

Why do we need an Oxygen Scavenger & which one should we use?

By Ian Penney

Introduction to Corrosion

Corrosion is the gradual deterioration of metals caused by air, moisture, or chemical reactions (such as with acids) on their surface. It is a natural process that converts a refined metal back into a more chemically stable oxide.¹ This process can be understood at a basic level: when we mine metals from the earth, they are typically found as metal oxides (like iron oxide). We use heat in furnaces to remove the oxide, producing pure molten metals. These refined metals are in a high-energy state due to the heat input and tend to revert to their natural state (oxide) through corrosion.

Most metals "want" to corrode, except for precious metals like silver, gold, or platinum, which are mined in their pure form and do not corrode. Their lack of reactivity and scarcity make these metals valuable.

Oxygen Corrosion

Oxygen corrosion occurs when metals degrade in the presence of dissolved oxygen, leading to the formation of insoluble deposits due to rapid oxidation. Significant quantities of oxygen, combined with water and electrolytes, can cause severe corrosion reactions on metal surfaces.

Oxygen acts as a cathodic depolarizer, removing the hydrogen ion film from the cathode surface during electrochemical corrosion, which allows corrosion to continue. Simply put, oxygen promotes corrosion. Methods like coating, painting, or blanketing with inert gases (e.g., nitrogen) can reduce the exposure of metals to oxygen, preventing corrosion in both air and water environments.

Oxygen Scavengers in Water Treatment

In water, oxygen is a dissolved gas, and its concentration is directly proportional to the water's temperature. This principle is used in steam boilers, where the boiler feedwater is preheated to as high a temperature as possible to reduce oxygen content. Reducing oxygen concentration can significantly prevent different types of corrosion, such as crevice, pitting, galvanic, and intergranular corrosion.

The rest of this paper discusses some common chemical oxygen scavengers used to reduce corrosion and their respective pros and cons.

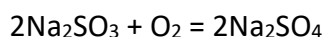
Common chemical oxygen scavengers:

- Sodium sulphite (& sodium metabisulphite)
- Tannin
- DEHA (N, N-diethylhydroxylamine)
- Hydrazine (carbohydrazide)
- Erythorbic acid (sodium erythorbate)

Sodium sulphite (Na_2SO_3)

The most widely used material for oxygen scavenging in industrial water treatment applications is sodium sulphite. It is the least expensive and most active product for low to medium pressure boilers. Sodium sulphite is usually supplied as a catalysed product (i.e. cobalt catalyst) which speeds up the reaction rate for the conversion of sulphite to sulphate incorporating the oxygen present.²

Reaction



Dosage rate is 8ppm sulphite per ppm of O_2 // Residual sulphite in boiler @ 30-70ppm³.

Pros

- Inexpensive
- Fast reaction rate when catalysed.
- Effective up to 600psig boilers
- Easy field test available (i.e. feedwater / boiler)

Cons

- Adds to dissolved solids level (TDS)
- Does not promote passivation.
- Can form undesirable boiler scales.

Tannin

Tannin does not add to the boiler TDS so reduces the need for blow down hence saves energy. Feedwater tannins have a dual corrosion protection mechanism since they not only remove the oxygen but also form a corrosion resistant tannate film on the boiler steel.² Tannins are natural organic compounds derived from plants. Tannins have been found to help stabilise boiler pH as well as inhibit the formation of organic deposits. It was not possible to find a reaction formula for tannin and oxygen for this paper as there are many types of tannin-based products in use across the industrial water applications. However, a general formula for the formation of the corrosion resistant tannate film is shown.

Reaction



Dosage rate is N/A as tannin per ppm of dissolved O₂ // Residual tannin in boiler @ 120-160ppm³.

Pros

- Acts as an oxygen scavenger as well as forming a tannate protective layer.
- Provide a level of dispersion capability.
- Does not add to dissolved solids level (TDS)
- Suitable for low or variable feed water temperatures
- Suitable for protecting idle and intermittently used boilers.

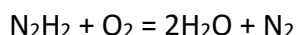
Cons

- Suitable for low pressure boilers only
- Adds significant 'colour' to the boiler water making other field tests difficult.

Hydrazine (N₂H₄)

Hydrazine can be used for oxygen scavenging in high pressure boiler applications as it does not add to the dissolved solids level (TDS) of the boiler water. It also benefits from promoting the conversion of red iron oxide (hematite) into black iron oxide (magnetite) which function as a protective barrier on the metal surfaces. Research into hydrazine has unfortunately identified it as a potential carcinogen and as such its use in industry has reduced even with its inherent benefits.

Reaction



Dosage rate is 1ppm hydrazine per ppm of O₂ // Residual hydrazine in boiler @ 0.1-1.0ppm³

Pros

- Fast reaction rate
- Effective for high pressure boilers
- Promotes black iron magnetite formation.
- Easy field test available (i.e. feedwater / boiler)
- Does not add to dissolved solids level (TDS)

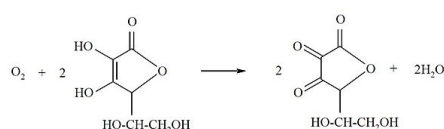
Cons

- Classed as potential carcinogen

Erythorbic acid (Sodium Erythorbate)

Erythorbic acid (aka vitamin C) is a non-volatile organic oxygen scavenger that can be used as an alternative to hydrazine in low to medium pressure boilers. Like hydrazine, it does not add to the dissolved solids level (TDS) of the boiler water. Erythorbic acid also benefits from promoting the conversion of red iron oxide (hematite) into black iron oxide (magnetite) which function as a protective barrier on the metal surfaces. However, unlike hydrazine erythorbic acid is on the GRAS (Generally Recognised as Safe) list of food additives so it finds widespread application in steam production associated with the food industry. Erythorbic acid converts oxygen to water and carbon dioxide in the boiler.

Reaction



Dosage rate is 11ppm erythorbate per ppm of O₂ // Residual level in boiler @ 15-30ppm³.

Pros

- Effective for low to medium pressure boilers
- Promotes black iron magnetite formation.
- Easy field test available (i.e. feedwater / boiler)
- Does not add to dissolved solids level (TDS)

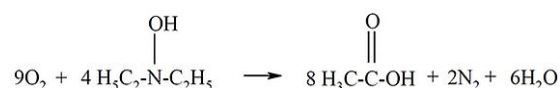
Cons

- Degradation of erythorbic acid can form weak acids (carbonic acid)
- Can add to the requirement for pH correcting condensate treatments.

DEHA (Diethylhydroxylamine)

DEHA is a volatile amine commonly used as an oxygen scavenger in medium and high-pressure boiler applications. Decomposition of DEHA starts from 280°C, however the byproducts of DEHA, amines are alkali in nature and as such are helpful in raising pH of condensates. This reduces the consumption/need for neutralizing amines.

Reaction



Dosage rate is 1.2ppm DEHA per ppm of O₂ // Residual level in boiler @ 0.1-1.0ppm³

Pros

- Effective for medium to high pressure boilers
- Volatile so can offer corrosion protection post boiler.
- Promotes black iron magnetite formation.
- Easy field test available (i.e. feedwater / boiler)
- Does not add to dissolved solids level (TDS)
- Has low toxicity so safe and easy to manage?

Cons

- Reacts with moderate speed at pH levels < 9.
- DEHA does not have FDA approval so cannot be used for steam production which directly contacts food.

Summary

This paper provides an overview of some common oxygen scavengers used today. While each chemical has its advantages and disadvantages, the reader should conduct additional research to fully understand the suitability of each option for specific applications.

References:

1. ScienceDirect <https://www.sciencedirect.com>
2. BS 2486:1997 Recommendations for Treatment of water for steam boilers and water heaters. Available from <https://shop.bsigroup.com>
3. Midwest Water Treatment <https://www.midwestwt.com/oxygen-scavenging>
4. Water Technology Report <https://watertechnologyreport.wordpress.com>