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A study of the pH performance in protecting carbon steel from corrosion compared to chemical compounds acting as corrosion inhibitors

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Abstract

The main objective of this research is to study the corrosion rates of carbon steel in low-salinity water, where the total dissolved solids (TDS) does not exceed 15.00 parts per million (ppm). This research was conducted by determining the corrosion rates of carbon steel, measuring the weight loss of carbon steel coupons immersed in water, and studying the effect of pH on reducing the corrosion of carbon steel coupons compared to some well-known chemical compounds, such as NaNO2 and Na3PO4, which are used as corrosion inhibitors in aqueous environments such as cooling systems, water tanks, pipes, pumps, and some other industrial processes.

From the results obtained, we concluded that at a pH 10, carbon steel was protected from corrosion, as evidenced by the low corrosion rates. In other words, the expensive chemical compounds used in chemical treatment as corrosion inhibitors could be replaced by adding caustic soda to raise the pH to 10. This would reduce the costs of chemical treatment processes for carbon steel used in low-salinity water systems

Introduction

Corrosion is considered one of the most serious problems facing industries, as aquatic environments are indispensable in industries and are considered one of the most important causes of corrosion. Corrosion is one of the most important factors causing economic losses and loss of safety due to damage to industrial units and facilities. Carbon Steel is one of the most widely used metals in their structural construction. When Carbon Steel is exposed to corrosion processes, changes in its physical and chemical properties occur. This leads to the deterioration and destruction of its properties resulting from chemical, physical, or electrochemical reactions between the metal and its surrounding environment, such as water .(1)

Therefore, numerous studies and research have been conducted to find ways to combat and reduce corrosion, protect these facilities and industrial units from damage, and reduce losses by protecting them from corrosion. One of the most common methods for protecting carbon steel from corrosion is the use of corrosion inhibitors. Nitrite and phosphate compounds are the most commonly used, but the high cost of chemical treatment of these materials has prompted the search for alternatives that reduce costs. ***(2)***

- Type of Corrosion Inhibitors

A corrosion inhibitor is a chemical additive, which, when added to a corrosive aqueous environment, reduces the rate of metal wastage. It can function in one of the following ways:

-Anodic inhibitors

as the name implies an anodic inhibitor interferes with the anodic process.

$$Fe \rightarrow Fe^{++} + 2e-$$

P

A

If an anodic inhibitor is not present at a concentration level sufficient to block off all the anodic sites, localised attack such as pitting corrosion can become a serious problem due to the oxidising nature of the inhibitor which raises the metal potential and encourages the anodic reaction .

Anodic inhibitors are thus classified as “dangerous inhibitors”. examples of anodic inhibitors include Nitrite (NO_2).(3)

-Cathodic Inhibitors

the major cathodic reaction in water systems is the reduction of oxygen.

$$\frac{1}{2}O_2 + H_2O + 2e \rightarrow 2OH^-$$

There are other cathodic reactions and additives that suppress these reactions called cathodic inhibitors. They function by reducing the available area for the cathodic reaction. This is often achieved by precipitating an insoluble species onto the cathodic sites. Zinc ions are used as cathodic inhibitors because of the Precipitation of Zn (OH) 2 at cat cathodic sites as a consequence of the localised high pH.(4)

Cathodic inhibitors are classed as safe because they do not cause localised corrosion.

- ***Used corrosion inhibitors***

1- Mainly anodic: Nitrites

Metal surfaces can be passivated (when there is no difference in potential between the anode and cathode areas and corrosion is minimized) by formation of a thin, impervious film that is formed by the addition of nitrite.

Nitrite are considered to be anodic inhibitors and provide passivation corrosion protection because they react and bond with the metal at the point of potential metal loss by forming a thin, protective, mono-molecular film, thus minimizing the anodic corrosion reaction and reducing metal loss.(5)

2-Mainly cathodic: Polyphosphates .

Polyphosphates form a protective film that acts as a barrier to the corrosive medium. This is due to the transfer of cations to the cathode and their deposition on the surface of the metal to be protected.

Corrosion Monitoring Methods

There are several methods, the most important of which are:

- Weight Loss Coupons

The principle of the weight loss coupons is very simple , A sample of the material in question of known weight is exposed to the process for a period of time. After it is carefully removed cleaned and weighed the change in weight is used to calculate the metal loss, which can be expressed as an annual loss rate (in millimeters or millimeters per year).(6)

- ***Experiments***

The corrosion rates of carbon steel in aqueous media were studied by comparing two different types of corrosion inhibitors: sodium nitrite at a concentration of 400 ppm as NO2 and phosphate at a concentration of 15 ppm as PO4. ***These concentrations are often used in chemical treatment processes for industrial waters containing dissolved solids less than 1500 ppm.***

The effectiveness of the corrosion inhibitors was compared to that of a pH 9 and pH 10 in protecting carbon steel from corrosion.

Tests were conducted on carbon steel coupons used to measure corrosion rates. Many of these coupons were obtained from an oil company and manufactured specifically for such studies.
By accurately measuring the difference between their weights before and after the experiment, and for specific time periods, corrosion rates can be accurately calculated.
Corrosion coupons are a simple and effective tool for quantitatively estimating the rate of corrosion and provide a visual indication of the type and form of corrosion.

- *Material and methods reagents*
    - $NaNO_2$ (98.9% purity)
    - Na_3PO_4 (98 % purity)
    - NaOH (99 % purity)
    - Distilled water was used to prepare the solution.

The coupons to be studied were thoroughly cleaned and their initial weight determined before the experiment. The piece of metal to be studied was tied to a thin plastic string, suspended from a holder, and immersed in the sample. The time the coupons were immersed was recorded as the start time of the experiment, and the required immersion time was calculated accordingly. After each week, the coupons were removed from the solution, dried, cleaned , and accurately weighed

Then we return the coupons to the sample after cleaning its surface well and weighing it. We calculate the difference in weight (ΔW) of the coupons after each week, and through the difference in weight we can calculate the corrosion rate (mpy)during the study period (five weeks). (7)

- ***Sample Testing***

Duration of the Study Five Weeks and water samples were 400 ml .
1- The first sample: A water sample free of any additives .
2- The second sample has a PH of 9 adjusted by adding sodium hydroxide .
3- The third sample has a PH of 10 adjusted by adding sodium hydroxide.
4- In the fourth sample The corrosion inhibitor $NaNO_2$ was added at a concentration of 400 ppm as NO2
5- In the fifth sample The corrosion inhibitor Na_3PO_4 was added at a concentration of 15 ppm as phosphate PO4 .

- Steps to measure corrosion rate using the weight-loss method:

1- Weigh the coupons using a sensitive balance and calculate their original weight in milligrams (W).
2- The surface area exposed to the solution is calculated in cm^2 (S).
3- Immerse the coupons in the medium (solution) for a sufficient period of time (T), measured in days, until corrosion occurs.
4- Remove the coupons from the corrosive medium (solution), wash them with distilled water to remove traces of the solution, and then dry and clean them of corrosion products.
5- Weigh the coupons after immersion (W),then calculate the change in weight.
6- The weight loss is calculated using the following equation:
Weight of coupons before immersion - Weight of coupons after immersion = (ΔW) Weight Loss .(8)

-Final weight and internal corrosion rate calculation from the following equation (9) :

$$CR= \frac{(W1 - W2) \times 365}{S*D(T2-T1)*0.00256}$$

Where:
CR: Internal corrosion rate estimated in [MPY].
[MPY]: milli-inches per year.
W1: Weight of the test coupons before placing it inside the tube [g].
W2: Weight of the test coupons after removing it from the tube [g].
S : Surface area of the coupons exposed to corrosion [cm2].
D: Density of the material from which the metal coupons is made [g/cm3].
T1: Date the coupons was placed [day].
T2: Date the coupons was removed [day].

➢ Inhibitor Efficiency

Using the following equation, the average efficiency of each corrosion inhibitor can be calculated by comparing it to the untreated sample over the same period . (10)

$$\% \text{ Protection} = \frac{(M_b - M_1) \times 100}{M_b}$$

Where:- M_b = The mpy reading for the blank .
M_1 =The mpy reading for the sample .

❖ *Results and discussion*

By studying the corrosion rates obtained during the testing period, as shown in the Table (1). the following points can be summarized:

	samples				
	Blank Corrosion rate	***PH 9 Corrosion rate***	***PH 10 Corrosion rate***	***NaNO2 Corrosion rate***	***PO4 Corrosion rate***
First week	1.4 mpy	0.42 mpy	0.01 mpy	0.0 mpy	0.5 mpy
Second week	3.9 mpy	3.4 mpy	0.10 mpy	0.0 mpy	1.0 mpy
Third week	4.2 mpy	3.7 mpy	0.11 mpy	0.03 mpy	3.2 mpy
Fourth week	4.77 mpy	3.8 mpy	0.11 mpy	0.14 mpy	4.4 mpy
Fifth week	6.1 mpy	3.8 mpy	0.11 mpy	0.65 mpy	4.7 mpy

Table (1) shows the corrosion rate

- ➢ The first, untreated sample exhibited the highest corrosion rate compared to the other samples, as illustrated in Figure (1). The initial reading in the first week was 1.4 mpy, and the corrosion rate subsequently increased, reaching 6.1 mm/year by the end of the five-week experiment. This was the highest corrosion rate obtained.

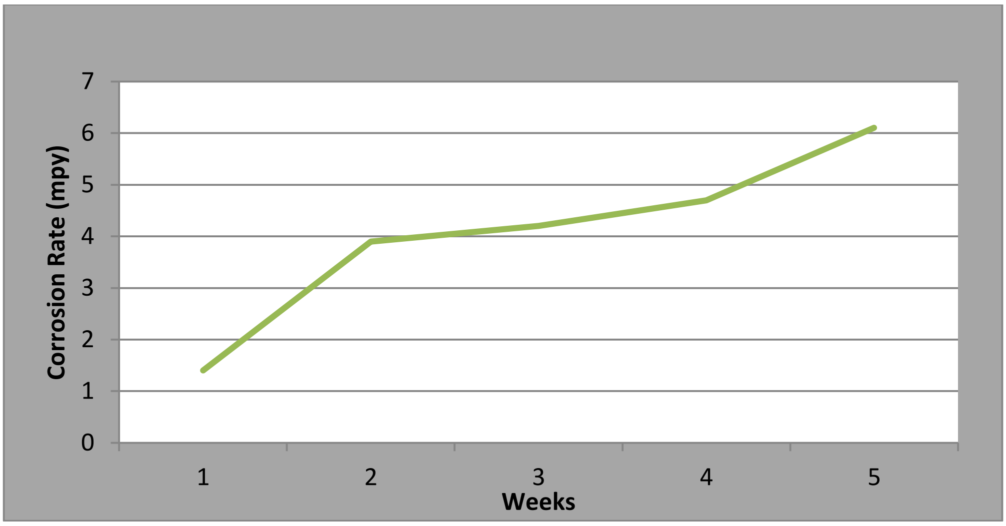

Figure (1) Blank sample

- The corrosion rate in the first week for the second sample, **at pH 9**, was 0.4mpy. As shown in Figure (2), these readings are considered good compared to the first untreated sample . In the second and third weeks of the same sample, there is an increase in the corrosion rate compared to the first week, where it was 3.4 *mpy* and 3.7 *mpy* . In the fourth and fifth weeks, there is a slight and almost constant increase in corrosion rates of 3.8 *mpy*. Overall the corrosion rates in this sample are considered high.

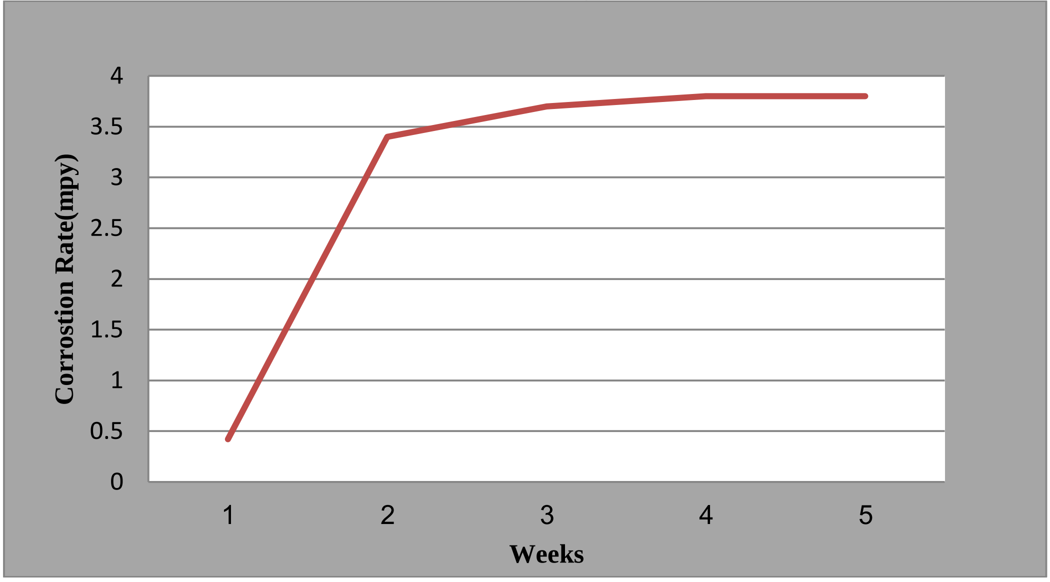

Figure (2) Sample PH 9

- In the third sample at **pH 10**, the corrosion rate in the first week was 0.01*mpy*, which is considered a very low rate. After that, there is a slight increase in the corrosion rate until it reached 0.11mpy, as shown in Figure (3). These corrosion rates are considered very satisfactory. In such a case, the metal is protected from corrosion due to the iron oxide layer that forms when the pH value is high(alkaline).

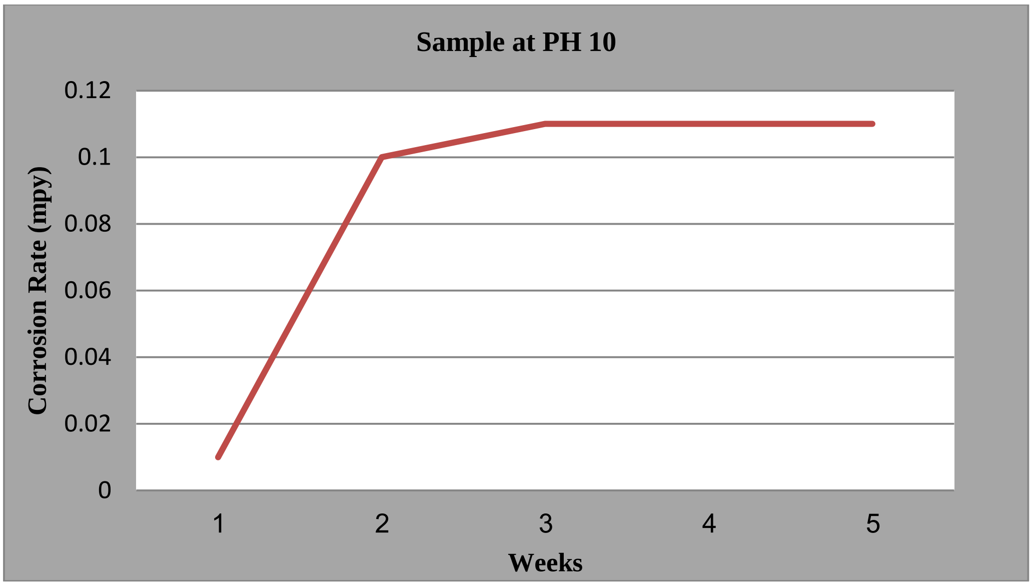

Figure (3) Sample PH 10

- As for the fourth sample, treated with a corrosion inhibitor at a concentration of 400 ppm as Nitrite, the corrosion rates in the first and second weeks were zero, the best corrosion rates obtained, as shown in Figure (4). The corrosion rate began to increase gradually from the third to the fifth week until it reached 0.65 mpy. The reason for the low corrosion rates in this sample is the layer that forms, where sodium nitrite acts as an inhibitor of anodic corrosion. Nitrite forms a protective layer of gamma iron oxide on the metal surface.This layer is formed by the reaction of nitrite with dissolved oxygen .

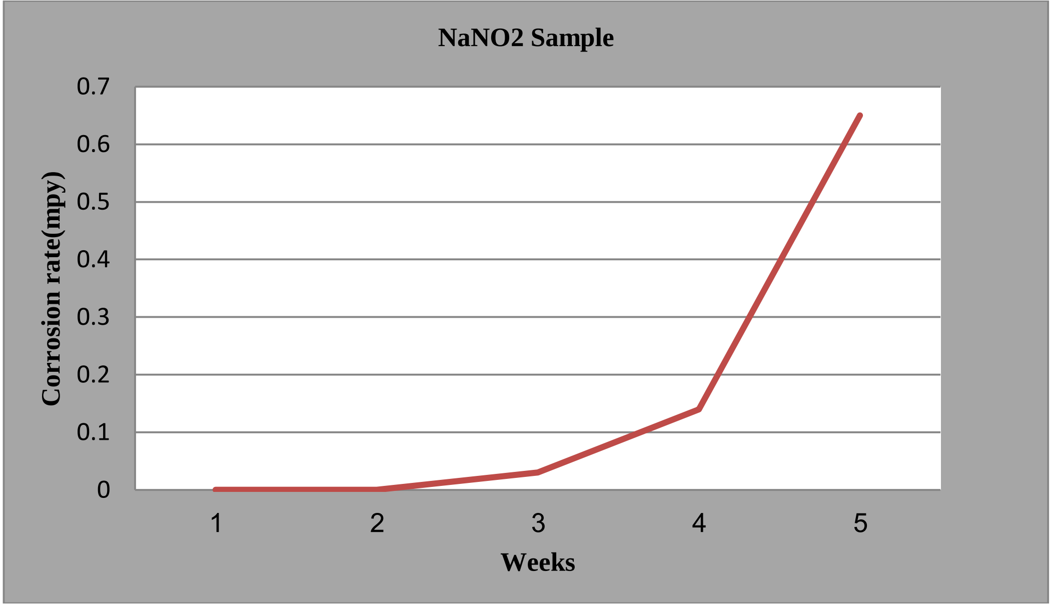

Figure (4) 400 ppm as NO2

- When studying the corrosion rates in the fifth sample, as shown in Figure (5), we observe an increase in corrosion rates starting from 0.5 *mpy* in the first week until reaching the highest corrosion rate of 4.7 *mpy* in the fifth week.
  The reason for the high corrosion rates in this sample is that polyphosphate has the ability to bind with calcium Ca^+ and magnesium Mg^+ ions present in water.Therefore, some of the polyphosphate is lost through reaction with the hardness instead of protecting the Coupons surface .

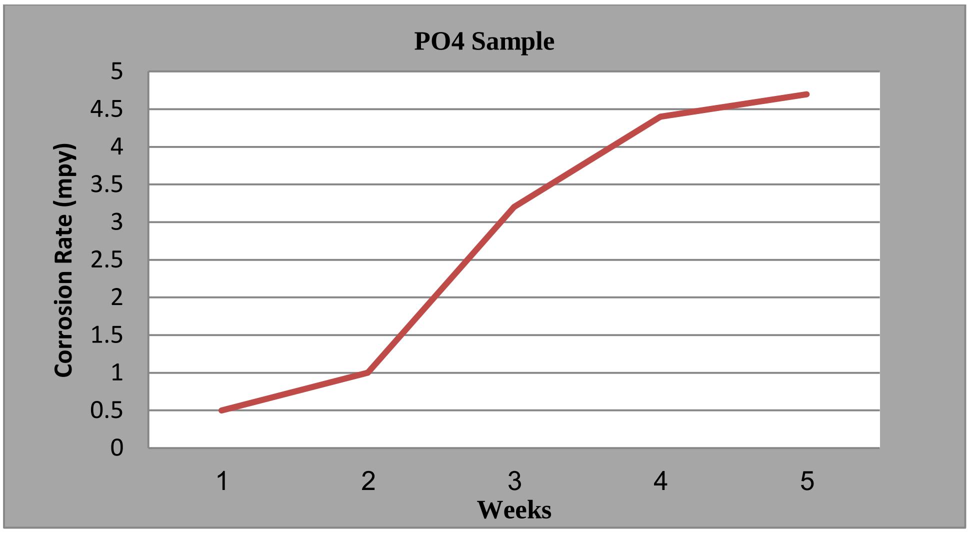

Figure (5) 15 ppm as PO4

- **Average corrosion rates**

The longer the duration of the corrosion rate testing and the subsequent calculation of the average corrosion rate, whether in field or laboratory tests, the greater the accuracy and reliability of the results.

Figure (6) (11) shows the average corrosion rates during the testing period(35 days).

It is evident that the sample with a pH of 10 showed the best reading at a concentration of 0.088 mpy, while the sample treated with sodium nitrite (NaNO2) came in second at a concentration of 0.1 mpy. These are excellent results, and the treatment processes successfully protected the metal from corrosion.

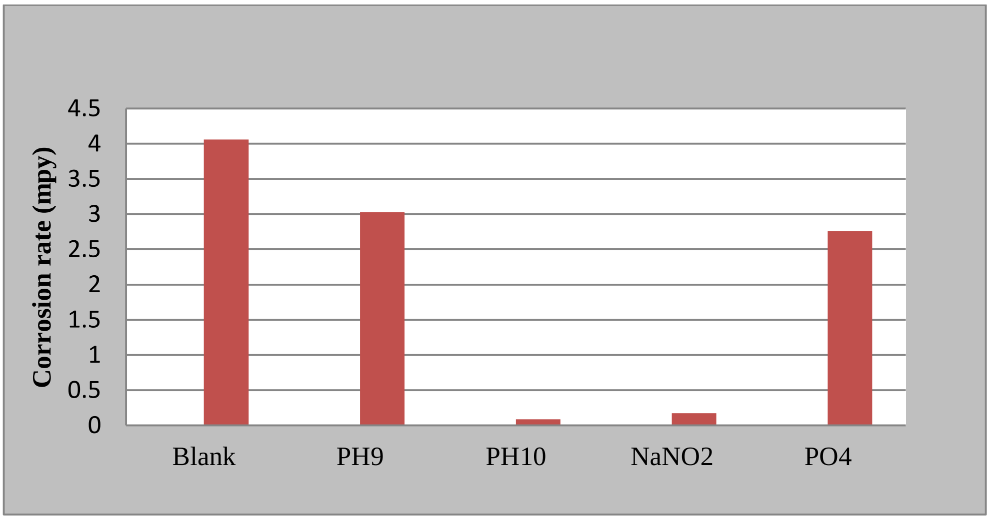

Figure (6) Average corrosion rates (35 days)

- ***Percentage efficiency in corrosion protection***

By studying the corrosion protection efficiency of the coupons compared to the untreated sample, as shown in Figure (7) , we found that the third sample with a pH 10, and the fourth sample treated with sodium nitrite (NaNO2), had the highest corrosion protection efficiency compared to the other samples, with efficiencies of 90% and 99%, respectively, which remained relatively stable throughout the testing period .

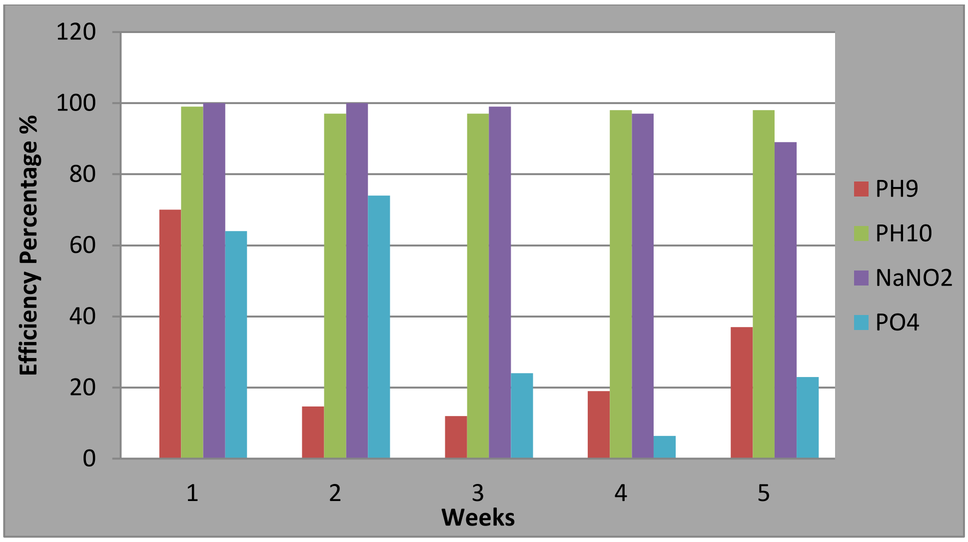

Figure (7) corrosion protection efficiency

➢ Conclution

Protecting industrial units from corrosion is crucial for human and equipment safety and for minimizing environmental pollution. By studying the results obtained, we can reduce the cost of chemical treatment processes for industrial units using cooling water with a total dissolved solids (TDS) level of 1500 ppm. These systems often use expensive corrosion inhibitors containing active ingredients such as sodium nitrite ($NaNO_2$) and polyphosphate (Na_3PO_4).

These inhibitors can be replaced by adding caustic soda to achieve a pH of 10. This value should not exceed 10 to avoid another type of corrosion that occurs at pH levels above 10.8 .

Caustic soda is less expensive than corrosion inhibitors and does not require close monitoring or laboratory testing .

➢ Recommendation:

1. Apply this experiment to a field sample after adjusting the pH of the water system to 10 with a dissolved salt concentration not exceeding 1500 ppm to compare the results obtained in the field with those obtained in the laboratory.

2. Repeat the experiment under the same conditions with a pH value of 10 for a longer period to determine the duration of the corrosion protection efficiency.

3. Repeat the experiment with a higher salt concentration to study the effect of this increase on corrosion rates.

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