NTSB DOM 13

**QUESTIONS** 

**AND ANSWERS** 

### Oxygen Scavengers



Close-up of "pit" formation — the characteristic oxygen attack mechanism.



#### **Oxygen Corrosion**

#### Is oxygen corrosive?

Yes. Oxygen is a highly reactive gaseous element. In the presence of steel, the corrosion rate of oxygen doubles for each 30°F rise in temperature. For example, in a boiler system operating at 400 psig and 444°F, the corrosion rate for oxygen is 256 times more reactive than at room temperature.

## How does oxygen attack metal surfaces?

Oxygen forms localized corrosion areas referred to as "pits." This distinctive formation is readily distinguishable from acid attack, caustic gouging or chelate corrosion. (See Figure 1.) Oxygen pits can rapidly "drill" through metal surfaces, leading to metal fatigue and failure.

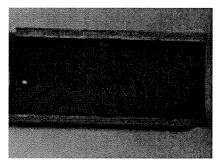


Figure 1 — Oxygen attack occurs as a distinctive pit formation

## What is the oxygen corrosion mechanism?

Oxygen corrosion is an electrochemical process similar to a simple battery. Iron dissolves at the anode and releases electrons which are subsequently consumed by oxygen at the cathode. (See Figure 2.) Pitting is the result of this localized mechanism.

Anode:  $Fe^0 \rightarrow Fe^{+2} + 2e^-$ 

Cathode:  $2e^- + H_2O + 1/2O_2 \rightarrow 2OH^-$ 

## Where can oxygen corrosion occur in a boiler system?

Because oxygen is a gas, it will "flash" into the condensate system, turbines, and other steam operated equipment. Every metal surface of the boiler system is vulnerable to oxygen attack.

## Why is oxygen corrosion a serious problem?

As oxygen corrodes the boiler metal, it dissolves the iron surface. This weakens the metal site, but more importantly, sends dissolved iron into the boiler. This dissolved iron can deposit onto boiler tubes, causing overheating and tube failure.

#### **Oxygen Scavenging**

## How can oxygen corrosion be minimized?

Oxygen control is generally both a mechanical and chemical process. The majority of oxygen in the boiler feedwater is typically reduced to less than 20 parts per billion (ppb) by heating the water to reduce its solubility and releasing it out of the system via venting (deaeration). Since even very low levels of oxygen will cause corrosion, a chemical scavenger is used to supplement mechanical deaeration to reduce the level to zero. For more information on mechanical deaeration, see Nalco TECHNIFAX® 148.

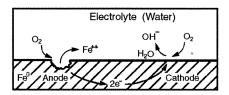


Figure 2 — In the basic corrosion cell, iron dissolves at the anode while oxygen reacts to form hydroxide ions at the cathode

# Can an oxygen scavenger be used if the plant currently does not deaerate the feedwater?

Yes. Oxygen scavengers are effective at high oxygen levels, but mechanical deaeration is more efficient and cost-effective in the long run. Oxygen corrosion cannot be completely inhibited by chemicals alone. There is no real substitute for good mechanical deaeration. Chemicals are most effective when used only to polish a properly operating system.

## Should oxygen scavengers be fed with other products?

No. Oxygen scavengers should *not* be mixed with other chemicals because this may result in a complete loss of product activity.

The addition of water to a *liquid* oxygen scavenger may also result in a loss of product activity. Dilution water contains oxygen, which is consumed by the scavenger and reduces the overall effectiveness of the product. All liquid oxygen scavengers should be fed neat (undiluted).

## What Nalco chemicals can be used for oxygen scavenging?

- Sodium sulfite based:
   NALCO® 19P NALCO® 2549
   NALCO® 1720 NALCO® 7408
   NALCO® 1722
- Proprietary formulations: NALCO® 1700 NALCO® 1721 NALCO® 1710 ELIMIN-OX®

Table 1 — Oxygen scavenger characteristics

	O <sub>2</sub> Scavengers						O <sub>2</sub> Scavengers & Passivators		
	19P	1720	1722	2549	7408	1710	1721	1700	ELIMIN-OX
Form	Dry	Liquid	Liquid	Dry	Liquid	Liquid	Dry	Liquid	Liquid
Max. pressure	900	900	900	900	900	1500	900	2500	Unlimited
Catalyzed	Yes	Yes	Yes	Yes	No	Yes	Yes	No	No
Passivates	No	No	No	No	No	No	Yes	Yes	Yes
Adds solids	Yes	Yes	Yes	Yes	Yes	Trace	Yes	Trace	No
Spray attemperation	No	No	No	No	No	Yes	No	Yes	Yes
Superheater lay-up	No	No	No	No	No	No	No	No	Yes
Boiler lay-up	Yes	Yes	Yes	Yes	Yes	No	Yes	No	Yes
FDA approved	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes	No*
USDA approved	No	No	Yes	Yes	No	No	No	Yes	No

<sup>\*</sup>Can be used in boilers which are FDA regulated for pulp and paper mills only

Each of these chemicals is a strong reducing agent which quickly removes oxygen from boiler feedwater. (See Table 1.) To determine the maximum recommended boiler pressure for each product, see Figure 3.

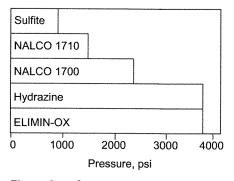


Figure 3 — Oxygen scavenger pressure limits

## What types of sodium sulfite are available?

Sodium sulfite is a highly effective oxygen scavenger and is available in several forms:

Uncatalyzed sulfite — The reaction of sulfite with oxygen is very slow at temperatures below 200°F. Without a catalyst, it takes up to ten minutes to reduce the oxygen

content of water from the saturation point to 70% with sodium sulfite at room temperature. This type of product is recommended only when the application cannot tolerate the presence of a cobalt catalyst (catalyst beds, food applications, etc.).

Catalyzed sulfite — The catalyst, usually a cobalt salt, speeds up the reaction rate of sulfite at low temperatures (<240°F). A fully saturated oxygen solution can be completely deoxygenated in as little as 30 seconds. A potential drawback is that the catalyst can be deactivated or precipitated by improper feed application, such as water dilution or mixing with caustic.

Decharacterized sulfite — This is a term used by the USDA. It refers to specific chemicals which must be removed from sodium sulfite for the product to be USDA and FDA approved. Sulfite which is not decharacterized has the ability to give meat a red or "fresh" appearance. Nalco's two decharacterized products are both catalyzed.

## What are the disadvantages of using sodium sulfite?

Several costly disadvantages are inherent with using sodium sulfite as an oxygen scavenger. These problems occur regardless of whether the sulfite is catalyzed or uncatalyzed.

- Adds solids to the boiler Additional solids to the boiler contributes to an increased blowdown requirement. Blowdown is literally "money down the drain." It is a direct loss of energy and increases water treatment costs.
- Cannot be used for spray attemperation The solids contribution of sodium sulfite would cause superheater and turbine deposits. Also, since chemical feed must occur after the attemperation water take-off point, all equipment upstream of that point would be subject to oxygen corrosion and costly repairs.

 Cannot be used at boiler pressures above 900 psig. Sodium sulfite begins to decompose at approximately 600 psig and is complete at 900 psig. The decomposition products are H<sub>2</sub>S and SO<sub>2</sub>, both highly corrosive gases, which can cause catalyst poisoning and severe corrosion on steam operating equipment.

#### What is NALCO 1710?

NALCO 1710 is a nonvolatile, organic oxygen scavenger which can be used as a direct replacement for sulfite without the associated dissolved solids contribution.

## What are the advantages of using NALCO 1710?

- Minimal solids added to the boiler
   — Less boiler solids means lower conductivity levels and lower blowdown rates, thereby saving energy dollars.
- No poisoning of catalyst beds Unlike sulfite, NALCO 1710 will not poison hydrogen, ammonia or methanol catalysts with sulfur dioxide or hydrogen sulfide.
- Can be used for spray attemperation
   — Because it breaks down to volatile components, the unique chemistry of NALCO 1710 permits it to be added upstream of the spray attemperation takeoff point which provides more equipment protection from oxygen attack.
- Can be used at boiler pressures up to 1500 psig Unlike sulfite, which has a pressure limit of 900 psig, NALCO 1710 can be used up to pressures of 1500 psig. The decomposition products of NALCO 1710 are completely volatile and have been proven not to adversely affect steam operated equipment.

 Reduced sodium level variation in the boiler feedwater — Lower variation will reduce the problems in maintaining the proper Na:PO<sub>4</sub> ratio in phosphate-based programs. This enhances boiler corrosion protection and fouling control by eliminating the control conflict between the oxygen scavenger and internal treatment programs.

## Can NALCO 1710 actually save money over sulfite?

Yes. Since NALCO 1710 does not contribute dissolved solids to the boiler, this product may pay for itself within the first year of treatment. For example, in a typical 400 psig boiler using 500,000 lb/hr of feedwater which is conductivity limited, the savings in energy and water cost can be as high as \$200/ day or \$70,000 per year! The return on investment (ROI) for using a NALCO 1710 program can be over 500% while only slightly raising the cost of chemical treatment. For an estimate of your potential blowdown savings, contact your local Nalco representative.

## How is a NALCO 1710 program monitored?

Iron, copper, and oxygen testing are recommended to monitor the oxygen consumption of the product. Oxygen residual testing provides an extra measure of insurance, especially during upsets. Your Nalco representative can provide the necessary product monitoring guidelines.

# How does the performance of Nalco's oxygen scavengers compare?

At typical boiler feedwater temperatures (>210°F), sulfite, NALCO 1710 and NALCO 1700 provide the fastest oxygen scav-

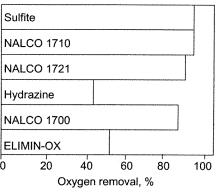


Figure 4 — Oxygen scavenger performance (240°F)

enging properties, whereas, NALCO 1721, hydrazine, and ELIMIN-OX all provide superior protection from oxygen by also providing metal passivation. (See Figure 4.)

#### **Metal Passivation**

#### What is metal passivation?

Metal passivation has traditionally been considered to be the reduction of hematite to magnetite in iron-based boiler tubes. Actually, it is a process by which bare metal surfaces form a protective oxide film. The passive film is very thin and dense. It is distinguishable from the base metal by the coloration. In the case of carbon steel, this protective film is magnetite  $(Fe_3O_4)$  and is black in color.

## Can oxygen scavengers enhance metal passivation?

Yes. Hydrazine has traditionally shown passivation properties and Nalco has developed several proprietary products which effectively enhance metal passivation.

# What Nalco oxygen scavengers can be used for metal passivation?

- NALCO 1700
- NALCO 1721
- ELIMIN-OX

Each of these chemicals is an excellent metal passivator which quickly forms a protective oxide layer on the boiler metal surface. (See Table 1.)

## What are the disadvantages associated with hydrazine?

- Generates ammonia One of the decomposition products of hydrazine is ammonia (NH<sub>3</sub>). At concentrations above 0.5 ppm, ammonia will attack copper in the presence of oxygen.
- Suspected carcinogen Hydrazine is a suspect carcinogen, therefore, handling is a special concern. Precautions, records, and special equipment may be required to avoid inhalation or frequent exposure to hydrazine.
- Slow reaction rate At low temperatures, hydrazine is slow to react. Slow reaction time means there is always the possibility of oxygen attack, even with hydrazine in the system, unless very high levels are maintained.

# Can the low temperature reaction of hydrazine be catalyzed to speed it up?

Yes. Although a catalyst helps at ambient temperatures, it is of little value at boiler operating temperatures. Even catalyzed hydrazine reacts more slowly than the uncatalyzed form of sulfite at low temperatures.

#### What is NALCO 1700?

NALCO 1700 is a highly effective oxygen scavenger that also enhances metal passivation. NALCO 1700 is nonvolatile and the ingredients are listed as Generally Recognized As Safe (GRAS) by the FDA for use as boiler water additives. NALCO 1700 is also approved for use in USDA regulated meat and poultry applications. NALCO 1700 cannot be used in dairy applications.

## What are the advantages of NALCO 1700?

- Minimal solids added to the boiler
   — Less boiler solids means lower conductivity levels and lower blowdown rates, thereby saving energy and water treatment dollars.
- Can be used for spray attemperation
   — Because it breaks down to volatile components, the unique chemistry of NALCO 1700 permits it to be added upstream of the spray attemperation takeoff point which provides more equipment protection from oxygen attack.
- Provides metal passivation —
   Passivation is the extra measure of protection that helps improve system reliability. Less corrosion means less downtime and fewer repairs.
- Can be used at boiler pressures up to 2500 psig — NALCO 1700 begins to decompose at temperatures associated with pressures of approximately 1800 psig. The decomposition products of NALCO 1700 are completely volatile and have been proven not to adversely affect steam operated equipment.
- Fast reaction rate At typical feedwater temperatures (>210°F), NALCO 1700 is nearly 100% faster than hydrazine.

## Will NALCO 1700 carry over into the steam?

No. NALCO 1700, under boiler conditions, is a nonvolatile substance that will not carry over. It is acceptable for turbines, evaporators, and other steam operated equipment.

## Will NALCO 1700 adversely affect condensate polisher resin?

Unlike some oxygen scavengers which can carry over into the steam, NALCO 1700 cannot foul or adversely affect condensate polisher resin.

#### What is NALCO 1721?

NALCO 1721 has been specially formulated to provide the scavenging power of catalyzed sulfite and metal passivation properties of NALCO 1700. This product offers sulfite users the additional benefits of metal passivation and protection against oxygen attack.

#### What is ELIMIN-OX?

ELIMIN-OX is an all-volatile oxygen scavenger which can be used in all types of boilers, except where FDA or USDA compliance is required.

# Is ELIMIN-OX just a catalyzed form of hydrazine?

No. ELIMIN-OX oxygen scavenger contains carbohydrazide which reacts directly with oxygen. At temperatures above 300°F, it begins to break down to hydrazine. ELIMIN-OX is unique in that both the product and its byproducts are oxygen scavengers and metal passivation enhancers.

### What are the advantages of using ELIMIN-OX?

- Wet lay-up of boilers and superheaters

   Oxygen protection is as important when a boiler comes down as while it is on line. When properly used, ELIMIN-OX helps prevent oxygen damage and continues to passivate metal surfaces during wet lay-up.
- Once-through boilers The superior metal passivation properties of ELIMIN-OX make it the product of choice for oncethrough systems.
- Fast reaction rate At typical feedwater temperatures (>210°F), ELIMIN-OX is nearly 15% faster than hydrazine.
- No handling concerns Unlike hydrazine, ELIMIN-OX poses no special handling problems.
- No solids added to the boiler —
   Zero boiler solids means lower
   conductivity levels and lower
   blowdown rates, thereby saving
   energy and water makeup
   dollars.
- Can be used for spray attemperation
   — Because it breaks down to volatile components, the unique chemistry of ELIMIN-OX permits it to be added upstream of the spray attemperation take-off point which provides more equipment protection from oxygen attack.
- Provides metal passivation —
   Passivation is the extra measure of protection that helps improve system reliability. Less corrosion means less downtime and fewer repairs.

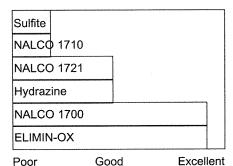


Figure 5 — Metal passivation performance (240°F)

Unlimited boiler pressures —
 ELIMIN-OX can be used for any boiler operating pressure. The decomposition products of ELIMIN-OX are completely volatile and have been proven not to adversely affect steam operated equipment.

# How are NALCO 1700, NALCO 1721 and ELIMIN-OX programs monitored?

Testing procedures have been developed to monitor residual NALCO 1700, NALCO 1721 and ELIMIN-OX products present in the system.

Additional iron, copper, and oxygen testing are recommended to monitor the passivation properties and oxygen consumption of the products. Oxygen residual testing provides an extra measure of insurance, especially during upsets. Your Nalco representative can provide the necessary product monitoring guidelines.

NALCO 1710  NALCO 1721  Hydrazine  NALCO 1700  ELIMIN-OX	Poor	or God	od	Excelle	nt
NALCO 1721 Hydrazine	ELIMIN	IMIN-OX	-		
NALCO 1721	NALCO				
	Hydraz	drazine			
NALCO 1710	NALCO	LCO 1721			
	NALCO	LCO 1710			
Sulfite	Sulfite	fite			

**Figure 6** — Metal passivation performance (>300°F)

#### How does the performance of Nalco's metal passivators compare?

Temperature has an effect on the performance of certain metal passivators. (See Figures 5 and 6.) At typical feedwater temperatures (>210°F), hydrazine has only moderate passivation properties, whereas, NALCO 1700, NALCO 1721 and ELIMIN-OX provide excellent metal passivation. At boiler operating conditions (>360°F), all products provide full metal passivation protection. ELIMIN-OX has also been shown to be significantly more effective than DEHA and MEKO as a volatile oxygen scavenger in both lab and field studies.

# How will I know which product is best for my plant?

Nalco can provide technical service, consulting and chemicals for total boiler control of your plant. Productivity improvement through decreased energy losses, reduced downtime, and superior corrosion protection are goals that Nalco shares with your plant. Your local Nalco representative will be happy to conduct a survey of your particular application and recommend a cost-effective program for your use.

NALCO CHEMICAL COMPANY ONE NALCO CENTER - NAPERVILLE, ILLINOIS 60563-1198

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