

The Effect of pH and TDS on The Corrosion Rate of Carbon Steel

Mirs. Nuha. H. AL- Hasen

College of Eng.-University of Basrah.

Abstract : The aim of this paper is to reduce the corrosion rate by controlling the pH value, the polarization technique was used in this research in acidic, neutral and basic solutions. The corrosion rate was studied for carbon steel in filtered water, raw water and de-mineralized water under static condition at room temperature and 1 atm. Also, the effect of total dissolved solid (calcium , magnesium and sodium) on the corrosion rates was studies.

تأثير pH والأملاح الذائبة الكلية على معدل التآكل في الصلب الكربوني

م.م. : نهى هادي الحسن

قسم هندسة المواد - كلية الهندسة
جامعة البصرة

الخلاصة: إن هدف هذه المقالة هو تقليل معدل التآكل بالسيطرة على قيمة pH تحت الظروف المسكنة، استخدمت تقنية الاستقطاب في المحاليل الحامضية ، المتعادلة والقاعدية حيث تمت دراسة معدلات سرعة التآكل للفولاذ الكربوني في الماء المرشح و الماء الخام و الماء الايوني في ظروف ساكنة عند ضغط 1 جو وبدرجة حرارة الغرفة. كما تمت دراسة تأثير المواد الصلبة الذائبة (الكالسيوم والمغنيسيوم والصوديوم) على معدل التآكل.

ENGLISH SYMBOLS		
Symbols	Definition	SI Units
A	Area of corroding electrode	cm ²
A _c	Surface area	cm ²
CR	Corrosion rate	mpy
b _a	Tafel slope for the anode region	
b _c	Tafel slope for the cathode region	
d	Density of corroding metal	g/cm ³
E	Potential	V
Z	Equivalent weight of the corroding metal	g
K _c	Constant	mg/l
I	Current	A
I _{corr}	Corrosion current	nA
T _c	Time	hr
TDS	Total dissolved solid	
W _c	Weight loss	mg

1. Introduction

The measurement of pH in high temperature aqueous systems has been a major challenge in physical chemistry and in the power generation industry for over the five decades, and accurate pH measurements are still not routinely performed at temperatures above 100°C. However, several significant developments have been made to improve pH measurement techniques in high temperature subcritical and supercritical aqueous solutions[1]. In this work pH was measured at 32 °C.

The effect of acidic function and TDS on the corrosion behavior of carbon steel investigated in filtered water, raw water and de-mineralized water. The influence of the acidic function can

manifest itself either through its action in passive film, or by changing the nature of the electrolyte in the vicinity of the electrode surface. Wranglen [2] showed that anodic polarization curves clearly indicated that investigated carbon steel, and the different pH value used as a comparison, are in passive state at static condition, however, the passivation current density is much lower for the carbon steel. The formation of NH₄⁺ ions at the interface between the passive layer and the electrolyte, causes a locally increased pH value of the electrolyte close to the electrode surface, which makes for easier passivation of the carbon steel [2].

Linear polarization resistance is particularly useful as a method to rapidly identify corrosion upsets and initiate remedial action, thereby prolonging plant life and minimizing unscheduled downtime. The technique is utilized to maximum effect when installed as a continuous monitoring system, this technique has been used successfully, in almost all types of water-based, corrosive environments. Some of the more common applications are:

- Cooling water systems
- Secondary recovery system
- Amine sweetening
- Waste water treatment systems
- Pickling and mineral extraction processes
- Hydrocarbon production with free water [2].

2. Principle of Measurement

When a metal/alloy electrode is immersed in an electrolytically conducting liquid of sufficient oxidizing power, it will corrode by an electrochemical mechanism. This process involves two simultaneous complementary reactions, at anodic sites, metal will pass from the solid surface into the adjacent solution and, in so doing, leave a surplus of electrons at the metal surface. The excess electrons will flow to nearby sites, designated cathodic sites, at which they will be consumed by oxidizing species from the corrosive liquid [3].

The corrosion current (I_{CORR}), generated by the flow of electrons from anodic to cathodic sites, could be used to compute the corrosion rate by the application of a modified version of Faraday's Law:

$$CR = \frac{I_{CORR} \times z}{A \times d} \times 12867 \dots\dots (1)$$

Where, CR : Corrosion rate in "mils per year" (mpy)

E : Equivalent weight of the corroding metal (g)

A : Area of corroding electrode (cm^2)

d : Density of corroding metal (g/cm^3) [4].

3. Materials and experimental details

The chemical composition of the tested carbon steels [wt.%]: 0.3% C, 1.2% Mn, 0.05% P, and 0.06% S, Fe for balance. we test

this composition by surface analysis in general company for fertilizers-southern region of Basrah.

The electrochemical corrosion tests were performed using an EG & G PARC-US, model 350A; a saturated calomel electrode (SCE) was used as the reference electrode, provided with computer based design X-Y recorder, electrometer, compensation modules model 356 IR and electrochemical cell including three electrodes system.

The chemicals purchased from (BDH) chemical company: Sodium hydroxide, Acetone, and emery paper in different grade (120, 320, 400, and 600).

4. Apparatus and Instruments

4.1. Conductivity Meter

Conductivity meter (Jenway PCM3) was used for measuring electrical conductivity of the tested solutions. The instrument was calibrated for TDS measurements.

4.2. pH Meter

Model M62 pH meter was used to determine the pH values of the tested solutions.

4.3. Potentiodynamic Scan

A potentiodynamic scan an electrochemical corrosion measurement system model 350A Corrosion Measurements Console (EG & G PARC-US), is a qualitative experiment to assess the passivation tendencies of a metal

sample. The currents measured during a potentiodynamic scan can easily range over 6-7 decades, so it is possible appreciate the 9 or 10 decades of automatic current ranging with a Gamry Potentiostat, for quantitative investigation of the corrosion properties of materials with this method, three standard electrode cell have been used (as shown in figure (1) below).

I-Working electrode: this term was used rather than anode because the investigations of anodic behavior alone is not limited; cathode behavior are also be examined, the surface area of its must be at lest 1 cm² to convert current measurement into current density.

II-Counter (auxiliary) electrode: It can be used any material that will not introduce contaminating ions into the electrolyte, usually a carbon rode is used and Pt or Au can also used with success.

III-Reference electrode: Reference electrode present to provide a very stable datum against which the potential of the working electrode can be measured [3].

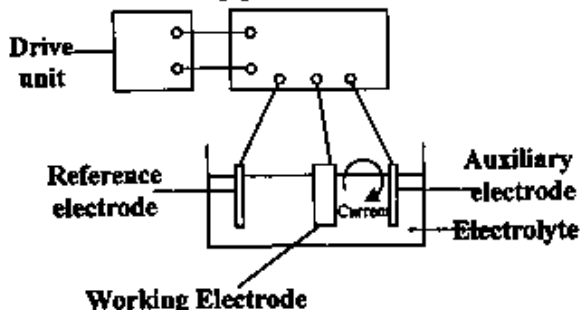


Fig.(1) Extrapolation arrangement for determining polarization curve

4.4. Weight Loss Measurements

The weight loss measurements were performed to investigate the effect of pH values on corrosion rate of CS, by using demineralized water as a corrodent at different pH values, the NaOH was used to raise the pH above 7, and the HCl to lower the pH below 7. Where, pH can be found by this equation:

$$pH = -\log \left[\frac{\text{weight}}{\text{molecular weight}} \right] \dots\dots (2)$$

After Grinding and polishing processes for the samples which were carried out using Buchler LTG, instrument model Buchler Ecomet II, the samples were immersed completely alone in a closed container at the same time. So, weight of each sample was determined after a specified period of time (3 days each of immersion within 1 month duration) then, the corrosion rate was estimated as below:

$$CR = \frac{K_c \cdot W_c}{A_c \cdot T_c \cdot d} \dots\dots (3)$$

where; K_c: constant (534), T_c: time (hr), W_c: weight loss (mg), A_c: surface area (cm²), CR: corrosion rate (mpy), d : density of material (g/cm³). [note: the samples have 1 cm² surface area].

5. Results and discussion

5.1. Weight Loss Measurements

The results of weight loss calculations after 3 days each of immersion within 1 month duration are shown in figures (2) and (3),

where the specimens are accurately weighted to the 4th decimal of gram. From these figures it can be observed that weight loss increases as time increases at pH 2, 3, and 6, but weight loss increased slightly at pH 8 and decreased at pH 8.4, 9, and 12. From Fig.(3) it can be seen that the best pH with minimized weight loss is equal to 8.4.

The corrosion rates increased when TDS increase as shown in figures (4) & (5) at pH 7.5 & 8, where corrosion rates in filtered water less than in raw water at the same pH.

From figure (4) it can be seen that the best pH with minimized corrosion rate is equal to 8 & 1800 TDS (calcium and magnesium). But under certain conditions such as the presence of salts, although in alkaline solutions; the corrosion rate increase with time to a greater value in de-mineralized water with $\text{pH} > 7$.

These results above occurred because that the pH values below 4, hydrogen ion replaces oxygen as the oxidizing agent, pH below 8, essentially all the alkalinity is in the form of bicarbonate, and the pH is significantly above 9, most of the alkalinity is in the form of carbonate and hydroxyl [5].

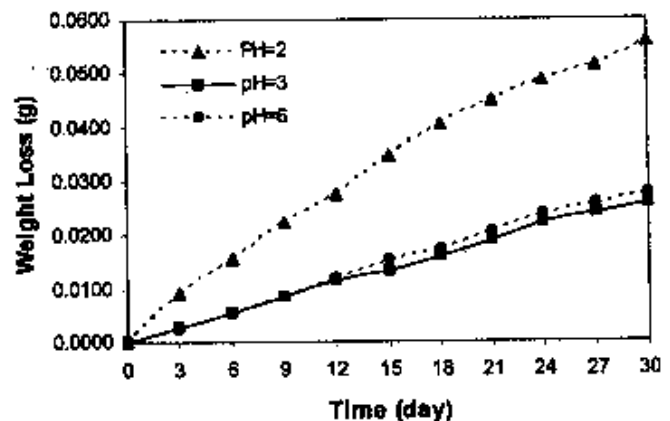


Fig.(2) The relationship between weight loss and time in de-mineralized water at pH 2 , 3 & 6 for CS.

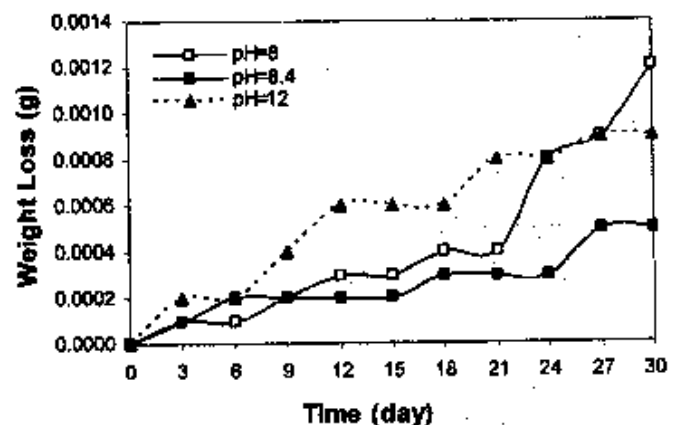


Fig.(3) The relationship between weight loss and time in de-mineralized water at pH 8 , 8.4 & 12 for CS.

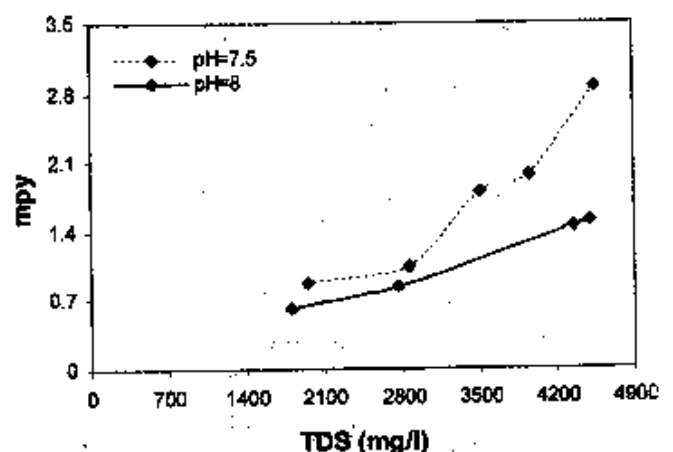


Fig.(4) The relationship between corrosion rate (mpy) and TDS in filtered water at pH 7.5 & 8 for CS.

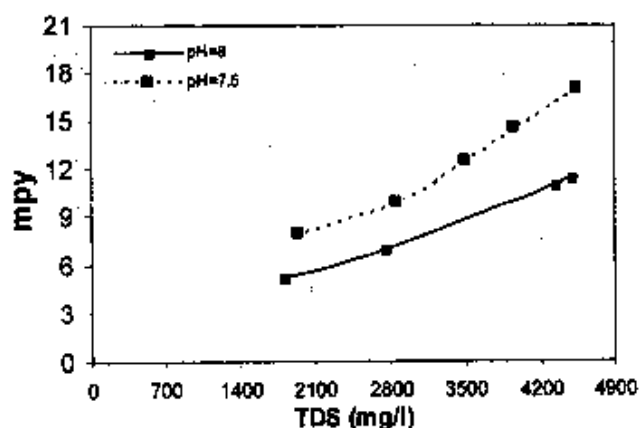


Fig.(5) The relationship between corrosion rate (mpy) and TDS in raw water at pH 7.5 & 8 for CS.

5.2. Anodic polarizations

The values of the electrochemical parameters obtained in raw and filtered water, at 32 °C are shown in table 1. ,and Figure(6) showed that the corrosion rate in raw water greater than corrosion rate in filtered water, these measurements based on Tafel plots in which the specimen is scanned from the open circuit potential to a value ± 250 mV ,while recording potential versus logarithm current density at stagnant condition, this data can yield Tafel constants which are used to compute corrosion rates,during polarization at all current densities ranging from $(0-10^6)$ nA/cm² the potential was slightly drifted within the applied range ± 250 mV.The results of all polarization experiments are presented as plot of the electrode potential compared to the standard calomel reference electrode in volts versus logarithm current density in nA/cm² . The anode potential is displaced in appositve

direction by the anodic polarization and the cathode potential in a negative direction by the cathodic polarization, the corrosion potential and the corrosion current is appear as a point of intersection between the two rectilinear polarization curves [2],the results in table (1) are similar to the results in reference[6],where the corrosion rates of carbon steel are more than 0.6mpy which depended on many factor such as percent of carbon content and bacterial effect.

However, anodic and cathodic sites continually shift position, and they exist within a continuously conductive surface, making direct measurement of I_{CORR} impossible. small, externally-imposed, potential shifts (ΔE) will produce measurable current flow (ΔI) at the corroding electrode. The behavior of the externally imposed current is governed, as is that of I_{CORR} , by the degree of difficulty with which the anodic and cathodic corrosion processes take place. The greater the difficulty, the smaller the value of I_{CORR} , and the smaller the value of ΔI for a given potential shift. In fact, at small values of ΔE , ΔI is directly proportional to I_{CORR} , and hence to the corrosion rate. This relationship is embodied in the theoretically derived Stern-Geary equation [3]:

$$\Delta E/\Delta I = \frac{b_a \times b_c}{2.3 I_{CORR} (b_a + b_c)} \quad \dots\dots (4)$$

Where; b_a : Tafel slope for the anode region.
 b_c : Tafel slope for the cathode region. i_{corr} :
 Corrosion current, ΔE : potential difference (V)
 and ΔI : current difference (A).

The most popular application of electrochemical corrosion techniques is the determination of the rate of uniform corrosion. Based on the Stern-Geary relationship, the measurement of corrosion rate with electrochemistry has a theoretically sound foundation and is used every day in thousands of laboratories with excellent results. The two electrochemical techniques for corrosion rate determination are polarization resistance and Tafel plots, where, Tafel plots allow the direct measurement of the corrosion current from which the corrosion rate can be quickly calculated [7].

Table (1) Electrochemical results of CS polarized in raw water (TDS=27 mg/l) and filtered water at 32 °C, 1atm and under static conditions .

medium	b_c Volt/decade	b_a Volt/decade	R_p Ohm	i_{corr} nA/cm ²	E_{corr} Volt	Corrosion rate mpy
Raw water	0.319	0.138	8.168E3	5.121E3	-0.393	2.366
Filtered water	0.226	0.196	3.162E4	1.440E3	-0.436	0.665

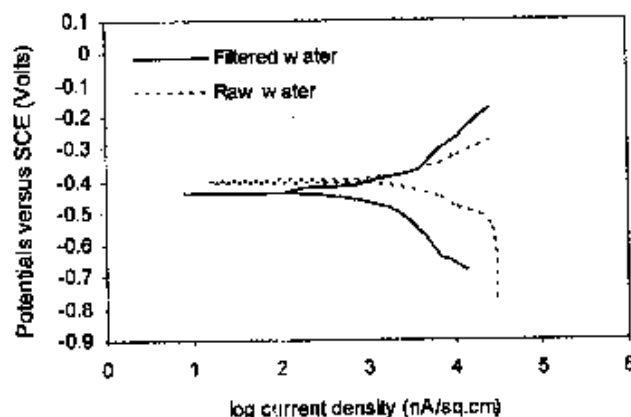


Fig.(6) Polarization curve for CS in filtered water and raw water at 32 °C, 1atm.

6. Conclusion

- I. The corrosion rate is very dependent on the pH value and the environmental conditions with increasing TDS.
- II. The weight loss increases with time. But, due to the influence of the environmental conditions the linearity of the change of corrosion rate with time can not be expected, the weight loss was found at minimum value in de-mineralized water at pH 8.4, and greater value in de-mineralized water at pH 2.
- III-The rate of corrosion was found at minimum value in 1800 TDS in filtered water and raw water at pH 8.

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