Control of Flow-Accelerated Corrosion in Steam Generators
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Preface

In 2012, the author gave a paper on flow-accelerated corrosion at the 73rd Annual International Water Conference. [1] The following discussion incorporates many details from that paper, and also includes new information.

Introduction

Thanks to extensive efforts by personnel at organizations such as the Electric Power Research Institute (EPRI), the International Association of the Properties of Water and Steam (IAPWS) [2], and by power plant chemists around the world, it has been shown that the reducing environment produced by oxygen scavengers initiates and propagates flow-accelerated corrosion (FAC) in the feedwater system and other components of high-pressure steam generators, including heat recovery steam generators (HRSGs). Since 1986, FAC-induced attack has caused numerous failures, some with fatalities, at a number of power plants in the U.S. Yet, specifications for many new power plants both domestically and globally, and in which the condensate/feedwater system contains no copper alloys, continue to call for oxygen scavenger feed to the condensate. This document is a response to this misguided trend.

Old Chemistry

When I began my utility career in 1981, conventional wisdom said that any dissolved oxygen which entered the condensate/feedwater system of utility boilers was harmful. At that time, over 50 percent of the power produced in the U.S. came from coal. Coal-fired units typically have complex condensate/feedwater networks with numerous feedwater heaters. Common feedwater heater tube materials during the heyday of large coal plant construction included Admiralty metal (a copper-zinc alloy) for low-pressure heaters and often copper-nickel alloys for high-pressure heaters. The prevalent thinking during this era was that any trace of dissolved oxygen (D.O) would cause corrosion, and indeed dissolved oxygen can cause severe corrosion of copper alloys. Therefore, virtually all feedwater systems for high-pressure steam generators were equipped with a deaerator for non-condensable gas removal. A properly operating deaerator can lower D.O. concentrations to 7 parts-per-billion (ppb).

However, even this residual D.O. concentration was still considered harmful, so chemical deaeration was also adopted at virtually all plants. The workhorse for many years was hydrazine (N_2H_4), a reducing agent which reacts with oxygen as follows:

$$N_2H_4 + O_2 \rightarrow 2H_2O + N_2\uparrow$$
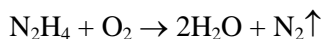
Hydrazine proved advantageous because it does not add any dissolved solids to the feedwater, it reacts with oxygen in a one-to-one weight ratio, and it is supplied in liquid form at 35% concentration.

More importantly, hydrazine will passivate oxidized areas of piping and tube materials as follows:

$$N_2H_4 + 6Fe_2O_3 \rightarrow 4Fe_3O_4 + N_2\uparrow + 2H_2O$$

$$N_2H_4 + 4CuO \rightarrow 2Cu_2O + N_2\uparrow + 2H_2O$$

Hydrazine residuals were typically maintained at relatively low levels of perhaps 20 to 100 part-per-billion (ppb). Oxygen scavenger treatment was coupled with feed of ammonia or an amine to maintain feedwater pH within a mildly alkaline range, which evolved to 9.0 to 9.3 for mixed-metallurgy feedwater systems and 9.2 to 9.6 for all-ferrous systems.

$$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$$

The program of ammonia/reducing agent feed became known as all-volatile treatment reducing [AVT(R)].

Due to the suspected carcinogenic nature of hydrazine, alternative chemicals such as carbohydrazide, methyl ethyl ketoxime, and others gained popularity. Regardless, all still had the same purpose, to establish a reducing environment in the feedwater circuit, thus inhibiting oxidation of metal. The technique became a standard in the industry.

"This changed in 1986. On December 9 of that year, an elbow in the condensate system ruptured at the Surry Nuclear Power Station [near Rushmere, Virginia.] The failure caused four fatalities and tens of millions of dollars in repair costs and lost revenues." [3]. Researchers learned from this accident and others that the reducing environment produced by oxygen scavenger feed results in single-phase flow-accelerated corrosion (FAC).
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Fig. 1. Single-phase FAC. Note the orange peel texture. Photo courtesy of Dave Johnson, ChemTreat.

The attack occurs at flow disturbances such as elbows in feedwater piping and economizers, feedwater heater drains, locations downstream of valves and reducing fittings, attemperator piping, and, most notably for the combined-cycle industry, in low-pressure evaporators.

The effect of single-phase FAC is outlined in the next illustration.

Fig. 2. Photo of tube-wall thinning caused by single-phase FAC. Photo courtesy of Dave Johnson, ChemTreat.

Wall thinning occurs gradually until the remaining material at the affected location can no longer withstand the process pressure, whereupon catastrophic failure occurs. Following is a brief examination of the chemistry behind single-phase FAC. When a steam generator is placed in service, carbon steel feedwater piping and waterwall tubes form a layer of protective iron oxide known as magnetite (Fe_3O_4). Magnetite is actually a composition of FeO (with iron in a +2 oxidation state) and Fe_2O_3 (with iron in a +3 oxidation state).

The combination of a reducing environment and localized fluid flow disturbances causes dissolution of ferrous ions (Fe^{+2}) from the metal and metal oxide matrix.
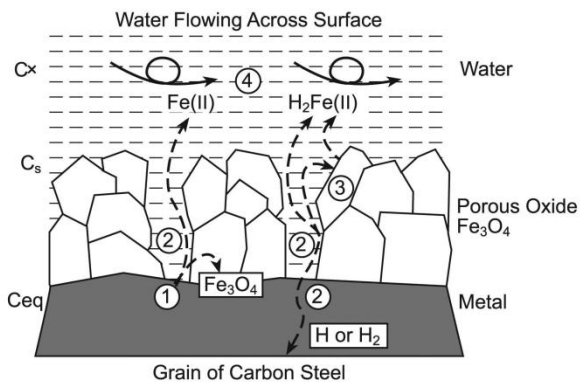

Fig. 3. Diagram of single-phase FAC mechanism. Source: Reference 3.

Results from EPRI show that iron dissolution is greatly influenced by not only reducing conditions but also by solution pH and temperature.
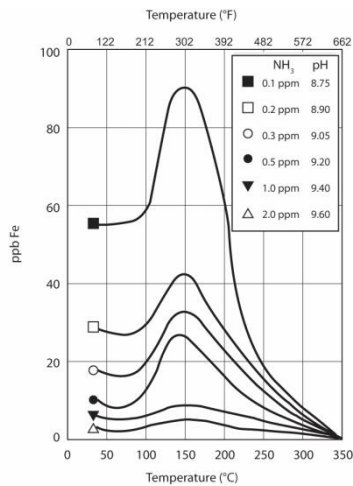
Fig. 4. Carbon steel matrix dissolution as a function of pH and temperature. Source: Reference 3.

As Figure 4 illustrates, corrosion reaches a maximum at 300° F. Thus, feedwater systems and HRSG low-pressure evaporators are particularly susceptible locations. Also note the influence of pH on the corrosion characteristics.

The quest to maintain a non-detectable oxygen residual in feedwater systems led to FAC issues at many coal-fired power plants. I observed this directly at one of my two former utilities. At the plant in which I worked, a feedwater heater drain line failed due to FAC, shutting down an 800 MW supercritical unit. Infinitely more serious was FAC-induced failure of an attemperator line in 2007 at another of the utility's stations, which killed two workers and seriously injured a third.

This brings us to the heart of this document. In large measure, coal plant personnel have recognized the problem of single-phase FAC, and have adopted alternative feedwater treatment methods to mitigate the issue. However, I regularly review combined-cycle proposals in which the developer specifies an oxygen scavenger feed system.

Solutions to Single-Phase FAC and Changing the Oxygen Scavenger Mindset

The following discussion primarily focuses upon HRSGs, but the general chemistry is also applicable to coal-fired units, and indeed most of the original developments came at coal-fired plants. The figure below illustrates the generic layout of a very common HRSG style, a triple-pressure unit.

Deaerator (DA)

HP SH Steam

IP SH Steam

LP SH Steam

IP SH Steam

Steam Injection
to CT
(if used)

LP
Drum

IP
Drum

HP
Drum

Crossover

HP IP
Steam Turbine

LP

Condenser

CT
Exhaust

Reheater

DA
Pump

FW
Pump

Attemperation
Water

Combustion
Turbine

Condensate
Storage

Makeup
System

LP
Blowdown

IP
Blowdown

HP
Blowdown

Steam
from IP
(if used)

Condensate
Polisher
(if used)

Condensate
Pump

Legend
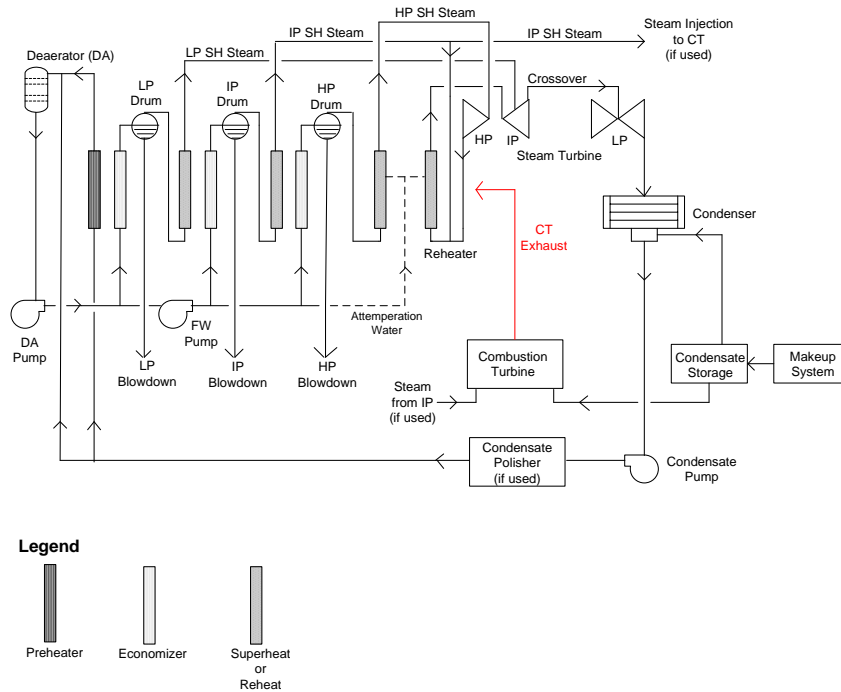
Preheater   Economizer   Superheat
or
Reheat

Fig. 5. A common HRSG style, three-pressure drum design.

HRSGs by their very nature typically have many waterwall tubes with short-radius elbows. Thus, the HRSG contains many spots for single-phase FAC, particularly in the low-pressure (LP) economizer and evaporator, where the temperatures are at or near 300^oF. A primary method to mitigate this attack is selection of proper feedwater treatment, which we will now examine.

Approximately 40 years ago, researchers and chemists in Germany and Russia began using a program known as oxygenated treatment (OT) to minimize carbon steel corrosion and iron dissolution in supercritical steam generators. The key component of the program was, and still is, deliberate injection of pure oxygen into the condensate/feedwater network to establish oxygen residuals of up to 300 ppb. What chemists discovered is that in very pure feedwater (having a cation conductivity ≤ 0.15 μS), the oxygen will intersperse and overlay magnetite to generate a tenacious and very insoluble film of ferric oxide hydrate (FeOOH). OT typically lowered feedwater iron concentrations to 1 ppb or less, and, as researchers have subsequently confirmed, greatly minimized single-phase FAC. Now, OT is the preferred feedwater treatment for most once-through utility steam generators around the world. Common in the United States is an oxygen residual range of 30 to 150 ppb, with a recommended pH range of 8.0 to 8.5.

Although OT has been successfully applied to drum boilers, another program has evolved that is very popular for condensate/feedwater in drum units. It is known as all-volatile treatment oxygenated [AVT(O)]. With AVT(O), oxygen that enters from condenser air in-leakage is allowed to remain without any oxygen scavenger/metal passivator treatment. It should be noted at this point that OT and AVT(O) are not permissible for feedwater systems containing copper alloys, as the oxygen would simply be too corrosive to the metal.

At this point, an issue regarding HRSG configuration must be introduced to proceed with the discussion. Figure 5 illustrates a three-pressure system with an LP circuit that EPRI refers to as a "stand-alone LP (SALP) configuration. [4] As can be seen, separate branches from the main feedwater line feed each circuit.

In many multi-pressure HRSGs, the entire feedwater stream flows through the LP circuit for pre-heating with distribution then to the IP and HP circuits.

When researchers first developed AVT(O), the following guidelines appeared.

- Feedwater pH range, 9.2-9.6
- Feedwater D.O. concentration, 1-10 ppb
- Condensate and feedwater cation conductivity, ≤ 0.2 µS/cm

It is now known that an even higher pH of up to 9.8 or thereabouts in the LP circuit will further inhibit single-phase FAC. Complexity arises in this regard from the HRSG configuration. If the low-pressure circuit is SALP, tri-sodium phosphate (Na_3PO_4) or caustic (NaOH) can be utilized to establish the desired pH range. However, if the LP circuit serves as the pre-heater for the IP and HP circuits, these solid alkalis cannot be employed, as they could be directly transported to the steam via the attemperators. Only ammonia or an amine is suitable in this case. Space does not permit a detailed discussion of ammonia and amine chemistry and their likenesses and differences, but perhaps this issue can be addressed in another paper.

Dissolved oxygen guidelines have changed also. The original AVT(O) program relied solely on oxygen that entered the condensate through condenser air in-leakage. But, as most experienced plant chemists and engineers know, this can be quite variable. The old rule of thumb for proper condenser conditions is a limit of 1 scfm (standard cubic feet per minute) of air in-leakage per 100 MW of capacity. However, I have worked with units in which the air in-leakage ratio was significantly higher, but where the condenser vacuum pumps had sufficient capacity to remove the gases. If the feedwater dissolved oxygen concentration is too low, not enough oxygen may be present to form the FeOOH protective layer. Modern guidelines now call for a 5 to 10 ppb dissolved oxygen concentration in the feedwater. In oxygen deficient systems, one method that has been employed to improve chemistry is to close the deaerator vents. In others, a supplemental feed of pure oxygen may be required. This scenario closely relates to OT, as mentioned above.

Single-phase FAC control can also be addressed in large measure by materials selection. For HRSGs in the design phase, preparing the specifications to include the addition of a small amount of chromium to FAC-susceptible spots virtually eliminates the corrosion. A primary example is LP waterwall elbows. Fabrication of the elbows from 1¼ or 2¼ chrome alloy (T-11 and T-22, respectively) can provide great benefit. While this alloy addition adds some cost to the project, the materials are quite resistant to FAC.

Two-Phase FAC

Many steam generators, regardless of type, are susceptible to two-phase FAC. As the name implies, this corrosion mechanism occurs where water flashes to steam, resulting in a mixed-phase fluid. For conventional units, feedwater heater shells and heater drains are common locations for two-phase FAC, but this equipment is not common for HRSGs. However, deaerators also experience two-phase fluid flow. As fluid flashes upon entering a deaerator, oxygen departs with the steam. Thus, the water that impinges upon metal surfaces does not maintain an oxidizing environment. Also, the pH of entrained water droplets within the steam is usually lower than the bulk water pH. The combination of these factors often initiates FAC.

Fig. 5. Two-phase FAC in a deaerator. Photo courtesy of Tom Gilchrist (ret.), Tri-State G&T.

As has been noted, elevated pH will help to mitigate FAC, but the HRSG configuration dictates how the maximum treatment allowed. If the LP system is utilized for heating of feedwater to the IP and HP circuits, solid alkali treatment (tri-sodium phosphate or caustic) of the LP circuit is not permissible. Control of pH can only be accomplished by ammonia or an amine.

As with single-phase FAC, a method to combat two-phase FAC is fabrication of susceptible locations with chromium-containing steel. Again, this adds cost to the project.

References

1. B.Buecker, "The Continuing Crusade Against Oxygen Scavenger Use in All-Ferrous Steam Generators"; from the Proceedings of the 73rd Annual Meeting, International Water Conference, November 12-16, 2012. (The paper received the 2013 IWC Paul Cohen Award.)
2. The IAPWS offers many documents for free viewing. Their web site is www.IAPWS.org.
3. *Cycle Chemistry Guidelines for Combined-Cycle/Heat Recovery Steam Generators (HRSGs)*, EPRI, Palo Alto, CA: 2006. 1010438.
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Biography

Brad Buecker is Process Specialist with Kiewit Power Engineers, Lenexa, KS. He has over 33 years of experience in the power industry much of it with City Water, Light & Power in Springfield, IL and at Kansas City Power & Light Company's La Cygne, KS generating station. Buecker has written many articles and three books on steam generation topics, and he is a member of the American Chemical Society, the American Institute of Chemical Engineers, the American Society of Mechanical Engineers, the Cooling Technology Institute, the National Association of Corrosion Engineers, the ASME Research Committee on Power Plant & Environmental Chemistry, and the Electric Utility Chemistry Workshop planning committee. He has a B.S. in Chemistry from Iowa State University with additional course work in fluid mechanics, energy and materials balances, and advanced inorganic chemistry.