

If you would like a more detailed version of this report, please request “SOS” from bcavano@scrantonassociates.com along with your e-mail address.

Sulfites for Oxygen Control

Robert R. Cavano – Scranton Associates, Incorporated

A. Introduction

Oxygen is present in all water supplies, though at widely varying concentrations. Unless limited, it can cause corrosion throughout the entire steam generation system. In addition to weakening the metal, this attack generates metallic oxides that become or form troublesome deposits. And while oxygen provides a major pitting challenge on its own, additional forms of corrosion are accelerated by its presence.

Carbon dioxide reduces the pH of the condensate causing grooving and generalized thinning of piping. It is well known, moreover, that oxygen and carbon dioxide are synergistic in their activity to increase corrosion.

Oxygen dissipation and deactivation are the most common methods of control, carried out by mechanical or chemical means or by a combination of the two. Other popular methods of protecting the metal in a boiler are passivation and filming inhibitors. The most common chemical scavengers, by far, are based on sulfites and bisulfites, an approach that can be highly effective if boiler pressures are not too high, and total solids are kept within prescribed limits.

B. Oxygen Corrosion

Corrosion is primarily a phenomenon in which the metal surface hosts a network of galvanic cells. In the presence of water, there is a tendency for ions to go into solution at the anode, resulting in hydrogen being released at the cathode. This creates an electrochemical potential which promotes iron corrosion. When sufficient oxygen is present, these reactions are accelerated in a process described as depolarization. In the absence of adequate scavenging, the various forms of iron oxide are converted to hematite.

“Pitting” is an especially distressing condition which quickly destroys the integrity of a metal. Within a pit, iron contributes to reactions that form black iron oxide. If the process were to stop here, the coating could provide good protection. But the process goes on with a continuing formation of ferric hydroxide. As the temperature of the water rises, more oxygen leaves the solution, no equilibrium is reached or magnetic coating formed, and corrosion continues until the oxygen is exhausted.

C. Sources of Oxygen

A major obstacle in planning any boiler treatment program is the difficulty of estimating the oxygen present in a system or being added with the make up. Temperature is an especially critical factor. Since oxygen is not an ionizable gas, its solubility is much more temperature dependent than is carbon dioxide. Low temperature make up water contains as much as 10 mg/L of oxygen and hot feedwater about 3 mg/L. A variation from 40° F to 80° F in our water source results in a drop in oxygen content from 13 ppm to 8 ppm.

Concentrations of oxygen are usually expressed as cubic centimeters per liter (cc/L) or milliliters per liter (ml/L) [numerically the same]. Oxygen may also be reported by weight: 1 cc/L or ml/L of dissolved oxygen equals 1.43 mg/L. 1 mg/L of oxygen then equals 0.699 cc/L (or ml/L).

D. Oxygen Limits

Even very low levels of oxygen can cause corrosion. Table I shows the concentrations which must be complied with in deaerated water if corrosion to steel is to be avoided:

Table I – Oxygen Limits (mg/L)

Type of Water	Maximum Oxygen Concentration (mg/L)
Cold Water	0.300
Hot Water	0.100
Low Pressure Boilers (<250 psi)	0.030
High Pressure Boilers	0.005

Another set of upper limits for corrosion prevention has been established by the American Boiler Manufacturer' Association (ABMA):

Table II – Oxygen Limits in Boilers

Drum Operating Pressure (psig)	0 – 450	451 - 900
Dissolved Oxygen (mg/L)	< 0.040	< 0.007

E. Deaeration

Efficient deaeration is necessary to minimize boiler and condensate corrosion. Mechanical deaeration ordinarily reduces oxygen to a residual of less than 0.04 mg/L. In a multistage deaerator, the amount of oxygen can be further reduced to 0.007 mg/L or less. Since the maximum oxygen content of higher pressure boilers should be between 0.005 and 0.007 ppm (as mg/L), both deaeration and chemical treatment are usually necessary.

F. Sulfite Treatment

Since it is not possible to remove all dissolved oxygen by physical means, traces of it usually still remain, and no matter how small they are, cause significant corrosion unless chemical agents are introduced. This oxygen may be controlled by feeding sodium sulfite in quantities sufficient to react with the oxygen and, in addition, adding enough to constitute a comfortable excess.

The sulfites (whether sulfite or bisulfite, sodium or potassium) have become, because of their low cost, the first choice for scavenging. Sodium sulfite is sold as a powder -- as is, catalyzed, or decharacterized. Liquid versions are often available as aqueous sodium sulfite or metabisulfite solutions.

Products based on sulfite react with oxygen to form sodium sulfate. Solids introduced through this reaction can become a problem as pressures go up, so the use of sulfite is limited to lower pressure installations. The sulfite/oxygen reaction is inhibited by chelants, by contaminants in the feed water, or by treatment chemicals.

Users of sodium sulfite often express concern with its slow and incomplete solubility. Realizing that metabisulfite is more readily soluble (38% @ about 43° F), many have used that alternative. Several suppliers now mix metabisulfite with sulfite to lower the pH and improve the solubility of the sulfite and possibly of the “catalyst”.

G. Sulfite Dosage

The amount of oxygen scavenger required in a boiler water is related to the concentration of dissolved oxygen, the residual level of scavenger specified, and the percent of blow down performed. Water temperature, water composition, and reaction time also have considerable impact on the ultimate quantity of scavenging chemical needed:

$252/32 = 7.88$ parts pure sodium sulfite per part oxygen by weight;

$190/32 = 5.94$ parts of metabisulfite [becomes bisulfite in water] per part of oxygen by weight;

$7.88/0.97 = 8.12$ (adjustment for activity of commercial sodium sulfite);

$8.12 \times 1.43 = 11.61$ parts sulfite when oxygen is stated as parts per unit volume;

$(252 + 32)/(32)(0.97) = 9.15$ parts sulfate created per part of oxygen.

Sulfite dosage figures can alternatively be developed as:

1 ml/L dissolved oxygen = 0.0715 mg/L (or lbs oxygen/million lbs water) [$0.05 \times 1.43 = 0.0715$]. This requires 0.58 lbs of sodium sulfite/million pounds of water [$0.0715 \times 8.12 = 0.58$], or 4.83 lbs of sodium sulfite/million gallons of water [$0.58 \times 8.33 = 4.83$].

Praise the Lord who allows us to convert from among the various sources of sulfite:

Table III – Sulfite Conversions

*If dosage is stated as 100 mg/L of sodium sulfite, we may use 75 mg/L of metabisulfite
If 100 mg/L of sulfur trioxide is called for 157 mg/L of sodium sulfite may be substituted.*

Sodium Sulfite (Na₂SO₃)	100	133	157	197
Sodium Metabisulfite (Na₂S₂O₅)	75	100	119	148
Sulfur Trioxide (SO₃)	63	84	100	124
Sulfur Dioxide (SO₂)	51	68	80	100

H. Speed of Reaction

For good corrosion control in a boiler, rapid reaction is sought between oxygen and the chemical scavenger. A slow reaction rate could allow traces of oxygen to enter the boiler even in the presence of an excess of sodium sulfite. Factors determining the rate at which this reaction takes place are: the purity of the water, the residence time in a system, the location of the chemical feed, the levels of dosage, the temperature of the water, its pH, and the presence and concentration of catalysts. The performance of sodium sulfite is very sensitive to catalysis from trace amounts of manganese, copper, iron, nickel, or cobalt.

The sulfite/oxygen reaction is known to be inhibited by some alcohols, phenols, amines, and thiosulfate. Other contaminants or organic treatment chemical such as corrosion inhibitors, scale inhibitors, and biocides may also slow down reaction time. A slow reaction can present a problem at early phases in a system and require the use of catalysts or feeding techniques that provide maximum time for the reaction to occur. The reaction rate for sulfite appears to be the fastest of all of the scavengers, followed by erythorbic acid and DEHA. Slower rates, in general, have been reported for hydroquinone, carbohydrazide, and hydrazine.

I. Catalyzation

A catalyst is defined as a substance that changes a reaction rate without being consumed in the process. In some smaller systems, stray metals may perform as sulfite catalysts. Rarely is the amount of iron or copper arising from contamination or corrosion sufficient to catalyze sulfite in larger systems. In addition, the presence of large quantities of these metals may be undesirable because of the potential for iron or cobalt "poisoning" of polymers and the risk of copper plating out on metal surfaces, and may have to be removed.

Erythorbates have been widely used as anti-oxidants for food products. They are able to reduce stray metals, sequester them, and maintain them in a system thereby preventing oxidation and precipitation. This also makes erythorbate useful, when present in sufficient amounts, as a stabilizer for concentrated solutions of sodium sulfite. When the materials are used together, we have low-cost scavenging with effective passivation, and possibly even some catalyzation.

For lower erythorbate content, the same sequestering process releases it from solution as it is diluted and as alkalinity increases in the boiler. This allows any free erythorbate present to catalyze the sulfite/oxygen reaction and validates it as a safe, non-metallic agent of catalysis.

The usual catalyst for sulfite had been cobalt sulfite or cobalt chloride at levels of less than 0.1% (as Co). One problem with the use of catalyzed sulfite was that the cobalt was precipitated from solution by phosphates or pH values above 8.3. In order to avoid deactivating the catalyst, the product, consequently, had to be fed prior to the introduction of phosphates or chelating agents.

For many years, the cobalt in catalyzed sulfite went directly to the bottom of the feed tank and never fully participated in the process. Later approaches used a sulfite/metabisulfite blend to assure lower pH for better sulfite and cobalt solubility. Since cobalt has now been described by the National Toxicology Program to be “reasonably anticipated to be a human carcinogen”, its use as a catalyst has largely been abandoned.

J. Decharacterization

USDA requires that sulfites shipped to food plants be decharacterized:

“ To promote handling of preparations containing sodium nitrate, sodium sulfite, sodium bisulfite, and sodium metabisulfite in a manner as to prevent their use in meat products, such preparations must be adequately decharacterized.”

It is difficult to design decharacterized liquid sulfite products which are sufficiently concentrated since lignosulfonate solubility requires high alkalinity which, in turn, reduces sulfite solubility. One remedy is to start with metabisulfite and decharacterize it by the addition of a hydroxide. This can yield a neutral solution congenial to the solubility of some metallic catalysts. Decharacterization is most often achieved either by making sodium hydroxide or potassium hydroxide part of a liquid product or by incorporating 5% of lignosulfonate in a dry formula.

K. Feeding and Dosage

We should consider how to introduce scavengers so as to achieve maximum speed of reaction. They should be fed continuously, and if possible, in a concentrated form. To provide ample time for reaction, the scavenger should be fed as far ahead of the boiler as possible. If we dilute these scavengers too early, much of the product will be used up on the oxygen from the dilution water and from the ambient air.

Sodium sulfite is alkaline (pH 9-10 for a 1% solution), while solutions of sodium bisulfite are mildly acidic. The low pH (<5) of sodium metabisulfite, in addition to allowing more concentrated products, prevents the solution from reacting with atmospheric oxygen too quickly.

L. Residuals

In addition to the sulfite necessary for reaction with the oxygen present, we must also select a residual level sufficiently large to handle additional incursions. This residual becomes a further means of verifying that all oxygen has been controlled and that a reserve of sulfite is available for future demands.

M. Concentration and Blow Down

Deposits of suspended and dissolved solids result from impurities in the make-up or from treatment chemicals (including sulfite). When their levels exceed certain limits, precipitation occurs and scale forms. Maximum permissible concentrations may be determined for specific materials or from the total alkalinity or solids content of the water.

To be sure that we do not exceed these limits, quantities of concentrated boiler water must be regularly removed and replaced with better water. This periodic or continuous drainage is referred to as blow down (BD) and expressed as $\% \text{ BD} = (100)(\text{quantity of BD})/(\text{quantity of feed water})$.

N. Passivation

The term “passivation” describes the process by which a protective film is formed on metal surfaces, a passive film distinguishable from carbon steel by its black color. Should we be able to develop such a protective film, we must continue to work to assure its quality and durability.

While “passivation” sounds appealing and is a good marketing tool, the mechanism and possible consequences of this state are complex. We must decide whether passivation alone is a legitimate reason for choosing an oxygen scavenger. Those who have used filming amines for condensate treatment realize that they are taking chances if they don’t neutralize the aqueous medium in addition to providing surface protection. We suggest that, for the problem at hand, you try to go after the oxygen and control it. If you get some passivation, so much the better!

Hydrazine and other organic scavengers provide passivation properties far beyond those available with sulfite. Sulfite preferentially reacts with oxygen in the presence of metal oxides, while hydrazine preferentially reacts with the metal oxides themselves. This accounts for the superiority of sulfite as an oxygen scavenger and of hydrazine as a passivating agent. These comments are now somewhat academic in that hydrazine is so hazardous to work with and all of the organic materials are so much more expensive than sulfite.

O. Sulfite Degradation

At temperatures as low as 490° F, sulfites begin to form corrosive gases. The extent reached is a function of boiler pressure and sulfite concentration, and is reflected in reduced pH values. The gases leave the boiler with the steam and the resulting acid condensate, unless neutralized, attacks turbine blades and other sections of the system.

Substantial generation of corrosive gases does not usually begin until 535° F but the range between desirable magnetite formation (428°F) and the start of degradation (490° F) is relatively narrow. In order to avoid excessive quantities of these gases, sulfite residuals should be carefully controlled.

P. Volatility

Distribution ratios are familiar to us as indications of the ability of neutralizing amines to volatilize and remain with the steam and condensate. Sulfite, hydroquinone, erythorbate/erythorbic acid, and carbohydrazide are not volatile and consequently have DRs of zero, while hydrazine has a DR rating of close to zero. There are several oxygen scavengers which volatilize with the steam (DEHA, MEKO) and can be used for this function, alone or in combination with other scavengers.

Q. Contact with Foods

Boiler water additives may be safely used in the preparation of steam that will contact food, under conditions published in 21 CFR, Ch. 1, 173.310 – Food and Drug Administration. From the approved substances in this list, we select several of interest from part c):

sodium sulfite (neutral or alkaline)
sodium lignosulfonate
sodium hydroxide

sodium metabisulfite
cobalt sulfate (as catalyst)

Part d) of CFR 173.310 indicates that **no** hydrazine is acceptable in the steam that contacts food products. No other volatile oxygen scavengers are mentioned.

Ammonium hydroxide is not listed in 173.310 but is accepted in 184.1139 as suitable for direct addition to human food in the GRAS (Generally Accepted as Safe) category. Erythorbic acid, suggested as a scavenger or catalyst for oxygen, is also acceptable in food products and consequently listed in the GRAS classification.

FDA advised some companies making boiler water treatments that they “should” use food grade sulfite if the steam comes in contact with food. Tedious semantic discussion with regulators established that “should” did not mean “must”. No sulfite ingredients are known to be volatile. Volatile amines approved in this section are not available in food grade versions so no universal and comprehensive instruction prevails for the list.