Oxygen Control For High- and Low-Pressure Boiler Water Systems

QUALICHEM

Commissioned by Rick Whittington Consulting on Behalf of QualiChem
Author: Sarah Greesonbach, Greesonbach Creative
Editor: Tess Kennedy, Rick Whittington Consulting

H1 Introduction

When treating a boiler water system, it's important to understand how dissolved oxygen can threaten the boiler water environment and what choices can mitigate the effects of dissolved oxygen and provide an efficient and reliable boiler system. The problems that arise will depend on the available tools and the system's needs and specifications.The ultimate goal is to analyze the situation quickly and accurately to identify the most effective technique for dissolved oxygen corrosion control and prevention.

Commercial and Institutional boiler water systems offer unique challenges to those attempting to treat or prevent dissolved oxygen corrosion. Unlike Industrial boiler systems, which often make use of deaerators and have different system requirements, Commercial and Institutional boiler systems typically make use of less intricate pre-boiler feedwater systems but still require careful monitoring proper operation.

Read on for an overview of the factors that affect boiler water system dissolved oxygen control for Commercial and Institutional boiler water systems and the mechanical and chemical best practices for maintaining those systems.

H1 Dissolved Gases and Dissolved Oxygen Corrosion Control

The dissolved gases present in water, specifically oxygen, cause boiler water systems prone to problems with dissolved oxygen corrosion if gone untreated. The presence of dissolved oxygen enhances the environment necessary for the complex electrochemical reaction that results in corrosion.

Dissolved oxygen corrosion is a complex electrochemical process. In effect, iron is dissolved at the anode and releases electrons. These electrons are then consumed by oxygen at the anode. In essence, iron in the presence of water with dissolved oxygen in it, forms iron hydroxide. In turn, the iron hydroxide, again in the presence of water with dissolved oxygen it, forms hydrated iron oxide (rust). The result of this localized corrosion mechanism is a pit-like, pockmarked depression on the system metallurgy.

H2 Problems associated with dissolved oxygen

Dissolved oxygen is so corrosive in hot water that small concentrations can cause serious problems. Since this corrosion is localized pit in nature and can cover a large area, with pits varying in shape and size and characterized by sharp edges at the surface. These pits penetrate the metal surface and can cause leaks. This corrosion process liberates corrosion by-products which can deposit on pre-boiler and boiler heater transfer surfaces. This in turn reduces the overall efficiency and reliability of the boiler water system.

H2 Sources of dissolved oxygen

There are several major sources of oxygen in an operating system, including poor deaerator operation; low temperature feedwater; in-leakage of air on the suction side of pumps; the breathing action of receiving tanks; and leakage of undeaerated water used for pump seals. The acceptable dissolved oxygen level will depend on many factors, from water temperature, pH, flow rate, and dissolved solids content to the metallurgy and physical condition of the system. There are various guidelines surrounding oxygen limits, but the generally accepted American Society of Mechanical Engineer (ASME)'s limit is less than 7 ppb.

H3 Oxygen corrosion mechanism - The perpetuation of corrosion

[INSERT BETZ GRAPH “How corrosion perpetuates itself once initiated in boiler systems”]

Simplified, the metal loss occurs from the anodic area (anode). Iron, Fe^0, is lost to the water and becomes oxidized to Fe^{+2} ion. Because of the formation of Fe^{+2}, two electrons are released to flow through the steel to the cathodic area (cathode). The dissolved oxygen in the water is reduced at the metal surface (cathode) and completes the electric circuit by using the electrons that flow to the cathode to form hydroxyl ions $(OH)^-$ at the metal surface.

By cutting off the environment’s dissolved oxygen supply, the opportunities for this corrosion reaction to occur or continue are reduced.

H3 The role of Temperature in reducing dissolved oxygen

Temperature is another important factor for helping to control dissolved oxygen corrosion in pre-boiler and boiler systems. As temperature increases the solubility of oxygen within that water will be decreased. This means that there will be less dissolved oxygen the higher the temperature of the water.

[INSERT BETZ GRAPH 2.3-1: SOLUBILITY OF WATER]

The amount of steam required to heat and deaerate the water depends on the amount of incoming water and its temperature. Determine the required temperature to achieve desired level of deaeration by referencing the graph above.

Nearly complete oxygen removal is required to meet industry standards for the allowable oxygen content and metal oxide levels in feedwater. This can be accomplished by efficient mechanical deaeration (using heat, steam atomization, and venting) and an effective and properly controlled chemical oxygen scavenger treatment program.

H1 Methods of Dissolved Oxygen Control

Controlling the amount of oxygen within a boiler water system is a vital part of maintaining system reliability and performance.

There are two best practices for reducing the amount of dissolved oxygen in a boiler system: mechanical and chemical treatment. Mechanical methods of dissolved oxygen removal alters the physical characteristics of the water to reduce the amount of dissolved oxygen. Chemical methods of dissolved oxygen removal employs water treatment chemistries to scavenge the remaining oxygen out of the boiler system.

It is best to make use of available mechanical methods to reduce dissolved oxygen rather than solely relying on chemical methods. When facing a situation in which a mechanical option is available, start with troubleshooting or optimizing the mechanical solution first.

Not only will optimizing the effectiveness of the mechanical options provide better deaeration, it will also help keep chemical usage to a minimum. This will help to establish a better relationship between the chemical service provider and the end user. customer and will help maintain a more consistent boiler water environment.

H2 Mechanical Removal

Mechanical removal is the most fundamental method of removing dissolved oxygen from hot water or feedwater tank boiler systems. It involves the manipulation of the water boiler system's physical environment, including temperature and pressure, utilizing steam injection.

Here's a brief overview of common methods of mechanical oxygen control:

> *H3 Hot water or feedwater tanks*
>
> Commercial and Institutional environments most often present with the configuration of feedwater or hot water tanks. A feedwater tank is the simplest form of equipment that can help to help reduce the amount of dissolved oxygen in a boiler system. This tank is typically the vessel for storing makeup water (city, softened or demineralized) and where the return condensate collects. This combined water is known as feedwater.
>
> These tanks often use steam sparging to increase the water temperature and drive the scrubbed oxygen out a vent. As the steam elevates the water temperature in the tank, oxygen is driven off. The higher the water temperature, the lower amount of dissolved oxygen will hold. The lower the amount of dissolved oxygen in the tank, the lower the amount of chemical oxygen scavenger required. Since steam is generally readily available, this is the most fundamental method of mechanical deaeration.
>
> *H3 Deaerators*
>
> Deaerators are more often used in larger commercial and institutional systems, as well as Industrial boiler systems. Deaerators are vessels that collect makeup water and condensate and direct it over trays or as a spray, countercurrent to a stream atmosphere. The released dissolved gases (oxygen) are removed via a vent on the vessel.
>
> These devices reduce dissolved gases, particularly oxygen, to a low level and have the added benefit of improving thermal efficiency by raising the water temperature. Deaerators also provide feedwater storage and proper suction conditions for boiler feedwater pumps. Efficient mechanical deaeration generally reduces dissolved oxygen to 7 ppb or less. For complete protection from oxygen corrosion, a chemical scavenger is required following mechanical deaeration.
>
> *H3 Performance checks*
>
> Continuous monitoring and on- and off-line spot checks are essential to ensure maximum oxygen removal in the effluent of the deaerator. For high-pressure systems, a continuous monitoring with an on-line oxygen meter recommend. For performance testing of the deaerator, the feed of the chemical oxygen scavenger is stopped for a brief period of time and the dissolved oxygen content of the effluent measured. A thorough offline internal inspection should be performed as often as possible.

H2 Chemical Removal

Chemical treatment for dissolved oxygen involves the use of specific chemicals to chemically "scavenge" the remaining trace amounts of dissolved oxygen from a boiler water system and provide an excess amount of the oxygen scavenger residual to the boiler for further insurance against dissolved oxygen corrosion.

Many factors can influence the best choice for an oxygen scavenger for a specific application. These include product cost, reaction speed, residence time in the system, temperature and pressure, pH and the end use of the steam. The type of water treatment chemical used to remove oxygen from a boiler water system will depend on the system's unique specifications.

Here's a look at several of the higher levels of selection considerations one should take into account before moving forward with a chemical water treatment choice:

H3 Pressure
Boiler water systems function at different pressures depending on the application. System pressure plays an import role in the selection of which water treatment chemicals are appropriate for oxygen scavenging.

Commercial and Institutional facilities tend to have low-pressure systems (generally 50 to 300 PSI), whereas Industrial applications tend to have high-pressure systems (over 600 PSI). System pressure determines which water treatment chemicals are appropriate for oxygen scavenging.

For example, in a high-pressure system, the feedwater quality needs to be very pure and free of dissolved solids to avoid causing scale. Addition of a non-volatile oxygen scavenger such as sulfite will add dissolved solids to the boiler. Besides the increased need to blow the boiler down due to the increased solids (resulting in a direct loss of energy and water) it can lead to deposition and boiler tube overheating. The decomposition products from sulfite can form at the higher pressures and can lead to the formation of corrosive sulfur compounds.

Additionally, for Industrial environments, feedwater may be used as attemperating or desuperheating water into a steam line.Again using sulfite in high pressure applications would contaminate steam and negatively affect operations down line. Low-pressure systems favor sulfite products. They readily react with oxygen at feedwater Sulfite is inexpensive and safe to use.

H3 Feed System Metallurgy
When evaluating chemical options, one also needs to consider the metallurgy of the chemical injection lines.The materials of compatibility can vary depending on the oxygen scavenger selected. The oxygen scavenger product may react unfavorably with the metallurgy causing corrosion leading to leaks in tubing and piping.

H3 FDA approval
FDA requirements can dictate which chemical scavengers are allowed within the boiler water system. Plants that require FDA certification must make use of allowed oxygen scavengers and controlled below the maximum allowable levels.[1]

[1] http://www.gpo.gov/fdsys/pkg/CFR-2011-title21-vol3/pdf/CFR-2011-title21-vol3-sec173-310.pdf

H3 Safe Handling and Environmental Acceptance

Responsible chemical handling practices are important for personnel safety and environmental compliance. When selecting the proper oxygen scavenger, know the intended system requirements and the potential exposure constraints of the location where the chemical will be used.

For example, sulfite products have minimal health and environmental impact, whereas Hydrazine is toxic and a suspected carcinogen/mutagen. Special precautions are required to make sure the chemical is used for the appropriate application and in the appropriate area.

H3 Different Types of Chemical Oxygen Scavengers

By definition, oxygen scavengers are reducing agents. They are used to provide a favorable reducing condition at the metal surface. The term ‘oxygen scavenger’ refers to chemicals that facilitate chemical reactions that consume the dissolved oxygen from a system decreasing the likelihood of oxygen induced corrosion damage.

Oxygen scavengers can be volatile organics or inorganic in nature.

H4 Inorganic scavengers

Inorganic materials are the most basic chemicals with relatively simple chemical structure. The most widely used inorganic scavengers used within this classification are sulfites and meta- and bisulfites. Sulfites and bisulfites are variations on the same chemistry.

The environment of the boiler water system will influence which form of sulfite to use. For example, solutions of sodium sulfite have a more neutral pH whereas metabisulfite has a more acidic pH. If the makeup water has a naturally occurring high alkalinity metabisulfite can be used not only to help scavenge dissolved oxygen, but also has the added benefit to reduce boiler water alkalinity.

Sulfite easily reacts with dissolved oxygen but the reaction rate is slower in waters below 200 deg F. It is a standard practice to add a catalyst to help accelerate the reaction rate. The catalyst for inorganic sulfite oxygen scavengers is usually cobalt sulfate. More on this later.

H4 Organic scavengers

Organic scavengers are compounds derived from a hydrocarbon or hydrocarbon-based chemicals. These molecules tend to be volatile and can travel with the steam to provide downstream benefits. These molecules do not contribute solids to the boiler water.

Many organic chemical oxygen scavengers can enhance the formation a protective film on the metal of the boiler in a process called passivation. Passivating organic chemicals include DEHA, Carbohydrazide, Hydrazine, and Erythorbates.The best organic oxygen scavenger for a system will depend on the system’s requirements as discussed previously.

H3 Monitoring of Oxygen Scavengers

When a system has oxygen scavengers in it, the environment needs to be monitored for residual chemical scavengers. The first step is to monitor the stoichiometric balance of the environment to make sure that the appropriate chemical reactions occurred.

For example, if there is a certain amount of oxygen, the environment needs a certain amount of sulfites to counteract it. Stoichiometrically, the environment should balance out to show that everything has been converted.

In monitoring, aim to attain a sulfite residual from 30-60 ppm to establish a buffer of excess sulfite. That way, if the system experiences an adjustment in temperature or pressure, the excess sulfites will be consumed by the dissolved oxygen in the water.

To most accurately diagnose a customer's boiler water system symptoms, make sure to evaluate all of the possible causes of the excess oxygen to identify the most effective oxygen removal method for the situation. Effective maintenance and monitoring of the boiler water system— when active and during downtime and storage— are vital steps to ensure the long-term reliability and performance of the system.

Have a problem that goes beyond the basics of boiler system chemistry troubleshooting? Contact Qualichem at (540) 375-6700 or visit http://www.qualichem.com/ to find out why the Blender Matters and how we can help you with your blending and water teatment needs. QualiChem provides unparalleled technical support to the customers we blend for.

Established in 1989 with headquarters in Salem, Virginia, QualiChem develops and manufactures water treatment chemicals and metalworking solutions worldwide. The Water Treatment Division formulates and blends for regional sales and service companies. QualiChem is a quality-focused ISO 9001:2008 company. In addition to Water Treatment services, the company's Metalworking Fluids Division offers next-generation cutting and grinding fluids, straight oils, rust preventives, and metal cleaners.