Education Institute for

Equipment & Process Design

Oxygen Scavenger

DISSOLVED OXYGEN CONTROL

Dissolved oxygen can lead to severe corrosion in the economizer section and in the boiler and condensate systems. In the feedwater system, it will contribute to metals transport into the boiler, where deposition can lead to under-deposit corrosion and long term overheating. Dissolved oxygen enters the system via makeup water, which is often air saturated, or leaks into condensers or through pump seals.

The most common effect of dissolved oxygen is to increase the corrosion of the feedwater heaters. Copper and iron oxides are formed which break loose and travel to the boiler. These metal oxides deposit on the hottest part of the boiler tubes and create insulating deposits. From the heat transfer discussion in section 5.1, such insulating deposits increase the temperature gradient needed to provide a constant heat flux. The temperature rises on the tube wall, and overheating may result. Over a long time, such overheating can lead to metal fatigue and failure. Copper deposits can also lead to galvanic corrosion of steel (see chapter 4).

Oxygen problems are especially severe where ammonia is present in significant quantities. In the presence of oxygen, ammonia is very corrosive to copper. Ammonia is used for feedwater pH adjustment. It can also be formed from the thermal breakdown of hydrazine:

$$3N_2H_4 = N_2 + 4NH_3 \qquad (3\text{-}16)$$

or from hydrothermal breakdown of organic amines:

$$R\text{-}NH_2 + H_2O = ROH + NH_3 \qquad (3\text{-}17)$$

Where R is a general organic group like $(HO)CH_2\text{-}CH_2\text{-}$ (ethanolamine).

Ammonia cannot attack copper metal itself. It reacts only with copper ions in the +2 oxidation state (cupric). In the feedwater loop, these will be in the form of cupric oxide (CuO) and hydroxide ($Cu(OH)_2$). The cupric state can only form if oxygen is present. So it is the combination of ammonia AND oxygen that is aggressive to copper alloys. If oxygen is kept low by mechanical and chemical means then ammonia will not be a problem for copper.

However, maintaining low oxygen levels can be a difficult task. Oxygen enters the system from makeup water, cooling water leaks, condensate storage tank equilibration with the atmosphere, and pump seal leaks. Systems that are frequently laid up or which fluctuate widely in load may be more susceptible to air inleakage.

In high pressure boilers, the economizer section is very susceptible to oxygen corrosion. It is the first predominantly steel surface where dissolved oxygen can directly attack the metal. If oxygen is present in the feedwater, heavy iron oxide deposits and deep hemispherical pits can form in the economizer tubes.

In the boiler itself, dissolved oxygen can lead to oxygen pitting and tube failure. Pits are hemispherical, with sharp edges, and often have caps of corrosion products.

Methods for Dissolved Oxygen Removal

Two methods are available for removing dissolved oxygen from boiler water and steam systems: mechanical stripping, or deaeration (see section 4.3); and chemical oxygen scavengers. Oxygen scavengers are reducing agents that react with even the very low levels of oxygen left in water by good deaeration. They are normally added to the storage section of the deaerator, to allow time for reaction before the feedwater reaches the boiler.

Low pressure boilers sometimes do not include mechanical deaerators. In these systems, oxygen scavengers are required to do the whole job of dissolved oxygen removal. Obviously, much larger dosages are required in this case.

Oxygen scavengers fall into several classes. These include sulfites and ascorbates (non-volatile), and hydrazines, hydroquinones, hydroxylamines and ketoximes (volatile). Each of these is discussed in the following sections.

Sulfite

Sulfites are used in lower pressure boilers. They are non-volatile, and so add dissolved solids to the boiler. Sulfites are very reactive, and can reduce oxygen to 5 ppb if used correctly.

The reaction of sulfite with oxygen can be written as:

$$2SO_3^{-2} + O_2 = 2SO_4^{-2} \qquad 3\text{-}18$$

Above 430 °F (350 psia) sulfite reacts with iron oxide:

$$3Fe_2O_3 + SO_3^{-2} = 2Fe_3O_4 + SO_4^{-2} \qquad 3\text{-}19$$

Fe_3O_4 is magnetite, an intermediate valence form of iron oxide that forms good protective oxide films (passive films) under boiler conditions (low or zero oxygen levels). However, sulfite is not considered to be a good passivating agent because it does not passivate low pressure boilers, where sulfite is most often used. Passivation can be accomplished in high pressure boilers, but high dosages of sulfite are needed.

Sulfite is commonly supplied as sodium sulfite, Na_2SO_3; sodium bisulfite, $NaHSO_3$; ammonium sulfite, $(NH_4)_2SO_3$; or sodium metabisulfite, $Na_2S_2O_5$. All of these species hydrolyze (react with water), and at the usual boiler water pH range, the sulfite ion, SO_3^{-2}, is the active species present.

Sodium sulfite can decompose to sulfur dioxide (SO_2) and hydrogen sulfide (H_2S) in the boiler. For this reason, the use of sulfites is limited to boilers under 900 psig. The feed rate should be as shown in Table 3-5. divided by the boiler cycles. Up to 600 psig, residuals of 5-50 mg/L can be used; above 600 psig, 5-20 mg/L is the safe limit. Avoid large overfeeds.

TABLE 3-5
Sulfite Feed Requirements

Chemical	Name	mg/L SO_3 per mg/L O_2
Na_2SO_3	Sodium sulfite	7.88
$NaHSO_3$	Sodium bisulfite	6.5
$(NH_4)_2SO_3$	Ammonium sulfite	7.25
$Na_2S_2O_5$	Sodium metabisulfite	5.94

Although sulfite reacts slowly with oxygen at room temperature, it reacts very quickly at elevated temperatures. Also, the presence of minute quantities of oxidizable metal ions like cobalt (Co^{+2}) will greatly accelerate the rate of reaction with oxygen. Many water treatment suppliers supply catalyzed sulfite products, usually containing cobalt.

As discussed above, sulfite does not passivate metal surfaces well and should not be used for this purpose.

Hydrazine

Hydrazine is a very common oxygen scavenger. It is an inorganic reducing agent of great power. However, the reaction rate of hydrazine with dissolved oxygen is slower than the sulfite reaction, For this reason, plus difficulties in handling, hydrazine is used most often in high pressure boilers.

The reaction of hydrazine with oxygen is:

$$N_2H_4 + O_2 = 2H_2O + N_2 \qquad (3\text{-}20)$$

At temperatures greater than 250 °F, hydrazine reacts with metal oxides:

$$6Fe_2O_3 + N_2H_4 = 4Fe_3O_4 + 2H_2O + N_2 \qquad (3\text{-}21)$$

$$4CuO + N_2H_4 = 2Cu_2O + 2H_2O + N_2 \qquad (3\text{-}22)$$

Ferric oxide is reduced to the familiar black, protective magnetite film (equation 3-21), and cupric oxide is reduce to red cuprous oxide (3-22). These reactions passivate, or protect the metal surfaces in the boiler, so that hydrazine is used as a passivating agent as well as an oxygen scavenger.

Hydrazine decomposes in boiler water at 400-600 °F (250-1500 psia):

$$3N_2H_4 = 4NH_3 + N_2 \qquad (3\text{-}23)$$

Feed rates of about 5 times stoichiometric are required for good oxygen scavenging. For every 1 mg/L of oxygen feed about 5 mg/L of hydrazine. The excess will break down to ammonia in the boiler (equation 3-23) and may cause problems in copper condensate systems unless they are air free. Hydrazine is typically supplied as a 35% solution in water.

Hydrazine is listed as a carcinogenic compound and must be handled with proper precautions.

Carbohydrazide

Carbohydrazide is a derivative of hydrazine. It reacts readily with oxygen:

$$(NH_2NH)_2C=O + 2O_2 = 2N_2 + 3H_2O + CO_2 \qquad (3\text{-}24)$$

Decomposition: carbohydrazide first breaks down to hydrazine and carbon dioxide, and then decomposes to ammonia and nitrogen.

Reduction of metal oxides:

$$(NH_2NH)_2C=O + 12Fe_2O_3 = 8Fe_3O_4 + 3H_2O + 2N_2 + CO_2 \qquad (3\text{-}25)$$

$$(NH_2NH)_2C=O + 8CuO = 4Cu_2O + 3H_2O + 2N_2 + CO_2 \qquad (3\text{-}26)$$

Thus, the passivating properties of carbohydrazide are similar to hydrazine. However, the produced carbon dioxide adds to the potential for acidic condensate, and must be taken into account.

The feed rate is the same as for hydrazine: about 2.5 times stoichiometric, or about 5.6 mg/L per mg/L of oxygen.

Hydroquinone

Hydroquinone is a powerful reducing agent (scavenger). Its reaction with oxygen is:

$$2C_6H_4(OH)_2 + O_2 = 2C_6H_4O_2\text{ (benzoquinone)} + 2H_2O \qquad (3\text{-}27)$$

Hydroquinone is also a goof passivating agent for both steel and copper:

$$C_6H_4(OH)_2 + 3Fe_2O_3 = 2Fe_3O_4 + \text{misc. organic products} \qquad (3\text{-}28)$$

$$C_6H_4(OH)_2 + 2CuO \rightarrow Cu_2O + \text{mixed organic products} \qquad (3\text{-}29)$$

The feed rate of hydroquinone for oxygen scavenging is approximately 3 to 7 mg/L per 1 mg/L oxygen.

The oxidation product of hydroquinone, benzoquinone (equation 3-27) can also scavenge oxygen. Thus the stoichiometric relation does not fully apply.

Hydroquinone is more reactive than other oxygen scavengers, and scavenges effectively at temperatures below 180 °F.

Hydroquinone is very toxic, and must be handled in a well ventilated area. For this reason, it is rarely used in HVAC systems.

Diethylhydroxylamine (DEHA)

The hydroxylamines, mainly diethylhydroxylamine, DEHA, are also used effectively for oxygen control.

Reaction with oxygen:

$$4(C_2H_5)_2NOH + 9O_2 = 8CH_3COOH + 2N_2 + 6H_2O \qquad (3\text{-}30)$$

The reaction product, acetic acid, is neutralized to form acetate ions with hydroxide in the boiler.

Reactions with metal oxides:

$$\text{DEHA} + 6Fe_2O_3 = 4Fe_3O_4 + CH_3CH{=}NOH + CH_3CHO + H_2O \quad (3\text{-}31)$$

$$\text{DEHA} + 4CuO = 2Cu_2O + CH_3CH{=}NOH + CH_3CHO + H_2O \quad (3\text{-}32)$$

DEHA has passivating properties, as shown by (3-31) and (3-32), but it is less effective for that purpose than hydrazine and hydroquinone.

DEHA breaks down above 300 psig to form a small amount of ammonia plus organic acids and carbon dioxide.

The stoichiometric rate is 1.2 mg/L per mg/L O_2. Feed at 6 mg/L, a 5:1 stoichiometric excess.

DEHA is an amine, and is sometimes used to neutralize carbon dioxide (carbonic acid) in condensate, as well as to scavenge oxygen (section 7.4).

Methyethylketoxime (MEKO)

Methylethylketoxime (MEKO) is another scavenger, not as widely used.

Reaction with oxygen:

$$2CH_3(C_2H_5)C{=}NOH + O_2 \;=\; 2CH_3(C_2H_5)C{=}O + N_2O + H_2O \qquad (3\text{-}33)$$

Reaction with metal oxides:

$$2MEKO + 6Fe_2O_3 \;=\; 2CH_3(C_2H_5)C{=}O + N_2O + H_2O + 4Fe_3O_4 \qquad (3\text{-}34)$$

$$2MEKO + 4CuO \rightarrow 2\,CH_3(C_2H_5)C{=}O + N_2O + H_2O + 2Cu_2O \qquad (3\text{-}35)$$

MEKO also breaks down to ammonia and organic acids above 1800 psig, and at lower pressures if a large excess is fed to the boiler.

Feed rate: the stoichiometric rate is 4.7 mg/L per mg/L O_2; feed normally at 5 times the stoichiometric rate.

Ascorbate/Erythorbate

Ascorbic acid (vitamin C) and erythorbic acid, an isomer of ascorbic acid, are organic, non-volatile, non-toxic oxygen scavengers useful up to about 1500 psig.

Reaction with oxygen:

$$NaC_6H_6O_6 + \tfrac{1}{2}\,O_2 \;=\; C_6H_5O_6 + NaOH + \text{complex organics} \qquad (3\text{-}36)$$

Reduction of metal oxides:

$$NaC_6H_6O_6 + 3\,Fe_2O_3 \;=\; C_6H_5O_6 + 2Fe_3O_4 + NaOH \qquad (3\text{-}37)$$

$$NaC_6H_6O_6 + 2CuO \;=\; C_6H_5O_6 + Cu_2O + NaOH \qquad (3\text{-}38)$$

Feed rate: the stoichiometric rate is 12 mg/L active acid per mg/L O_2; feed at 5 times stoichiometric.

TABLE 3-6

Oxygen Scavenger Feedrates

Oxygen Scavenger	Operating Pressure, psig	mg/L Active / mg/L Oxygen
Sulfite	0 to 600	6-8 +20-50 mg/L residual (see Table 3-5)
Sulfite	601 to 900	6-8 + 5-10 mg/L residual (see Table 3-5)
Hydrazine	600 to >2500	5
Carbohydrazide	600 to >2500	5-6
Hydroquinone	300 to >2500	3-7
DEHA	150 to 600	6
MEKO	300 to 1800	25
Ascorbate/erythorbate	150 to 1500	60