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2002 Fall

Oxidation And Degradation Products Of Common Oxygen Scavengers

By John D. Zupanovich ChemTreat, Inc.

For many years, sulfite and hydrazine were the principal materials used to protect boiler systems from oxygen attack. When hydrazine became listed as a suspected carcinogen, a search began for a replacement.

During the search it became apparent that strong reducing agents (oxygen scavengers) should do more than react with and remove dissolved oxygen. They should also form protective oxide films on the metal surfaces of the steam/water system. Thus, the reaction with metal oxides is equally as important as the reaction with dissolved oxygen. During the past decade, a number of materials have been proposed for use as oxygen scavengers and metal passivators. The reactions are frequently very complex. This article is an attempt to explain the oxidation and degradation reactions of the more common oxygen scavengers in current use.

In each case, the material will react with oxygen, and with metal oxides. The efficiency of the reaction is dependent on time, temperature, concentration and system pH. In general, as the pH, time, and temperature increase, the reaction becomes more complete. Since time is usually of the essence, many materials are catalyzed to decrease the reaction time. As a rule, multi-valent metal ions such as copper and iron will increase the reaction rate. Certain organic compounds such as hydroquinone and its derivatives have also been found to be effective catalysts.

Sulfite

Sulfite reacts with and consumes dissolved oxygen in aqueous solutions:



At temperatures of 430°F and above, sulfite will react with iron oxide:



However, because sulfite begins to decompose at 250°F, this reaction is rarely encountered in boiler systems.

Sulfite is supplied to the water conditioning market via several common salts:

2002 Fall

Salt	Formula
Sodium Sulfite	Na ₂ SO ₃
Sodium Hydrogen Sulfite	NaHSO ₃
Sodium Metabisulfite	Na ₂ S ₂ O ₅
Ammonium Sulfite	(NH ₄) ₂ SO ₃

Each of these salts readily ionizes in aqueous solutions; solution pH levels determine which ions are released:

pH	Species Present
4-5	HSO ₃ ⁻
7	HSO ₃ ⁻ and SO ₃ ²⁻ (1:1)
8.5-9.0	SO ₃ ⁻

Because of the alkalinity and sodium found in most boiler feedwater and boiler water, sulfite ion is the species found regardless of the initial salt.

In the high temperature/pressure and alkaline atmosphere of the boiler, sodium sulfite will decompose. As a result, the sulfite salts are limited to pressures below 1250 psig.



Large amounts of sulfur dioxide and hydrogen sulfide gases are usually the result of an overfeed of the sulfite salt.

Both gases volatilize with the steam, reducing the condensate pH at the point of condensation. Generally, this is considered undesirable, but a deliberate overfeed of sulfite will frequently prevent the buildup of water soluble deposits found in turbines operating in the 600-900 psig range.

Hydrazine

Hydrazine has been used in high purity and high pressure systems (greater than 900 psig) where sulfite compounds in the steam could foul a catalyst, or where feedwater is used for attemperation.

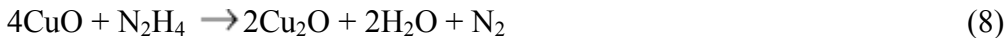
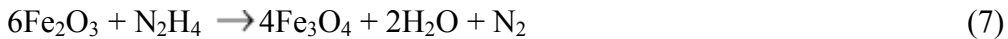
Hydrazine reacts with dissolved oxygen:

2002 Fall



The reaction is slow at ambient temperatures but increases as temperature and pH increases. The presence of a catalyst reduces the reaction temperature to ambient levels. However, the reaction rate is, at best, slower than that of sodium sulfite. Neither hydrazine nor its reaction products contribute dissolved solids to the boiler water. This has been an important feature of the use of hydrazine.

Hydrazine also reacts with CuO and Fe₂O₃ forming protective passive oxide films:



A reaction temperature of 250°F or higher is required for these reactions to take place.

Hydrazine begins to decompose at about 400°F and is virtually gone at 600°F. The reaction at the lower end of the temperature range is believed to be:



At the higher temperature the reaction appears to be:

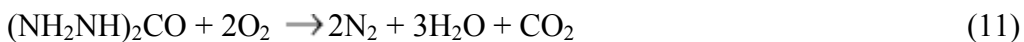


In either case, a significant amount of ammonia is formed when hydrazine decomposes.

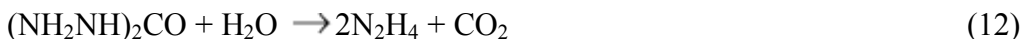
The ammonia can attack copper and copper alloys in the condensate and feedwater system. This is a good reason to keep excess hydrazine in the feedwater low.

Carbohydrazide

Carbohydrazide is the dihydrazide of carbonic acid. It can react with oxygen directly:



and indirectly through hydrolysis to hydrazine:

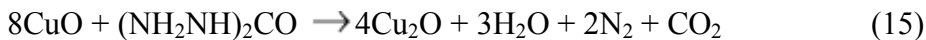
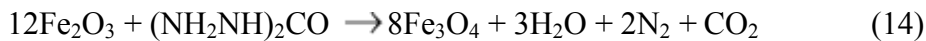


2002 Fall

At room temperature, reaction 11 takes place significantly faster than reaction 12, and slightly faster than reaction 13. However, at boiler feedwater temperatures, reaction 12 is fast enough to produce hydrazine in the boiler feedwater.

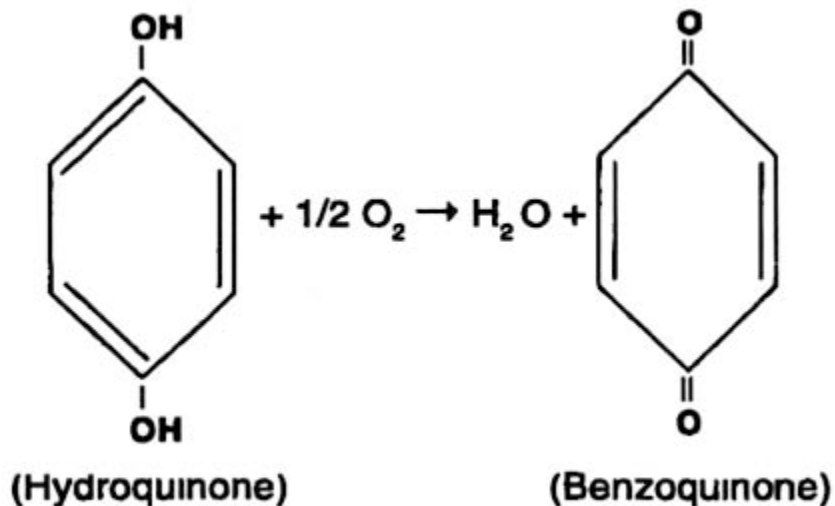
Carbohydrazide is relatively stable at or near room temperature. At elevated temperatures, hydrazine and carbon dioxide are released followed by the degradation reaction shown above for hydrazine.

Carbohydrazide reacts with iron and copper oxides to form protective passive oxides:



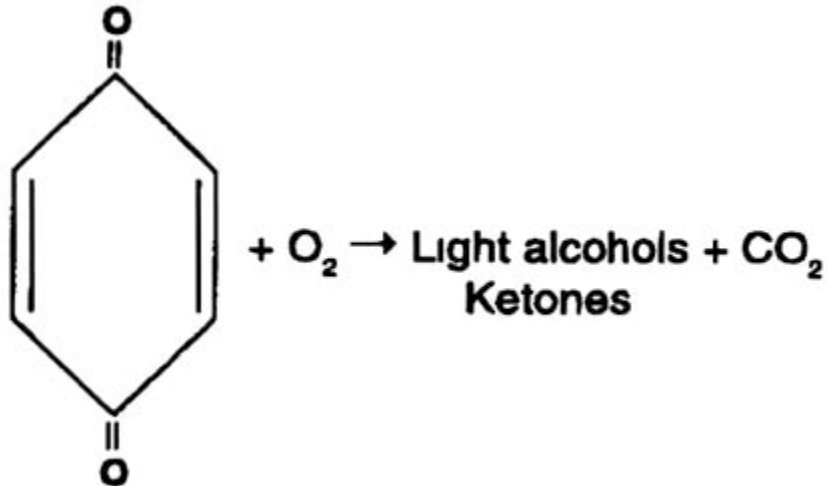
Hydroquinone

Hydroquinone reacts with dissolved oxygen in an aqueous system. The reaction rate is a function of temperatures, solution pH, and the ratio of hydroquinone to dissolved oxygen present in the system. Unlike the reaction of oxygen with sulfite or hydrazine, the hydroquinone reaction is quite complex and appears to go forward in more than one stage. Autoclave studies have shown that the first stage reaction is believed to be:



The Benzoquinone subsequently undergoes further reaction with dissolved oxygen:

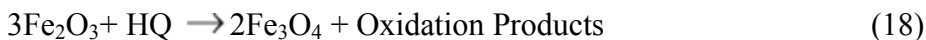
2002 Fall



Because the amount of hydroquinone required in a well-maintained system is small, the quantity of the final reaction products is very low. The end products have neither caused a problem, nor are problems to be expected. As a result of the secondary reaction, less than stoichiometric amounts of hydroquinone are frequently required to scavenge dissolved oxygen from boiler feedwaters

In autoclave experiments using high concentrations of hydroquinone at 2500 psig, some degradation to light alcohols and ketones were noted. However, there has been no measurable amount found under normal use concentrations in 2600 psi systems.

Because there is no nitrogen in the molecule, it does not contribute ammonia to the system. Hydroquinone will also form protective passive oxides with iron and copper.



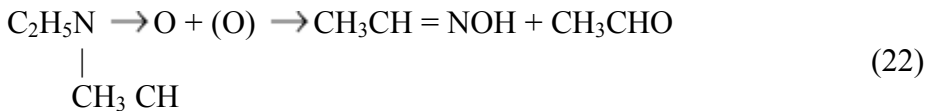
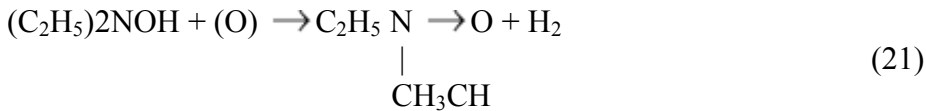
Diethylhydroxylamine (Deha)

Diethylhydroxylamine (DEHA) reacts with oxygen in aqueous solutions. The reaction rate is dependent upon solution pH, temperature, and the ratio of DEHA to dissolved oxygen. Similar to hydroquinone, the reaction of the DEHA with dissolved oxygen is quite complex and several reaction products have been identified. Theoretically, DEHA reacts with dissolved oxygen thusly:



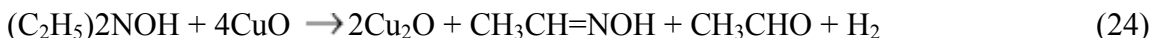
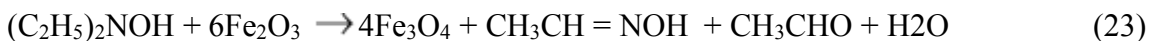
2002 Fall

In practice, the reaction does not proceed stoichiometrically to acetic acid. The first stage reaction with oxygen produces a nitron, which is further oxidized to acetaldoxime:



When sodium hydroxide is present in the boiler water, the acetic acid produced is trapped as sodium acetate and removed by blowdown. The other products are volatile and pass through the condensate system and are vented. In autoclave studies, with very high concentrations of DEHA, very small quantities of ammonia were found. A solution of 1000 mg/L DEHA, autoclaved for two hours produced 83 mg/L of ammonia. When reduced to typical use concentrations, the amount of ammonia contributed by DEHA would not be measurable.

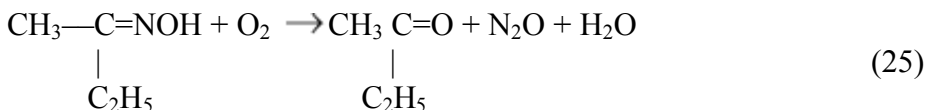
DEHA will also react with iron and copper oxides to form protective passive film:



DEHA degrades as the pressure increases above 1,250 psig. The major degradation product appears to be diethylamine, a volatile neutralizing amine that will contribute to the pH control of the condensate.

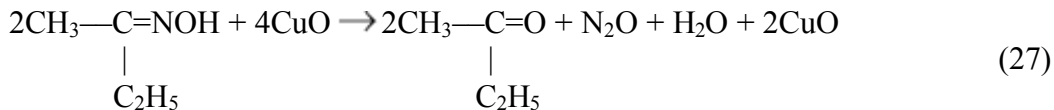
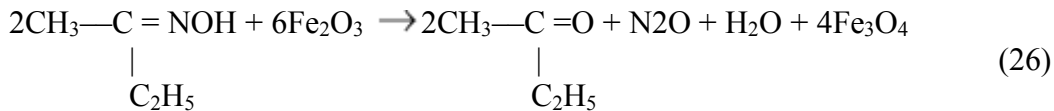
Methyl Ethyl Ketoxime

Methyl Ethyl Ketoxime (MEKO) reacts with dissolved oxygen in an aqueous system. The reaction is virtually non-existent at room temperatures, but at elevated boiler conditions it is reported to react with oxygen:



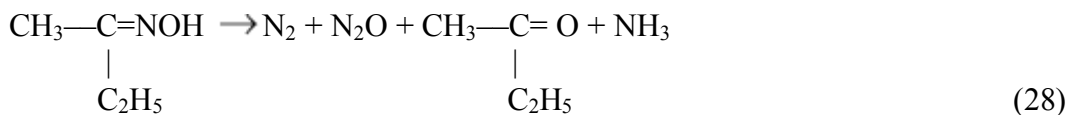
MEKO is claimed to react with iron and copper oxides to produce passive protective oxides:

2002 Fall



Because the reaction with oxygen is slow at low temperature, the reaction is probably also very slow under normal condensate temperature conditions.

MEKO will degrade under boiler conditions:



At 1800 psig MEKO will produce the same amount of ammonia that would be produced from an equivalent amount of nitrogen in the form of hydrazine.

Erythorbate

Erythorbate reacts with dissolved oxygen in aqueous solutions:



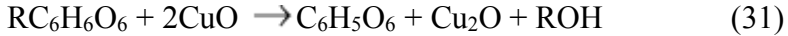
Note: R could be hydrogen, sodium or an amine.

However, as with most complex organic molecules, the reactions are also quite complex. The dehydroerythorbic acid readily hydrolyzes to 2,3-diketo-D-gluconic acid, which in turn can undergo further oxidation. Under alkaline conditions, the reaction can proceed to D-erythronate and oxalate, and finally to CO₂ and water. The final products will depend upon the amount of oxygen, the pH and the temperature during the reaction. The presence of metal ions also impacts upon which of the final reaction products are produced.

Erythorbate is a relatively strong reducing agent capable of reducing oxidized forms of iron and copper.



2002 Fall



As with oxygen, these reactions can proceed beyond the dehydroerythorbic acid. The path will be similar to that described for the oxygen reaction and the final products will be dependent upon the amount of oxidized metal, the pH, temperature, and level of exposure.

Erythorbates will degrade in aqueous solution. The pathway and route of degradation is dependent upon the chemical environment. The pH, temperature, the presence or absence of oxygen and the presence or absence of metal ions are all important parameters of the degradation reaction. Under acid conditions (without oxygen) the molecule degrades to carbon dioxide and furfural, under alkaline conditions (without oxygen) erythorbate is quite stable.

Conclusion

Oxygen scavengers remove dissolved oxygen in boiler water by a reduction reaction, and thereby inhibits corrosion caused by oxygen. The desirable functions of an oxygen scavenger are to have a chemical potentiality high enough to reduce oxygen, and a thermally decomposed reaction product that does not have an aggressive effect on the boiler or on the steam and condensate lines. These two conditions have been met for the above discussion of oxygen scavengers.

About the Author

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Technical Article Review Quiz

The Questions for the exam may be answered by reading and understanding the Fall 2002 Analyst Article titled "Oxidation And Degradation Products Of Common Oxygen Scavengers" by John Zupanovich. The correct answers are derived from that article and any disputed answers will be referred back to that article for justification.

- Oxygen Scavengers remove dissolved oxygen in boiler water by a,
 - Reduction reaction.
 - Oxidation reaction.
 - Precipitation reaction
 - Altering saturation pH
- Oxygen Scavengers will react with oxygen and with metal oxides, the efficiency of the reaction is dependent on,
 - Time.
 - Temperature and concentration.
 - pH
 - all of the above.
- Sulfite begins to decompose at,
 - 100°C
 - 250°C
 - 250°F
 - 100°F
- Sulfur dioxide and hydrogen sulfide gases are usually the result of an overfeed of,
 - amines.
 - hydrazine.
 - sulfite.
 - carbohydrazide.
- Hydrazine and its reaction products will,
 - not contribute to the dissolved solids in the boiler water.
 - increase dissolved solids in the boiler water.
 - decrease dissolved solids in the boiler water.
 - all of the above depending on temperature.
- DEHA degrades as the pressure increases above,
 - 1250 psig.
 - 100 psig.
 - 500 psig.
 - 5 psig.
- MEKO reacts with dissolved oxygen in an aqueous solutions at,
 - any temperature
 - elevated boiler water temperatures
 - the feedpoint to form magnetite
 - does not react with oxygen
- Erythorbate is a relatively strong reducing agent capable of reducing,
 - non-oxidized iron
 - non-oxidized copper
 - oxidized iron and copper
 - to form a neutralizing amine
- Carbohydrazide is relatively stable at or near,
 - room temperature
 - elevated boiler water temperatures
 - any temperature
 - 1250 psig
- Hydroquinone will contribute ammonia to the system when,
 - Benzoquinone consumes nitrogen
 - Hydroquinone consumes nitrogen
 - Hydroquinone reduces nitrogen to nitrite
 - Hydroquinone contains no nitrogen in the molecule