Oxygen removal from boiler water in high pressure boilers

Abstract
The most frequently encountered corrosion problems results from exposure of boiler metal to dissolved oxygen. Breakdown of the magnetite layer is almost because of mechanical and thermal stresses induced during boiler start up or shutdown. The presented study is related to oxygen removal from boiler water in high pressure boilers. The water in the deaerator must always be at its saturation point or a little bit higher. During normal operation, Deaerator effluent was found free of carbon dioxide with oxygen content in the range of 5 - 10 ppb. A major dose of hydrazine-ammonia-amine should be added to BFW downstream of the deaerator to remove this ppb oxygen and adjust pH. A relatively smaller dose is often injected into the deaerator to protect the deaerator itself. During short-term stoppages, wet preservation is recommended and suitable corrosion inhibitors should be added to the filling water. The water in the storage section of the deaerator should also receive a higher than normal level of hydrazine. The combined use of a filming amine and hydrazine may provide the best corrosion protection available for an idle steam / condensate system. Deaerator start up procedure should be carefully carried out. A comparison between deaerators normal operating condition and chemicals consumption was carried out for three different ammonia plants located in Abu Qir Fertilizers Co, Alexandria, Egypt.

Introduction
The most frequently encountered corrosion problems results from exposure of boiler metal to dissolved oxygen. Breakdown of the magnetite layer is often because of mechanical and thermal stresses induced during boiler start up, shutdown, and during rapid load swings. During normal boiler operation, the environment favors rapid repair of breaches in the magnetite. However, if excessive levels of oxygen are present, either during operation or outages, the cracks in the magnetite cannot be adequately repaired and corrosion commences.

First Principle - Henry’s Law
The solubility of non-condensable gases (O\textsubscript{2} and CO\textsubscript{2}) in water is very low. Eventhough they should be completely removed before entering the boiler to protect it from corrosion. Deaerator temperature and pressure specify the oxygen content. The lower the deaerators pressure the lower oxygen content in the water phase [1].

Deaerator operating condition
The reduction in the deaerator temperature results in a reduction in the deaerator pressure. For deaerators of 0.2 bar above atmosphere, the water is sprayed into a steam space where it is heated to within 1 - 2 °C above saturation temperature [2]. However, Lieberman [3] has reported that the water in the deaerator must always be at its saturation point. Hence deaerator pressure sets its temperature. The manufacturer [4] has reported that for high pressure boilers, the expected value for oxygen outlet deaerator and before injection is less than 20 ppb. Deaerators present in our ammonia plants produce effluents free of carbon dioxide with oxygen content in the range of 5 - 10 ppb during normal operation. Direct reaction of this residual oxygen with catalyzed hydrazine eliminates oxygen completely; hence water becomes suitable for feeding to high pressure boilers.

**Deaerator configuration**

Fig. 1 shows the principle of deaeration in an industrial deaerator [4]. The water to be deaerated is sprayed into the steam space via an automatically operating sprayer (A). The outlet cross section of the sprayer is varied by a spring loaded piston as a function of the load so that perfect spraying is achieved at any load. The steam is supplied via distribution tube (B) from which steam is conveyed into the water via smaller immersion tubes (C). There are bore holes in the lower section of the immersion tubes to insure a uniform distribution of the heating steam. The heating steam goes upward and flows under the sprayer to condense at the water jets. At the same time, the sprayed water is heated to boiling temperature (saturation point). The vapor containing the non-condensable gases escapes through one of the two vents (E) located next to the sprayer. Only 0.5 t/h vented steam is sufficient during normal operation of our deaerators. The cold contents of the vessel are also heated via (B) and (C). The rate of the in-flowing heating steam is controlled by a pressure controller. The feedwater is pumped out at the nozzle (H). The vessel is protected against overfilling by the overflow (F). The vessel is protected against over pressure by a safety valve (G). A pressure equalizing line (D) with a non-return valve is provided between the heating steam piping and the vessel steam space in order to prevent water from flowing back in case of a pressure drop in the heating steam piping. The water level is regulated to the specified value and controlled by level alarms (LAL, LALL, LAH, and LAHH).
Fig. 1: Deaerator 382D001.

A: water sprayer  
B: distribution tube  
C: immersion tubes  
D: pressure equalizing line  
E: vents  
F: overflow  
G: safety valve  
H: Boiler water outlet deaerator  
J: drain  
R: minor injection point  
S: sampling point in stoppage.

The vessel is drained via the nozzle (J) when necessary. Thermometers, pressure gauges and water level indicators are provided on the vessel to monitor the corresponding values. All measured values (flow rates, pressures, and temperatures ... etc) are checked hourly and recorded for the whole unit. Sample point “S” is useful only in the standstill condition. The main sample or online analysis points will be discussed later below.

Chemical treatment
Hydrazine of extreme activity is mixed with demineralized water in the hydrazine dosing station. In *plant III*, amine and ammonia are mixed with demineralized water in another dosing station (when ammonia is about 4% conc.), then combined with hydrazine stream in one header. Amine-ammonia dosing acts as pH buffer. A major dose of hydrazine-ammonia-amine (85% of the total amount required) is added to BFW downstream of the deaerator 382D001 to remove few ppb free oxygen and adjust pH. A relatively smaller dose (15% of the total amount required) is injected into the deaerator via connection (R) which is called minor injection point [4] (as shown in Fig. 1).

Oxygen sampling connected to online oxygen analyzer should be performed as close to the minor injection point as possible [6], because long residence time in sampling lines can allow hydrazine to further react and reduce oxygen reading to a very low immeasurable value. Also if in-leakage occurs, falsely high reading may be obtained. The expected oxygen outlet deaerator 382D001 and before injection is < 20 ppb [4] or within the range 5 - 10 ppb [8]. On the other hand, the distance between the major injection point and pH online analyzers is a maximum (Fig. 2) to allow for mixing effect and to reach the recommended pH value ( > 9). Table 1 suggests water quality limits of BFW regarding boiler operating pressure [5]. Table 2 compares the design and the actual analysis of BFW (in *plant III*).

![Fig. 2: Major injection point & online analyzers](image)
### TABLE I

**SUGGESTED WATER QUALITY LIMITS**

**BOILER TYPE:** Industrial watertube, high duty, primary fuel fired, drum type  
**MAKEUP WATER PERCENTAGE:** Up to 100% of feedwater  
**CONDITIONS:** Includes superheater, turbine drives, or process restrictions on steam  

**SATURATED STEAM PURITY TARGET:** See footnote

<table>
<thead>
<tr>
<th>Drum Pressure (psig)</th>
<th>0-300</th>
<th>301-450</th>
<th>541-600</th>
<th>601-750</th>
<th>751-900</th>
<th>901-1000</th>
<th>1001-1500</th>
<th>1501-2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedwater</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Dissolved Oxygen (mg/l)</strong></td>
<td>≤0.1</td>
<td>≤0.05</td>
<td>≤0.03</td>
<td>≤0.025</td>
<td>≤0.02</td>
<td>0.1</td>
<td>≤0.05</td>
<td>None detected</td>
</tr>
<tr>
<td><strong>Total Iron (mg/l Fe)</strong></td>
<td>≤0.1</td>
<td>≤0.05</td>
<td>≤0.03</td>
<td>≤0.025</td>
<td>≤0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>≤0.01</td>
</tr>
<tr>
<td><strong>Total Copper (mg/l Cu)</strong></td>
<td>≤0.05</td>
<td>≤0.025</td>
<td>≤0.02</td>
<td>≤0.015</td>
<td>≤0.015</td>
<td>≤0.01</td>
<td>≤0.01</td>
<td>≤0.01</td>
</tr>
<tr>
<td><strong>Total Hardness (mg/l CaCO₃)</strong></td>
<td>≤0.3</td>
<td>≤0.3</td>
<td>≤0.2</td>
<td>≤0.2</td>
<td>0.1</td>
<td>≤0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>pH range @ 25°C</strong></td>
<td>7.5-10</td>
<td>7.5-10</td>
<td>7.5-10</td>
<td>7.5-10</td>
<td>7.5-10</td>
<td>8.5-9.5</td>
<td>9.0-9.6</td>
<td>9.0-9.6</td>
</tr>
<tr>
<td><strong>Nonvolatile TOC (mg/l C)</strong></td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td><strong>Oily Matter (mg/l)</strong></td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td><strong>Boiler Water Limits</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Silica (mg/l SiO₂)</strong></td>
<td>≤150</td>
<td>≤90</td>
<td>≤40</td>
<td>≤30</td>
<td>≤20</td>
<td>≤8</td>
<td>≤2</td>
<td>≤1</td>
</tr>
<tr>
<td><strong>Total Alkalinity (mg/l CaCO₃)</strong></td>
<td>&lt;350</td>
<td>&lt;300</td>
<td>&lt;250</td>
<td>&lt;200</td>
<td>&lt;150</td>
<td>&lt;100</td>
<td>Not specified</td>
<td></td>
</tr>
<tr>
<td><strong>Free Hydroxide (mg/l CaCO₃)</strong></td>
<td>Not specified</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Unneutralized Conductivity (µmho/cm @ 25°C)</strong></td>
<td>&lt;3500</td>
<td>&lt;3000</td>
<td>&lt;2500</td>
<td>&lt;2000</td>
<td>&lt;1500</td>
<td>&lt;1000</td>
<td>≤150</td>
<td>≤100</td>
</tr>
</tbody>
</table>

**Footnote:** No values given because steam purity achievable depends on many variables, including boiler water total alkalinity and specific conductance as well as boiler design, steam drum internals and operating conditions. Since boilers in this category require relatively high steam purity, operating parameters must be set as low as necessary for the protection of the superheaters and turbines.
Table 2: BFW quality downstream the deaerator 382D001

<table>
<thead>
<tr>
<th>Item</th>
<th>Design figures [4]</th>
<th>actual figures</th>
</tr>
</thead>
<tbody>
<tr>
<td>free O₂</td>
<td>&lt; 20 ppb *</td>
<td>5 ppb (before major injection point)</td>
</tr>
<tr>
<td>pH</td>
<td>9 - 9.6</td>
<td>9.4 (after major injection point)</td>
</tr>
<tr>
<td>Hardness</td>
<td>Not detected</td>
<td>Not detected</td>
</tr>
<tr>
<td>SiO₂</td>
<td>&lt; 0.02 mg/l</td>
<td>Not detected</td>
</tr>
<tr>
<td>Total iron</td>
<td>&lt; 0.02 mg/l</td>
<td>Not detected</td>
</tr>
<tr>
<td>Conductivity</td>
<td>&lt; 0.2 μS / cm</td>
<td>6.9 μS / cm</td>
</tr>
<tr>
<td>Residual Hydrazine</td>
<td>&gt; 0.1 mg/l</td>
<td>0.3 mg/l</td>
</tr>
</tbody>
</table>

* Nalco figure is within the range of 5 – 10 ppb and ASME code figure is less than 7 ppb.

Comparing oxygen removal in three ammonia plants

The hydrazine and neutralizing amine specific consumption figures were measured based on monthly consumption data during a non-stop-plant operation (March 2007). Table 3 illustrates specific consumptions in the three plants. Deaerator conditions were collected for the three plants (table 4). BFW flow rate in plant I is close to that of plant III. It is remarkable that the oxygen analyzer downstream the deaerator 382D001 reads 5 ppb, because it is located before the major injection point, while it reads 0.4 ppb downstream the deaerator 52-2003 because the injection is completely into the deaerator. The old-fashion design of 52-2003 is the reason for such huge drum size. This explains why the complete dose is injected into 52-2003.

Deaerator size for plants II and III is almost the same. However, deaerator 82D001 (plant II) operates recently at a relatively lower efficiency (higher O₂ concentration downstream the deaerator and before the main injection). Therefore chemicals consumption for 82D001 is higher than expected. Inspection for 82D001 internals is necessary during the next annual plant shut down.

Figures 3-1, 3-2 and 3-3 illustrate the operating conditions of deaerators in the three plants. The efficiency of 382D001 is considered the best since deaerator temperature is one degree centigrade above saturation and free oxygen is 5 ppb. On the other hand, the huge size of 52-2003 makes it even difficult to reach the saturation point. For 82D001, the recorded operating temperature is typically the saturation point. This temperature could be a little bit increased if we increase the steam flow rate, but still this is not the reason for lower efficiency.
Table 3: Chemicals consumption during March 2007

<table>
<thead>
<tr>
<th>Plant</th>
<th>Hydrazine specific cons., g/m$^3$ BFW</th>
<th>Neutralizing amine specific cons., g/m$^3$ BFW</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>plant I</td>
<td>3.2</td>
<td>3.6</td>
<td>Large deaerator size and old-fashion design.</td>
</tr>
<tr>
<td>plant II</td>
<td>4.8 *</td>
<td>4.2 *</td>
<td>Efficiency of the deaerator is lower than expected.</td>
</tr>
<tr>
<td>plant III</td>
<td>2.7</td>
<td>3.1</td>
<td>Efficient deaeration.</td>
</tr>
</tbody>
</table>

* Consumption figure is higher than expected.

Table 4: Deaerator operating conditions for three plants

<table>
<thead>
<tr>
<th>Item in comparison</th>
<th>52-2003 (Plant I)</th>
<th>82D001 (Plant II)</th>
<th>382D001 (Plant III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deaerator pressure, barg</td>
<td>1.5</td>
<td>1.3</td>
<td>1.2</td>
</tr>
<tr>
<td>Deaerator temperature, °C</td>
<td>126</td>
<td>125</td>
<td>125</td>
</tr>
<tr>
<td>Saturation temperature, °C</td>
<td>127</td>
<td>125</td>
<td>124</td>
</tr>
<tr>
<td>BFW flow rate, m$^3$/h</td>
<td>349</td>
<td>310</td>
<td>352</td>
</tr>
<tr>
<td>Required steam vent, t/h</td>
<td>0.5</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>% chemical injection into deaerator</td>
<td>100</td>
<td>35</td>
<td>15</td>
</tr>
<tr>
<td>% chemical injection after deaerator</td>
<td>0</td>
<td>65</td>
<td>85</td>
</tr>
<tr>
<td>Free oxygen before main injection, ppb</td>
<td>0.4</td>
<td>15 – 20 **</td>
<td>5</td>
</tr>
<tr>
<td>BFW quality downstream the deaerator:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>9.3</td>
<td>9.4</td>
<td>9.4</td>
</tr>
<tr>
<td>Silica, mg/l</td>
<td>&lt; 0.02 mg/l</td>
<td>&lt; 0.02 mg/l</td>
<td>Not detected</td>
</tr>
<tr>
<td>Iron, mg/l</td>
<td>&lt; 0.02 mg/l</td>
<td>&lt; 0.02 mg/l</td>
<td>Not detected</td>
</tr>
<tr>
<td>Conductivity, µS/cm</td>
<td>7.7</td>
<td>8.5</td>
<td>6.9</td>
</tr>
<tr>
<td>Residual hydrazine, mg/l</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>

** 5 – 10 ppb had been recorded before at normal operation.

Demin. water, 353 m$^3$/h | vent, 0.5 t/h
Fig. 3-1: Operating condition of 382D001

SLS
18 t/h, 146 °C, 1.2 barg

135 °C

SLS from 303D004
130 °C, 1.7 barg

SLH, 220 °, 4.2 barg

85 % injection

O₂

pH

To BFW pump

Fig. 3-2: Operating condition of 82D001

Demin. water, 310 m³/h

vent, 0.4 t/h

12 t/h, 180 °C, 1.7 barg

130 °C, 1.7 barg

SLH, 240 °, 4.3 barg

35 % injection

O₂

pH

To BFW pump

Fig. 3-3: Operating condition of 52-2003

Demin. Water, 348 m³/h

vent, 0.5 t/h

240 °C, 1.55 barg

30 t/h SLH
255 °C, 4.2 barg

100 % injection

O₂

pH

To BFW pump
Catalyzed Oxygen scavenger

Hydrazine is a reducing agent that removes dissolved oxygen by the following reaction:

\[ \text{N}_2\text{H}_4 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{N}_2 \]

The decomposition products of hydrazine are ammonia and nitrogen. Decomposition begins at 204 °C and is rapid at 315 °C. The alkaline ammonia does not attack steel. However if enough ammonia and oxygen are present together, copper alloy corrosion increases. Close control of the hydrazine feed rate can limit the concentration of ammonia in the steam and minimize the danger of attack on copper-bearing alloys. Theoretically, 1 ppm of hydrazine is required to react with 1 ppm oxygen. In practice, 1.5 - 2 parts are required per part of oxygen. Many factors affect this reaction [6]. These factors include temp, pH, initial conc. of hydrazine, and initial conc. of dissolved oxygen. At temperatures higher than 100 °C the reaction is rapid. The reaction proceeds most rapidly at pH values of 9 – 10.

Certain materials catalyze the oxygen removal reaction. The most effective catalysts are the heavy metal cations (Fe, Cu, Co, Ni, Mn, …). Fig. 4 compares the removal of oxygen using a commercial oxygen scavenger and a catalyzed type [6].

The following conditions necessitate the use of catalyzed type:

- Low feedwater temperature.
- Incomplete mechanical deaeration.
- Short residence time.
- Use of economizers.
Hydrazine can also aid in the formation of magnetite and cuprous oxide as shown below:

\[
\begin{align*}
\text{N}_2\text{H}_4 + 6 \text{Fe}_2\text{O}_3 & \rightarrow 4 \text{Fe}_3\text{O}_4 + \text{N}_2 + 2 \text{H}_2\text{O} \\
\text{N}_2\text{H}_4 + 4 \text{CuO} & \rightarrow 2 \text{Cu}_2\text{O} + \text{N}_2 + 2 \text{H}_2\text{O}
\end{align*}
\]

**Idle operation / short-term shutdown**

During short-term stoppages, wet preservation is recommended. Suitable corrosion inhibitors should be added to the filling water and connection “S” is used for stand-still sampling. The water in the storage section of the deaerator should also receive a higher than normal level of hydrazine for two reasons [1]. First, this water will not be deaerated again before going to the boiler, so any oxygen that is dissolved will be available for boiler and water-line corrosion. Further, the deaerator vessel is not usually designed for corrosive conditions, and so would be susceptible to its oxygen attack.

The spaces above the water level in the boiler and in the deaerator may experience flash rusting, but this should not be too serious over very short periods of time. If the boiler is to remain idle for more than a day or two, it should be completely filled with deaerated water containing a substantial residual of scavenger [1]. Nitrogen blanketing of the steam space and the deaerator will help on longer shutdowns.

Steam / condensate lines are especially vulnerable during even brief shutdowns. Neutralizing amines, which are normally used for protection during operation, do little to prevent oxygen corrosion. Filming amines provide protection from carbon dioxide attack in the far end of steam / condensate lines, but in a non-operating system the film is not permanent. These amines will provide some corrosion protection for short idle times (a day or two) [1].

Hydrazine is fed to the water system during operation to help promote the formation of a magnetite film in the return lines. This surface is more corrosion resistant than the bare metal, and will provide some protection during short outages. The combined use of a filming amine and hydrazine may provide the best corrosion protection available for an idle steam / condensate system. Not only will the metal be protected by a resistant magnetite layer, but the amine film will keep oxygen-laden water and atmosphere away from the surface [1].

Demineralizers, even those that are freshly regenerated, will produce high hardness effluents when started up after an idle periods, due to ion reversal. To ensure that these trouble ions are not inadvertently sent to the boiler, the ion-exchanger should be rinsed prior to being put back into service.
Deaerator start up requires a special attention

1- Do not put the water sprayer into use without having ascertained that there is no air lift in the supply piping and that the piping is only filled with water.
2- Do not heat up the deaerator at a lower rate. The manufacturer gives allowable temp rise as follows: minimum = 2 °C/min, maximum = 6 °C/min
3- Never start up the deaerator at a higher starting level than LWL.
4- Never take the sprayer into full operation at once. Especially when during starting there is the danger of a rapid falling of the pressure when not enough steam is available. If the pressure remains constant it is allowed to gently increase the capacity of the sprayer.
5- To keep the deaerator as warm as possible (at a warm stop) close the vent valves.
6- When the oxygen analysis is satisfied, it is possible to close one of the two vent valves. 

*Note*: During the first start up of the plant, trisodiumphosphate or equivalent as specified by manufacturer is required for boiling out of steam drum and boiler beside NaOH and hydrazine.

Conclusion

During idle operation or short-term shutdown, the following check list should be considered.

Prior to shutdown
- Is pH > 9.0 ?
- Has filming amines been used ?
- Is there a volatile oxygen scavenger in condensate ?
- Are there high levels of oxygen scavenger in boiler and deaerator ?

During shutdown
- Is BFW circulated to prevent temperature drop ?

Prior and during startup
- Has BFW iron been monitored ?
- Have demineralizers been rinsed to achieve suitable quality effluent ?
- Have more frequent bottom blowdowns been carried out ?

This list was successfully executed in our plants, hence it provides a better corrosion control.

A comparison between deaerators operating conditions in three ammonia plants was reported. It considers deaerator temperature, pressure, size, the location of injection points, and the analysis of boiler water just downstream the deaerator. It is remarkable that higher chemical consumption reflects lower deaeration efficiency based on the same water flow rate.
References


