2
- gouging of brasses by Ammonia and somewhat by CO_2
- bumping and priming in the steam generator
- large non condensibles therefore low condenser vacuum.

(d) Organic matter if not controlled may lead to foaming in the steam drum, asphaltic deposits and the generation of CO_2 in the system.

There is no true internal treatment for organics other than blowdown. Externally, organic matter is removed from make-up water in the clarifier and in the carbon filters.

The consequences of not controlling organic matter are:

- foaming in the steam drum
- asphaltic deposits in the steam drum
- generation of CO_2.

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