

## Reducing of Corrosion Rate in Boiler Tubes by Using Oxygen Scavengers

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### Abstract

The corrosion behavior of carbon steel at different temperatures 100,120,140 and 160 °C under different pressures 7,10 and 13 bar in pure distilled water and after adding three types of oxygen scavengers Hydroquinone, Ascorbic acid and Monoethanolamine in different concentrations 40,60 and 80 ppm has been investigated using weight loss method. The carbon steel specimens were immersed in water containing 8.2 ppm dissolved oxygen (DO) by using autoclave. It was found that corrosion behavior of carbon steel was greatly influenced by temperature with high pressure. The corrosion rate decreases, when adding any one of oxygen scavengers. The best results were obtained at a concentration of 80 ppm of each scavenger. It was observed that hydroquinone is the best among the other scavengers in reducing the corrosion rate at the temperatures and pressures of this investigation and most efficient in the consumption of oxygen especially 80 ppm, it reduces the concentration of oxygen in water from 8.2 to 0.8 ppm, while the ascorbic acid reduces the oxygen concentration to 1.4 and monoethanolamine reduces the concentration of oxygen to 1.9 . It has been observed that hydroquinone reacts with oxygen quickly and at low temperatures while the other scavengers react slowly with oxygen.

**Key Words:** Boiler feed water (BFW), boiler tubes, dissolved Oxygen (DO), oxygen corrosion, oxygen scavengers.

### Introduction

Boiler tubes are constructed primarily of carbon steel to improve its mechanical properties in order to withstand extreme operating pressure and temperature and the medium for heat transfer is water, the potential for corrosion is high. The corrosion of boiler is divided into internal corrosion (water side) and external corrosion (Fire side). There are also a number of locations in a boiler system where various types and amounts of corrosion occur. [1] 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 equipment piping. The cause of water side corrosion is primarily due to the presence of dissolved oxygen and carbon dioxide.

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. [2]

The most harmful of the dissolved gases in water is oxygen. It is present in all water supplies, though at widely varying concentrations. Oxygen is highly corrosive when present in hot water. Even small concentrations can cause serious problems. Because pits (small but deep pinpoint holes) which is the most common type of corrosion in boilers can penetrate deep into the metal. Additionally, iron oxide generated by the corrosion can produce iron deposits in the boiler. For that matter any system that is exposed to dissolved oxygen is under threat.

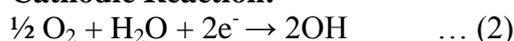
Hence it is essential to know this threat well in advance and accordingly try to minimize. Water can contain up to (9) ppm dissolved oxygen (DO) at room temperature and atmospheric pressure. As the temperature increases, the solubility of oxygen decreases, but water under pressure can hold higher amounts of dissolved oxygen. [3]

Oxygen corrosion occurs through an electrolytic process (electrochemical reaction) using the boiler system metal (usually iron) as current path and boiler water as an electrolyte. In this reaction the iron is oxidized (anodic reaction) and released into the water. The electrons from oxidation released and absorbed by dissolved oxygen (cathodic reaction). The reaction is: [4]

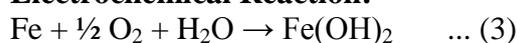
**Anodic Reaction:**



**Cathodic Reaction:**



**Electrochemical Reaction:**



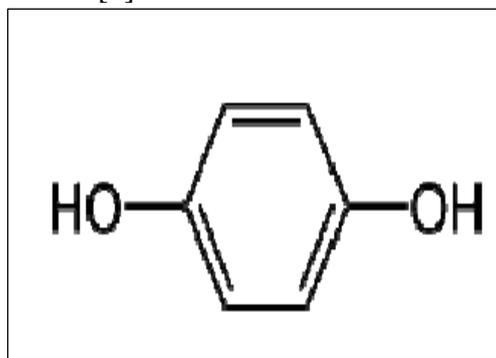
To control the corrosion due to oxygen, the feed water should be free from oxygen. Various methodologies

were adopted to remove the dissolved oxygen from boiler water and steam systems. To reduce corrosive dissolved gases from makeup water most plants use some variation of a deaerator. 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 oxygen in water can be removed by using chemical agents called oxygen scavengers, which are reducing agents such as sodium sulfite ( $\text{Na}_2\text{SO}_3$ ), hydrazine ( $\text{N}_2\text{H}_4$ ), hydroquinone (HQ) Diethylhydroxyl-amine (DEHA), ( $\text{C}_6\text{H}_4(\text{OH})_2$ ), methylethylketo-xime (MEKO) and other chemical compounds that can control (DO). It is of critical importance to select and properly use the best chemical oxygen scavenger for a given system. [5]

Three oxygen scavengers (Hydroquinone, Ascorbic acid and Mono- ethanolamine) were selected. These compounds tested for the first time in Iraq.

**Hydroquinone (HQ)**

Hydroquinone is an aromatic compound derived from phenol. It is a crystalline powder. It is well known for its antioxidant properties. Its chemical name is (Benzene-1,4-diol) and its molecular formula is ( $\text{C}_6\text{H}_6\text{O}_2$ ). The structure of hydro- quinone is shown below: [6]





The rectangular carbon steel alloy specimens of dimensions (3 x 1.5 x 0.2 cm) have been used. Before each experiment, one specimen was abraded in sequence under running tap water by using emery paper of grade number (80, 220, 400, 600, 1000) respectively, washed in distilled water, dried with clean tissue, immersed in acetone and dried with clean tissue, immersed in benzene and dried with clean tissue, and then dried with an air blower, then kept in desiccators over silica gel until use (ASTM G1, 2004).

Table 1, Composition of carbon steel

Element	%
Iron ( Fe)	99.437
Carbon (C)	0.156
Manganes (Mn)	0.29
Sulphur (S)	0.007
Silicon (Si)	0.1
Phosphorus (p)	0.01

After preparing the specimen and regulation of water pH, for each experiment the specimen weighted and recorded ( $w_1$ ) then hanged inside the autoclave by insulated wire to prevent any attachment with another metal in the autoclave which cause galvanic corrosion, then (250 ml) of pure water or a solution of water with known value of concentration ( 40, 60 or 80 ppm) put in the autoclave. The autoclave was closed tightly, and  $N_2$  gas was injected providing no leaking occur. After that the temperature regulator turned on and set it to the required temperature. Once the temperature reached to the required value,  $N_2$  gas injected to raise the pressure inside the autoclave to the required value. From that time, the test period started. The exposure time was (2) hours for each experiment. After (2) hours, the heating cut off, the specimen was removed and cleaned by

washing it with running tap water using a plastic brush, then the specimen was immersed in cleaning solution for (10) minutes with continuous stirring to remove the corrosion products then washed with tap water followed by deionized water and dried, after that the specimen was weighed and represented as ( $w_2$ ).

The surface area of the specimen is (10.8)  $cm^2$ .

The corrosion rate was estimated in MPY (Mils penetration per year) which is a unit of measurement equal to one thousandth of an inch.

$$Mils\ per\ year(mpy) = \frac{534\ W}{DAT}$$

Where:

mpy: mils per year.

W: weight loss in milligrams.

D: density in grams per cubic centimeter.

A: area in square inches.

T: time in hours.

## Result and Discussion

### 1- Temperature Effects

The effect of temperature in the range (100,120,140,160) indicates that higher temperature increases the electrochemical reaction and hence increase corrosion rate of carbon steel, figure (2), but when adding any one of the used oxygen scavengers to water at the same temperature leads to reduce the effect of temperature on corrosion rate. It is observed that (80) ppm of any scavenger give best results and it was found that hydroquinone is more stable and more effective than the other scavengers at different temperatures, figures (3,4 &5)

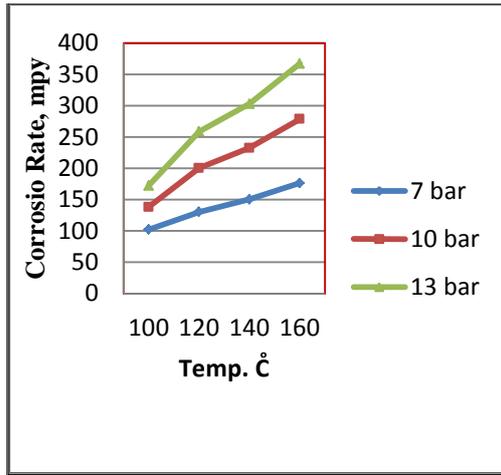


Fig. 2, Temperature and corrosion rate with pure water

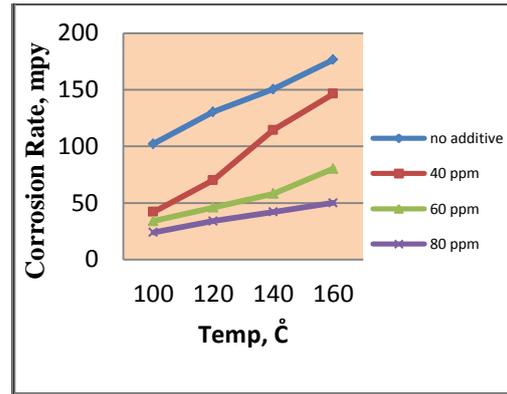


Fig. 5, Temperature and corrosion rate at (7) bar with different concentrations of Ethanolamine

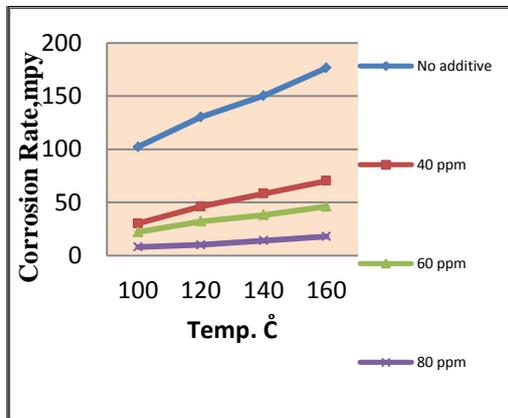


Fig. 3, Temperature and corrosion rate at (7) bar with different concentrations of Hydroquinone

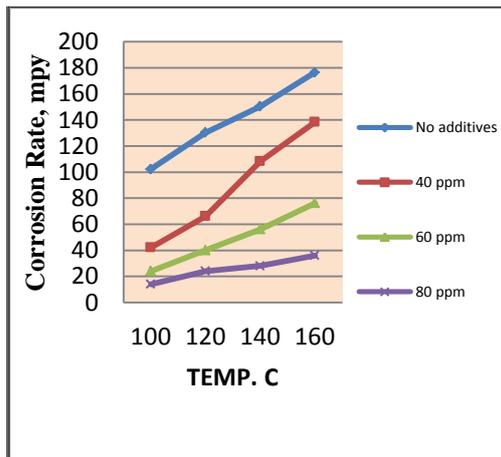


Fig. 4, Temperature and corrosion rate at (7) bar with different concentrations of Ascorbic acid

## 2- The Effect of Pressure

It was observed a positive relationship between the corrosion rate and pressure (rate of corrosion tends to increase with rising pressure). It is known; however that pressure alters the thermodynamics of corrosion and increases the solubility of oxygen and the rate of solution. The reason behind this varying effect of pressure probably depends on the alteration of other corrosion limiting factors, or on the modification of their synergistic actions. Figure (6) shows the effect of pressure on corrosion rate of carbon steel with distilled water with no addition and figures (7 to 9) show how the scavengers decrease the effect of pressure on corrosion rate at 100 C°.

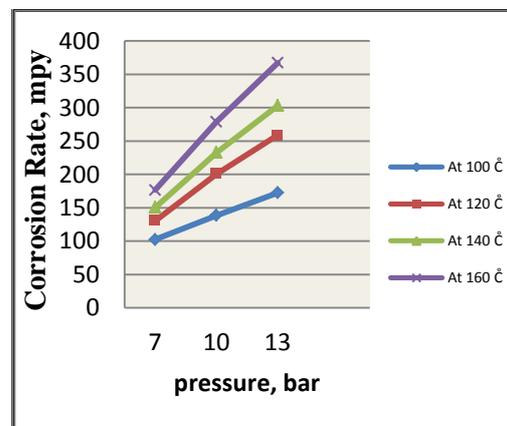


Fig. 6, the relation between pressure and corrosion rate with distilled water

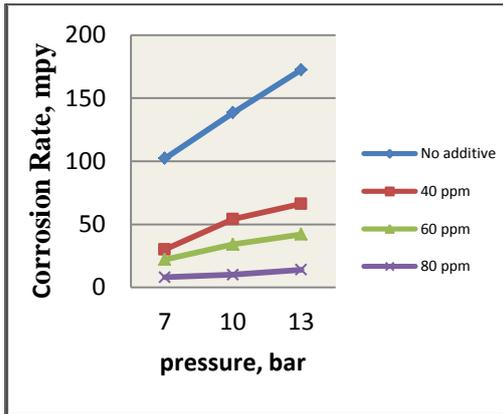


Fig. 7, the relation between pressure and corrosion rate with different concentrations of Hydroquinone solution at 100 °C

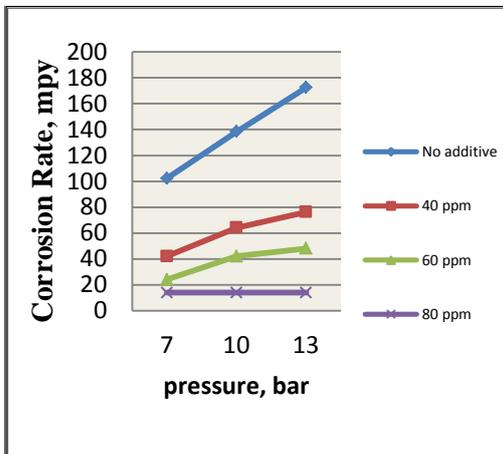


Fig. 8, the relation between pressure and corrosion rate with different concentrations of Ascorbic acid solution at 100 °C

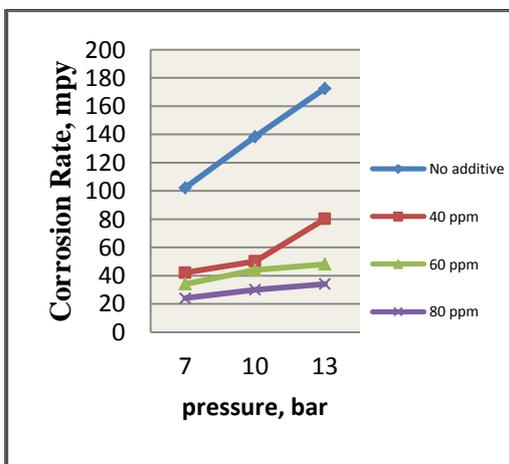


Fig. 9, the relation between pressure and corrosion rate with solution of different concentrations of Ethanolamine at 100 °C

### 3- The Effect of Scavenger Concentration

Oxygen scavengers were added to demineralized water in three concentrations (40, 60 and 80) ppm at different conditions of temperature and pressure. It can be observed an inverse relationship between the corrosion rate and the concentration of scavengers (rate of corrosion decreases with increasing the concentration of scavenger in solution at constant temperature and pressure).

The reason of this behavior, when increasing the concentration of reactants (scavenger) leads to the consumption of larger amount of dissolved oxygen leading to reduce the rate of corrosion. [13]

Figures from (10) to (18) show the relation between corrosion rate and the concentration of scavengers at constant pH (9) and different conditions of temperatures and pressures.

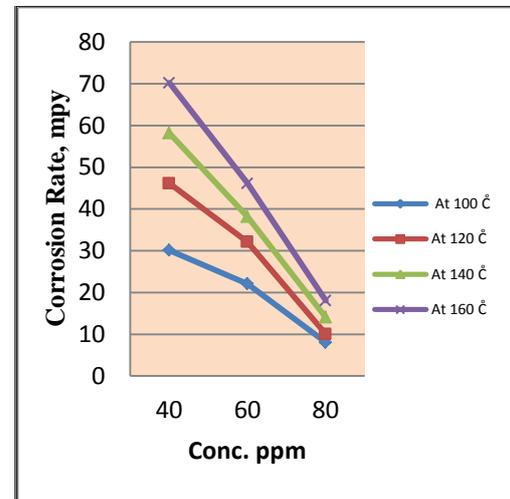


Fig. 10, the relation between concentration of Hydroquinone and corrosion rate at different temperatures and (7) bar

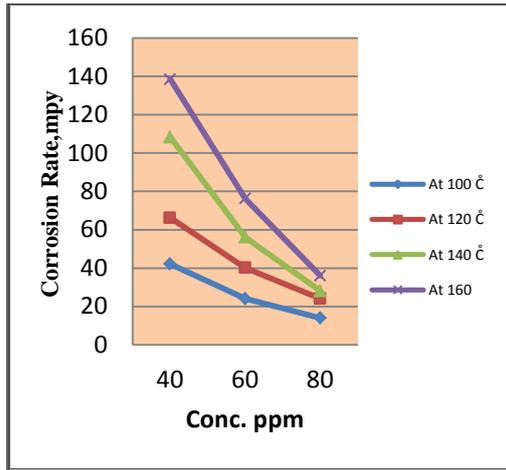


Fig. 11, the relation between concentration of Ascorbic acid and corrosion rate at different temperatures and (7) bar

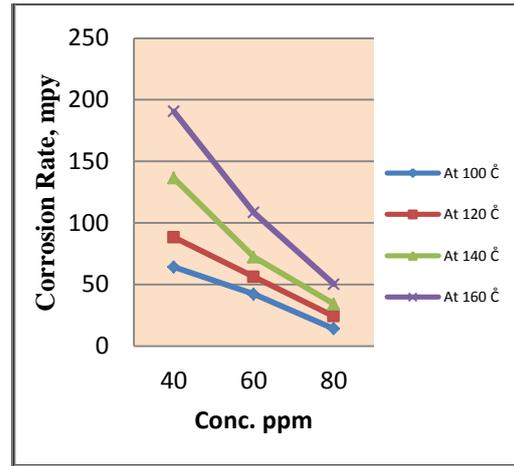


Fig. 14, Concentration of Ascorbic acid and corrosion rate at different temperatures and 10 bar

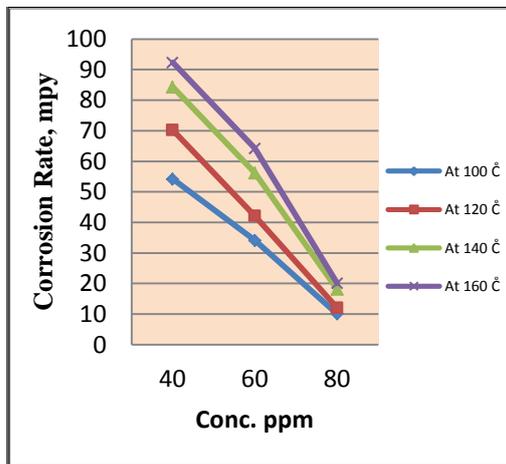


Fig. 12, concentration of Ethanolamine and corrosion rate at different temperatures and (7) bar

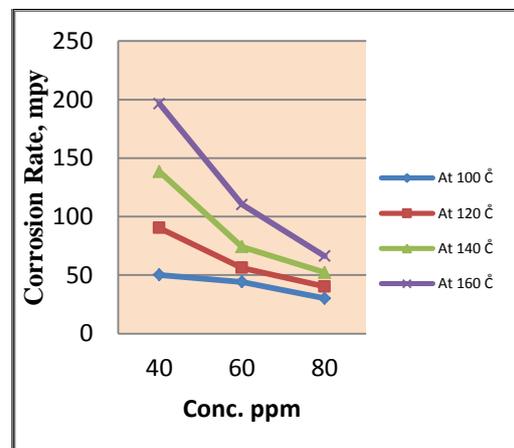


Fig. 15, Concentration of Ethanolamine and corrosion rate at different temperatures and 10 bar

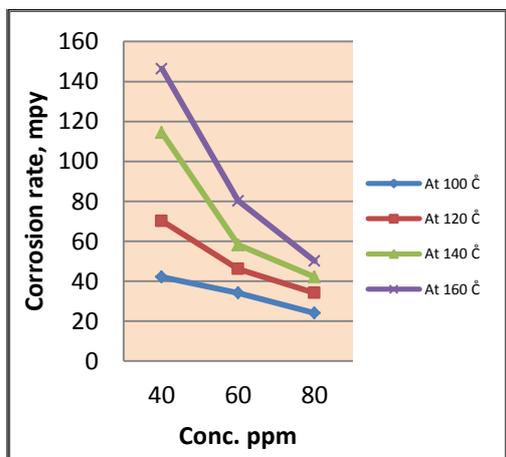


Fig. 13, Concentration of hydroquinone and corrosion rate at different temperatures and 10 bar

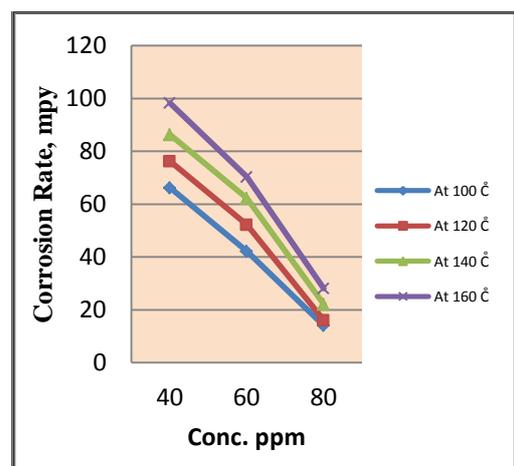


Fig. 16, concentration of Hydroquinone and corrosion rate at different temperatures and 13 bar

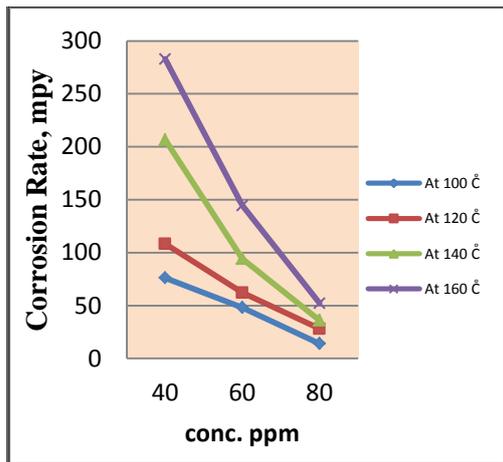


Fig. 17, Concentration of Ascorbic acid and corrosion rate at different temperatures and 13 bar

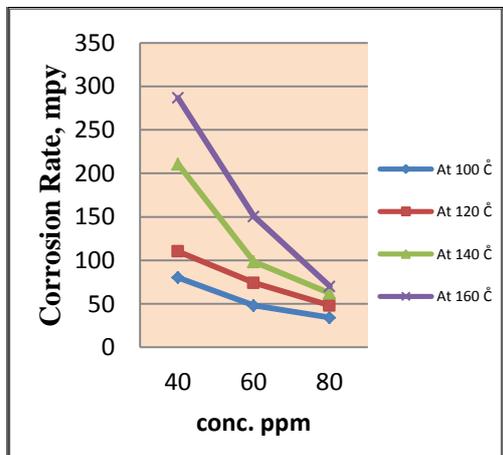


Fig. 18, Concentration of ethanolamine and corrosion rate at different temperatures and 13 bar

**Measurement of Dissolved Oxygen**

Winkler method and (DO) meter were used to find the concentration of dissolved oxygen. It was found that dissolved oxygen in pure water equal to (8.2) ppm at (25) °C. The same method was used in determining the concentration of dissolved oxygen after adding each scavenger. The concentration of dissolved oxygen was measured after (24) hours of preparation solutions of (40,60 and80) ppm of each scavenger to ensure completing the reaction between scavengers and oxygen, The (DO) values after adding each concentration of scavengers is shown in Table (2).

**Determining the Speed of Reaction between Dissolved Oxygen and Scavengers**

Winkler method and digital (DO) meter were used to find the concentration of dissolved oxygen in solution of water and (80) ppm of each scavenger every (5) minutes for half an hour after adding each scavenger at (25) °C. Figure (19) shows the rate of oxygen consumed by plotting the concentration of (DO) with time. It has been observed That Hydroquinone reacts rapidly with oxygen at (25) °C while the other scavengers (Ascorbic acid and Ethanolamine) react slowly with oxygen at the same temperature.

Table 2, the remained DO after adding different concentration of scavengers

Scavenger	Dissolved Oxygen, ppm			
	0 ppm	40 ppm	60 ppm	80 ppm
Hydroquinone	8.2	3.8	2.2	0.8
Ascorbic acid	8.2	4.7	2.6	1.4
Ethanolamine	8.2	5.3	3.7	1.9

This means that Hydroquinone reacts with oxygen quickly, even at low temperatures, while Ascorbic acid and Ethanolamine need high temperatures to increase the speed of reaction and may need to add oxidation catalysts to increase the speed of reaction with oxygen and their efficiency. [13]

This analysis is important for the evaluation of the used scavengers in this research. It gives an indication about the reaction speed, Residence time in the system which effect on ability of the scavenger to remove oxygen as well as the preferred choice of the places in boiler system where the injected scavenger gives the best results.

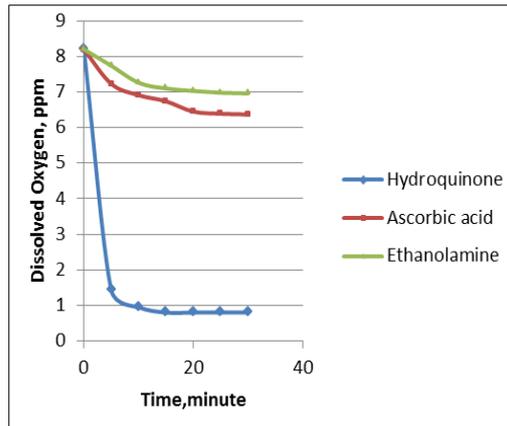


Fig. 19, Reaction Rates of Oxygen Scavengers at 25 °C and pH 9

### Conclusion

- 1- The corrosion rate of carbon steel in water at constant pressure and (pH) increases with temperature.
- 2- The corrosion rate of carbon steel decreases when adding oxygen scavengers.
- 3- Oxygen Scavengers react with dissolved oxygen in water and they work on the consumption of oxygen.
- 4- Oxygen Scavengers differ among themselves in susceptibility removal of oxygen, The reason for this difference is mechanisms of the chemical reaction of each scavenger at the same conditions.
- 5- The best results were obtained when adding (80) ppm of each scavenger because of consumption the most of DO.
- 6- Hydroquinone is the best of the others in oxygen scavenging at different conditions.
- 7- Hydroquinone reacts quickly and spontaneously with dissolved oxygen in water at low temperatures while ascorbic acid and monoethanolamine react slowly with dissolved oxygen at the same conditions.

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