

ORGANIC CHEMICALS

Oxygen Scavengers





SELECTION GUIDE FOR OXYGEN SCAVENGERS

Oxygen Scavengers

Corrosion by oxygen in the boiler can be controlled by the addition of an “oxygen scavenger” to the preboiler section of the steam generating system. It is generally fed, along with other treatment chemicals, as an aqueous solution to the feedwater either just upstream or, preferably, just downstream of the deaerator, although it is sometimes added into the return lines to scavenge oxygen in the condensate.

The most widely used materials in this application are sodium sulfite (Na_2SO_3) and hydrazine (N_2H_4), both of which are usually sold as catalyzed systems to enhance reactivity with oxygen at lower temperatures and pressures. Quinones and cobalt salts are typically used as catalysts. Sulfite is the least expensive and most active (when catalyzed) for lower and medium pressure boilers [up to 600 psig (42 bar abs)]. In its reaction with oxygen, sodium sulfite produces sodium sulfate, which contributes solids to the circulating boiler system:



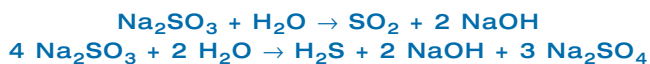
Thus, in high pressure and supercritical boilers, where any solids constitute a severe problem, sulfite cannot be used.

The theoretical dosage of sodium sulfite, or the number of parts of Na_2SO_3 required to consume 1 part of O_2 , can be calculated based on its reaction with oxygen described above:



Therefore, about 8 parts of Na_2SO_3 are fed to the boiler to consume each part of oxygen. Typically, residual concentrations of sulfite of up to 20 ppm are maintained in the boiler.

Sulfite also breaks down at pressures as low as 600 psig (41 bar abs) resulting in the formation of sulfur dioxide or hydrogen sulfide, by either of two routes:



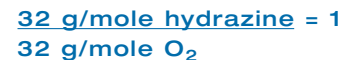
Both are corrosive gases which leave the boiler with steam, resulting in low pH steam and condensate and potential attack throughout the system.

Sulfite is an effective oxygen scavenger, but it is non-volatile and does not leave the boiler with the steam, thus providing no protection in the condensate system. Sulfite also does not reduce hematite to magnetite and is ineffective in repassivating boilers with existing rust.

The oxygen scavengers used in the higher pressure boilers, and the ones with which diethylhydroxylamine (DEHA) competes most directly are hydrazine and catalyzed hydrazine. Hydrazine does not produce corrosive gases at high temperatures and pressures, and in application, reacts with oxygen to form nitrogen and water:



In calculating the theoretical requirement of hydrazine for scavenging oxygen, a value of 1 part per part oxygen is obtained:



In operation, a 100% excess of hydrazine is used. Boiler residuals of 1 ppm hydrazine are typically maintained.

Hydrazine does not contribute solids to the system, so boiler blowdown, or the mechanical removal of solids from the after-boiler section as sludge, is reduced. It also promotes the formation of the protective magnetite film on the boiler tubes and drum, and converts red iron dust (hematite) to magnetite. It is because of these passivation effects that an excess of scavenger to oxygen is required when changing a boiler system from a non-passivating scavenger to one which passivates.

Hydrazine is not without limitations. It is not considered “volatile”, so it does not leave the boiler with the steam to scavenge oxygen and passivate metal throughout the system. In boilers operating above 400°F (205°C), it can degrade to ammonia and volatilize with steam, and, in the presence of oxygen, attack metals containing copper:



Finally, and most importantly of late, is the inclusion of hydrazine on the OSHA and NIOSH lists as a suspect carcinogen. Papers and sales literature presenting laboratory and field data on “hydrazine alternatives” abound, and include those listed in Tables 1 and 2. Each claims to be a safe and effective material for boiler protection through oxygen scavenging, but the levels required and optimum conditions for use vary.

Carbohydrazide is a volatile oxygen scavenger, contributes no solids to the system, reacts readily with oxygen at low temperatures and pressures, and passivates the metal of the boiler system. Carbohydrazide can (and does) break down to hydrazine above temperatures of 350°F (180°C) to scavenge oxygen, but this conversion is not necessary



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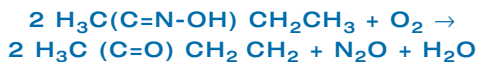
for oxygen scavenging activity because it reacts directly with oxygen:



The theoretical dosage required to scavenge one part O₂ is 1.4 parts carbohydrazide. It should be noted that in its reaction with oxygen, carbohydrazide creates carbon dioxide, a gas that when dissolved in the condensate as carbonic acid, H₂CO₃, results in corrosion in the return line. Carbohydrazide cannot be used in applications where the steam comes into contact with food.

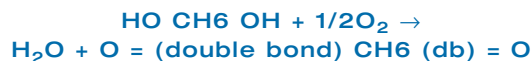
Erythorbate, however, is generally regarded as safe (GRAS) by the FDA and can be used in food processing applications. It, too, is a metal passivator and contributes no solids to the system. It has a theoretical dosage level of 11 parts per oxygen (as O₂). Erythorbic acid is non-volatile. It will remain in the boiler, and will not travel with the stream to control oxygen corrosion in the condensate.

Methylethylketoxime, or MEKO, is a volatile oxygen scavenger which displays metal passivating characteristics. It reacts with oxygen to form methyl ethyl ketone, nitrous oxide, and water:



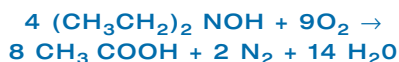
Its theoretical dosage is 5.4 parts per part of oxygen.

Hydroquinone, which has been used to catalyze the reaction with O₂ of some of these oxygen scavengers, has been examined and proven to be effective itself in lowering O₂ levels to the 1-2 ppb range. It reacts with oxygen to form benzoquinone:



and has a theoretical dosage level of 6.9 parts per part O₂. It is extremely reactive with oxygen at the lower boiler temperatures and pressures, and is volatile in higher pressure systems. It does not degrade to ammonia, so it is safe for use with copper-containing alloys.

Diethylhydroxylamine, or DEHA, is a volatile metal-passivating oxygen scavenger which reacts with oxygen to form acetate, nitrogen and water:



In theory, 1.24 parts of DEHA react with 1 part of oxygen, but in application, a dosage of 3 : 1 DEHA to O₂ is recommended. It is generally true that all oxygen scavenger requirements in the field are larger (by up to a factor of 10) than projected by calculations.

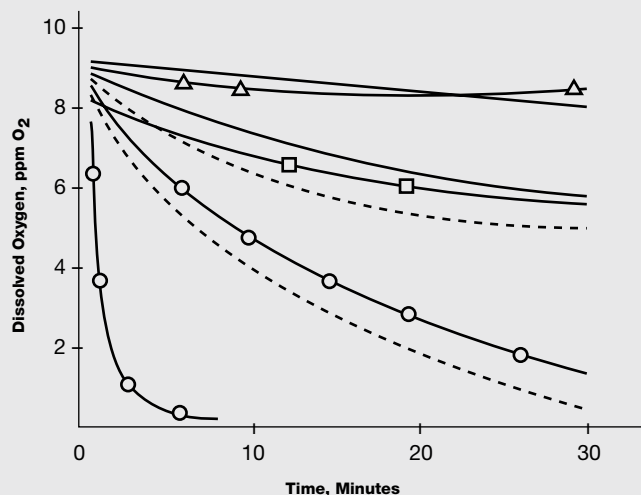
DEHA has other advantages over each of the above-mentioned O₂ scavengers. It has higher volatility and metal passivating characteristics than sulfite, hydrazine and erythorbate, and can be used more safely than hydrazine. Less DEHA is required than erythorbate and methylethylketoxime in theoretical considerations. It offers toxicity advantages over carbohydroxide in that it does not yield hydrazine under use conditions.

Relative to the other scavengers, catalyzed and uncatalyzed DEHA show excellent reactivity (e.g., rate of reaction) with oxygen. Catalyzed sodium sulfite is by far the most reactive oxygen scavenger available in the industry which accounts for its use in low pressure systems. Among the preferred scavengers for higher pressure systems, DEHA has the highest rate of reaction with oxygen (Fig. 3 and 4). At 70 °F (21° C) and pH 8.5, DEHA lowers the level of dissolved oxygen from 9-4 ppm in 10 minutes, whereas with carbohydrazide, catalyzed hydrazine, and erythorbate, dissolved oxygen levels are still above 7 ppm. In thirty minutes, the O₂ levels for DEHA were below 1 ppm compared to levels near 6 ppm for the other scavengers. At pH 11, catalyzed DEHA compared favorably in rate of reaction with catalyzed sulfite. In both cases, the DEHA was catalyzed with hydroquinone.

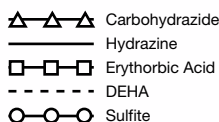
In considering thermal and oxidative degradation products, DEHA generates dialkyl amines, acetaldehyde, acetaldoxime and acetic acid, the last of which can promote low pH corrosion in the system and add to boiler deposits as sodium or calcium acetates. Several of the other scavengers, including erythorbate, MEKO, and hydroquinone also degrade into organic acids and negatively affect the boiler and after-boiler actions. As well, carbohydrazide produces CO₂ in its reaction with O₂, requiring additional prevention of corrosion due to low pH levels (as carbonic acid, H₂CO₃) in condensate return-lines.

For the most part, DEHA will find application as a replacement for hydrazine in medium and higher pressure boilers. In changing a steam-generating system from one to the other, a higher level of DEHA will be required at start-up to passivate the after-boiler and return-line sections of the system. After this has been accomplished, a 3 part DEHA per part oxygen dosage corresponds to a DEHA to hydrazine replacement ratio of 1.5.

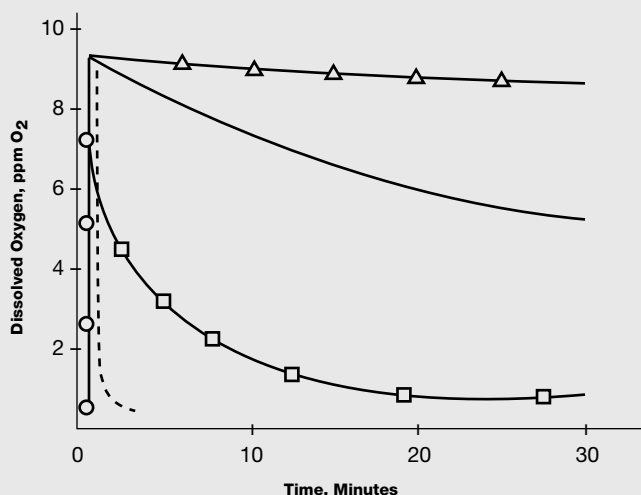
Reaction Rates of Oxygen Scavengers at 70°F and pH 8.5



The lower line for each product reflects the catalyzed version



Reaction Rates of Oxygen Scavengers at 70°F and pH 11



The Hydrazine, Sulfite, and DEHA used were catalyzed

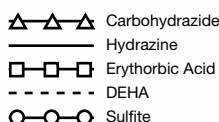


Table 1: Oxygen Scavengers

Chemical Name	Structure	Product Name	Supplier
Carbohydrazide	<chem>H2NHNCONHNH2</chem>	Eliminox®	Nalco
Erythorbate	<chem>OC(O)C(O)C(O)C(O)O</chem>	SurGard®	Nalco
Methylethylketoxime	<chem>CC(C)C(=N)O</chem>	Mekor®	Drew
Hydroquinone	<chem>Oc1ccc(O)cc1</chem>	Magni-Form®	Betz
Diethylhydroxylamine	<chem>CCN(O)CC</chem>	Steamate® Neutrox® Conquor	Dearborn Calgon

Table 2: Oxygen Scavengers

Name	Volatility as VLDR	Metal Passivator	Contributes Solids	Toxicity	Theoretical Dosage (per part O ₂)
Catalyzed Sulfite	non-volatile	N	Y		7.9
Catalyzed Hydrazine	0.08	Y	N	suspect carcinogen	1
Carbohydrazide	volatile	Y	N		1.4
Erythorbate	non volatile	Y	N	G.R.A.S.	11
Methylethylketoxime	volatile	Y	N		5.4
Hydroquinone	volatile	Y	N		6.9
DEHA	1.26	Y	N	relatively non-toxic	1.2

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