Corrosion of Carbon Steel and alloy Steel: effect of humidity and hydrochloric acid

Abdulkader A. Muhammad¹, Thamir A. D. M. S. Almula ¹*, Dyhia A. Sultan¹

¹ Engineering Technical College / Mosul, Northern Technical University NTU, 41002 Mosul, Iraq
* Email: thamir_own@ntu.edu.iq, thamir_own@yahoo.com

Abstract. The corrosion performance of hypo-eutectoid carbon steel, and alloy steel used in steam boilers at Al-Najibiyah Thermal Power Station in the Iraqi city of Basra was investigated. These metals were exposed to different media such as moisture and acids for (30, 45, and 60) days, then the rate of corrosion was calculated in a way of weight loss. The influence of carbon content, corrosive media and duration of immersion on samples of hypo-eutectic carbon steel and alloy steel were studied. The results showed an increase in the percentage of corrosion as a result of the increase in carbon content, and alloy steel has a high resistance to corrosion than carbon steel in the different corrosive media used in this study.

Keywords: Corrosion, Carbon steel, Alloy steel, Moisture, Hydraulic acid, Steam boilers

1. Introduction
The major technical challenges and the great cost directly correlated to corrosion, which is provide strong motivations for researchers and engineers and other technical scientist staff to improve a firm grasp development on the essential bases of corrosion. Adopting the fundamentals of corrosion is essential not only for recognizing corrosion mechanisms (an important achievement by itself), but also for avoiding corrosion by proper corrosion protection means as well as predicting the corrosion performance of metallic material within service conditions. Understanding the corrosion mechanisms is important for developing the design knowledge of corrosion resistance for alloys and to estimate the long-term performance of metallic material in corrosive environments [1].

Corrosion is defined in several forms, the most important of which are: metal decay caused by its interaction with the corrosion medium to which it is exposed; it is also known as metal damage as a result of chemical or electrochemical interaction with the atmosphere. Or the reverse procedure of extracting the raw materials from metal, i.e., restoring the metal to its original, free, natural form before it was extracted, or an electrochemical reaction of metals surrounded by soil or water chemicals. These conduction cells generate electricity as a result of the natural voltage difference between metals which results degradation of the more active metals [2-5].

The microstructure of the carbon steel which has been used in the current research consists of ferrite and pearlite, where the ferrite represents a single phase, while the pearlite represents two different phases, namely the ferrite and cement. The two different phases give distinct mechanical properties but...
are more susceptible to corrosion than the single-phase microstructure. The micro-galvanic corrosion cell is formed because of the expected voltage difference between the two microstructure phases [6].

The corrosion that will study in this research is wet corrosion, which includes electrochemical reactions, and this type of corrosion occurs only when the medium is an electrolyte, i.e. electricity conductor. This type of corrosion has been focused on which attack metallic parts, for example, corrosion of carbon steel in the presence of water, this type of corrosion is called galvanic corrosion attributed to the discovery of the Italian scientist Galvani. The Galvanic corrosion cell consists of two poles, one of which is the anode, and the other represents the cathode, and the voltage difference between the anode and the cathode can occur if the two poles of the cell are of different metals or of the same metal. In this research, the focus will be on the corrosion of the one metal, so that the single metal becomes two poles, one of which represents the anode, while the other represents the cathode [7].

Numerous researches and studies have been conducted in the field of metal corrosion, the researcher Raja and his colleagues [8] studied effect of carbon percentage on sulfuric acid corrosion rate (5% H_2\text{SO}_4) as Corrosion Medium, and concluded that corrosion rate increases with increasing carbon percentage in steel due to increased surface area of micro-galvanic corrosion cell. Batis and Rakanta [9] studied the effect of carbon percentage on corrosion resistance in the atmosphere and found that steel containing 0.08% C more corrosion-resistant than steel containing 0.30% C, and that is due to decreasing the area of corrosion cells and the two researchers showed that corrosion resistance in carbon steel decreases with increasing carbon content. Takasaki and his colleagues [10] investigated the influence of corrosion exposure period on corrosion rate for mild steel and concluded that increasing the time of exposure reduces corrosion rates, and studied the effect of \([\text{SO}_4]^-\), \([\text{CL}]^-\) ions on corrosion rates in mild carbon steel and showed that the corrosion rates rise with the concentration of ions.

Wall F. D and his colleagues [11] also studied the effect of corrosion exposure time on corrosion rate, where they found a decrease in corrosion rate through time, they explained that by the presence of rust and corrosion layers that tend to decrease the rate of corrosion, and these layers may form protective membranes that reduce the interaction of the metal surface with the corrosion medium. Corvo F. and his colleagues [12] concluded that the cause of variation in the corrosion rate of carbon steel in the air media is the difference in the chloride ions Cl^- concentration that cause accelerated corrosion, especially in areas exposed to rain, for continuous periods or in marine areas, the increasing of chloride ions concentration rises the conductivity, which increases the reaction rate of the electrochemical, as a result it increases the rate of corrosion.

Increasing the concentration of chloride ions Cl^- would maximize the weight loss of carbon steel and increase conductivity as well, demonstrating that increased concentration of NaCl leads to increased corrosion rates. Corrosion is closely related to the quality of metal exposed to corrosion and to the quality of the corrosive medium, there are several types of corrosive media that produce different types of corrosion, and the most important of these are the atmosphere, water, soil, acids and salts. When conducting tests and examinations related to corrosion phenomenon in a certain media and for a particular metal, it is necessary to carefully analyze both the medium and the metal, in order to determine the type of corrosion which will result, and consequently to conclude the methods to protect it [13]. The researcher R. M. Azoor and his colleagues provided the foundation for the presence of the optimal moisture level, which results to relatively great corrosion rates in soil. the corrosion rates of cast iron in silt, sand and clay were observed at various degrees of saturation [14].

Previous research shows that the researchers compared the corrosion of different types of carbon steel under different conditions of humid atmosphere and acidic media such as sulfuric acid and also studied the impact of the duration of corrosion exposure on the rate of corrosion.

In the present study, corrosion of low, medium and high carbon steels in wet and acidic media will be studied and compared with the corrosion of alloy steel used in the steam boilers at Al-Najibiyah Thermal Power Station in the Iraqi city of Basra under the same conditions.
2. Experimental work

2.1 Material
In this study, three types of hypo-eutectoid steel were used, which are characterized by the wide range of usage in engineering and industrial applications, these types of steel contain different carbon content, as well as a sample of alloy steel, which is used in steam boiler at the Najibiyah Thermal Power Station in the Iraqi city of Basra was taken, and is shown in figure 1. The chemical analysis of the specimens used in this research was carried out using a metal spectroscopy device shown in figure 2(a, b), to determine the carbon content and other chemical constituents, in order to obtain reliable results, three readings were taken and the average of these readings was adopted. Tables 1 and 2 show the chemical composition of carbon steel and alloy steel, respectively.

| Table 1. Ultimate tensile strength values and elongation to fracture. |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Type | Chemical composition (%) |
|-------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
|      | Fe % | AL  | Mo  | Ni  | Cr  | S   | p   | Si  | Mn  | C   |
| S1   | 0.006 | 0.014 | 0.041 | 0.112 | 0.012 | 0.112 | 0.041 | 0.014 | 0.006 | Ba |
| S2   | 0.017 | 0.072 | 0.22  | 0.231 | 0.037 | 0.231 | 0.22  | 0.072 | 0.017 | Ba |
| S3   | 0.041 | 0.043 | 0.083 | 0.027 | 0.002 | 0.04  | 0.027 | 0.083 | 0.043 | Ba |

| Table 2. The chemical composition of alloy steel studied. |
|------------------|------------------|------------------|------------------|------------------|------------------|
| S4   | Chemical composition (%) |
|      | Mn  | Cu  | Ni  | Mo  | Fe % |
| Alloy steel | 0.54 | 0.16 | 0.1  | 0.01 | Ba |

2.2 Heat treatment of specimens
Normalizing is a heat treatment process apply to carbon steel to restore the metal to its equilibrium state. This process was performed on the carbon steel specimens to restore them to their equilibrium state, namely, ferrite and the Pearlite [15]. To investigate the effect of the microstructure of carbon steel on corrosion resistance in different media, normalizing process was carried out for carbon steel specimens used in the research by heating them to a temperature above the crystallization temperature by 30-50 °C, and then maintained at this temperature depending on the thickness of the specimen [15]. The specimens were then removed from the oven and left to cool in still air until room temperature. Table 3 shows the
retention time and temperature of the normalizing process performed on the carbon steel specimens used in this research.

**Table 3.** The retention time and temperature of normalizing process performed on carbon steel.

| Retention time (min.) | Normalizing temperature (℃) | Carbon content |
|-----------------------|-----------------------------|---------------|
| 30                    | 900                         | 0.11          |
| 30                    | 850                         | 0.385         |
| 30                    | 800                         | 0.64          |

2.3. **Heat treatment of specimens**
Carbon steel specimens were prepared for microstructure test by conventional method including: grinding and smoothing by using sandpaper of SiC with (320, 600, 800, 1000, 1200) degree and electrical polishing followed by the etching process using the nital solution, which consists of the following percentages: 2% concentrated nitric acid and 98% methanol. Figure 3 shows the microstructure of carbon steel specimens that have been heat treated by normalizing process.

![Figure 3. Microstructure of carbon steel specimens that have been heat treated by normalizing process](image)

3. **Corrosion tests**

3.1. **Exposure period to corrosive medium**
First period: 30 days (720 hours)
Second Period: 45 days (1080 hours)
The third time: 60 days (1440 hours)

3.2. **Corrosive media**
Saline solution: saline water was used, 5% g of sodium chloride (NaCl) added to (95% g) of distilled water, where it was ascertained that sodium chloride was completely dissolved in water before immersion of the specimens. Acid solution: diluted hydrochloric acid was used (5% Vol HCl).

3.3 **Calculating the rate of corrosion in a way of weight loss**

3.3.1 **Calculating the weight loss**
Weight loss was calculated as follows:
- The specimens were cleaned before the weight was measured with diluted HCL 10% concentration, then swap with filtered water then alcohol then finally dried.
• The weight of each specimen was accurately found by using a sensitive electronic balance (Sartorius) Germany-made, with a precision of 0.1 mg, where the original weight was recorded.
• The specimens are placed in the corrosive media so that they are suspended with insulating filaments and completely immersed in the glass basin containing the corrosive media.
• After the exposure period is finished, the specimens are removed from the corrosive medium and cleaned from resulting rust layers by using a soft brush and water, and then cleaned the eroded layers using a diluted hydrochloric acid solution (HCl) without affecting the metal. Then the specimens are washed with distilled water and alcohol, then dried and each weight is measured to find the final weight. In order to calculate the change in weight ($\Delta w$) which is the difference between the original weight (the weight of the specimen before the corrosion test) and the final weight (the weight of the specimen after the corrosion test and removal of corrosion residues).

3.3.2 Calculating the rate of corrosion
Corrosion rate was measured in Mils per year (mpy) depending on the main function, which is the weight loss ($\Delta w$) during the period of the test ($T$). The test constants in this study are: density of steel ($D$), surface area exposed to corrosion ($A$). The following equation has been adopted to compute the rate of corrosion:

$$CR(\text{mpy}) = \frac{k \times \Delta w}{D \times A \times T}$$

(1)

where $CR$ is the corrosion rate, and $K$ is a constant value equal $3.4 \times 10^6$.

The corrosion rate can also be calculated in millimeters per year and is usually called the corrosion penetration rate.

Corrosion penetration rate is given as follows:

$$CR (\text{mm/y}) = \frac{87.6 \Delta w}{D \times A \times T}$$

(2)

4. Results and discussion
The main objective of this research is to study the effect of moisture and acid solution on the corrosion of carbon steel and alloy steel at different time intervals (30, 45, 60 days). Figures 4, 5, 6, 7, 8, 9, and 10 show the results of corrosion tests. The results in figure 4 show the extent to which the carbon content affects the corrosion rates of hypo-eutectoid steel in the corrosive media during exposed period (30 days). It has been shown that when the carbon content increases in the three types of carbon steel which are adopted in the current research, the corrosion rates increase, this increase is gradual and somewhat similar to the linear relationship.

The Carbon steel corrosion rate of 0.64% C is higher than that of carbon steel with the lowest carbon content of 0.112% C, which means that the corrosion rate rises with the increase in carbon content. Corrosion rates depend on the type of carbon steel in general and on its microstructure in particular, where the change in carbon content affect the microstructure of steel. The microstructure of the hypo eutectoid steel composed of alpha ferrite and pearlite with different percentage depending on carbon content.

The increase in corrosion rates, with the increase in carbon content, is caused by the fact that increasing the carbon content leads to an increase in the proportion of pearlite, leading to an increase in the number of galvanic corrosion cells. The pearlite is a two-phase microstructure composed of alpha ferrite and cementite ($\text{Fe}_3 \text{C}$), Which reflects the best installation of the galvanized cells represented by the anode, which is the cementite and the cathode, which is the alpha ferrite, and then the pearlite represents the galvanic corrosion cell because of the voltage difference between the cathode and the anode, between the ferrite and cementite when they exist together and when the electrolyte is available. As a result, with the increase in the carbon content in the hypo-eutectoid steel, the anodic area (the area of the galvanic corrosion cells) represented by the pearlite, leading to maximize in the rate of corrosion.
Figure 5 shows the rates of corrosion of hypo-eutectoid steel in the corrosive media during 45 days. The results show that corrosion rates are increasing as carbon content increases, and this increase is also gradual. Figure 6 shows the rates of corrosion of hypo-eutectoid steel in the corrosive media during 60 days. The results show that when the carbon content of hypo-eutectoid steel increases, the corrosion rate increases, and this increase is gradual. The highest carbon content of 0.64% C is the highest in corrosion rate compared with the other carbon steel used, and the lowest corrosion rate occurred for carbon content of 0.11% C.

The corrosion rate increases with the increase in carbon content due to the change in the microstructure, which leads to the increase of the cementite phase and the decrease of the ferrite phase, thus increasing the anode area with the increase of the carbon content that leads to the increase of the corrosion rates. The results show that there is a variance in the corrosion rates of hypo-eutectoid steel by changing the corrosive medium, which indicates the important role played by the corrosive medium that affect the corrosion rates.

Figure 4. Effect of carbon content on corrosion rates during 30 days.

Figure 5. Effect of carbon content on corrosion rates during 45 days.

Figure 6. Effect of carbon content on corrosion rates during 60 days.

Figure 7. Effect of wet weather exposure period on the corrosion rate of carbon steel.
Figure 8. Effect of acidic solution exposure period on the corrosion rate of carbon steel

Figure 9. Corrosion rates for carbon steel and alloy steel in a wet weather during different time periods

Figure 10. Corrosion rates for carbon steel and alloy steel in an acidic solution during different time periods

All the results shown in Figures 4, 5, and 6 indicate that corrosion rates of carbon steel in acidic media were higher than those of wet media, the results show that corrosion rates vary from one medium to another depending on the nature of the medium and the severity of its effect. Figure 7 shows the effect of wet weather exposure period on the corrosion rate of carbon steel. Figure 7 show the results that corrosion rates decrease gradually with increased exposure period in wet weather. It seems that the lowest corrosion rates were obtained within a 60-day exposure period, while the highest corrosion rates were obtained during a period of 30 days.

The reason for the decrease in corrosion rates with increasing in exposure period is due to the slow rate of electrochemical reaction caused by the formation of a membrane or layers of corrosion residues on the surface of carbon steel that impedes the persistence of electrochemical corrosion, thus reducing corrosion rates. And due to the depletion of dissolved oxygen in corrosive medium as well. At the beginning of the corrosion test, the electrochemical reaction occurs rapidly resulting in high corrosion rates, but over time the dissolved oxygen is reduced, increasing the concentration of hydrogen ions that accumulate at the anode, which inhibits corrosion reactions.
This is called polarization and the value of acidic function (pH) is also affected by the concentration of dissolved oxygen, since the acidity and the base of the medium are affected by the value of PH. If (pH< 6) the medium is acidic and have a very high effect on the metal, if the value of (pH=7) the medium will be neutral, and the medium will be alkaline if (pH>8) which is the least influential medium in steel.

Figure 8 shows the effect of corrosion exposure period in acidic solution on the corrosion rates of the hypo-eutectoid steel. It is clear from the figure that the corrosion rates gradually decrease with increasing exposure period to corrosive medium, it seems that the lowest corrosion rates were obtained during a 60-days exposure period, and the highest corrosion rates were obtained during a 30-days exposure period. Also, as the case in figure 4, the reason for the decrease in corrosion rates with increasing in exposure period is due to the slow rate of electrochemical reaction caused by the formation of a membrane or layers of corrosion residues on the surface of carbon steel that impedes the persistence of electrochemical corrosion, thus reducing corrosion rates.

It is therefore possible to conclude that the longer the time for immersing, the greater the carbon steel resistance to corrosion and rust, because increasing the time of the immersion provides an opportunity to complete the interaction between the immersion solution (corrosive medium) and the surface of the metal, and this helps to form a layer of corrosion residues on the surface of the metal then increase its thickness and form an obstacle to the persistence of electrochemical corrosion.

Figure 9 shows that the corrosion rate of alloy steel is greater than that of the three types of carbon steel during the 30-days exposure period in wet weather. While in the 45-days exposure period, the corrosion rate of alloy steel is higher compared with carbon steel of 0.11% C and 0.358% C, and less than that of 0.64% C. In the 60-day exposure period, the corrosion rate of alloy steel is lower than the corrosion rate of carbon steel of 0.358% C and 0.64% C, and higher than the corrosion rate of carbon steel of 0.11% C. It is concluded that the corrosion rate of alloy steel in wet weather decreases at a greater rate with increasing exposure period compared with the reduction in the corrosion rate of carbon steels.

Figure 10 observes the corrosion rates of carbon steels and alloy steel in an acid solution at different time periods. The figure shows that the corrosion rate of alloy steels is lesser than the corrosion rate of carbon steel 0.64% C, unlike the other two types of carbon steel 0.11% C and 0.358% C, the corrosion rate of alloy steel is greater than that of these two types of carbon steel.

5. Conclusion
From the previous results obtained from this study, it can be concluded that the low carbon steel (0.11%C) has higher corrosion resistance than that of medium carbon steel (0.358%C) and high carbon steel (0.64%C) in the wet and acid corrosive media, this indicates that the corrosion resistance decreases with increasing carbon content, however, this decrease in corrosion resistance is more pronounced in the case of acid medium. It is also noticed that the corrosion rate decreases with increasing the exposure duration to wet and acid corrosive media for the three types of carbon steels. In the wet medium, it is noticed that the corrosion rate of alloy steel which is used in the steam boilers at Al-Najibiyah Thermal Power Station in the Iraqi city of Basra is higher than that of the three types of carbon steels after 30 days, but begins to decrease whenever the exposure duration exceeds 30 days. So, after 45 days the corrosion rate of alloy steel is less than that of high carbon steel, and it is nearly equal to that of medium carbon steel. After 60 days, it is noticed that the corrosion rate of alloy steel is lower than that of high carbon steel and medium carbon steel, but slightly more than that of low carbon steel. In the acid medium, it is noticed that the corrosion rate of alloy steel is lower than that of high carbon steel, but still higher than that of medium carbon steel and low carbon steel for the three-exposure duration 30, 45, and 60 days.
References

[1] Shaw, B. (2003). ASM handbook volume 13a: corrosion: fundamentals, testing and protection. D. Stephen, ASM International, Materials Park, Ohio, USA. Singh, AK, & Quraishi, MA (2010). Effect of Cefazolin on the corrosion of mild steel in HCl solution. Corrosion Science, 52(1), 152-160.

[2] Fontana, M. G. (2005). Corrosion engineering: Tata McGraw-Hill Education.

[3] Hou, X., Gao, L., Cui, Z., & Yin, J. (2018). Corrosion and protection of metal in the seawater desalination. Earth Environ Sci, 108, 022037.

[4] Takasaki, S., & Yamada, Y. (2007). Effects of temperature and aggressive anions on corrosion of carbon steel in potable water. Corrosion Science, 49(1), 240-247.

[5] Stephen, C. (2003). Galvanic Corrosion. University of Delaware, USA.

[6] Shreir, L. L. (2013). Corrosion: corrosion control: Newnes.

[7] Roberge, P. R. (2000). Handbook of corrosion engineering: McGraw-Hill.

[8] Raja, V., Baligidad, R., & Shankar Rao, V. (2002). Effect of Carbon on Corrosion Behavior of Fe3 Al Inter-metallic's in 0.5 N Sulfuric acid. Journal of Corrosion Science, 33, 521-533.

[9] Batis, G., & Rakanta, E. (2005). Corrosion of steel reinforcement due to atmospheric pollution. Cement and concrete composites, 27(2), 269-275.

[10] Trethewey, K. R., & Chamberlain, J. (1995). Corrosion for science and engineering.

[11] Wall, F., Martinez, M., Missert, N., Copeland, R., & Kilgo, A. (2005). Characterizing corrosion behavior under atmospheric conditions using electrochemical techniques. Corrosion Science, 47(1), 17-32.

[12] Corvo, F., Minotas, J., Delgado, J., & Arroyave, C. (2005). Changes in atmospheric corrosion rate caused by chloride ions depending on rain regime. Corrosion Science, 47(4), 883-892.

[13] Garcia, K., Barrero, C., Morales, A., & Greneche, J. (2008). Lost iron and iron converted into rust in steels submitted to dry–wet corrosion process. Corrosion Science, 50(3), 763-772.

[14] Azoor, R. M., Deo, R. N., Birbilis, N., & Kodikara, J. (2019). On the optimum soil moisture for underground corrosion in different soil types. Corrosion Science, 159, 108116. doi:https://doi.org/10.1016/j.corsci.2019.108116

[15] Brooks, C. R. (1996). Principles of the heat treatment of plain carbon and low alloy steels: ASM international.