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Study the Effect of the Corrosion Medium on the Corrosion Rates of Oil Pipes Made of Carbon Steel and Reinforced with a Composite Material

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ABSTRACT

External corrosion of buried pipelines is easily influenced by the complex subterranean environment, including soil resistivity, pH, dissolved ion concentration, water content, and coating state. For pipelines to be intrinsically safe, external corrosion rate prediction is therefore crucial. This paper studied the effect of immersion medium on the corrosion rates of samples made of low-carbon steel. The samples were taken and prepared using cutting, grinding, and cleaning the surface of the samples. A polymeric coating was produced of an epoxy-based superimposed material and reinforced with silicon carbide particles (SiC), zinc oxide powder (ZnO), and titanium dioxide powder (TiO_2). The mixing ratio of the two components is 3:1. The samples were immersed amid the oil, Majnoon field in Basra Governorate in Iraq, as well as the use of sulfuric acid ($H2SO_4$) and hydrochloric acid (HCL) as corrosion media. The lowest corrosion rates were obtained for the titanium dioxide-coated specimens in sulfuric acid and hydrochloric acid, which were 0.00009 mm/y and 0.0001 mm/y respectively. The weight loss of the specimens immersed in sulfuric acid was higher than those immersed in hydrochloric acid.

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Study the Effect of the Corrosion Medium on the Corrosion Rates of Oil Pipes Made of Carbon Steel and Reinforced with a Composite Material

دراسة تأثير وسط التأكل على معدلات التأكل لانابيب النفط المصنوعة من الصلب الكاربوني والمعززة بمادة متراكبة

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الملخص

يتأثر التآكل الخارجي لخطوط الأنابيب المدفونة بسهولة بالبيئة الجوفية المعقدة، بما في ذلك مقاومة التربة، ودرجة الحموضة، وتركيز الأيونات المذابة، ومحتوى الماء، وحالة الطلاء. لذلك، لكي تكون خطوط الأنابيب آمنة جوهريًا، فإن التنبؤ بمعدل التآكل الخارجي أمر بالغ الأهمية. درست هذه الورقة تأثير وسط الغمر على معدلات تآكل العينات المصنوعة من الفولاذ منخفض الكربون. تم أخذ العينات وإعدادها باستخدام القطع والطحن وتنظيف سطح العينات. تم إنتاج طلاء بوليمري من مادة متراكبة تعتمد على الإيبوكسي ومعززة بجزيئات كربيد السيليكون (SiC) ومسحوق أكسيد الزنك (ZnO) ومسحوق ثاني أكسيد التيتانيوم (TiO_2). نسبة خلط المكونين هي 3: 1. تم غمر العينات وسط النفط، حقل مجنون في محافظة البصرة في العراق، وكذلك استخدام حامض الكبريتيك (H_2SO_4) وحمض الهيدروكلوريك (HCL) كوسط تآكل. تم الحصول على أقل معدلات التآكل للعينات المطلية بثاني أكسيد التيتانيوم في حامض الكبريتيك وحامض الهيدروكلوريك، والتي بلغت 0.00009 مم/سنة و0.0001 مم/سنة على التوالي. كان فقدان الوزن للعينات المغمورة في حامض الكبريتيك أعلى من فقدان الوزن للعينات المغمورة في حامض الهيدروكلوريك.

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Nomenclature Symbol	Description	Unit
ΔW	Weight lost [Eq. (1)]	(gm)
w	Weight sample [Eq. (1)]	(gm)
CR	Corrosion rate [Eq. (3)]	(mm/y)
K	Constant value 87.6 [Eq. (3)]	
D	Density (g/cm^3) [Eq. (3)]	
A	Surface area [Eq. (3)]	(cm^2)
T	Exposure time [Eq. (3)]	(hours)

subscripts symbols	
i	Initial weight before immersion [Eq. (1)]
o	Weight after immersion [Eq. (1)]
m	mean [Eq. (2)]

Abbreviations Table

Symbol	Description Unit		
LM	Levenberg-Marquardt's	CNN	Convolutional Neural Networks
RF	Random Forest	RMSE	Root Mean Square Error
DNN	Deep Neural Network	ASTM	American Society Testing Material
		FESEM	Field Emission Scanning Electron Microscopy

Introduction

One of the main issues facing the oil and gas sectors, which costs enormous quantities of money annually, is pipeline corrosion. The coating serves as the pipes' initial line of protection from the corrosive soil where they are buried. The paint's rate of adherence to the metal surface determines how well it works. Among the elements that improve long-term coating efficiency are initial adhesion and durability in contact situations. In the oil and gas sector, pipelines play a critical role in safely transporting products, both onshore and offshore. Usually, carbon steel is used to make them. As a result, one of the main threats to the pipeline's serviceability is corrosion. Pipeline corrosion is dependent on time, and as pipes age, they corrode more and more (Birkland and Dann, 2018). Therefore, it is necessary to assess and predict the corrosion growth rates to avoid pipeline failures or leakages. In addition, prediction of corrosion growth rate can be used to carry out risk assessment to make decisions by pipeline operators (Zardasti, L., et al., 2015). Composite materials are materials that are produced by combining two or more different materials or components in a way that produces materials that satisfy specific chemical, mechanical, and physical specifications. One or more continuous phases submerged in a continuous phase make up a composite. The continuous phase is referred to as the matrix, whereas the discontinuous phase, which is often stronger and harder than the continuous phase, is called the reinforcement phase (Khidhir and Alhaffaf, 2019). Metals are being replaced by composites in machine tools more and more. They perform better than metals at high temperatures and do not experience potentially hazardous flaws like fatigue and fractures since they are stronger and lighter. Furthermore, the adoption of novel and cutting-edge materials that not only reduce dead weight but also absorb shock and vibration through specially designed microstructures has become increasingly important due to the need for composite for lighter construction materials and more seismic-resistant structures. Nowadays, composites are widely employed in the strengthening and rehabilitation of older structures that need to be adapted to become earthquake-resistant or to fix damage brought on by seismic activity. In contrast to traditional materials like steel, the qualities of a composite material can be created with the structural concerns considered. Both material and structural design are involved in the creation of a composite structural component (Ngo, T.-D.,2020). The gas pipelines move gases from the source of their generation to end customers over great distances. The first set of characteristics of gasoline pipeline systems are their alignment with predefined requirements on the delivery region and series webpage, their low value in terms of opportunity utilization, their high funding, their low operating costs, and their long payback period (European, 2013). The capacity risk associated with the transit fuel pipeline system is related to corrosion degradation and operational stress. Approximately five percent of Slovakia's gross national product is lost to corrosion each year in gas-producing companies (Burda, 2007). The importance of the gasoline pipeline corrosion problem entails each discount of their supplier existence and polluting of the environment in emergencies (Hagarová, 2015). This suggests the high monetary relevance of protection costs for underground systems. Among the most prominent studies and research published in reducing and limiting corrosion such as:

According to Alfred, B.O. et al., (2022), this work created a neural network-based model for forecasting the rate of corrosion in gas and oil pipelines. To improve predicted accuracy, the model's training was optimized using Levenberg-Marquardt's (LM) backpropagation technique. MATLAB was used to validate the created model. A 97%

accuracy rate was later found when the model was tested using an industrial dataset; this represents improvements of 17.7% and 6.6% over the Abbas artificial neural network model and the Obaseki analytical model, respectively. (Obaseki, Martins, et al. 2023) This research aimed to create a multiphase flow simulation model that takes erosion into account when calculating the rate of corrosion of gas and oil pipelines. Apart from corrosion caused by carbon dioxide (CO_2) and hydrogen sulfide (H_2S), the current model additionally considers the effects of chloride concentrations. The current model is easily relevant for estimating corrosion rates for industrial applications since it assesses and reflects a thorough grasp of corrosion in a saline environment. According to the model's output, the forecast accuracy is roughly 85%. The accuracy of the model's predictions is confirmed by field data collected in a variety of environmental settings. The current model's predictions and the field data agree quite well. (Fang, Jian, et al. 2023) This study used OLI Studio Corrosion Analyzer, a program built on strict first principles, to simulate hundreds of corrosion scenarios of natural gas and crude oil pipelines. With simulation, thousands of datasets were produced. Following that, two machine learning algorithms Random Forest (RF) and Cat Boost were created and applied to forecast the internal corrosion rate (CR) by pipeline operating conditions. The models for crude oil pipeline CR forecasts included five key features temperature (T), molar concentrations, velocity (v), and pH value (pH) to achieve high prediction accuracy. Similarly, by employing six crucial features stream composition, pressure (P), velocity (v), and temperature (T) the models for natural gas pipeline CR forecasts were able to achieve excellent prediction accuracy. In terms of forecasting the internal corrosion rates of pipelines carrying natural gas and crude oil both the RF and Cat Boost Corrosion Rate models performed admirably. (Guang, Yu, et al 2024) By extracting corrosion characteristics data, a deep neural network (DNN) was utilized to estimate the exterior corrosion rate of underground pipes. Additional weighting operations of corrosion components are conducted using an attention method. The results of the analysis of the external corrosion factors dataset, data reduction, and standardization of the DNN-attention mechanism model demonstrate that the primary governing elements are pipeline age and soil bulk density, while sulfate ion concentration and redox potential have less of an impact. In comparison to convolutional neural networks (CNN), CNN-residual, and DNN, the external corrosion rate value predicted by the DNN-attention mechanism model is the one that is closest to the true reality, with an evaluation index root mean square error (RMSE) of 0.0064 and prediction accuracy of 91.91%. Using a publicly available pipeline corrosion dataset, demonstrates that it is reasonable to use the DNN-attention mechanism to estimate the exterior corrosion rate of a pipeline. (Chohan, Imran Mir, et al. 2024) The purpose of this study is to look at how seawater characteristics such as temperature, pH, and salinity affect the microhardness and exterior corrosion behavior of carbon steel pipes used for offshore oil and gas. 28 days of immersion experiments were conducted in accordance with ASTM G-1 guidelines, replicating controlled artificial marine habitats with different temperatures, salinities, and pH levels. Analysis of the corrosion morphology is also done using field emission scanning electron microscopy (FESEM). According to the findings, the corrosion rate can be lowered by 28% by raising the salinity from 33.18 to 61.10 ppt. The corrosion rate, on the other hand, is significantly impacted by changes in seawater pH; a drop in pH from 8.50 to 7 results in a 42.54% rise in corrosion rate. On the other hand, the most significant factor was the seawater temperature, which led to a 10.99% decrease in the microhardness of offshore pipes and a 76.13% increase in corrosion rate. Every year, corrosion costs the energy sector billions of dollars. Unfortunately, there aren't enough publicly available datasets on pipeline corrosion, which makes it challenging to precisely forecast and stop corrosion. However, previous studies have indicated protection methods using Agaricus Bisporus as an environmentally

friendly inhibitor for mild steel against corrosion at room temperature. However, our current study proposes a new and effective method for protecting carbon steel from corrosion by coating carbon steel with a polymeric coating consisting of a nanocomposite material and studying the effectiveness of the coating in reducing the corrosion rates of low carbon steel, especially when immersed in acidic media and crude oil media. The polymeric coating from a polymer-based composite material reinforced with inorganic materials with specific weight ratios and certain volumetric portions of the reinforcing material to be coated on the external and internal surfaces of transport and production pipelines to reduce the corrosion phenomenon in pipelines of production lines because of exposure to the atmosphere, moisture, sunlight, and other external conditions. The coating is tested after it has been manufactured to specifications, and various checks are carried out to ensure that it is effective for its intended purpose.

MATERIALS AND METHODOLOGY

An unsaturated Polypol3455 epoxy was used as matrix material, manufactured by the Turkish company (Poliya Composite Resins and Polymers, Inc.). The Turkish company (Akpa Organic Peroxides, Initiators and Paint Driers) type (Akperox A1) mixed with a ratio of 3 g of hardener for each 100 g of unsaturated epoxy resin. Silicon carbide particles (SiC), commercially known as carborundum Figure 1 shows microscopic images of the particles used in the research, and Table 1 shows the mechanical and physical reinforcement characteristics. Table 2: Properties of Epoxy according to International Standards**.**

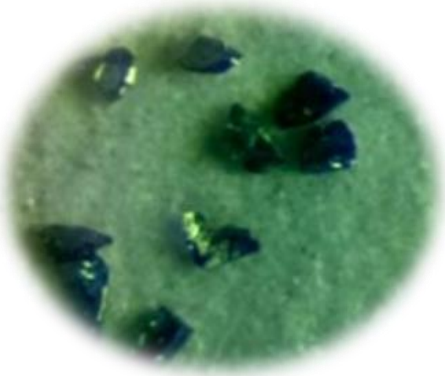


Fig. 1. micrographs of the particles used in the research (80X).

Table 1: Mechanical and Physical Characteristics of Reinforcement

Reinforcement Type	Modulus of elasticity (Gpa)	Poissons ratio	Specific heat (J/g.°C)	Thermal conductivity (W/m.k)	Density (g/cm3)
SiC	200-300	0.2	0.67	52	3.2
ZnO	800	0.358	0.494	23.4	5.61
TiO2	177.24	0.27	683	4.8	4.23

Table 2: Properties of Epoxy according to international standards.

Density (gm/cm3)	Young's Modulus (GPa)	Poisson,s ratio	Coefficient of thermal expansion 10-6	Tensile strength (Mpa)	Percent Elongation%
1.2 - 1.5	2 - 4.5	0.38	75	40 - 90	2

Sample preparation of carbon steel, low carbon steel (B), is used. Pieces of medium-carbon steel were taken, and due to the presence of some sediments and rust on the surface, the grinding process was carried out as well as the cleaning process with the use of a brush. After the cleaning process was completed, mechanical operations were carried out, which included cutting and grinding, until all samples were obtained in a parallel manner with rectangular dimensions (length = 34mm, width = 25mm, thickness = 5mm). The samples

were punctured with an electric drill from one of the angles with a diameter of 3 mm to hang them amid corrosion. The samples were cleaned by both fine and coarse sandpaper, where the type of paper was used (AA-400), (AA-80). After all the cleaning, cutting, and drilling operations are completed, the samples are washed with distilled water and dried using an electric dryer, and each sample is weighed separately by the scale and on the scale. The samples were classified so that all four samples were selected with each other so that they are close. Weigh it and write the sample number on it as shown in Figure 2 and Table 3. Show weigh each sample before immersion in the acid.

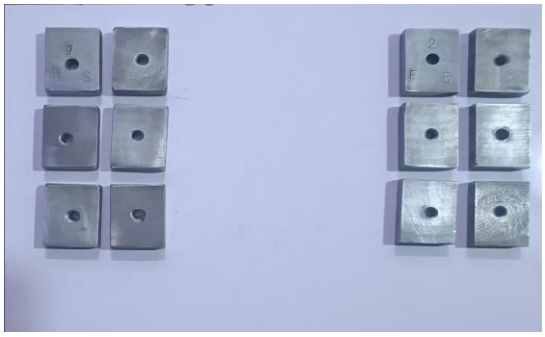


Fig. 2. Low carbon steel samples test

Table 3: Weigh each sample before immersion in the acid.H_2So_4 and HCL and Oil

Immersion time (day)	Sample Number	Sample Weight (gm)(Wo)	Sample Weight (gm)(Wo)
15,45	B1(METALIC)	65.7	67.7
	B2(PURE)	68.2	67.5
	B3(ZnO)	68.0	69.0
	B4(SiC)	67.3	68.5
	B5(Oil)(TiO_2)	66.0	66.0
	B6(TiO_2)	65.1	67.7

The sample coating was prepared by mixing epoxy resin with SiC particles according to selected weight ratios, mixing manually for ten minutes, and then adding the hardener gradually according to the mixing ratio of 3:1. The second layer was mixing epoxy resin with zinc oxide powder ZnO and adding the hardener. While the third layer was mixing epoxy with titanium dioxide powder TiO_2 and adding the hardener. Figure 3 shows the reinforcing powders, while Figure 4 shows the epoxy and hardener.

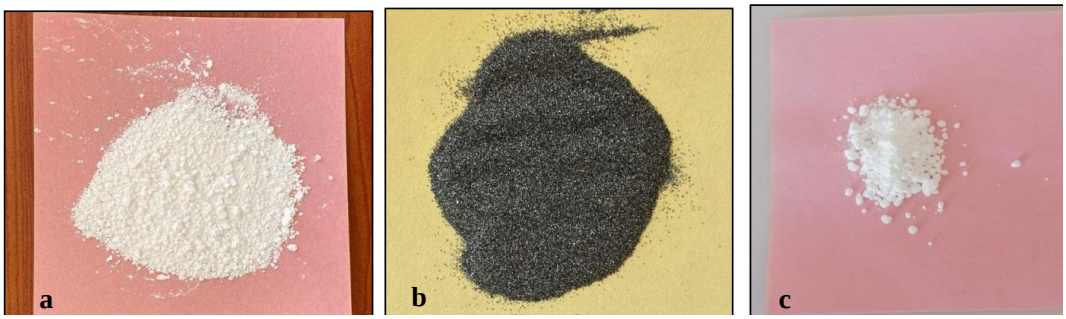


Fig. 3. Reinforcing materials used in polymer coatings: a. zinc oxide powder, b. silicon carbide particles, and c. TiO2 powder



Fig. 4. Epoxy and hardener used in polymer coatings

EXPERIMENTAL TEST

The first test was immersion. The first period lasted 15 days (360 hours), and the second period lasted 45 days (1,080 hours). The second test was corrosive media; majnoon oil was used as the corrosion medium. Acid (10% H_2SO_4) and (5% HCl). Corrosion tests were carried out on the pre-prepared carbon steel samples by completely immersing them. In liquid corrosion selected so that they were hanging thread dielectric completely immersed in the glass aquarium, which contains the circles of various corrosion, and after it was suspended vertically in the basins glass designed for this purpose left open any exhibition basins to air during the specified period, we have all corrosion tests were carried out at room temperature, as shown in Figure 5. After the period of exposure to the corrosive medium ended, the samples specified for that period were removed from the corrosive medium and then cleaned of the rust layers and sediments using a soft brush and water first. The samples were washed with distilled water and then dried with an electric dryer.



Fig. 5. Low - carbon steel samples in a container during immersion medium

Each sample to find the final weight to calculate the weight lost, I have used the most in this search method Weight Loss to calculate the rate of corrosion, a method called this method sometimes by gravimetric method, which is widely used to find, especially those general corrosion rates that cause significant weight loss. Steps to measure the corrosion rate by the method of weight loss:

Preparation of samples with certain geometric shapes, and the most used of these shapes is rectangular. Weigh the samples with a sensitive scale and calculate their original weight (W_o) in milligrams in the samples as shown in Figure 6. Calculate the surface area exposed to solution (A) in cm^2. Submerge the samples in the medium (solution) for a sufficient period (T) measured in days until it is corrosion.



Fig. 6. Low carbon steel Sample weight

The samples were removed from the edible medium (solution), then washed with distilled water to remove the effects of the solution, then dried and cleaned from corrosion products. Weigh the samples after immersion (W), then calculate the weight change. The lost weight is calculated by the following equation: (Chohan et al., 2024; Pearson and Cousins, 2016).

Weight lost (ΔW) = weight of the sample before immersion - weight of the sample after immersion

$$\Delta W = W_i - W_o \quad \text{..... Eq. (1)}$$

Mean weight loss = total weight lost for all samples/3

$$\Delta W_m = \frac{\sum \Delta W}{3} \quad \text{..... Eq. (2)}$$

The unit of measure of the rate of corrosion (corrosion in millimeters per year and written as (mm/year) or (mm/y), depending on the main function, which is the loss in weight (ΔW), during the test period (T). As for the test constants in this research, they are steel density (D), and area exposed. The following equation was used to calculate the corrosion rate (Chohan et al., 2024; Pearson and Cousins, 2016).

$$CR = \frac{K^* \Delta W}{D^*A^*T} \quad \text{..... Eq. (3)}$$

Where:

CR: Corrosion rate

K: a constant value equal to (87.6) until the corrosion rate becomes measured in (mm/y)

ΔW: Weight lost (mg).

D: the density of the steel (7.85g/cm3).

A: Surface area exposed to abrasion (cm2). T: exposure time in hours (hours)

The area of the surface subject to corrosion is calculated by the following equation and Figure 7:

$$A = 2 * [(a * b) + (b * t) + (a * t)] \text{ .....(4)}$$

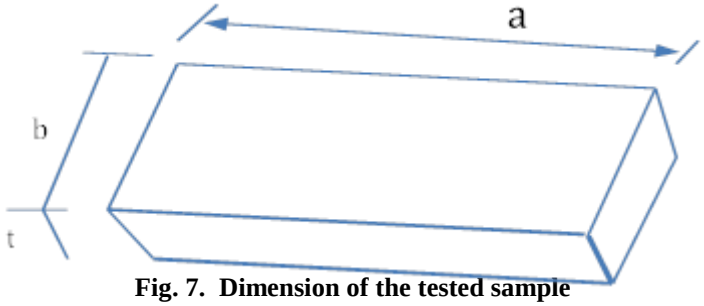


Fig. 7. Dimension of the tested sample

where:

a: sample length.

b: sample width.

t: the thickness of the sample.

RESULTS AND DISCUSSIONS

Effect of sulfuric acid on weight loss and corrosion rates

The weight loss of the samples was calculated through equation 1, and according to the results in Table 4, a significant change was noticed in the weight loss before immersion and after immersion in sulfuric acid (Fig. 8). The amount of old and new weight loss for low carbon steel samples shows the gradient of weight loss for samples coated before immersion, the amount of weight loss over periods of 15 days, and the weight loss during 45 days. Where the highest values of weight loss were recorded in the samples coated with zinc oxide and the metal sample, and the reason is that the zinc oxide powder has a weak resistance to corrosion with sulfuric acid, and for the metal sample in a sample free from the coating layer, the effect of the acid was on the surface of the sample directly. As for the samples immersed in oil, it has been proven that the weight loss changed during the specified periods, and therefore we need longer periods to obtain a noticeable difference in the weight loss of the samples immersed in oil. The reason is also due to the high acidity of sulfuric acid and the effect of oil immersion medium on corrosion rates. As for the corrosion rates, they were calculated according to equation 3.3, and the results were recorded. We notice the values of the corrosion rates vary between the samples during the periods immersed in them. The lowest corrosion rate was recorded for the samples immersed in sulfuric acid and coated with titanium dioxide, compared to other samples that were dipped in oil and coated The average weight loss was calculated through equation 3.2, and the results were like the coated samples in losing weight compared to the uncoated metal sample. The highest percentage of weight loss compared to the sample coated with titanium dioxide. As for the sample immersed in oil and coated with titanium dioxide, it was noted that the average weight loss was confirmed.

Table 4: Show The lost weight

H_2SO_4					
Immersion time (day)	Sample Number	Sample Weight (gm)(W_i)	Sample Weight (gm)(W_o)	lost weight(ΔW) = $W_i - W_o$	CR (mm/y)
15	B1(METALIC)	65.7	63.8	1.9	0.0025
	B2(PURE)	68.2	66.7	1.5	0.002
	B3(ZnO)	68.0	66.1	1.9	0.0025
	B4(SiC)	67.3	67.0	0.3	0.0004
	B5(Oil)(TiO_2)	66.0	66.0	0	0
	B6(TiO2)	65.1	64.6	0.5	0.0006
45	B1(METALIC)	63.8	60.5	3.3	0.001
	B2(PURE)	66.7	65.3	1.4	0.0006
	B3(ZnO)	66.1	65.4	0.7	0.0003

	B4(SiC)	67.0	63.3	3.7	0.001
	B5(Oil)(TiO_2)	66.0	66.0	0	0
	B6(TiO_2)	64.6	64.4	0.2	0.00009

Effect of HCl on weight loss and corrosion rates

The weight loss of the samples was calculated through equation 3.1, and according to the results in Table 5 and Figure 9, a significant change was observed in the weight loss before immersion and after immersion in hydrochloric acid, Figure 9. The amount of old and new weight loss for low carbon steel samples shows the gradient of weight loss for samples coated before immersion, the amount of weight loss over periods of 15 days, and the weight loss during 45 days. Where the highest values of weight loss were recorded in the samples coated with zinc oxide and the metal sample, and the reason is that the zinc oxide powder has a weak resistance to corrosion with hydrochloric acid, and for the metal sample in a sample devoid of the coating layer, the effect of the acid was on the surface of the sample directly. As for the samples immersed in oil, it has been proven that the weight loss changed during the specified periods, and therefore we need longer periods to obtain a noticeable difference in the weight loss of the samples immersed in oil. The reason is also due to the high acidity of hydrochloric acid and the effect of oil immersion medium on corrosion rates. As for the corrosion rates, they were calculated according to equation 3.3, and the results were recorded. We note that the values of the corrosion rates are very close between the samples during the periods immersed in them. The lowest corrosion rate was recorded for the samples immersed in hydrochloric acid and coated with titanium dioxide compared to other samples immersed in oil and coated samples. As for the metallic sample, we noticed a clear change in weight loss and corrosion rates. Since the surface of the sample was not coated with a superimposed material, the effect of the acid was clear on the surface of the sample. The average weight loss was calculated through equation 3.2, and the results were similar to the coated samples in losing weight and less weight loss for the samples coated with titanium dioxide. As for the sample immersed in oil and coated with titanium dioxide, it was noted that the average weight loss was proven.

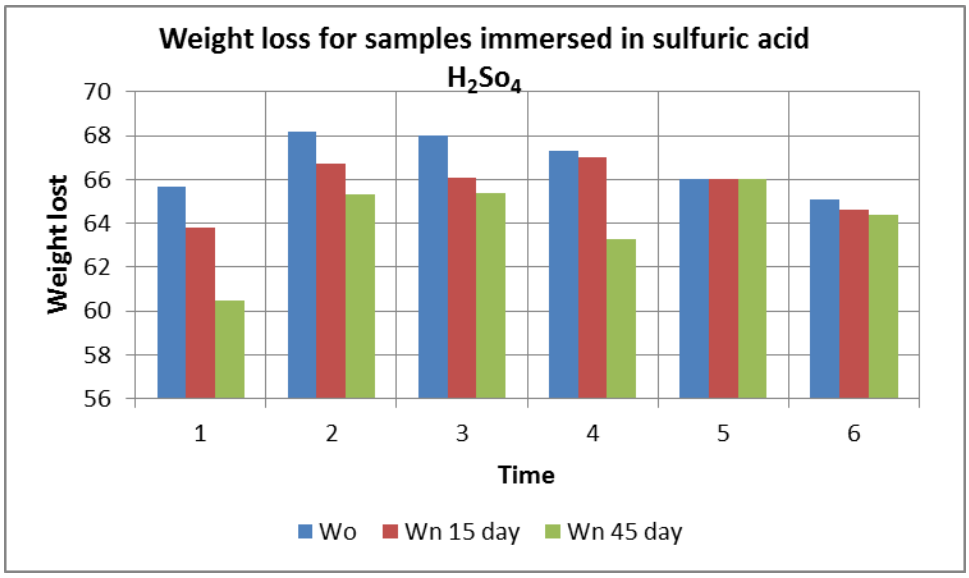


Fig. 8. Amount of old and new weight loss of low carbon steel samples

Table 5: Show The lost weight

HCL					
Immersion time (day)	Sample Number	Sample Weight (gm)(W_i)	Sample Weight (gm)(W_0)	lost weight(ΔW) = $W_i - W_o$	CR (mm/y)
	B1(METALIC)	67.7	66.1	1.6	0.002

15	B2(PURE)	67.5	66.3	1.2	0.001
	B3(ZnO)	69.0	67.6	1.4	0.001
	B4(SiC)	68.5	68.4	0.1	0.0001
	B5(Oil)(TiO2)	66.0	66.0	0	0
	B6(TiO2)	67.7	67.6	0.1	0.0001
45	B1(METALIC)	66.1	65.0	1.1	0.001
	B2(PURE)	66.3	66.2	0.1	0.0001
	B3(ZnO)	67.6	67.5	0.1	0.0001
	B4(SiC)	68.4	68.3	0.1	0.0001
	B5(Oil)(TiO2)	66.0	66.0	0	0
	B6(TiO2)	67.6	67.5	0.1	0.0001

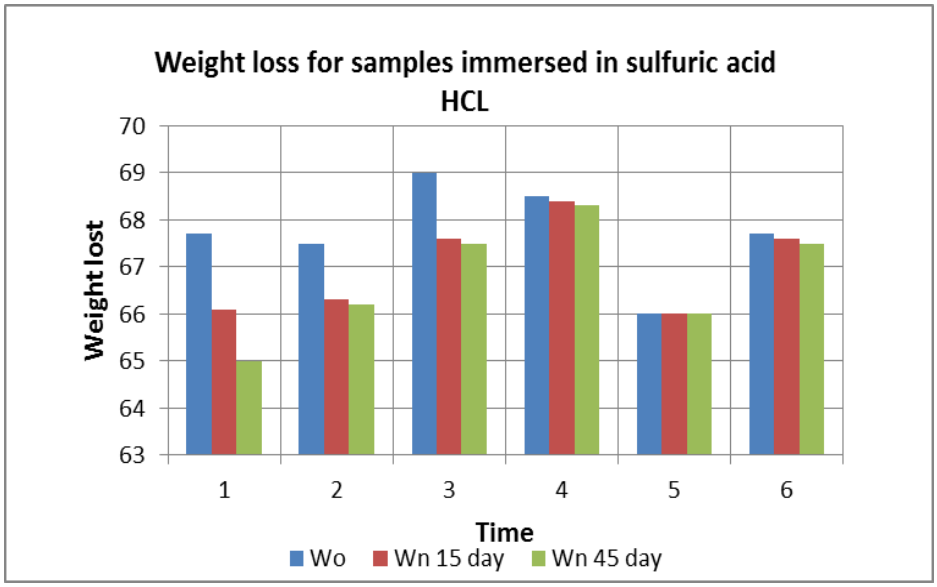


Fig. 9. Amount of old and new weight loss of low carbon steel samples

Conclusion

The results showed that the amount of weight loss for samples immersed in sulfuric acid was higher than the amount of weight loss in hydrochloric acid. The reason is due to the high acidity of sulfuric acid compared to hydrochloric acid, in addition to the dilution ratio of hydrochloric acid reaching 5% compared to 10% sulfuric acid. The corrosion rate of steel samples coated with titanium dioxide is significantly lower than the rest of the samples coated with silicon carbide particles and zinc oxide powder. This is because titanium oxides do not dissolve in water, dilute acids, or concentrated hydrochloric acid. And titanium dioxide powder, which is not easily dispersed when mixed and has high resistance to precipitation, so that the produced coating is more stable and satisfactory. Note that the steel sample coated with titanium dioxide and immersed in oil maintains its weight and the lack of corrosion rate compared to the values of weight loss and corrosion rate for the same percentages of coating the sample but immersed in acids with oil.

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