

CORROSION of BOILER TUBES in SOUTH BAGHDAD ELECTRIC STATION

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ABSTRACT

The corrosion of low carbon steel boiler tubes in demi water had been investigated. The purpose of this investigation was to determine the change produced in corrosion behavior of the carbon steel as a result of the specific presence of chloride and copper ions in the water under different temperatures.

For low carbon steel experiments, the temperature was taken in three levels (125, 175, and 215°C) under about 27 bar pressure and 1500 rpm in autoclave. Using weight loss technique, the corrosion rate ranges from (85 to 789 gmd) for low carbon steel boiler tubes.

INTRODUCTION

Corrosion can cause serious problem to the safe and economic operation of a wide variety of industrial installations. However, in order to understand a corrosion problem or situation, it is very important to be able to recognize the type of problem one is dealing with [1].

Water is a naturally occurring substance; because except in rare cases it is not sufficiently pure, it cannot be used for human consumption or in industry without some form of treatment. The main use of water in industry is the transfer of heat and the production of steam. Cooling water is used extensively in every manufacturing process, in fossil and nuclear, fueled steam

plant and attendant steam generation dominate the power generating field [1].

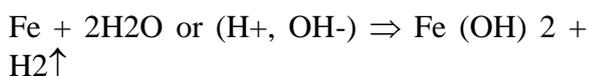
Water in the boiler section is heated to high temperature (260-315°C). The water is deaerated (usually by Na₂SO₃ addition) to reduce the O₂ content less than (50 ppb) in a well operating boiler. Some boilers are operated with zero solid water. High-purity water was used in the boiler; deaeration is obtained by adding volatile hydrazine or hydrazine

Replacement which is called carbohydrazid: A to control the pH and also reduce the O₂ content [2].

Carbon steel is widely used in chemical process plants for several important reasons. For one; it is low in cost, easy to fabricate, strong, and performance specifications are

well defined. However, the general corrosion resistance of carbon steel is low in certain environment. Most iron occurs naturally as stable oxide, and iron that had been processed into steel tend to return to that form [3].

Iron and steel corrode in water to form various compounds depending upon the temperature and other environment conditions. Theoretically, iron should react with water in the absence of air to form ferrous hydroxide:



However, even extremely small quantities of dissolved O₂ in water will produce ferric ions which color the ferrous hydroxide to green.

The up normal chemical control (i.e., ammonia dosing) and up normal operating conditions (i.e., steam and water velocities) may lead to a leakage in the condenser tubes causing dissolution of Cu from the Cu-Ni alloy. Drops of raw water may enter from the cooling side (tubes) to steam side (shell) holding contaminants (i.e., Cl⁻, SO₄⁻², SiO₂, O₂,

organic mater in addition of Cu⁺²). So, this polluted water will enter the boiler where the corrosion problem will initiate because of high temperature (380 °C), and high pressure (60 bar).

In this investigation, the interest lies in corrosion behavior of iron a widely used in the steam power plant with demi water as corrosive media.

EXPERIMENTAL WORK

Specimens Preparation

Specimens of low carbon steel with dimensions of about (3 cm ×1.5 cm) and (0.51 cm) thickness rectangular in shape were used exposing about 4.5 cm² surface area to the corrosion media

Cleaning procedure

Specimens were cleaned by washing with detergent and flushed with tap water followed by deionized water, degreased by analar benzene and acetone, then annealed in vacuum at 600°C for 1 hour and cooled under vacuum to room temperature. Finally, they were stored in a desicator over a silica gel to be used.

Specific treatment

Specimens carbon-steel were abraded in sequence using emery paper of grade number 220, 320, 400, and 600 then washed with running tap water followed by deionized water, then dried with clean tissue, degreased with benzene, dried, degreased with acetone, dried, and finally left to dry for one hour in a desicator over silica gel. Weighing the specimens were carried out using 4 decimals digital balance and its dimensions were measured with a vernier.

Experimental procedure

The tests were carried out using a standard reactor (autoclave) as shown in Fig. (1) Made of stainless steel and consist of pressure gauge and thermocouple which are sealed in stainless steel probe, internal agitator with stirring shaft hanged on it a specimen, safety pressure discs which protect the operator and the equipment from accidental destructive pressure. Also consists of fitting for nitrogen feed. The carbon steel rectangular shape specimens were placed in taflon frame as shown in Fig. (1) Hanged on rotating shaft at constant speed of 1500 rpm in a reactor pressure vessel (autoclave) containing 250 ml of corrosive solution.

Before starting the experiment, the pressure was raised to 32 bar in the reactor for leakage checking by using pure nitrogen (98.0%), after that the pressure was reduced to the desired value of (i.e., 27 bar).

After they were exposed for one hour to the desired temperature of (125, 175, 215) °C and pressure of (27) bar. The specimens were cleaned with running tap water using a brush, followed by deionized water, dried with clean tissue, then degreased with benzene, dried, degreased with acetone, dried, left for one hour, then the weight loss was measured and the corrosion rate was obtained.



Fig (1) Auto-clave system for corrosion rate measurement under high temperature and pressure

RESULTS AND DISCUSSION

Corrosion Behavior of Low Carbon Steel Pipes Used in Boiler

The influence of temperature (125, 175, and 215°C), chloride concentration as NaCl (0.5, 50.25, and 100 ppm) beside copper concentration Cu+2 (0.005, 0.0125, and 0.02 ppm), were studied using weight loss technique. The experiments were designed according to factorial method and 27 runs have been achieved as shown in Table (1).

It is important to mention here that the rotational mixer speed during the experiment was fixed at (1500 rpm) and the pressure at (27±1) bar.

Effect of Temperature

The rate of metallic corrosion is dependent on temperature like most chemical reactions. Experiment at different temperatures and fixed flow velocity solution containing different concentration of Cl^- and Cu^{+2} ions as NaCl and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ respectively, were carried on flow velocity was expressed as rotational mixer speed at 1500 rpm. Fig. (2) shows the result of activation energies of low carbon steel obtained as log corrosion rates versus temperature reciprocal using Arrhenius form, a linear relationship was obtained giving different activation energies (7.75, 4.58, 3.935, and 2.89 kcal/mol) depending on the Cl^- and Cu^{+2} ions concentration in the solution.

The values of activation energy (7.75 kcal/mol) indicates that at 0.5 ppm chloride and 0.005 ppm copper, the reaction is to some extent slow while when the copper concentration was increased to 0.02 ppm in the same time fixing the chloride concentration at 0.5 ppm, the reaction become faster (i.e. activation energy= 4.58 kcal/mole < 7.75 kcal/mole).

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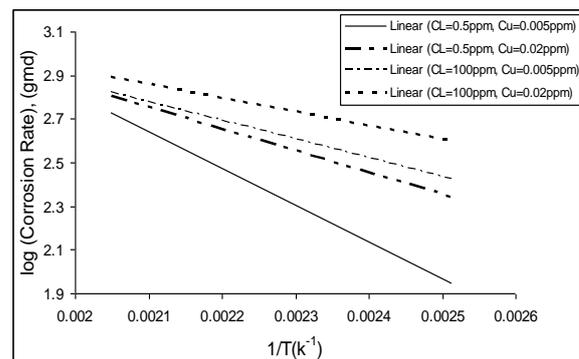


Fig. 2 Arrhenius plot for the corrosion rate of low carbon steel at different concentration of chloride and copper ions

Table (1) Corrosion rate results of factorial experimental runs for the boiler. Low carbon steel Pipes achieved in the autoclave

Run No.	Temperature (°C)	Chloride (ppm)	Copper (ppm)	C.R.* (gmd)
1	125	0.5	0.0050	85
2	125	0.5	0.0125	142
3	125	0.5	0.0200	213
4	125	50.25	0.0050	172
5	125	50.25	0.0125	230
6	125	50.25	0.0200	307
7	125	100	0.0050	266
8	125	100	0.0125	349
9	125	100	0.0200	401
10	175	0.5	0.0050	293
11	175	0.5	0.0125	341
12	175	0.5	0.0200	454
13	175	50.25	0.0050	382
14	175	50.25	0.0125	451
15	175	50.25	0.0200	513
16	175	100	0.0050	457
17	175	100	0.0125	524
18	175	100	0.0200	591
19	215	0.5	0.0050	506
20	215	0.5	0.125	595
21	215	0.5	0.0200	609
22	215	50.25	0.0050	591
23	215	50.25	0.0125	641
24	215	50.25	0.0200	721
25	215	100	0.0050	667
26	215	100	0.0125	739
27	215	100	0.02	789

* All corrosion rate valued in the last column are recorded from putting the sample in the corrosive media waiting until reaches the required temperature then 1 hr exposure time

Similarly, when the chloride concentration was increased to its maximum value. Fixing the copper concentration at its minimum value, the reaction goes faster (i.e. 3.94 and 2.89 kcal/mol) indicating that chloride concentration leads the reaction to be under diffusion control. In the closed system as in this study no oxygen is permitted to escape. As a result of the rise in temperature, the corrosion rate increases steadily with the temperature.

Figs. (3 - 5) show the effect of increasing temperature on the corrosion rate of carbon steel pipes at different concentrations of Cl^- and Cu^{+2} ions. It is clear that:

1. Generally, the corrosion rate is higher as the Cl^- ions increases at different Cu^{+2} ions concentration.
2. At all concentrations of Cl^- ions where the Cu^{+2} increases the corrosion rate increase with the temperature. This can be attributed to Cu^{+2} ions acting as cathode with respect to the carbon steel which act as anode. So, increasing Cu^{+2} ions cause an increase in the corrosion rate.

Finally, the results indicate that the corrosion attack proceeds by linear kinetics throughout the temperature range (125-215°C) studied in presence of Cl^- ions range (0.5-100 ppm) and Cu^{+2} ion range (0.005-0.02 ppm).

Accordingly, it is evident that since the experimental results show that corrosion process follows linear rate law, it's the chemical surface reaction which controls the kinetics in this case.

The same results was found by Kameswari[4] in his study of the relative corrosion resistance of different boiler steels in presence of sugar can, phosphates, sulfate, and chloride of sodium as the ash contains. He found that the weight loss data as function of temperature and time follows linear kinetics.

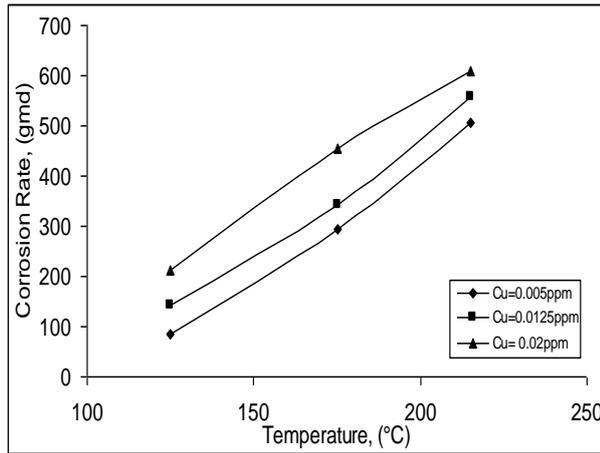


Fig. 3 The effects of temperature on the corrosion rate of carbon steel at different copper concentration and chloride

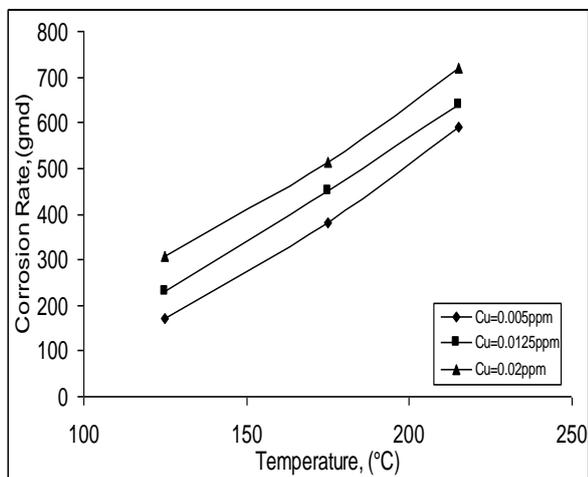


Fig. 4 the effects of temperature on the corrosion rate of carbon steel at different copper concentration and chloride

Effect of Chloride

Figures (6 - 8) show the effect of increasing the Cl^- ions concentration on the corrosion rate of low carbon steel pipe at different concentrations of Cu^{+2} ions for elevated temperature. In the sodium chloride solution, the conductivity is greater hence additional anodes and cathodes can operate. It can be stated that:

1. Generally the corrosion rate increases with increasing Cl^- ions

concentration at all Cu^{+2} concentration for all temperatures.

2. At certain temperature, corrosion rate increase with increasing Cl^- and Cu^{+2} ions concentrations.

The effect of Cl^- ions on the corrosion rate can be explained as follows: Chloride ions are able to destroy passive films formed on metals such as iron, and increase the corrosion rate of attack.

This behavior result from the conflicting effect of rising solution conductivity. Higher solution conductivity faster or greater physical separation between the anodi and permits the formation of cathodic product $\text{Fe}(\text{OH})_2$ at a distance from the steel surface. Because $\text{Fe}(\text{OH})_2$ formed in this way cannot provide a protective layer, the corrosion is not inhibited, so, a change in concentration of a salt can influence the corrosion rate.

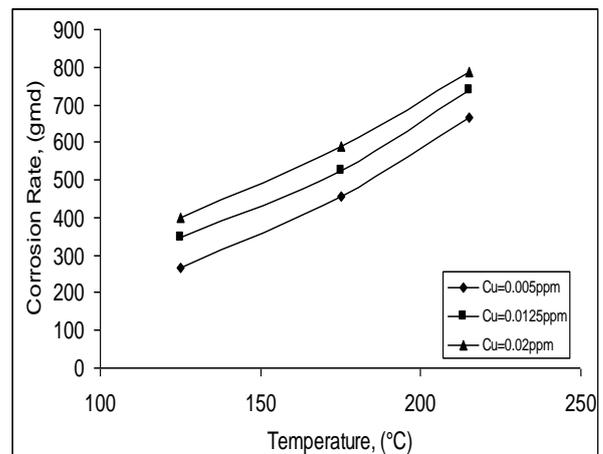


Fig. 5 The effects of temperature on the corrosion rate of carbon steel at different copper concentration and chloride

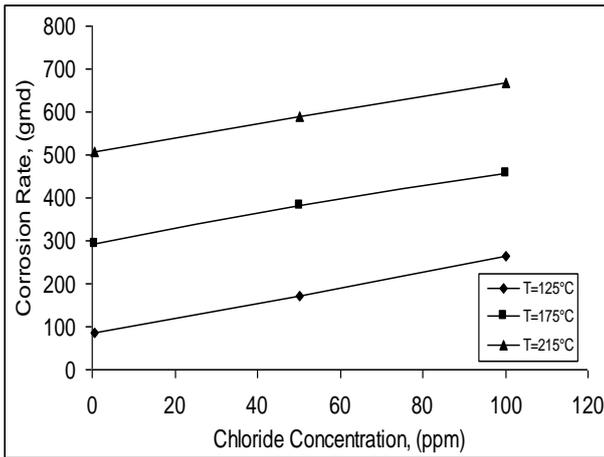


Fig. 6 the effects of chloride ion on the corrosion rat of carbon steel at different temperature and copper concentration of

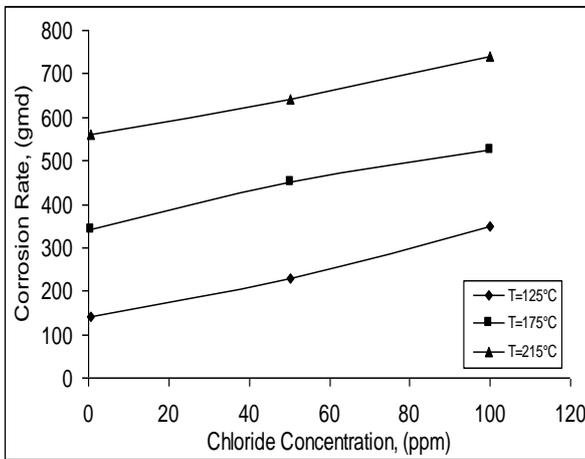


Fig. 7 The effects of chloride ion on the corrosion rate of carbon steel at different temperature and copper concentration

Effect of Copper

Figures (9 - 11) show the relationship between the corrosion rate of low carbon steel and the concentration of Cu+2 ppm in the solution with different Cl⁻ ion concentration at various temperature levels. It can be stated that:

1. The corrosion rate increase with increasing Cu+2 ion concentration at all Cl⁻ ion concentration for all temperatures.
2. At a given temperature, corrosion rate increase with increasing Cu+2 and Cl⁻ ions concentration.

As the result of up normal operation i.e., the presence of high concentration of ammonia in aerated water which leads to corrode the copper alloy followed by forming oxide layers, transferred to the boiler and deposited their causing increasing the corrosion rates of carbon steel.

Iron dissolves by displacing another metal which is already in solution in the electrolyte. This may be noted by submerging iron in copper solution. When this is done, the iron goes into solution in the electrolyte and the copper is deposited upon the iron [5].

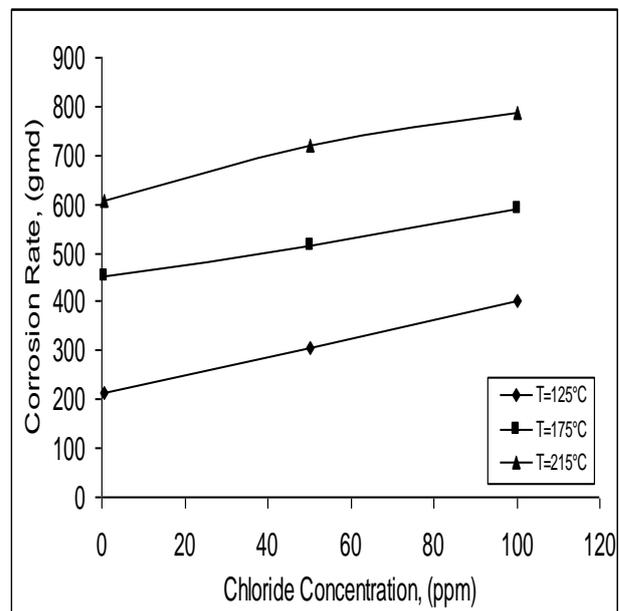


Fig. 8 The effects of chloride ion on the corrosion rate of carbon steel at different temperature and copper concentration of (0.02 ppm)

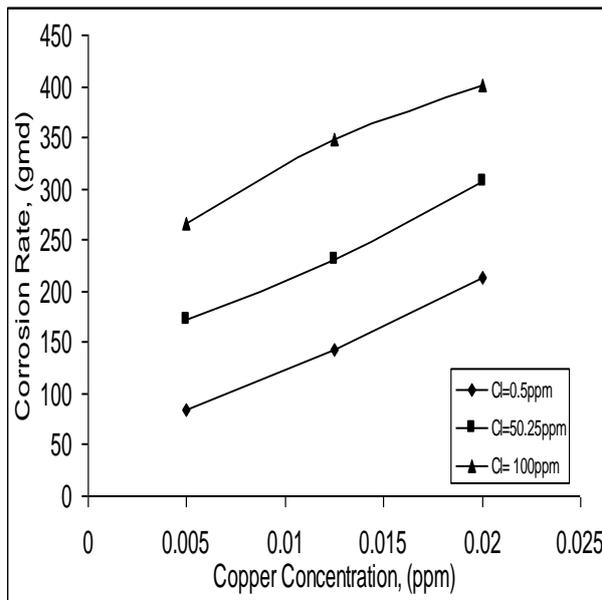


Fig. 9 The effects of copper ion on the corrosion rate of carbon steel at different chloride concentration and Temperature (125°C)

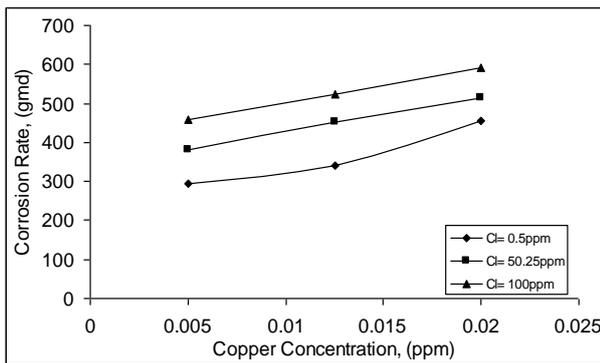


Fig. 10 The effects of copper ion on the corrosion rate of carbon steel at different

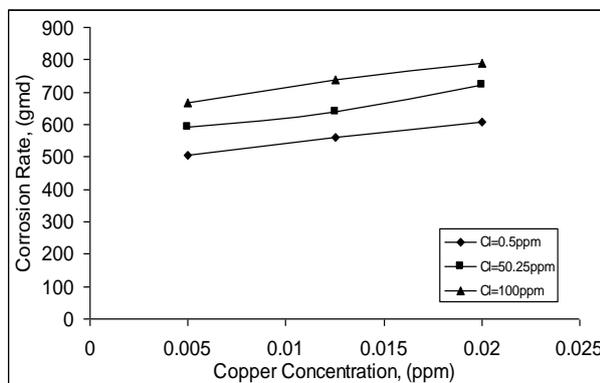


Fig. 11 The effects of copper ion on the corrosion rate of carbon steel at different

CONCLUSIONS

On the basis of the results presented The corrosion rate of boiler carbon steel tubes in water showed no minimum value in all experiments, (i.e. the higher the value of one variable when the second variable was fixed led to higher corrosion rate.

REFERENCES

- 1-NACE Basic Corrosion Course, Houston, Texas, (1970).
- 2-D. B. Gardner, Material Protection, Vol. 2, No. 4, p.54-61, (1962).
- 3-Gary N. Kirby, Grawford & Russell, Inc., Chemical Engineering Journal, Vol. 86, No. 6, p.72, (1979).
- 4-Kemeswari S., The International Corrosion Congress, Florence, Italy, April, Vol. 2, p.2613, (1990).
- 5-Powell, Sheppard T., "Boiler Feed Water Purification", McGraw-Hill Book Company, New York

