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Measurement of Corrosion Rate in Storage Tank of Crude Oil

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Abstract

The aim of this work is to measure and analyze corrosion problems in storage tanks to find solutions. ASTM A283-C specimens are used for studying the corrosion rate of tank bottoms by two factors of crude oil: the first is salt content, and the other is sulfur percentage. Also, some specimens were coated with a special epoxy to determine the efficiency of corrosion resistance. The specimens immersed in crude oil with a high sulfur content suffered from a high corrosion rate. The maximum corrosion rates of every specimen were calculated, which at the sulfur percentage (5.4399 wt%) as corrosive medium were equal (2.49395 mm/year). While the other specimens for salt content did not suffer from any significant corrosion during the immersion period (six months), the coated specimens with epoxy were not affected by any corrosion.

Keywords: weight loss, sulfur percentage, salt content, carbon steel plate, and epoxy coating.

قياس معدل التآكل في خزانات النفط الخام

الخلاصة:

الهدف من هذا العمل هو قياس وتحليل مشاكل التآكل في خزانات النفط الخام لإيجاد الحلول المتعلقة بها. تم استخدام عينات ASTM A283-C لدراسة معدل تآكل قيعان الخزانات مع الاخذ بنظر الاعتبار عاملين مهمين في النفط الخام: الأول هو محتوى الملح، والآخر هو نسبة الكبريت. حيث تم طلاء بعض العينات بإيبوكسي خاص لتحديد كفاءة مقاومة التآكل. عانت العينات المغمورة في النفط الخام ذي المحتوى العالي من الكبريت من معدل تآكل مرتفع. تم حساب معدلات التآكل القصوى لكل عينة، والتي كانت متساوية عند نسبة الكبريت (5.4399٪ وزنيًا) كوسيط تآكلي (2.49395 مم/ سنة). بينما لم تعاني العينات الأخرى لمحتوى الملح من أي تآكل كبير خلال فترة الغمر (ستة أشهر)، و لم تتأثر العينات المطلية بالإيبوكسي بأي نوع من التآكل.

1. Introduction:

Through the development of the oil industry and transportation, there has been a high and increasing requirement for storage tanks. However, corrosion is a common problem in storage tanks. As well, “corrosion” can be defined as the phenomenon of materials weakening caused by their interaction with the surrounding environment. Damages caused by corrosion have a great influence on the life of tanks, with increasing damages. There are two main reasons for corrosion in storage tanks [1]: First, corrosion is affected by external environmental factors and the nature of crude oil in tanks. The aggressive corrosion of crude oil is caused by non-hydrocarbon impurities such as water, sulfur-containing substances, and mineral salts. Various protection mechanisms to control the corrosion in crude oil tanks have been developed, including corrosion inhibitors, cathodic protection, and coating. Coating protection deals with the disconnection of metal surfaces from the corrosive environment, such as epoxy coats.

It has been observed recently that there is an increase in the salt content and the sulfur percentage dissolved in crude oil above the recommended values (the salt content recommends reducing to less than 30 and the sulfur percentage to less than 2% in the crude oil) for the purpose of designing crude oil storage tanks, especially after the addition of new fields of crude oil, so that the salt content exceeded 100 ppm and the sulfur percentage exceeded 3 wt%. It is expected that the values will increase in the near future. Hence the aim of this research, which is to increase the amounts of both salts and sulfur in crude oil, to know the extent of their corrosion effects on the crude oil storage tanks, and to suggest epoxy coatings as an answer for decreasing the corrosion rate. However, the corrosion of material in crude oil can be explained with many chemical concepts, as given below [2].

1.1. Corrosions caused by elemental-sulfur:

The corrosion behavior by sulfur is usually indeed quickly, Crude-oil commonly have sulfur with different configurations such Hydrogen Sulfide (H_2S), Thiophenes (C_4H_4S), Sulfoxides, Mercaptans (CH_3SH) which represent compounds that cause significant corrosion of metals known as Sulfidation corrosion that can be localized or general in the crude oil of storage tank [3].

1.2. Corrosions caused by salt:

The corrosion rate in crude oil which content salts depending on hydrochloric acid concentration where the corrosion rate increases with increase in the acid concentration. However, salt important role on the ability of formation Hydrochloric acid especially with water presence in crude oil in higher temperature. Crude-oil can contain many types of salts which related to occurrences of crude-oil such as Sodium Chloride (NaCl), Calcium Chloride ($CaCl_2$), and Magnesium Chloride ($MgCl_2$). Under certain conditions salts are broken down into Hydrochloric acid (HCl) [3]:

$NaCl + H_2O \rightarrow NaOH + 2HCl$ -------------- (1)

$HCl + Fe \rightarrow FeCl_2 + H_2$ ---------------------- (2)

2. Experimental Work:

2.1 Specimen Preparation: In experimental tests (27) specimens from carbon steel (ASTM A283-Gr.C) [4] the same material as plate used in construction of storage tank with dimensions (100mm * 100mm * 6mm) as shown in Figure (1), and the composition chemical was as shown in Table (1).

Fig. (1): Tested sample

Table (1): The chemical composition of tested samples

Elements	Carbon	Manganese	Phosphorous	Sulfur	Silicon	Copper
Samples	0.19	0.84	0.022	0.014	0.36	0.27
A283-Gr.C	0.24 Max.	0.90 Max.	0.035 Max	0.040 Max.	0.40 Max.	0.20 Min.

2.2 Corrosive Media:

Nine experiments of corrosive media using crude oil were prepared with a sample size of 2000 ml, as shown in Figure (2), the first four tests to study the effect of salt content on the tested specimen. The dissolved salt content was changed by adding weight percentages of the sodium chloride solution to the crude oil. The other four types of corrosive media are for the purpose of studying the effects of sulfur percentage. They were changed by adding pure sulfur to crude oil when the temperature was about 85°C and stirring the corrosive medium every day for 30 minutes and for 15 days before immersing specimens. As for the ninth experiment, it was considered a reference to measure the effect of salt and sulfur contents. However, the salt content is measured by the electrometric method according to (ASTM D3230) [5], and the sulfur percentage is measured by the energy dispersive X-ray method according to (ASTM D4294) [6] as shown in Table (2).

Fig. (2): The Experiment of corrosive media

Table (2): Corrosive Medium shows Salt content and Sulfur percentage foe Crude Oil

Experimental No.	Corrosive Medium	Density (g/cm^3)	Salt Content (ppm)	Sulfur Percentage (wt%)
1(Ref)	Crude Oil 1	0.8954	78	3.1429
2	Crude Oil 2	0.9086	180	3.1429
3	Crude Oil 3	0.9121	298	3.1429
4	Crude Oil 4	0.9106	455	3.1429
5	Crude Oil 5	0.9172	526	3.1429
6	Crude Oil 6	0.9384	78	3.6394
7	Crude Oil 7	0.9324	78	4.1967
8	Crude Oil 8	0.9182	78	4.9415
9	Crude Oil 9	0.8946	78	5.4399

2.3 Corrosion Rate Measurement:

Weight loss is one of the cheapest, easiest, and most widely accepted strategies for exploring corrosion rates. Several investigators have used immersion investigation followed by the mass loss method for calculating corrosion rates. The mass loss experiment procedure is given in the ASTM-G1 standard [7]. This standard offers the overall procedures for cleaning material samples. The two most essential pieces of data measured are the initial weight of the piece of metal before exposure to a corrosive environment and the weight of the cleaned metal piece after corrosion. The test samples were weighed using a balance with high sensitivity (0.01 gram). Procedures for the preparation of metal specimens for testing, the removal of corrosion products following completion of the process, and the evaluation of the corrosion damage that resulted. Focus is put on processes linked to the measurement of the corrosion rate by mass loss. In certain cases, a strong and closely bonded oxide is the corrosion result, which challenges the methods of ordinary mechanical and chemical removal. The mechanical technique given is intended to separate corrosion products without extensive base metal damage. This helps to accurately measure the mass loss of materials or alloys that has happened from exposure to the corrosive environment. Mechanical processes are regularly consumed to eliminate heavily crusted products of corrosion.

Procedure cleaning for carbon steel specimens after immersion period using a non-metallic (rubber) bristle brush and a soft polishing refined water slurry utilized to eliminate corrosion product according to ASTM G1 [7]. In this technique the level of corrosion could be detected without hard procedure and employ complex tools. The generality significant things are required for metallic specimen with adequate form in order to the surface area of material specimen in addition need to be calculated as a characteristic of equation. Eq. (3) clear up the factors of corrosion rate caused in technique of mass loss and the factors as stated below [7]:

$$CR = \frac{87600 * W}{A_{sur} * t_{exp} * \rho} \quad \text{.....................................} \ (3)$$

Where: CR= Corrosion Rate (mm/year), W= Loss Weight (gram), A_{sur}= Surface Area of Specimen (cm^2), t_{exp}= Exposure Time (hours), and ρ= Density (g/cm^3).

2.4 The Inspection of Hardness:

It was done for testing the change of tested specimens’ hardness due to corrosion. The instrument was Krautkramer MIC 20 hardness tester. According to hardness gauge of Vicker’s commonly hardness rate explains as a number amount connected to the inspected site in material surfaces. In further understanding of the theory after inspect procedure of hardness, could be expressed using the formula mentioned below [8].

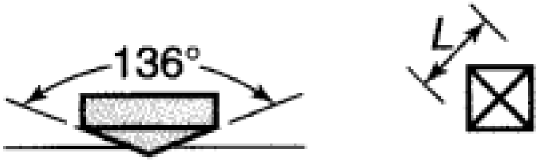

Fig. (3): Indenter of Vicker's hardness-tester

$HV = \frac{1.854\, F^2}{D^2}$ .... (4)

Where:

HV =Vickers Hardness

F =Applied force on the surface of material

D =Diagonal distance of square

In hardness inspection procedure, force is applied through a pyramid form diamond indenter and diagonal distance on the surfaces of metal that are generated using the indenter of hardness tester. Using Equation (4) the Vicker's hardness numbers are evaluated although the specified Vicker's hardness values are given as the reading in digital Vicker's hardness tester.

2.5 Coating:

paint (coating) is material which using as obstacle between material and its environment so it's corrosion resistance. There are some kinds of coatings classified as organic, inorganic, and metallic [9].

Organic paints help as an obstacle that are comparatively thin, between a specimen with environment. There are many organic paints utilized in different activities for combatting corrosion such as epoxy. Epoxy paints are versatile organic coating which could be used anywhere for any applications but might fade in sun lights. In this research, specimens were prepared before coating by polishing with a many metallographic grades (180- 500- and 800) of emery paper then cleaned with refined water and dried in a stream of air at room-temperature to remove all oil, tar, grease, salt, and other contaminants. The coating was applied as a three-layer epoxy, with a minimum coating thickness of (250 µm) then it's left to dry for two weeks at room-temperature and atmospheric pressure before exposing to solution test. This procedure was done according to API 652 [10] and NACE RP0184 [11].

3. Results and Discussions:

The corrosion rate was calculated by measuring the specimen weight loss over the period of immersion time and the exposed surface area of the specimens in corrosive media from crude oil, which is done using Equation (3). The cleaning procedure is repeated six times within the immersion period (six months) monthly for weighting the loss determined after each cleaning by weighting the specimens. The results of measuring the corrosion rate of specimens in salt and sulfur solutions in crude oil are shown in Table (3).

When measuring the corrosion rate of carbon steel plates immersed in crude oil with a salt content, the corrosion was very little and equal for those specimens. This is due to the presence of sulfur dissolved in crude oil. here, there was no effect of salts on the specimens due to the absence of water in crude oil, it is considered the most influential factor in corrosion resulting from the presence of hydraulic acid, especially at low temperatures.

While the result shows the difference in corrosion rate of sulfur content crude oil, the least corrosion rate was detected in carbon steel, as assumed at the start of the current's research. The greatest effect was observed on specimens in sulfur media, where a high corrosion rate was found, and it increased with the percentage increase of dissolved sulfur in the crude oil, as shown in Figure 4. Also, considering that corrosion arises in faster rate, i.e., corrosion's start to happen after the drop of the passive film when the sulfur content is almost (5 wt%). The maximum corrosion rates of every specimen with exposing time were calculated, and crude oil (9) as the corrosive medium was equal to 2.49395 mm/year. Increasing and decreasing in mass could be attributed to many reactions, which may happen, but the creation of passive film by the carbon steel for protecting itself through the conditions was exposed to other explanations. As well, when there was a break in the passive film, the metal corroded, and vice versa.

Results showed good corrosion's resistance of the coated carbon steel specimens were a high comparison with the results obtained from uncoated carbon steel specimen. This is due to coated resistance samples against crude-oil impurities that is higher than those of uncoated samples. The layer of coatings relative to the uncoated samples has disallowed the direct contact between crude-oil impurities (CO_2, H_2S, O_2, N_2, salts.... etc.) and the metallic surfaces. This impurity is considered the main reason for corrosion's problem. Rates of chemical reactions between these impurities and metal surfaces might be accelerated due to changes in the concentration of impurities. However, when the concentration of impurities increases, the rate of corrosion increases, and this is identical to the previous results that have been obtained by many researchers.

3.1 Material Hardness:

After a period of 208 days had been measure the decrease of hardness after corrosion. Where carbon steels specimens showed reduction of hardness as shown in Figure (5).

According to the hardness variant values of carbon steel plate for the crude oil storage tank little decrease was detected as consequence. using illustration of additionally study, there could be concluded the asymmetric distributions of hardness and as well little the hardness values reductions were occurred on each kind of the carbon steel specimens

The reduction analyzing of hardness values with the immersion time period in the corrosive medium for carbon steel plate, perfectly there cannot be distinguish any sequence or relation. Though there could be recognized several unanticipated situations as the increment observation of the hardness values at once. The carbon steel plate hardness values can be changed by the inspection location and as consequence this cause several of results were noticed in the inspection. After formation of corrosive compounds on carbon steel plate surfaces stability of metal surfaces will be reduced due the tendency of removing those compounds. The hardness decreasing values also take place with under these circumstances. Finally, the asymmetric variation of the reduction of the hardness also can be concluded as some variations of values due to the position on the metal surface and due to the asymmetric corrosion’s distributions on the metal surface.

4. Conclusions:

For concluding, the low-carbon steel corroded at a very low and acceptable rate in salt content crude oil because of the non-corrosive nature of organic hydrocarbons, especially when water is not found, while the specimen in sulfur content showed a high corrosion rate. The behavior of carbon steel plate specimens depends on their microstructure, which suffers from initial corrosion in selective areas that contain ferric phases due to their sensitivity to corrosion. The type of reaction between the carboxylic acid in the crude oil and the metal plate led to corrosion of the carbon steel specimens. When metal corroded, it experienced a loss of mass. The dissolution of metallic ions contributed to the reactions of corrosion, thus reducing the pH of the two by the evolution of hydrogen ions. After removing the carbon steel specimen, an increase in pH started due to the introduction of oxygen and a neutralization reaction occurring, forming water. From the results, simple and cheap methods of inspection for corrosion could be designed. It was found that epoxy coating could offer significant protection as a physical barrier against corrosive crude oil and various elements to which the metal is exposed. The following remarks could complete this work:

1. Crude oil has an important effect on the corrosion of carbon steel plates, and the effects are considerably different for crude oil according to the salt content and sulfur percentage.
2. The effects of coating on the speed and quality of corrosion rate and crude oil gave lower values of corrosion rate while coating.

Table (3): The results of measuring corrosion rate for specimens in salt and sulfur solutions in crude oil.

Exp. No.	**Corrosive Medium**	**Weight loss (g)**						**Corrosion Rate (mm/y)**
		30 days	**64 days**	**94 days**	**126 days**	**156 days**	**208 days**	
1 (Ref)	Crude-oil 1	Non	Non	Non	1	2	3	0.03297
2	Crude-oil 2	Non	Non	Non	Non	1	2	0.02148
3	Crude-oil 3	Non	Non	Non	1	2	3	0.03297
4	Crude-oil 4	Non	Non	Non	Non	1	2	0.02148
5	Crude-oil 5	Non	Non	Non	Non	1	2	0.02148
6	Crude-oil 6	Non	Non	2	3	4	5	0.05498
7	Crude-oil 7	2	3	4	6	7	8	0.08798
8	Crude-oil 8	2	5	11	17	21	28	0.30199
9	Crude-oil 9	36	80	131	167	197	229	2.49395

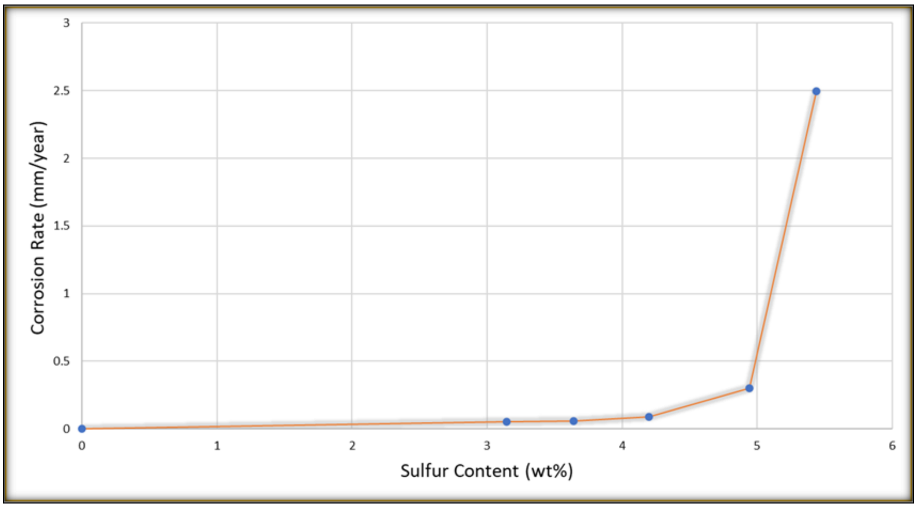

Fig. (4): Corrosion rate increases with the percentage increasing of dissolved sulfur in the crude oil

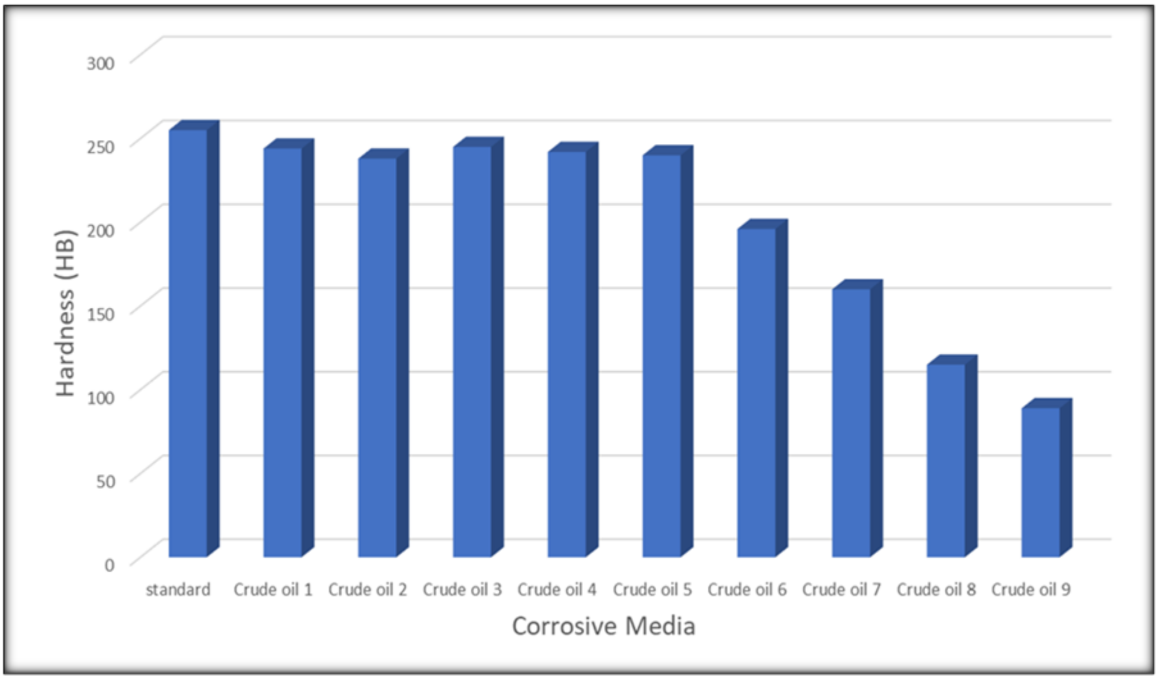

Fig. (5): Hardness values

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