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## **Boiler Systems – Chemical Treatment**

*By Irvin J. Cotton, Arthur Freedman Associates, Inc. and  
Orin Hollander, Holland Technologies, Inc.*

**This article is the third of a three part series on boilers. In part one, the authors discussed boiler design and classification. Part two discussed boiler components. In part three, the authors discuss the various chemistries used in boiler water treatment.**

### **Chemical Treatment**

In boiler operations or in any other endeavor, it is important to following established guidelines for reliable operation. In the area of boiler operations, some guidelines that are available include:

- ASME Consensus on operating practices for the control of feedwater and boiler water chemistry in modern industrial boilers - Book No. 100367.
- ASME Consensus for the lay up of steam generating systems practical guide to avoiding steam purity problems in the industrial plant (ASME CRTD, Vol. 35).
- ASME Boiler and Pressure Vessel Code - Recommended rules for care of power boilers.
- Electric Power Research Institute (EPRI), Project 2712: Consensus Guidelines on Fossil Plant Cycle Chemistry.

There are numerous problems that commonly occur in boiler systems. These can be classified as follows:

Pre-Boiler corrosion (boiler make-up and feedwater system)

Boiler system corrosion

Boiler system deposition

Carryover of steam purity problems

Condensate system corrosion

### **Important Issues**

Understanding boiler system design as discussed in part 1 is very important to effectively chemically treat the systems. Treatment philosophies are as follows:

- Solubilizing type chemical treatment programs should not be used in a fire tube boiler due to design and control issues.
- In hot water boilers systems, treatment should consist of normal phosphate type programs; however, especially when oxygen ingress is common, high levels of sodium nitrite (1500 mg/L) may be more effective.

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- With higher heat transfer systems, in addition to requiring high quality feedwater, should utilize solubilizing or coordinated PO<sub>4</sub>-pH programs.
- HRSG's systems must always be treated using demineralized or equivalent feedwater and an equilibrium PO<sub>4</sub> type chemical treatment.
- Proper lay-up, start-up and shutdown procedures must be in place.
- All applicable regulations must be followed.
- Systems should be monitored as per established guidelines and inspected effectively when required.

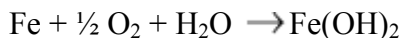
### **Preboiler Corrosion**

Most of the oxygen present in feedwater is removed in the deaerator by so-called "mechanical means." The scrubbing section of deaerators heat incoming water by mixing it with steam. The solubility of oxygen and other dissolved gases is greatly reduced at elevated temperatures and most of the gases are vented to the atmosphere. In industrial boiler feedwater systems, such treatment usually reduces the oxygen concentration to below 20 µg/L (ppb).

Because oxygen can be harmful to feedwater systems even at this low concentration, chemicals are generally fed to the storage section of the deaerator to react with the remaining molecular oxygen. Oxygen scavengers do not actually remove oxygen in the sense that mechanical deaeration does. Instead, the scavengers react with oxygen to render it harmless by reducing it to a lower oxidation state. Reduced oxygen is incapable of initiating pitting attack.

Dissolved oxygen in the feedwater can attack the feedwater line, heaters, and the economizer. Oxygen induced corrosion of low carbon steel is an electrochemical reaction and often results in localized pitting of the metal surface. The rate of reaction and severity of this type of corrosion will depend upon the level of dissolved oxygen, temperature, and pH of the feedwater.

Corrosion of steel is a spontaneous electrochemical reaction that occurs between iron and oxygen. The overall reaction is:



Oxygen attack on steel can be decreased by maintaining an alkaline pH and limiting the oxygen concentration.

The factors affecting oxygen scavenging reaction rates include:

- Oxygen concentration
- Presence of a catalyst
- Reaction time

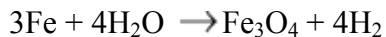
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- pH
- Temperature
- Scavenger feed rate and decomposition

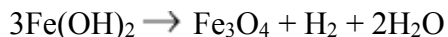
Oxygen scavengers in use include sulfites, hydrazine, carbohydrazide, hydroquinone, erythorbic(ascorbic) acid, diethylhydroxylamine (DEHA) and methylethylketoxime (MEKO) [Editor-see Fall 2002 issue of *The Analyst*, page17, for details on the chemistry of oxygen scavengers].

### **Boiler System Corrosion and Deposition**

A magnetite layer forms on boiler system metal surfaces under normal conditions according to the following overall reaction:



Ferrous hydroxide [ $\text{Fe}(\text{OH})_2$ ] is believed to be an intermediate in this process, converting to magnetite above 100°C according to the Schikorr reaction:



The resulting protective metal oxide acts as a barrier against further corrosion, which passivates the metal and inhibits further oxidation. There are three principal steps in the growth of any metal oxide layer:

- Surface reactions at the metal/oxide and at oxide/environmental interfaces.
- Transport of chemical species through the oxide by diffusion.
- Deposition of oxides from the circulating boiler water.

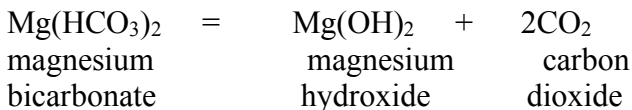
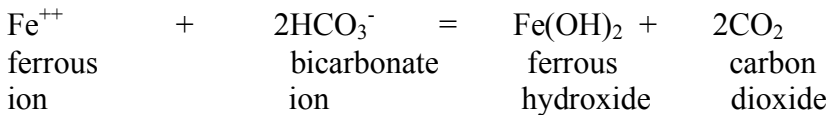
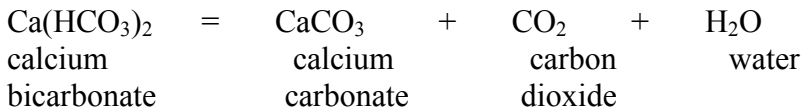
Iron oxidation in boilers results in the formation of two magnetite layers. The outer layer is porous, is easily penetrated by water and aggressive ions, and is the site of surface reactions. The inner layer is relatively less porous, and its growth is determined by diffusion of chemical species through the layer.

Deposition is the accumulation of material on boiler surfaces that can cause overheating as well as circulation restrictions. Both conditions frequently result in unscheduled outages.

Many solids, soluble in boiler feedwater, precipitate in the boiler water. This happens due to change in chemistry of water when going from feedwater to boiler water conditions, and/or retrograde solubility characteristics of some salts. One of the more significant chemical changes in feedwater to boiler water is the production of carbonate which will

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combine with calcium to form calcium carbonate, a relatively insoluble salt. Magnesium hydroxide and iron oxide are also produced by changes in water chemistry.



Calcium, magnesium, iron, copper, aluminum, silica and to a lesser extent silt and oil, are common contaminants in boiler feedwater that can form deposits. This results in scale that is crystallized directly on tube surfaces and/or sludge deposits consisting of various salts that have precipitated elsewhere. Scale forms where it can be tolerated least - on high heat transfer surfaces.

There are several basic approaches to selecting industrial internal boiler water treatment for the control of deposition: solubilizing programs, precipitation programs, and for high purity water systems, coordinated phosphate - pH programs.

Precipitating programs add phosphate to form calcium phosphate complexes in an alkaline environment. The precipitate (generally  $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$  - hydroxyapatite) is relatively non-adherent and is removed through boiler blowdown. Synthetic polymers are added to condition the precipitates to minimize deposits. Generally, polyacrylates and polymethacrylates of a specified molecular weight and concentration are used. The carboxylate portion of the polymer is the active site, which changes the charge on the deposit, and helps maintain cleaner heat transfer surfaces. Some newer phosphorous-based active polymers have also been effectively used.

Solubilizing programs chemically react with the ions that form deposits, such as calcium, magnesium, iron and copper. Chelants are typically used in these programs. The chelant attaches to the metal cation at two or more points to provide exceptional stability. The metal chelate formed is water-soluble. When the chelate is stable, precipitation does not occur. While there are many substances having chelating properties, EDTA has been commonly used for boiler feedwater treatment in the past. More commonly, proper levels of polymers are used. If sufficient concentration of some synthetic polymers are fed,

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solubilization can occur. Solubilizing programs can be combined with precipitating programs to provide other approaches.

Higher-pressure boilers using demineralized makeup water generally have a large percentage of condensate returns and high heat flux areas. It is these conditions, more than the operating pressure that makes high-pressure boilers prone to caustic attack; thus, they require specialized treatment. Boiler water with this characteristic has the potential of dissolving the protective magnetite layer when highly concentrated. Steam generating units supplied with demineralized or evaporated makeup water, or pure condensate, may be protected from caustic damage by using a system of treatment known as coordinated pH/phosphate control.

Avoidance of caustic corrosion can involve several different measures, depending on the cause of the problem. One step is to maintain caustic-free bulk water in addition to keeping the system free of deposits. This can be accomplished with a coordinated phosphate-pH program in which sodium phosphates act as buffering agents. Disodium phosphate reacts with potentially corrosive caustic to generate trisodium phosphate.



Coordinated pH/phosphate programs are normally maintained between 2.6 to 2.8 molar ratio of sodium to phosphate.

As was found with the phosphate precipitation and solubilizing control programs, the use of dispersants will improve the coordinated pH/phosphate program performance in terms of deposit control.

### **Steam Purity**

Steam is used for a variety of uses such as process heating, direct process injection, equipment drive, and possibly power generation. Whatever the end use, steam purity is always a concern. Some of the concerns and results of poor steam purity are as follows:

- Deposition on turbine blades which can result in loss of turbine efficiency, corrosion of turbine blades and rotors, stress corrosion cracking of turbine components as well as deposition on the turbine over-speed trip valve resulting in potential damage to the turbine and possible injury to operating personnel.
- Potential for superheater failure on boilers or steam generators so equipped.
- Potential for failure of steam lines due to carryover induced stress corrosion cracking. This situation could also result in potential injury to operating personnel.
- Potential for process contamination

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In summary, steam purity is important to effective and efficient operation.

Maintenance of effective boiler water level control, minimizing exceeding maximum load rating and rapid load changes, use of good boiler feedwater and attemperation water quality and use of effective steam purification equipment will minimize steam purity problems.

ASME Guidelines specify maximum boiler water concentrations recommended as a function of pressure to maintain good quality steam.

Use of a chemical antifoam agent is recommended especially where chemical contamination, which can cause foaming, is possible.

A program of closely monitoring steam using proper ASTM sampling nozzles and techniques on a continuous basis will minimize steam contamination and its associated problems.

### **Condensate System Corrosion**

Condensate systems are complex and spread over a significant area. A detailed understanding of the piping, equipment and conditions is required to select the best approach both from an operational and mechanical (venting, avoiding ingress of oxygen, protection during downtime) standpoint and from a chemical treatment approach is required. Key to success is effective monitoring and control.

The problems resulting from iron and copper corrosion in condensate systems are not confined to the piping and equipment damaged or to loss of water and energy when condensate is lost. Corrosion products and process chemicals from corrosion-caused leaks, if returned to the boiler, can contribute to the formation of damaging boiler deposits, reducing reliability and increasing operating and maintenance costs.

Iron can corrode in water even in the absence of oxygen. In a condensate system the water contains varying amounts of contaminants that promote the corrosion reaction, the most common being dissolved oxygen and carbon dioxide. In the presence of oxygen, the corrosion of iron proceeds rapidly. Oxygen corrosion is easily recognized by hemispherical pitting. Oxygen pitting begins at weak points in the iron oxide film and continues at the same location.

Oxygen can enter the condensate by direct absorption of air, by introduction with the feedwater and subsequent flashing over with the steam. Depending on the plant and operation, either source could predominate.

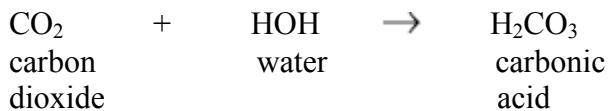
With proper mechanical deaeration and chemical oxygen scavenging, virtually all oxygen

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can be eliminated from boiler feedwater. Good system design is required to minimize air contact with the condensate and subsequent oxygen absorption. Condensate receiving tanks are common points in the system for air-condensate contact

The corrosion of copper by oxygen generally results in the formation of cupric oxide, and the reaction is in most cases self-limiting. If, however, copper complexing agents such as ammonia are present, the copper oxide film is complexed and washed away, and further oxidation of the base metal takes place. High concentrations of carbon dioxide in the condensate system, at lower pH values (less than 8) have an effect similar to ammonia in dissolving the copper oxide film. Both conditions, high ammonia concentrations and low pH with carbon dioxide, should be avoided in systems containing copper-bearing equipment.

Carbon dioxide results from the breakdown of alkalinity in the boiler water. As carbon dioxide dissolves in water, it causes the pH to be depressed by increasing the hydrogen ion concentration as shown in the reaction sequence below:



Carbonic acid promotes the iron corrosion reaction and results in acid attack of metal. Use of neutralizing amines to neutralize acids and elevate pH and application of filming amines can provide corrosion protection.

### **Summary**

Boilers operate under a wide variety of pressures, steaming rates, service cycles and applications. Designs vary widely. All these combine to place requirements on operating procedures, water quality, and chemical treatment. This three part series has been an overview of these factors. A future article will elaborate on chemical treatment matched to the specific combinations of water quality, boiler operating regime, boiler design, and end use of the steam. More details on boiler systems can be obtained from the *AWT Technical Reference and Training Manual*.

### **Additional Readings**

1. 2001 ASME Boiler and pressure vessel code, Section VII, ASME, New York, NY.
2. "Consensus on Operating Practices for the Control of Feedwater and Boiler Water Quality for the Control of Feedwater and Boiler Water Quality in Modern Industrial Boilers." ASME, Book No. 100367.
3. "Consensus Guideline on Fossil Plant Cycle Chemistry," EPRI CS 4829, Project 2712, June, 1986.



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4. "Guideline Manual on Instrumentation and Controls for Fossil Plant Cycle Chemistry," EPRI CS 5164, Project 2712-2, April 1987.
5. "Guideline for Water Chemistry Instrumentation and Control," Paper No. IWC 88-20, October 24-26, 1988.
6. "Annual Book of ASTM Standards: Water and Environmental Technology" - Philadelphia, PA: American Society of Testing and Materials, ASTM D1066 - Standard Practice for Sampling Steam, Vol. 11.01.
7. "Water and Steam in the Power Cycle Purity and Quality, Leak Detection and Measurement" - New York City, NY: American Society of Mechanical Engineers, ASME PTC 19.11, Part 11.
8. ASTM D 1192-94 "Standard Specification for Equipment for Sampling Water and Steam".
9. Groose, J.E. et al, "Trends in Water Sampling Technology For Evaluating Corrosion In Steam Generating Systems", National Association of Corrosion Engineers Meeting, March 1993
10. ASTM: D5540 "Standard Practice For Flow Control And Temperature Control For On-Line Water Sampling And Analysis".

**About the Authors:**

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**Technical Article Review Quiz**  
**2003 Spring**

The Questions for the exam may be answered by reading and understanding the Spring 2003 Analyst Article titled “Boiler Systems – Chemical Treatment, Part III“ by Irvin Cotton and Orin Hollander. The correct answers are derived from that article and any disputed answers will be referred back to that article for justification.

1. Steam deaeration usually reduces feedwater oxygen to less than:
  - a. 10 ppb
  - b. 20 ppb
  - c. 30 ppb
  - d. 40 ppb
  
2. Oxygen induced corrosion of low carbon steel is an electrochemical reaction and often results in:
  - a. Localized pitting
  - b. Gouging attack
  - c. Intergranular corrosion
  - d. Stress corrosion cracking
  
3. Which of the following is not used as a chemical oxygen scavenger
  - a. Sodium sulfite
  - b. Cobalt sulfate
  - c. Methylethylketoxime
  - d. Ascorbic acid
  
4. Internal boiler surfaces are protected from corrosion by the formation of a thin layer of:
  - a. Hematite
  - b. Ferrite
  - c. Magnetite
  - d. Calcium Carbonate
  - e. Ferrous Hydroxide

5. The primary purpose of “coordinated phosphate-pH” chemical treatments is to control:
  - a. Corrosion to Economizers
  - b. Scale in the boiler generating tubes
  - c. Carryover of boiler water into superheaters
  - d. Caustic corrosion to boiler tubes
  
6. The most common cause of steam condensate system corrosion is:
  - a. Ingress of carbon dioxide during downtime
  - b. Oxygen carryover from inadequate feedwater deaeration
  - c. Excess ammonia
  - d. Carbon dioxide
  - e. Carbonic acid
  
7. The primary purpose of a conventional phosphate chemical treatment is to:
  - a. Precipitate feedwater calcium as hydroxyapatite.
  - b. Prevent boiler corrosion.
  - c. Maximize “Cycles of Concentration”.
  - d. Enhance polymeric dispersant properties.
  
8. A “solubilizing” type of boiler water treatment:
  - a. Keeps scale forming feedwater metals from precipitating.
  - a. Is in liquid form versus dry form for ease of feeding.
  - b. Uses caustic soda to prevent scale in hot water boilers.
  - c. Is used to prevent carryover of solids in steam.
  
9. The most commonly used solubilizing chemical treatment is based on:
  - a. NTA
  - b. EDTA
  - c. Polyacrylate
  - d. DEAE
  
10. ASME Boiler Water treatment guidelines specify maximum boiler water concentrations as a function of pressure in order to achieve:
  - a. High quality steam
  - b. High purity steam
  - c. Low chemical cost
  - d. Deaerator efficiency

