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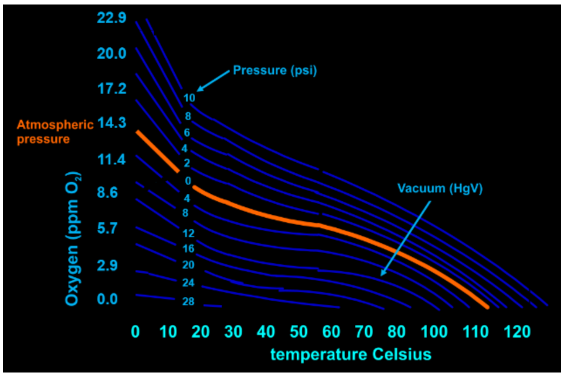
Oxygen Scavengers – which type to use?

What you should know about oxygen in boiler water

This is the first Marine Care article of a series on water treatment products. The subject of this paper is the use and need of oxygen scavengers in boilers, and the comparison of the types of oxygen scavengers used in these systems.

Introduction

Corrosion on the water side of boilers (including the feedwater and steam system) can have multiple causes. Prevention of corrosion is generally done by adding a mix of water treatment products to the boiler water. Different types of corrosion can occur in several locations of the boiler water system. Corrosion by dissolved oxygen (O2) is one of the general corrosion problems of the system as a whole and specifically for the steam generating part. In proper properly conditioned boilers (medium and high pressure), the steel surface of the boiler and steam system is protected through a high temperature reaction of water with the steel surface by another type of iron oxide called Magnetite (Fe3O4). This formation of Magnetite starts at temperatures above 100 °C in oxygen free and alkaline boiler water. Magnetite forms a passive layer that protects the underside steel surface against corrosion. When dissolved oxygen is present in boiler water, this reaction is disturbed. Oxygen reacts with steel surfaces to form a type of iron oxide called ferric oxide or hematite (Fe2O3), which cause pitting corrosion. To avoid this, oxygen levels in boiler water should be kept to zero. The solubility of oxygen in water is dependent on the temperature of the water and the pressure in the boiler. For example, at higher temperatures, less oxygen dissolves in water. However, with higher pressure, more oxygen can be dissolved. In Graph 1, the relation of dissolved oxygen, temperature and pressure is shown. The first physical treatment to remove oxygen from boiler water is high temperature and low pressure. This is achieved in the deaerator or hot well of the boiler system. It is important to keep the temperature of the hot well over 80 °C as the solubility of oxygen at 1 bar pressure is less than 1 ppm. To ensure a low level of dissolved oxygen in the entire water system of the boiler is kept, so called oxygen scavengers are added. Oxygen scavengers react chemically with the dissolved oxygen. The result of the chemical reaction and the formation of by products that can have an effect on the water and steam quality, is different for each type of oxygen scavenger used. This paper provides insight into the different types of scavengers, the chemical reactions they induce, as well as the advantages and disadvantages of each type of product.



Graph 1: Oxygen levels vs temp / pressure

Hydrazine

Hydrazine is historically the more commonly used oxygen scavenger for higher pressure boilers. However, due to its toxicity and related legislation, its use has been reduced and replaced with alternatives. One of the advantages of hydrazine is the absence of corrosive gas production. Hydrazine (N2H4) reacts with oxygen to form water and inert nitrogen gas. Hydrazine does not contribute to dissolving solids in the boiler water but does reduce the formation of sludge and requirements for blowdowns. The reaction rate of hydrazine is moderate to slow, and to raise the reaction rate catalysators are added to a hydrazine solution, forming catalyzed hydrazine. Quinones are commonly used to catalyze hydrazine solutions. Hydrazine acts as a passivator for the steel surface and promotes the formation of the protective magnetite film which converts the unwanted hematite to magnetite. Hydrazine is volatile so it will leave the boiler with the steam and at the same time passivate the steel surface while removing oxygen in the steam system. The degradation temperature of hydrazine is above 200 °C and will degrade to ammonia, nitrogen and hydrogen gas. Ammonia can cause corrosion to copper alloys, for instance copper condensate tubes.

(1) $N_2H_2 + O_2 \rightarrow 2H_2O + N_2$

Sodium sulfite

In low pressure boilers a commonly used oxygen scavenger is sodium sulfite (Na_2SO_3). Sulfite has the advantage of being inexpensive and highly reactive with oxygen. To raise the effect of sulfite a catalysator (most commonly) cobalt salts are used. In graph 2 the effect of addition of a catalysator is shown. The reaction of sulfite with oxygen forms sulfate which contributes to the total dissolved solids in the boiler water (2). Thus, sulfite-based products cannot be used in high pressure boilers. The rise of sulfate levels in boilers can cause deposit problems when hardness salts are present with insufficient complexing agents. Sulfate can react to form hardly removable gypsum scales ($CaSO_4$ / $MgSO_4$). Sulfite can break down by forming sulfur dioxide and hydrogen sulfide. Both these gasses are corrosive gasses and lower the pH value of the steam and condensate part of the boiler (3). Overdosing sulfite-based products can cause corrosion problems by exceeding amount of the corrosive gasses in the steam/condensate system. Sulfite does not passivate the steel surface neither does it contribute to the formation of magnetite due to the fact sodium sulfite decomposes at a temperature of 120 °C and the passivation reaction of sulfite starts at a temperature of 220 °C.

(2) $2Na_2SO_3 + O_2 \rightarrow 2Na_sSO_4$

(3) $5Na_2SO_3 + 3H_2O \rightarrow SO_2 + H_2S + 4NaOH + 3Na_2SO_4$

Sulfite products can be based on different type of initial chemicals (sodium sulfite, sodium metabisulfite, sodium hydrogen sulfite and ammonium sulfite) but in all cases by dosing the product reactive sulfite ions are released in alkaline boiler water.

DEHA

Diethylhydroxylamine (DEHA) is an oxygen scavenger which, depending on temperature and pH value, reacts quickly with dissolved oxygen. Through various complex chemical reactions DEHA reacts with oxygen to finally form acetic acid (or acetate), nitrogen and water. The formed acetate contributes to the total dissolved solids of the boiler water. DEHA has metal passivation properties, it reacts with the steel surface to form magnetite and with copper alloys to form a protective copper oxide layer. DEHA degrades into volatile dialkylamines which contributes to the pH control of the steam system and condensate. Not all DEHA in boiler water will degrade as in high pressure systems DEHA is volatile. Reaction rate of DEHA with dissolved oxygen depends highly on the pH value. At a higher pH value (around 11) DEHA reacts almost as quickly as sulfite while at a lower pH value (< 9) it reacts moderate, similar like hydrazine. DEHA can be used in all types of pressure boilers.

Carbohydrazide

Carbohydrazide is a volatile oxygen scavenger which reacts relatively slow with oxygen in comparison to other products (4). The reaction product of carbohydrazide is carbon dioxide, a gas that dissolves in water as carbonic acid, lowering the pH value of the steam and condensate. Carbonic acid can be corrosive to the steam and condensate part of the boiler and addition of condensate treatment chemicals or pH adjustment with ammonia is required. Some studies on high pressure steam system show the amount of formed carbon dioxide is limited and does not affect the cycle chemistry. At higher temperatures carbohydrazide decomposes to hydrazine as a result carbohydrazide (5) cannot be used for systems that are applied for food. The formed hydrazine reacts with oxygen (1) so there is no effect on oxygen scavenging properties when carbohydrazide degrades. Carbohydrazide has passivating properties due to the reaction with the steel surface to promote the formation of magnetite in the boiler system. Carbohydrazide can be used in all types of pressure boilers.

(4) $(NH_2NH)_2CO + 2O_2 \rightarrow CO_2 + 2N_2 + 3H_2O$

(5) $(NH_2NH)_2CO + H_2O \rightarrow N_2H_4 + CO_2$

Erythorbate

The oxygen scavenger Erythorbate, better known as vitamin C, can be used in food processing applications. It is a metal passivator, but only for the boiler part not the steam and condensate systems, as erythorbate is not volatile and therefor used in low and medium pressure boilers. Erythorbate reacts with oxygen through a series of complex chemical reactions. Oxalate is one of the intermediate reaction products, but the final reaction products are water and carbon dioxide. As with carbohydrazide, the formation of carbon dioxide in the condensate will lower the pH value and condensate treatment is required. Erythorbate reacts with the steel and copper surfaces to form protective passive films, but as a strong oxidizer it converts unwanted hematite into protective magnetite.

MEKO

Methylethylketoxime (MEKO) reacts with oxygen only properly at elevated temperatures and is unsuitable to dose in the deaerator part of the boiler. MEKO is volatile, thus does not contribute to the total dissolved solids and has passivating properties. The reaction products of MEKO with dissolved oxygen are organic acids, methyl ethyl keton (or MEK) and nitrogen oxides. At higher pressures MEKO decomposes into organic acids and ammonia.

Hydroquinone

In some cases, used as an oxygen scavenger, hydroquinone is more commonly used as a catalysator for the earlier discussed oxygen scavengers. It is added to DEHA or sulfite solutions to improve the reaction rate (lower reaction time) with oxygen. Addition of a catalysator is highly effective when pH values of boiler water is at lower end ($pH < 9$). See graph 2.

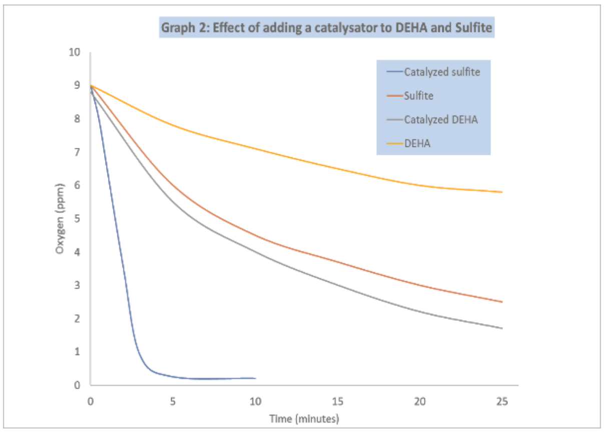


Table 1: comparison Oxygen scavengers

Name	Volatile	Raise TDS	Toxic	Passivator	Dosing Pp O_2	Degr. T / P	Reaction rate	Corrosive reaction products	Degradation products
Hydrazine	Y	N	Y	Y	1	200 °C	Slow	-	NH_3
Sulfite	N	Y	N	N	8	120 °C	Fast	SO_4^{2-}	H_2S & SO_2
DEHA	Y	Partly	N	Y	1,3	83 bar	Fast	Acetic acid	Diethylamine
Carbohydrazide	Y	N	N	Y	1,4	180 °C	Slow	CO_2	Hydrazine
Erythorbate	N	Y	N	Y	11	RT	Moderate	oxalate	CO_2
MEKO	Y	N	N	Y	5,4	90 bar	Very slow	N_2O	Acids, NH_3

Dosing points

Oxygen scavengers are preferably dosed furthest upstream of the system which is in most cases the Deaerator. The Deaerator is already the system were physically dissolved oxygen and carbon dioxide is removed. In case there is no option to dose oxygen scavenger to the deaerator, or as in smaller boiler system there is only a hot well, dosing can take place in the feed water line of the system. Last resort of dosing is to use the chemical dosing system of the boiler or steam drum. In case of the oxygen scavenger MEKO, it has no use to dose in the upstream part as reaction with oxygen at lower temperatures is too slow.

Testing

The amount of oxygen scavenger in boiler water should be analyzed regularly. It is important the analysis is started directly after taking the sample as oxygen from the air will react with the oxygen scavenger in the sample, resulting in faulty measurements. The test kit is easy to operate. An amount of sample is taken, and reagents added to give a coloration. The coloration is visibly checked with a color comparator giving the result in ppm oxygen scavenger. The test is applicable for every oxygen scavenger mentioned in the article.

Idle boiler and oxygen

In case a boiler is turned off for a period of time it is important to ensure the boiler is preserved properly to prevent corrosion problems. As mentioned in the first paragraph of the article warm water contains less dissolved oxygen than cold water. When shutting off a boiler, the water will cool down and oxygen is introduced to the boiler water. The amount of oxygen scavenger normally present in boiler water is insufficient to react with the oxygen introduced by cooling down. To preserve an idle boiler, it is best to add additional oxygen scavenger before cooling the boiler in the amount that reacts with 10 ppm dissolved oxygen. After cooling down the boiler water should be analyzed on presence of oxygen scavenger. The level of oxygen scavenger should be kept at 2 ppm minimum. In case a boiler is laid idle for longer period of time (over three weeks) protection against corrosion and further introduction is enhanced when the boiler is blanketed with 0,2 bar overpressure of nitrogen gas. During a longer period of time regularly monitor for the presence of sufficient amount oxygen scavenger and in case nitrogen gas is used, checking the pressure. When analyzing the water of an idle boiler, ensure to analyze the amount of hardness control (phosphates) as well. Ensure the amount of phosphates is at the higher end of the advised limit.

Conclusion

The choice of type of oxygen control product depends on several parameters; type of boiler, the utility steam is used for, type of water treatment chemicals used, budget, availability of the oxygen scavenger and expected performance. An overview of the comparison between the oxygen scavengers is given in tables 1 and 2. Most cost effective and highest reactivity with oxygen is sulfite, but sulfite has limitations, it can only be used in low and medium pressure boilers. Sulfite is not treating the steam and condensate system and contributes to the solids of the boiler water. DEHA has a good reactivity compared to other oxygen scavengers besides sulfite. The degradation and reaction products of DEHA are not corrosive and affect the steam / condensate system positively. Hydrazine should be avoided due to its toxicity and replaced by carbohydrazide or DEHA. In case steam is used in food processing only erythorbate based products can be used as oxygen scavenger.

Table 2: Overview application of oxygen scavengers

Name	HP Boiler	Cu present	Deaereator dosing	Passivator	Hematite to magnetite	Toxic	Condensate treatment required	Applicable for Food processing	Cost dosing ration
Hydrazine	Y	N	Y	Y	Y	Y	N	N	Low
Sulfite	N	Y	N	N	N	N	Y	N	Lowest
DEHA	Y	Y	Y	Y	N	N	N	N	Moderate
Carbohydrazide	Y	N	Y	Y	Y	N	Y	N	Low
Erythorbate	N	Y	Y	Y	Y	N	Y	Y	High
MEKO	Y	N	N	Y	N	N	N	N	High

Marine Care products

There are three types of oxygen scavengers available at Marine Care.

Caretreat Oxygen Scavenger
- based on catalyzed sulfite

Caretreat Oxygen Control DH
- based on catalyzed DEHA

Caretreat Oxygen Control CH
- based on Carbohydrazide