

DIETHYL HYDROXYLAMINE AS OXYGEN SCAVANGER FOR BOILER WATER TREATMENT

ANIL KHERA, N. ANBANANTHAN

Ion Exchange India Ltd

19/A, Phase II, Industrial Development Area,
Patancheru 502 319, Medak Dist, AP, India.

Waterside corrosion is a major problem in steam generation systems causing damage, inconvenience, down time, replacements and consequent financial losses every year. The corrosion can take place in pre-boiler, feed water systems, boiler drums & tubes and post boiler system comprising of steam and condensate equipments piping. The cause for corrosion is primarily due to the presence of dissolved oxygen and carbondioxide. The presence of dissolved oxygen is found as key cause of feed water, boiler water and even condensate corrosion in boiler system whereas carbon dioxide is known to cause corrosion in return line condensate system.

Oxygen corrosion occurs through an electrolytic process using the boiler system metal as current path and boiler water as an electrolyte. To control the corrosion due to oxygen, the feed water should be free of oxygen. Various methodologies were adopted to remove the dissolved oxygen. The dissolved oxygen in the feed water is partially removed by thermal deaeration. The removal of dissolved oxygen is not complete in this process and the residual dissolved oxygen is normally about 0.007 ppm. This low concentration can influence the corrosion. The residual dissolved in water oxygen can be removed by using 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. One of the oldest oxygen scavenger is sodium sulphite. In 1920, sodium sulphite

was first used as an oxygen scavenger. Later, hydrazine was first introduced in Germany in early forties. Due to the introduction of high pressure boilers, the demand for the use of hydrazine increased compared to sodium sulphite. Hydrazine is technically superior when compared to sodium sulphite especially in high pressure boilers. In addition to its oxygen scavenging capabilities, hydrazine could able to passivate ferrous metallurgy present in the boiler.

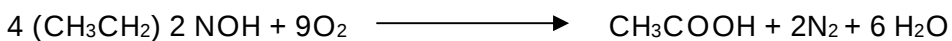
In early seventies, hydrazine was identified as a toxic substance and suspected carcinogen. With heightened sensitivity toward employee's health and safety, the water treatment industry directed their efforts towards the development of alternative oxygen scavenger. Many alternative oxygen scavengers were developed. These include catalysed diethylhydroxylamine (DEHA), carbohydrazide, methyl ethyl ketoxime (MEKO), hydroquinone, erythorbic acid etc. The catalysed oxygen scavenger – DIETHYLHYDROXYLAMINE (DEHA) was first introduced in India by Ion Exchange India.

Properties of DEHA

DEHA is a colourless to pale yellow transparent liquid. It is the derivative of hydroxyl amine. It is freely soluble in water. Chemically it is a reducing agent and hence it oxidizes. It reduces ferric ion and converts into ferrous ion. Thermally in presence of water, it decomposes. The details of the above chemical properties with reference to high temperature systems are discussed here.

Oxidation of DEHA

DEHA reacts with dissolved oxygen leaving to harmless byproducts. The overall reaction of DEHA with dissolved oxygen can be summarized as here below:



According to above equation 1.24 g of DEHA is required to remove 1 g of dissolved oxygen. However, in practice, it has been observed that about 4-ppm

of DEHA is required. It is, therefore, probable that the reaction does not follow the above direct path but involves various intermediate steps. Various mechanisms are available for such high consumption of DEHA in the literature.

Acetic acid is one of the major decomposition of DEHA. The acetic acid formed due to the decomposition of DEHA is retained by hydroxide alkalinity in boiler and is not found in steam. It gets converted into acetate salt and under most boiler conditions presence of it does not create any problems. However, in systems operated without hydroxide alkalinity, small portions of acetic acid at ppb level were observed. Such situations apply to high-pressure boilers where all volatile treatments are used. As the level of dissolved oxygen after deaerator is so small, the acetic acid level will also be correspondingly very low indeed. However, the presence of acetic acid does not mean that it is only originated from DEHA. Instances were reported especially in nuclear power plants that the acetic acid could also be formed due to the presence of organics in the feed water.

Apart from acetic acid nitrites, nitrates and acetaldehyde are also reported to be formed due to DEHA oxidation. Table 1 summarizes the various byproducts formed due to DEHA oxidation and their implications. Table 1 depicts the details of nitrites, nitrates and acetaldehyde.

OXIDATION PRODUCTS	Details
Nitrites and nitrates	Found only in boiler. Nitrite is found below 1000 psig and concentration of nitrite found is very low. Levels are insignificant for boiler operation.
Acetaldehyde	Is found almost entirely in steam due to low boiling point (21 deg c at atmospheric pressure). Its toxicity is low and does not pose any major problem in boiler operation.

Reduction of ferric ion

As iron is exposed to an aqueous environment, it begins to corrode leading to formation of rust Fe_2O_3 (Hematite). The iron in haematite is found in Fe^{3+} form. DEHA reduces Fe^{3+} to Fe^{2+} . The partial reduction of Fe^{3+} to Fe^{2+} leads to the formation of magnetite, Fe_3O_4 . The magnetite layer act as a passive layer and thus provides a protective barrier against the corrosive attack.

Thermal decomposition of DEHA

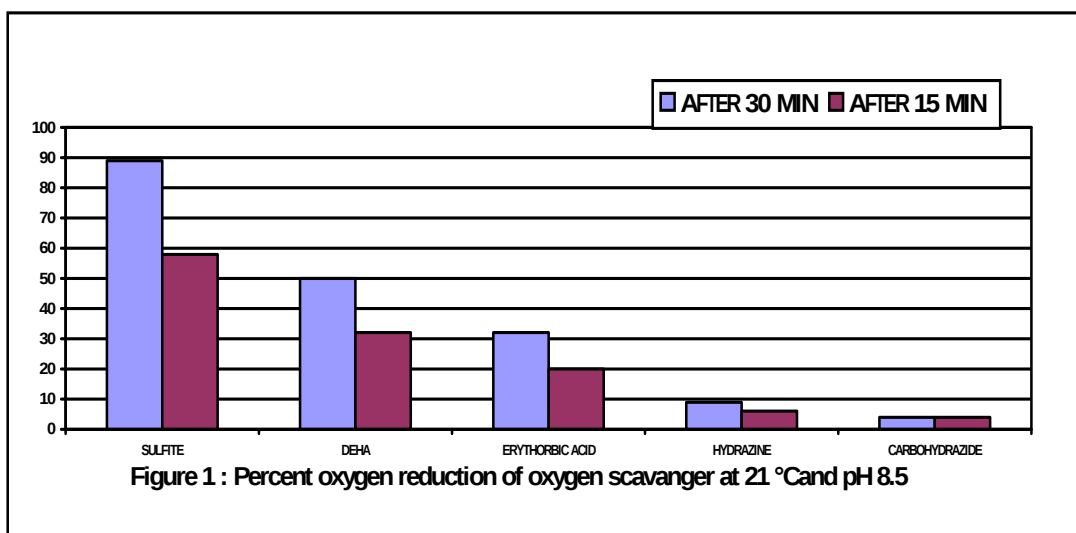
DEHA is thermally stable up 300 psig and some breakdown occurs at 1000 psig. The major thermal decomposition products appear to be diethylamine or ethylmethylaniline. It further decomposes to ammonia. But the quantities of ammonia formation are insignificant under most operating conditions. It is to be noted that the decomposition of DEHA initiates from 540 F only.

The byproducts of DEHA, amines are helpful in raising pH of condensates. This reduces the consumption of neutralizing amines. The formation of ammonia is very low and hence threat to yellow metallurgy in the system is very minimum when compared to hydrazine based treatment.

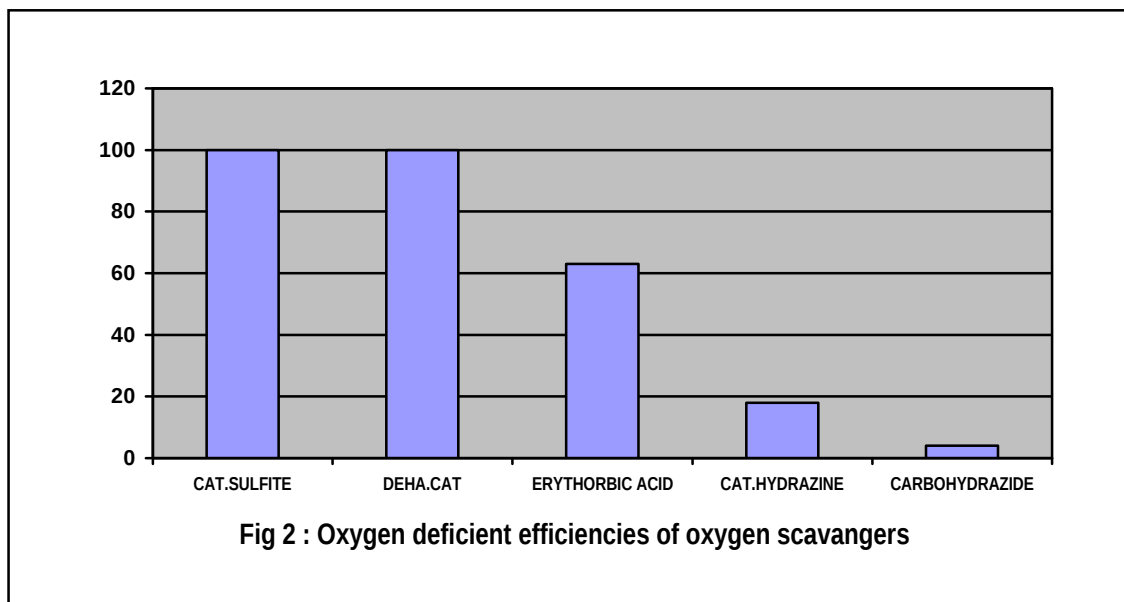
Advantages of DEHA over sulfite and hydrazine

Reaction kinetics

The reaction rate of reaction with dissolved oxygen depends upon pH, temperature and concentration of both DEHA and dissolved oxygen itself. Figure 1 depicts the sulfite reacts faster than hydrazine and DEHA at 21°C and pH 8.5 whereas DEHA reacts faster than Hydrazine. DEHA takes the second position in the spectrum. However, considering the high pressure operation, DEHA takes the first position. Moreover, when DEHA is catalyzed, the activity could be enhanced.



The catalyzed DEHA is nearly as fast as catalysed sulfite and much better than catalysed Hydrazine when tested at 21°C. Fig II shows the efficiencies of common oxygen scavengers at 21°C. The catalyzed DEHA performs equal to catalyzed sulphite. This shows that the DEHA based formulation performance exceeds all other common oxygen scavengers used in boiler water treatment.



Metal passivation

Sodium sulfite hardly has ability to reduce ferric ion to ferrous ion at low concentrations. The studies indicate that even hydroquinone and carbydhydrzide do not enhance pasivation. The role of DEHA as a reducing agent was discussed in earlier proves its efficiency. Hydrazine also behaves like DEHA on iron reduction. As hydrazine residuals are not present in condensate, the protection of iron metallurgy in the condensate area is seldom possible. In such instances, DEHA scores additional benefits over hydrazine.

Total dissolved solids

The total dissolved solids build up in the boiler water one of the primary disadvantages exists for sodium sulfite based treatment. Hydrazine and DEHA do not impart any dissolve solids build up in the boiler water.

Thermal decomposition byproducts

The oxidation product of sulfite and TDS in boiler water. The decomposition of sulfite has been observed at higher temperatures above 540 Deg F (950 psig). The decomposition products are usually sulphur dioxide and sodium sulphate which may lead to corrosive attack. The hydrazine decomposes to ammonia at 350F. This is corrosive to copper and its alloys. However, the corrosion is proportional to the ammonia concentration. Fig.3., compares the generation of ammonia in hydrazine and DEHA based steam generation system. The thermal degradation products of DEHA were discussed earlier and they do not have any significant impact on the corrosion of boiler metallurgy. Therefore, the use of DEHA provides additional benefit over sulfite and hydrazine.

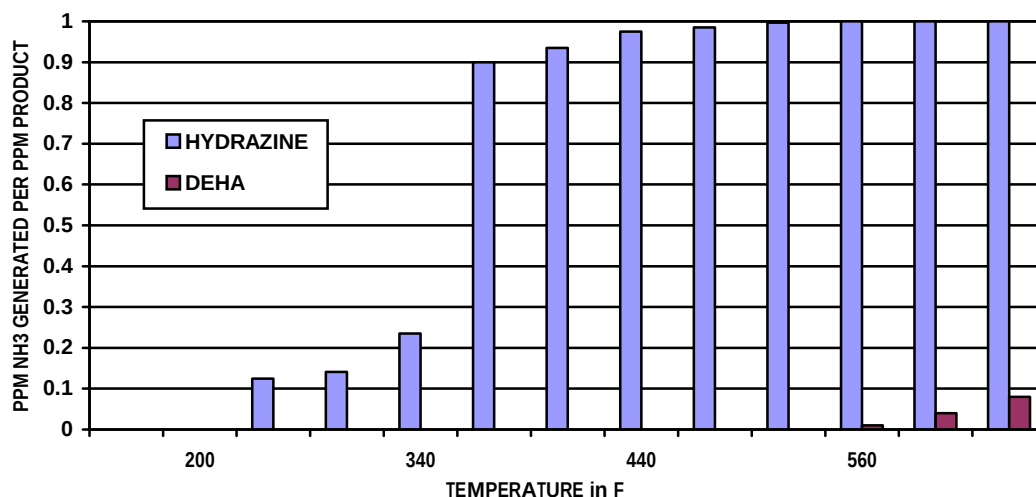


Figure :3 : Ammonia formation due to hydrazine and DEHA decompositon

Volatility

DEHA is highly volatile. This property provides additional advantage over sulfite and hydrazine. It travels with steam and reacts with dissolved oxygen, which often gets reingressed in steam and condensate system. DEHA residuals in steam passivate condensate lines whereas Hydrazine does not volatilise and reach such systems. The volatility of DEHA increases from 100 psig to 300 psig and then falls gradually at increasing pressures. DEHA, therefore, behaves in a similar manner as neutralizing amines. It would, therefore, be expected that volatility at high pressure will still be for giving residuals in steam.

Toxicity

The LD 50 value (rats, oral) of DEHA is >2000 mg/kg as against 50 mg/kg of hydrazine. This shows that the toxicity of DEHA is very low when compared to hydrazine.

The above comparisons confidently vouch for the superior performance of DEHA over hydrazine and sulphite which are well proven oxygen scavengers in steam generation systems. In addition to the above data, a few the case studies are summarized here below to reiterate the importance of DEHA.

Case history 1

A large paper mill operated with the following conditions. The co-ordinated phosphate with a reserve of 10-15 ppm in boiler water. Hydrazine was used as oxygen scavenger. Blend of neutralizing amines were used to prevent for condensate corrosion was being practiced. They wanted to replace hydrazine in view of its health hazards. The suggestion to use catalyzed DEHA was accepted.

Steam Generation	3,50,000 lbs/Hr
Operating Pressure	900 psig
Superheated steam temp. after attemperation	460 Deg C
Make up Water	DM
Feed Water	Deaerated
Condensate Recovery	50% (Not polished)
Cycles of Concentration	70

Initially 300 ppb of catalysed DEHA was used. Upon the use of DEHA the demand for neutralizing amines was reduced from 3 ppm to 2 ppm. They also monitor the levels of copper and iron. Results are reported in the following table. The Cu and Fe levels reduced by a factor of 10 over one year.

A new economizer was installed but was kept in moist condition before use. Therefore, it got corroded and the corrosion could be seen visually. The cleaning was not possible and hence they stated using catalysed DEHA with out cleaning. After a few months of use the economizer was found to be very clean.

This indicates the reduction capability of DEHA to convert ferric to ferrous ions. Thus it passivates the system and control further corrosion.

Case history 2

An utility plant operated at following conditions used DEHA instead of hydrazine. The steam generation was 8,50,000 lbs for average of 10hrs per day. It was operated at 850 psig. Regular monitoring systems were installed by the customer. Initially, the dissolved oxygen concentrations were measured and compared with their old data on hydrazine. The following table compares the measured dissolved oxygen values for hydrazine and catalyzed DEHA usage.

	After Deaerator	Feed Water	Condensate
With Hydrazine	7 ppb	5 ppb	10 ppb
With Catalysed	6 ppb	5 ppb	4 ppb

The above table enunciates that dissolved oxygen level dropped down in condensate when compared to hydrazine system. This indicates that DEHA should present in the condensate line to reduce the oxygen concentration. Therefore, the condensate was taken and analyzed for DEHA. The DEHA at such low concentrations is difficult to analyze by normal methods. Therefore, it is analyzed by indirect method. The method adopted was the reduction of Fe^{3+} ion to Fe^{2+} and complex it with a complexing agent. The complexing agent is 3-[2-Pyridyl]-5,6-diphenyl-1,2,4-triazine-4,4'-disulfonic acid-Na-salt). It forms a purple colour complex with iron at very low concentration. The analysis of DEHA in the condensate was proved its presence and the performance it imparts on corrosion control till the condensate line is established.

We addressed the properties of catalysed DEHA over other oxygen scavengers normally used in industrial boilers. Many field trials support the performance of DEHA in reduction of oxygen, reduced corrosion rate. Although, the DEHA possesses many advantages, one of the main disadvantage is its cost. In addition to the

cost of DEHA, the analysis of low concentration of DEHA is also cost prohibitive. Presently, the availability of indigenous DEHA test kit reduces the DEHA analysis cost significantly without affecting its analytical quality. Presently, many Indian industries hydrazine is still popularly being used in medium and high-pressure boilers. Therefore, the scope of the article is to create an awareness about the use of DEHA in place of hydrazine.

About the authors...

Mr. Anil Khera is presently the head of specialty chemicals operation of Ion Exchange India Ltd. He has got over 20 years of experience in the field of cooling and boiler water treatment. anil.khera@ionexchange.co.in

Dr. N. Anbananthan is presently the head of R&D team of Ion Exchange India Ltd. n.anbananthan@ionexchange.co.in
