The High Performance of Diethylhydroxylamine in Comparison with Hydrazine for the Removal of Dissolved Oxygen from Boilers of Power Plant

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ABSTRACT: *In boilers and hot water heating systems, hydrazine is used as one of the powerful reducing agents for eliminating oxygen. Due to the toxicity and carcinogenicity of this material, a suitable replacement named diethylhydroxylamine (DEHA) can be used. DEHA has low acute toxicity and animal tests do not show mutagenic activity. In this study, hydrazine, and DEHA as deoxygenation materials were used in boilers of Tarasht power plant in Iran (Tehran). In different months (May to November), deoxygenation was examined by these two substances. The oxygen removal value of DEHA was equal to hydrazine and sometimes far better than it. The rate of deoxygenation reaction of DEHA was 40 ppb in most months of the year, but the number of peaks in hydrazine was greater (2 peaks with 50 ppb and 1 peak with 60 ppb). Hydrazine analysis is time-consuming, as well as pollutes the environment. On the other hand, DEHA of tests was completed sooner. Also, DEHA as an economical material with low toxicity can be a good alternative to hydrazine in boilers. This material can prevent boiler corrosion by oxygen removal.*

KEYWORDS: *Hydrazine; Diethylhydroxylamine; Oxygen removal; Boiler.*

INTRODUCTION

Boilers are instruments containing shell and tube heat exchangers. Water boils and evaporates in these boilers, then converts to hot water with high pressure. Fossil fuel is used to generate heat, and the combustion gas can transfer through tubes of water. Also, passing the hot gas *via* the tubes containing water is possible [1]. The corrosion of the boiler is a great problem. There are two boiler corrosions; 1) internal corrosion (water side) and 2) external corrosion (fireside). Financial losses, increased time of relevant processes, and damage to the boiler are the consequences of waterside corrosion. The main cause of this corrosion is the presence of Dissolved Oxygen (DO) and carbon dioxide (CO_2) [2]. Hence, the removal of DO is essential for avoiding corrosion, negligible heat transfer, and a decrease in efficiency [3]. In the preparation of boiler feed water for electricity generation, semiconductor production, and making ultrapure water (UPW), DO removal is of considerable importance [4]. The standard DO concentration level should be kept constant (<10 ppb) in the boiler water of power plants [5].

Physical and chemical techniques have been reported for removing DO. Vacuum degassing, thermal degassing,

and use of membrane modules is the physical procedure. High cost and inflexibility are the drawbacks of this method. On the other hand, the addition of reducing agents is the chemical method [6,7].

Hydrazine is known as one of the powerful reducing agents, used to eliminate oxygen for preventing corrosion in boilers and hot water heating systems. The other applications of this compound are in the polymer, pharmaceutical, and dye industries. In addition, hydrazine and its derivatives are extensively utilized as explosives, gas generators, and high-energy rocket propellants due to its flammable property [8,9]. However, owing to the toxicity and carcinogenicity of this substance, it makes various difficulties related to human health. These problems include harm to the brain, DNA, liver, kidney, nervous system, and blood disorders. Mutation, nausea, dizziness, temporary blindness, and coma are the other side effect of this compound. Therefore, the permissible limit for its entry into the environment has been determined 1.0 ppm by the Environmental Protection Agency (EPA) [10-12]. The high solubility of hydrazine in water leads to its entry into subterranean water and soil, and penetrate the cycle of food [13].

A suitable replacement instead of hydrazine is diethylhydroxylamine (DEHA) because it possesses low acute toxicity (LD_{50}= 2190 mg/kg), and animal tests do not represent mutagenic activity [14]. The LD_{50} of hydrazine is 82 and 91 mg/kg in rats and rabbits, respectively. This is the dosage of hydrazine essential to kill 50% of a laboratory population of these species under test conditions. The same LD_{50} numbers for DEHA are 2190 and 1300 mg/kg in rats and rabbits, respectively. In terms of safety and handling standpoint, DEHA represents less than 10% of hydrazine toxicity. Hydrazine has also been identified as a suspected animal carcinogen by the U.S. government. DEHA can improve equipment reliability and efficiency, as well as it can minimize overall condensate system corrosion decreasing the related maintenance costs [15]. According to the industrial condition today, the use of DEHA as a corrosion inhibitor is probably increasing. Furthermore, due to the complex compatibility related to hydrazine usage, DEHA has been applied in sugar, paper, and pulp industries instead of hydrazine [16].

In this study, dissolved oxygen removal related to the boilers of the Tarasht power plant was investigated using hydrazine and DEHA. The effect of these materials in deoxygenation process was evaluated in different periods times.

EXPERIMENTAL SECTION
Chemicals
Hydrazine hydrate 55%, N,N-diethylhydroxylamine, sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), methylene blue (MB), sodium thiosulfate ($Na_2S_2O_3$), glycerol, potassium hydroxide (KOH), and 4-(Dimethylamino) benzaldehyde were purchased from Merck.

Apparatus
Dissolved oxygen (DO) meter (Model Hana) was used to measure dissolved oxygen before the injection of hydrazine and DEHA and also during the deoxygenation process. Thermo scientific spectrophotometer and DR 5000™ UV-Vis spectrophotometer were used to record the absorption spectra. A Mettler digital scale with a precision of 0.01 g (Jadever) was utilized to measure chemicals.
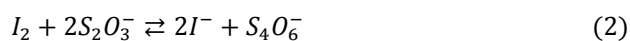
Determination of hydrazine
One method of measuring hydrazine is iodometry. 5 mL of the diluted sample was transferred to the Erlenmeyer flask and 0.5 mL H_2SO_4 (2 Eq/L) was added. Then, 2 mL of NaOH (2 Eq/L) was added to the solution. 10 mL of 0.1 Eq/L iodine solution was added to it. The resulting solution was collected in a 250 mL Erlenmeyer flask and stored in a dark place for 3 h. After this time, 2.5 mL of H_2SO_4 (2 Eq/L) was added to the solution. Then, titration with $Na_2S_2O_3$ with a concentration of 0.1 Eq/L was performed to obtain a yellow color. Finally, a small amount of starch was added and the titration was continued until the dark blue color of the solution became colorless.

Iodine reacts with hydrazine in alkaline and neutral environments according to the following formula.

$$2I_2 + N_2H_4 \rightleftarrows 4HI + N_2 \tag{1}$$

According to this formula, an extra amount of I_2 enters the environment, and a portion of it is converted to iodide ions. Then, the extra iodine is titrated with $Na_2S_2O_3$.

$$I_2 + 2S_2O_3^- \rightleftarrows 2I^- + S_4O_6^- \tag{2}$$

In an acidic pH, hydrazine also reacts with iodine, but the interactions are much slower [17].

Determination of water-soluble oxygen concentration
Colorimetry is one of the most common methods for measuring the compounds in the solution. The pH, the amount of dissolved oxygen and the amount of free chlorine can be measured by this method. MB is used

Fig. 1: Color change of solution in oxygen measurement using the colorimetric method

to measure water-soluble oxygen. MB was reduced with a reducing agent such as glucose in an alkaline environment. The sampling hose was placed inside the cylinder. After 10 min overflow of the sample, the hose was gently pulled out so that no bubbles formed in the container. About 2 mL of the reduced MB solution was slowly poured into the container from inside the burette. The container in the water was closed with a rubber cover. Then, the container was taken out from the water and shaken vigorously [18]. Finally, the color of the sample was compared with the standards and the oxygen concentration was reported (Fig. 1).

MB solution

125 mg of MB and 1.2 g of glucose were dissolved in 50 mL of distilled water. Then, this solution was poured into the 500 mL volumetric flask and diluted up to the mark with glycerol.

Potash solution

30 g of KOH was dissolved in distilled water and diluted up to the mark in a 100 mL volumetric flask.

Reduced MB solution

50 mL of MB solution (250 mg/L) was mixed with 1 mL KOH (30%). The solution was kept somewhere until it becomes colorless. Then, it was poured into the burette and covered with one layer of vaseline.

Preparation of initial standard solution of MB

4.7 mL of MB solution (250 mg/L) was poured into the 500 mL volumetric flask and diluted to the mark with distilled water. Herein, MB (2 mol) was combined with 1 mol oxygen.

Preparation of secondary standard solutions

The secondary standard solutions were prepared by diluting the initial standard solution. 10, 20, 30, 40, 50, and 100 mL of these solutions were poured into the cylinders and diluted to the mark with distilled water except in the last cylinder [18].
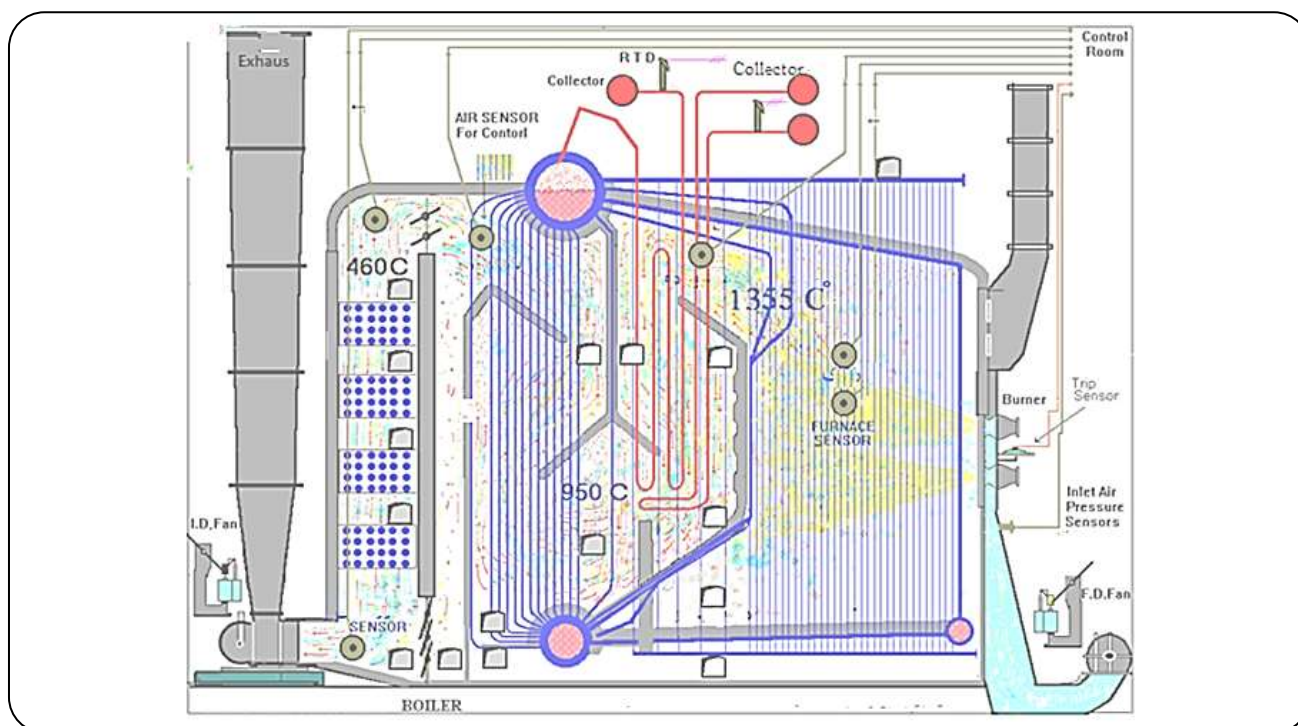
Boiler structure of Tarasht power plant

The boiler (Scheme 1) is the part where water is converted to steam with a temperature of 420 to 450 $^\circ$C with a pressure of 4000 kPa. The boiler has six burners in two rows of three, and the furnace air is under suction. First, water enters pipes called economizers. To provide the oxygen needed by the burners, a propeller called F.D.fan (Fig. 2a) is used, which is located next to the boiler. Air enters the furnace through this propeller and through pipes that go from the below ground to the boiler. The air oxygen is consumed by the flame, and the combustion gases are sucked via another propeller called the I.D. fan (Fig. 2b) and come out of the furnace. This propeller is located at the end of the boiler and moves the combustion gases to the end of the boiler. Before these gases leave the boiler, the gases pass through the economizer pipes and heat the water inside them, then pass through the suction propeller and go to the chimney. Each boiler has a chimney with a height of 24 m.

RESULTS AND DISCUSSION
Hydrazine and DEHA results

Deoxygenation was assessed by hydrazine and DEHA at different periods (May to November). As can be seen in Fig. 3 (a) and (b), deoxygenation of hydrazine and DEHA were equal, and in some cases, the DEHA had better

Scheme 1. The schematic of boiler structure of Tarasht power plant.

(a)   (b)

Fig. 2: (a) F.D.fan plus chimney and (b) I.D.fan in Tarasht power plant.

performance. Therefore, it can be a good alternative to hydrazine. As shown in Fig. 3 (a), the rate of deoxygenation reaction related to the hydrazine was low in May (40 ppb) but in June the amount of oxygen increased and this indicates that the deoxygenation was not done well. These studies continued until November, which showed fluctuations. On the other hand, the diagram of oxygen changes at the time of injection of the DEHA has shown that the fluctuations existed only from June to July (Fig. 3b). These results indicate better performance of DEHA than hydrazine. Due to the low

toxicity and low cost of DEHA, as well as its better efficiency than hydrazine, its use is recommended.

Comparison with other oxygen scavengers

Some scavengers for diminishing the dissolved oxygen are given in Table 1. The most common chemical oxygen scavenger is sodium sulfite used in boiler systems with low pressure. In addition, the catalyzed form of this material is available, which leads to an increase in the rate of the reaction with the dissolved oxygen. Hydrazine like the other oxygen

Table 1: Oxygen scavengers used in steam generating systems.

| No.	Scavenger	Primary reaction
1	Hydrazine	$N_2H_4+O_2 \rightarrow 2N_2+2H_2O$
2	Sodium sulfite	$2Na_2SO_3+O_2 \rightarrow 2Na_2SO_4$
3	Carbohydrazide	$(H_2N^-NH)_2CO+2O_2 \rightarrow 2N_2+3H_2O+CO_2$
4	N,N-Diethylhydroxylamine	$4(CH_3CH_2)_2NOH+9O_2 \rightarrow 8CH_3COO^-+9H^++2N_2+6H_2O$
5	Hydroquinone	$C_6H_4(OH)_2+1/2O_2 \rightarrow C_6H_4O_2+H_2O$
6	Erythorbate	$C_6H_4O_6+1/2O_2 \rightarrow C_6H_5O_8+H_2O$
7	Methyl ethyl ketoxime	$2CH_3(C_2H_5)CNOH+O_2 \rightarrow N_2O+2CH_3(C_2H_5)CO+H_2O$
8	DEHA	$4(C_2H_5)_2NOH + 9O_2 \rightarrow 8CH_3COOH + 2N_2 + 6H_2O$

(a)   (b)
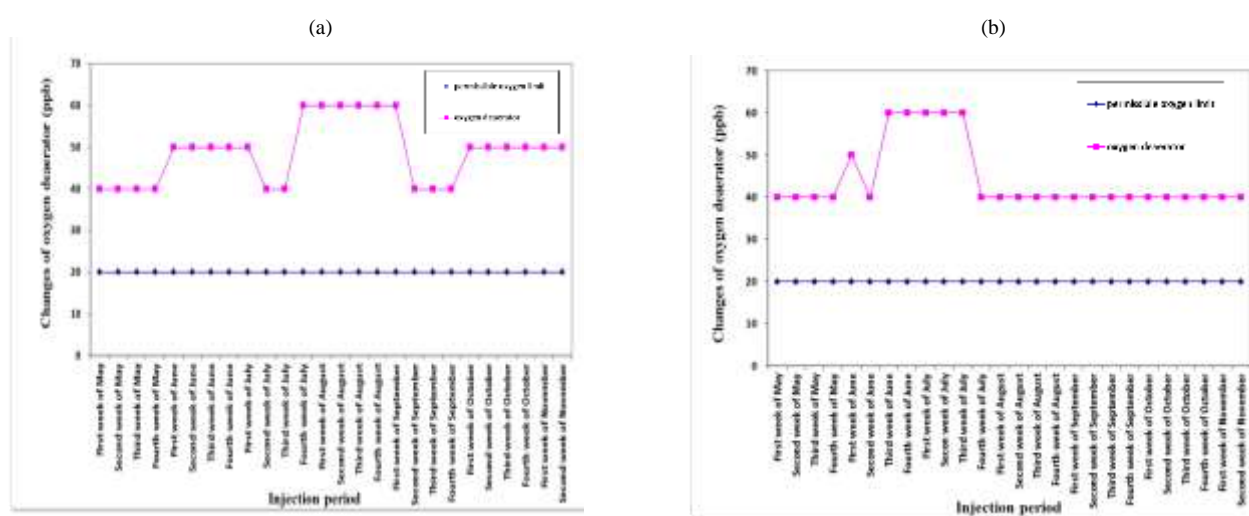
Fig. 3: Changes of oxygen deaerator at the time of (a) hydrazine injection (May 2019 to November 2019) and (b) DEHA injection (May 2020 to November 2020).

scavenger has been used in boilers with higher pressure. However, owing to its status as a suspect carcinogen, its usage has decreased in the industry. Hence, alternatives to hydrazine have been proposed. Carbohydrazide, erythorbate, diethylhydroxylamine, hydroquinone, and methylethyl ketoxime are the most common materials. Fast complete oxygen elimination under normal boiler feedwater temperature and pH conditions is one of the advantages of DEHA. Also, its low toxicity, makes it safe and simple to use in typical boiler application systems [19].

CONCLUSIONS

In this study, the results related to the functional properties of DEHA showed that its application is more useful than hydrazine. Therefore, it can be selected as a suitable alternative to hydrazine. This alternative can help the environment. DEHA has been effective for boilers with medium pressure. DEHA consumption is twice as much as hydrazine, but economically its cost is less. It also possesses better performance from an environmental point of view.

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