



# مجلة جامعة بنغازي الحديثة للعلوم والدراسات الإنسانية علىم الحكرية عصفة

العسدد الثالث عشر

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حقوق الطبع محفوظة

# شروط كتابة البحث العلمي في مجلة جامعة بنغازي الحديثة للعلوم والدراسات الإنسانية

- الملخص باللغة العربية وباللغة الانجليزية (150 كلمة).
  - 2- المقدمة، وتشمل التالي:
  - نبذة عن موضوع الدراسة (مدخل).
    - الدراسة.
    - الممية الدراسة 🍫
    - اهداف الدر اسة.
  - المنهج العلمي المتبع في الدر اسة.
  - 3- الخاتمة. (أهم نتائج البحث التوصيات).
    - 4- قائمة المصادر والمراجع.
- 5- عدد صفحات البحث لا تزيد عن (25) صفحة متضمنة الملاحق وقائمة المصادر والمراجع.

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## DETECTION OF SULPHATE REDUCING BACTERIA IN CRUDE OIL STORAGE TANKS IN TOBRUK REFINERY, LIBYA

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#### Abstract

The present study is related to an engineering problems caused due to the presence of sulfate reducing bacteria (SRB) which associated produced water in oilfield. This study has been conducted on the crude oil storage tanks at Tobruk refinery to detect the sulfate reducing bacteria which causing corrosion. The samples of study were collected from eight storage tanks at different positions and at different levels from tanks bottom are 35 cm, 85 cm and 140 cm, were found to be contaminated with sulfate reducing bacteria. The chemical results indicated that the SRB occurs intensively in the lower portions of tanks and decreasing toward the top and their activity is concentrated in the area of tanks bottom which reach vertically to level about 1.5 meters because of the presence of sludge and the remains of associated water in crude oil. The chemical analysis of the collected samples from storage tanks revealed that the concentrations of  $Fe^{2+}$  and  $Fe^{3+}$  fluctuate in the storage tanks ranging from 9.10-23.0 mg/l and 17.4-36.0 mg/l respectively, indicating that the degree of corrosion which is a function of SRB. Also, it can be noticed that  $S^{2-}$  exhibit a wide variation in content which attributed to SRB in tanks, whereas, the highest content recorded in Tank 02 (324  $\mu$ g/l) while the lowest value in Tank 05 (54  $\mu$ g/l). The study was suggested a treatment system and treatment program to eliminate from bacteria. Also, it recommended that the sulfate reducing bacteria can be eradicated from crude oil by using biocide chemicals. Three different classes of chemicals namely Jofcide 5622 (Phosphonium sulfate based chemical), Jof cide 5692 (Gluteraldehyde) and Jof cide 5672, were can be obtained from Jowfe Oil Technology Company and evaluated for their biocide killing performance.

**Index Terms**: Storage tanks, Tobruk refinery, crude oil, sulfate reducing bacteria, corrosion, biocide chemicals, concentration.

# الكشف عن البكتيريا المُغَترِلَة للكبريتات في مستودعات تخزين النفط الخام بمصفاة طبرق، ليبيا

إبراهيم محمد أبوالليل<sup>1</sup>، عبد الله موسى سعيد<sup>2</sup>، عبد الرازق اليسيري<sup>3</sup> ( قسم الهندسة النفطية، كلية الهندسة، جامعة طبرق<sup>1</sup>. قسم الكيمياء، كلية العلوم، جامعة خليج السدرة<sup>2</sup>. شركة الجوف للنفط<sup>3</sup>)

الملخص:

تتعلق هذه الدر اسة بإحدى المشاكل الهندسية الحبوية في الصناعة النفطية والناجمة إز اء البكتريا المُختَزلة للكبريتات المصاحبة للمياه المُنتجة مع النفط. حيث أجريت هذه الدراسة على ثمانية مستودعات تخزين النفط الخام بمصفاة طبرق للكشف عن البكتريا المُختَزلة للكبريتات والمُسببَة للتآكل. حيث تبيَّن من العينات المأخوذة من مواضع مختلفة و على ثلاثة ارتفاعات و هي 35 سم، 85 سم و 140 سم من قاع الخزانات بنمو هذه البكتريا المُختَزلة. لقد أظهرت نتائج التحليلُ الكيميائي عن زيادة تركيز هذا النوع من البكتيريا في الأجزاء السفلِّي من الخزانات ويقلُّ تدريجياً كلما اتجهنا لأعلى، كما يتزايد نشاطها حتى يصل لمستوى حوالي 1.5 متر من قاع الخزان بسبب وجود الرواسب الطينية Sludge والمياه المصاحبة لإنتاج النفط الخام. كما أظهر التحليل الكيميائي أيضاً لعينات الدراسة أنّ تركيز بعض الكاتيونات متل Fe<sup>2+</sup> وFe<sup>3+</sup> يتباين من خزان لأخر بمدى يتراوح ما بين 9.10-23.0 ملجم/لتر و 17.4-36.0 ملجم/لتر على التوالي، ما لوحظ أيضا التفاوت في محتوى الكبريتات -S<sup>2</sup> الناجم عن البكتريا المختزلة في الخزانات حيث سُجلت أعلى القيم في الخزان رقم 2 بتركيز 324 ميكروجرام/لتر بينما كانت أقل القيم في الخزان رقم 5 وهي 54 ميكروجرام/لتر. لقد تضمنت هذه الدراسة منظومة للمعالجة وبرنامج يمكن تطبيقه للتخلص من هذه البكتريا، كما أفادت أيضا عن إمكانية التخلص من البكتريا المختزلة للكبريتات في المستودعات النفطية باستخدام المضادات البكتيرية. حيث أن هنالك ثلاث مجموعات مختلفة منَّ هذه الكيماويات المضادة للبكتيريا والتي يُطلق عليها Jofcide 5622 (كبريتات الفوسفونيوم) Jofcide 5692 (جلوتر ألديهايد) و Jof cide 5672 والتي يمكن الحصول عليها من شركة الجوف للتقنية النفطية.

**المصطلحات الدالة:** مستودعات التخزين، مصفاة طبرق، النفط الخام، البكتريا المُختزِلة، الكبريتات، التآكل، الكيماويات الحيوية.

#### **1. Introduction**

Corrosion is the destructive attack of a material by reaction with its environment. The serious consequences of the corrosion process have become a problem of worldwide significance. In addition to our everyday encounters with this form of degradation, corrosion causes plant shutdowns, waste of valuable resources, loss or contamination of product, reduction in efficiency, costly maintenance, and expensive over design; it also jeopardizes safety and inhibits technological progress. Corrosion control is achieved by recognizing and understanding corrosion mechanisms, by using corrosion-resistant materials and designs, and by using protective systems, devices, and treatments. Major corporations, industries, and government agencies have established groups and committees to look after corrosion-related issues, but in many cases the responsibilities are spread between the manufacturers or producers of systems and their users.

This study will focus mainly on the sulphate reducing bacteria (SRB) associate with produced water in oil and gas fields and how it can affect corrosion of materials by reducing the sulphate group (SO<sub>4</sub>) to release hydrogen sulphide which causes the corrosion.

In oilfield microbiology, bacteria and fungi are the subdivisions of prime concern. Bacteria may be one of several shapes but all consist of a single cell having a low level of internal organization and ranging in size from ( $1\mu$ m to  $10\mu$ m). Bacteria comprise the broad class of microorganisms of greatest to us in water handling. The bacterial cell has little visible structure, even when examined with an electron microscope.

#### 2. Location of Study

The study will be conduct on the petroleum refinery in Tobruk (Figure 1). The project of Tobruk oil refinery has been implemented by the National Petroleum Institution to satisfy some requirements of petroleum products. The job of refinery facility is to separate the crude oil into different products, the processes of separation take place under atmospheric distillation. The maximum capacity of production about 21,500 bbl/day. The main petroleum products of the refinery are diesel, light naphtha, heavy naphtha and kerosene.

#### 3. Study Importance

The importance of this study is to spotlight on the causes of corrosion due to the bacterial activity which leads to the damage of metallic surfaces of petroleum equipment.

#### 4. Problem Statement

The statement of problem is represented by the serious corrosion effect of petroleum equipment e. g. separator units, transport pipelines, storage tanks etc. due to the presence of sulfate reducing bacteria (SRB) which associated water in oilfield.

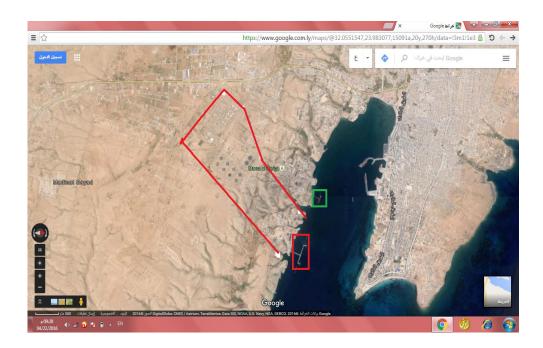
#### 5. Study Objective

The main objective of this study can be categorized as following:

- **1.** The detection of sulfate reducing bacteria (SRB) in the storage tanks of crude oil in Tobruk refinery that associated water in oilfield and causing corrosion problems.
- 2. Suggesting the procedure treatment to eradicate bacteria.



**3.** Recommended by the proper treatment chemicals of biocides.



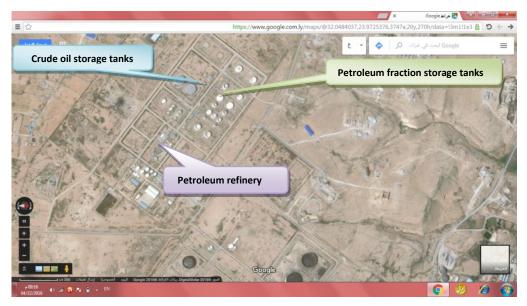


Fig. 1 Satellite image showing location of Tobruk refinery and storage tanks

#### 6. Materials and Methods

This study has been carried out on the crude oil storage tanks in Tobruk refinery to detect the sulphate reducing bacteria which causing the corrosion in storage tanks. The description of process treatment is described below:

A full technical survey was performed on eight storage tanks of crude oil throughout collecting samples to detect the sulphate reducing bacteria which causing the corrosion in different parts of their occurrence in all storage tanks in refinery of different sides and at different heights from tanks bottoms (35 cm, 85 cm & 140 cm).

The majority of the collecting samples representing a crude oil without associated water, whereas, these samples were washed by distilled water which has separated again from crude oil to subjected to the bacteria tests.

#### 7. Literature Review

At the end of the 19<sup>th</sup> century, the first reported suggestion that microorganisms might influence the metal corrosion process was made by Garret in 1891. He found that the corrosion of lead-sheathed cable was affected by the action of bacteria metabolites. Later reports provided evidence that iron and sulfur bacteria can be linked to the corrosion of the interior and exterior of water pipes<sup>[1]</sup>. Von Wolzogen<sup>[2]</sup> published the first paper that attempted to interpret MIC mechanisms in electrochemical terms. During the decades of the 1960<sub>S</sub> and 1970<sub>S</sub>, the cathodic depolarization theory (CDT) was the prevalent explanation for the corrosion of ferrous metal caused by sulfatereducing bacteria (SRB). At the same time, more mechanistic studies were published either objecting to or validating the anaerobic corrosion of iron by the cathodic depolarization theory<sup>[3]</sup>.

Tiller<sup>[4]</sup> mentioned that MIC problems were often subtle, hidden behind traditional corrosion, and often overlooked, suggesting that a sophisticated methodology and equipment for the detection and analysis was needed. Videla<sup>[5]</sup> stated that the participation of microbes could provoke or increase the corrosion of iron without changing the electrochemical mechanisms of corrosion. The microorganisms are capable of causing corrosion directly by converting element metal into metal ions. They can also secrete extracellular products that are corrosive in the absence of microbes.

Thierry and Sand<sup>[6]</sup>, MIC is not anew corrosion mechanism; it involves the activities of microorganisms in corrosion processes. All materials can be attached by microorganisms, including metals, minerals, organic materials and plastics. Therefore, MIC has become a multidisciplinary subject that integrates the field of materials science, chemistry, microbiology and biochemistry.

#### 7.1. Bacteria Which Cause Problems

Like all forms of life, bacteria use energy to carry on vital functions and to build new cells, that is, they have a metabolism. Bacterial metabolism is either anaerobic (without oxygen, called fermentation) or aerobic (with oxygen, called respiration). In the oil fields, the most common and troublesome organisms are anaerobic sulphate reducing bacteria (SRB) of the genus desulfovibrio. They obtain energy from organic compounds available in the water by the following reaction:

$$4H_2 + SO_4^{-2} + 2H^+ \rightarrow 4H_2O + H_2S + Energy$$

Major problems in oil and gas operations result from the biogenic formation of hydrogen sulfide ( $H_2S$ ) in the reservoir. The presence of  $H_2S$  results in increased corrosion, iron sulfide formation, higher operating costs, and reduced revenue and constitutes a serious environmental and health hazard. As previously stated, bacteria can contribute to both corrosion and plugging. Bacteria can affect the corrosion process in oilfield systems in several ways.

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#### 7.2. Microorganisms and Corrosion.

When pure metals or their alloys are exposed to water, corrosion occurs immediately. Corrosion is an electrochemical process consisting of two partial reactions, an anodic reaction by which metal becomes corroded and a cathodic reaction where some species are reduced. In some cases, the presence of microorganisms affects the corrosion reactions by forming a biofilm on the metal surface although a new electrochemical mechanisms are present in the corrosion process<sup>[7]</sup>. The dissolution of metals both directly and indirectly related to the activities of microorganisms is known as microbiologically influenced corrosion (MIC) or biocorrosion.

#### 7.3. Sulfate Reducing Bacteria (SRB)

Sulphate-reducing bacteria(SRB) are abundant in natural habitats such as marine and fresh water sediments or sludges and play a key role in the biogeochemical sulfur cycle<sup>[8-10]</sup>.

Sulphate reducing bacteria, known as Desulfuvibrio Desulfuricans in the scientific community, is also referred to as SRB. These bacteria are nonpathogenic (i.e., they are not capable of causing disease) and they are anaerobic bacteria (i.e. they require an oxygen free aqueous environment), but they are capable of causing severe corrosion of iron material in a water system because they produce enzymes which have the power to accelerate the reduction of sulphate compounds to the corrosive hydrogen sulphide, thus SRB act as a catalyst in the reduction reaction.

#### 7.4. SRB and Metal Surfaces

Steel and iron surfaces act as a substratum for microbial communities to form biofilms. Owing to oxygen consumption by aerobic microorganisms, biofilms are largely anaerobic at the metal surface, which creates a niche for anaerobic bacteria. Fermentation of decaying biomass also takes place. Fermentation products, such as lactate, acetate, butyrate, and propionate are used as electron donors for sulphatereducing bacteria (SRB). At the steel and iron surface, electrochemical corrosion occurs. Chemical dissolution of iron then results in the formation of hydrogen according to the following equation:

$$Fe + 2H^+ \rightarrow Fe^{+2} + H$$

Figure 2 and 3 show the mechanism of oxidizing hydrogen and electrochemical corrosion on metal surface respectively.

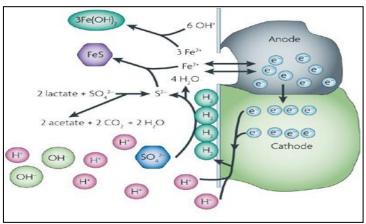


Fig. 2 Oxidizing of hydrogen on metal surface

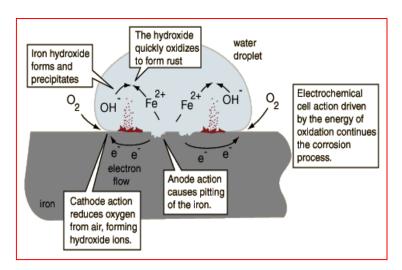


Fig. 3 Diagram showing electrochemical cell of the corrosion process

#### 7.5. Mechanism of MIC Due to SRB

Over the past decades, an extensive progress has been made to understanding the interaction between SRB activities within biofilm and the corrosion process of ferrous metal. Hamilton<sup>[11]</sup> raised the issue of the cathodic reaction with the participation of SRB during corrosion process in neutral anaerobic environment.

The overall reaction of MIC due to SRB can be expressed as:

$$4Fe + SO_4^{-2} + 4 H_2O \rightarrow 3 Fe(OH)_2 + FeS + 2OH^{-1}$$
(1)

Among many mechanisms proposed to explain how the metal dissolution proceeds in the presence of SRB, the cathodic polarization theory is the most prevalent explanation whereby protons may act as an electron acceptor at the cathode in the absence of oxygen<sup>[12]</sup>.

The typical reactions of this theory are provided below:

Anodic reaction: 
$$4Fe \Leftrightarrow 4Fe^{+2} + 8e^{-1}$$
 (2)

Electrolytic dissociation of water:  $8H_2O \Leftrightarrow 8H^{+1} + 8OH^{-1}$  (3)

Cathodic reaction:  $8H^{+1} + 8e^{-1} \Leftrightarrow 8H$  (4)

Cathodic depolarization by SRB:  $SO_4^{-2} + 8H \Leftrightarrow S^{-2} + 4H_2O$  (5)

Corrosion product:  $Fe^{+2} + S^{-2} \Leftrightarrow FeS$  (6)

Corrosion product: 
$$3Fe^{+2} + 6 OH^{-1} \Leftrightarrow 3Fe(OH)_2$$
 (7)

Overall reaction: 
$$4Fe + SO_4^{-2} + 4H_2O \Leftrightarrow 3Fe(OH)_2 + FeS + 2OH^{-1}$$
 (8)

On the other hand, Costello (1974) proposed that hydrogen sulfide,  $H_2S$ , instead of hydrogen ion could act as cathodic reactant, i.e.

$$2 H_2 S + 2e \Leftrightarrow 2HS^- + H_2$$
(9)

However, the scheme of iron corrosion by SRB based on reactions as suggested by the cathodic depolarization theory illustrated in Figure 4.

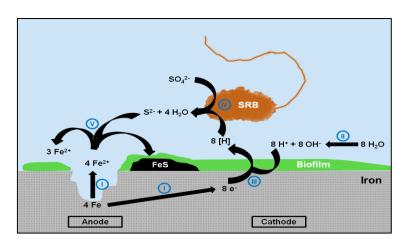


Fig. 4 Iron corrosion by SRB (I) Iron dissolution (II), Water dissolution (III), Proton reduction (IV), Bacterial sulfate reduction and (V) Sulfide precipitation<sup>[13]</sup>

#### 7.6. Problems Caused By Sulfate Reducing Bacteria

SRB are the most troublesome groups of organisms among all microorganisms involved in MIC of steels and other metals in oil, gas and shipping industries<sup>[14,15]</sup>. Considerable efforts have been focused on the influence of SRB on mild steels and alloys.

In oilfield water systems, however, SRB cause serious problems:

- 1. Production of sulphide, which is highly reactive, corrosive and toxic.
- 2. Corrosion of iron in the absence of air (anaerobic corrosion),
- **3.** Precipitation of amorphous ferrous sulfide due to plugging and diminishes the injectivity of water injection wells.
- 4. Contamination (souring) of fuel gas with  $H_2S$ .
- 5. Some sulfate-reducing bacteria play a role in the anaerobic oxidation of methane.

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^{2-} + HS^- + H_2O$$

$$\tag{10}$$

#### 7.7. Corrosion By Hydrogen Sulfide.

Corrosion of steel by  $H_2S$  has been one of the major problems in the oil industry since 1940. The presence of hydrogen sulphide ( $H_2S$ ) and free water can cause severe corrosion problems in oil and gas pipelines. Internal corrosion in wells and pipelines is influenced by temperature,  $CO_2$  and  $H_2S$  content, water chemistry, flow velocity, oil or water wetting and composition and surface condition of the steel. A small change in one of these parameters can change the corrosion rate considerably<sup>[15]</sup>.

A probable mechanism for Iron dissolution in aqueous solutions containing H<sub>2</sub>S based on the formation of mackinawite film:

$$Fe + H_2S \rightarrow Fe + HS^- + H^+$$
 (11)

 $Fe + HS^{-} + H^{+} \rightarrow Fe + S^{-} + 2H^{+}$ (12)

 $Fe + S^{-} + 2H^{+} \rightarrow FeS + 2H$  (13)

 $2nFeS \rightarrow nFe_2S_2 \rightarrow FeS_{mackinawite}$ (14)

#### 8. Results and Discussion

After preparing the samples for testing, the investigations have been carried out to detect the suphate reducing bacteria in all studied crude oil storage tanks. The obtained results revealed that there is an intensive bacterial growth in the most of the studied samples, in spite of these storage tanks were completely dewatering to the minimum level and become ready for exporting.

Table 1 shows the obtained results of storage tanks at three different levels from tanks bottoms. The positive sing indicates the bacterial growth, while the negative sing denote to the un bacterial growth. From these results it is obviously that the sulphate reducing bacteria occur intensively in the lower portions of tanks and decreasing toward the top.

Tuble T Detection of suphate reducing success in storage tanks																		
Tank farm	Level 35 cm					Level 85 cm					Level 140 cm							
Tank 01	+	+	+	+	+	+	+	+	+	+	+	-						
Tank 02	+	+	+	+	+	+	+	+	+	+	+	-						
Tank 03	+	+	+	+	-	-							-	-	-	-	-	-
Tank 04	+	+	+	+	+	+							-	-	-	-	-	-
Tank 05	+	+	+	+	+								+	+	+	+	-	-
Tank 06	+	+	+	+	+	+							-	-	-	-	-	-
Tank 07	+	+	+	+	+	+							-	-	-	-	-	-
Tank 08	+	+	+	+	+	+							+	+	+	+	+	-

Table 1 Detection of suphate reducing bacteria in storage tanks

The bacterial activity is concentrated in the area of tanks bottom because of the presence of sludge and the remains of associated water in crude oil. Also, it can be noticed that the bacterial activity reach vertically to level about 1.5 meters from tanks bottom. This area of storage tanks needed to be treated against this bacteria by applying chemical biocides.

#### 9. Main Storage Tanks

Table 2 depicts the capacity and storage level for normally and maximum operations of storage tanks, while Table 3 shows the concentration of iron (ferrous % ferric) and sulphide as well as pH values.

Tank	Operation		Maximum				
	Level (m)	Capacity (bbls)	Level (m)	Capacity (bbls)			
Tank 01	16.200	358,184	17.375	384,308			
Tank 02	16.200	358,281	17.375	384,415			
Tank 03	16.200	358,285	17.375	384,411			
Tank 04	16.200	358,310	17.375	384,439			
Tank 05	16.200	357,340	17.375	381,263			
Tank 06	16.200	357,082	17.375	383,231			
Tank 07	16.200	357,185	17.375	383,339			
Tank 08	16.200	357,351	17.375	383,518			

Table 2 Capacity and storage level of storage tanks

The chemical analysis of the collected samples from storage tanks revealed that the concentrations of  $Fe^{2+}$  and  $Fe^{3+}$  fluctuate in the storage tanks ranging from 9.10-23.0 mg/l and 17.4-36.0 mg/l respectively, indicating that the degree of corrosion which is a function of SRB (Table 3).

Also, it can be noticed that  $S^{2-}$  exhibit a wide variation in content which attributed to SRB in tanks, whereas, the highest content recorded in Tank 02 (324  $\mu$ g/l) while the lowest value in Tank 05 (54  $\mu$ g/l) (Table 3).

		1		$\mathcal{O}$
Tank	Fe <sup>+2</sup> mg/l	Fe <sup>+3</sup> mg/l	Sulfide (S <sup>-2</sup> ) $\mu$ g/l	pН
Tank 01	23.0	36.0	124	6.41
Tank 02	15.20	24.50	324	6.21
Tank 03	13.70	20.40	129	6.56
Tank 04	9.10	17.40	171	6.55
Tank 05	4.10	4.90	54	6.43
Tank 06	20.2o	26.30	74	6.35
Tank 07	13.70	28.60	60	6.33
Tank 08	15.90	22.12	96.85	6.50

Table 3 Iron and sulphide content in the storage tanks

The bar graphs in Figures 5 & 6 reflect the amount of variation in the concentration of these ions in the storage tanks.

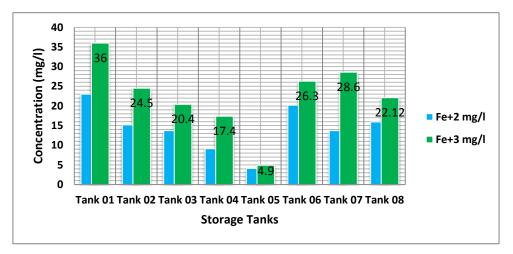


Fig. 5 showing the concentrations of Fe ions in the storage tanks

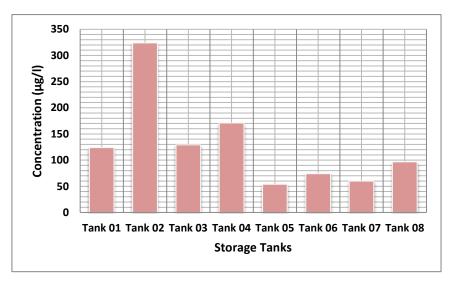
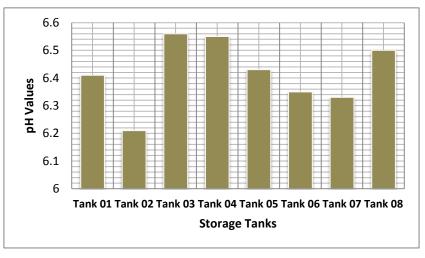


Fig. 5 Sulphide concentrations in storage tanks



On the other hand, the pH values also varies from tank to another, whereas, the highest value was recorded in Tank 03 and the lowest one in Tank 02 (Figure 7).

Fig. 7 pH values of storage tanks samples

#### **10. Treatment Process**

According to the obtained previous results, the treatment process to eradicate from suphate reducing bacteria in the storage crude oil tanks can be performed as the following procedure:

#### **10.1. Heaters and Circulation**

This process can be carried out by passing the crude oil through a heater to raise its temperature and soluble the waxes through a circulation process continue about five days to the single tank until temperature reach 115 °F (46 °C).

The tank circulation level will be at least 7.5 m, and the flow rate is about 1923  $m^3$ /hr at a flow line pressure ranging from 140-165 psi.

The mechanism of circulation process was illustrated in Figure 8, whereas, it will started from tank bottom at level 0.5 m which represent the oil storage tank outlet and come back to the position which represent the oil storage tank inlet, where it exist beneath the tank jetting system as a nozzles distributed over a large area at tank bottom at a level about 0.5 m in addition to the mixers at the middle of storage tanks and at the same level.

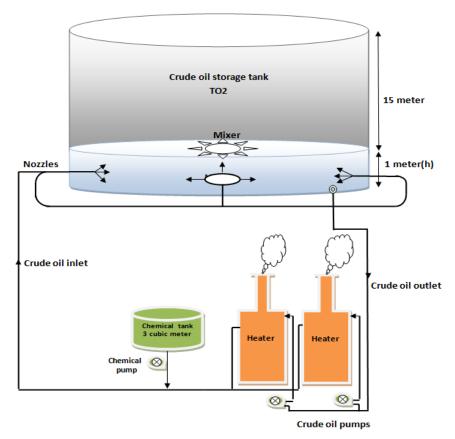


Fig. 8 Sketch illustrating chemical treatment method for tank bottom area

Total volume = 350,000 bbls

1 meter height = 21,500 bbls (crude oil + sludge + produced water)

#### **10.2. Treatment System**

The heaters system can be used in treatment process to use circulation system and design an injection system with tank its capacity at least 3  $m^3$  and an slugging pump exceeds 160 psi, whereas the injection point must be after the heater. Table 4 gives the range of heaters temperature and crude oil as well as storage tank target.

Table 4 Heaters temperature range

Crude	normal	Heater	inlet	crude		outlet	crude	Storage	tank
temperature		temperature			temperature			target temperature	
90 °F (32°C)		90 °F (3	2°C)		125 °F (3	51°C)		115 °F (46°	°C)

#### **10.3. Treatment Program**

The tank bottom area is the target of treatment at a level 1.0 m height because of the presence of this type of bacteria within this level according to the previous investigations.

At level 1.0 m height the tank could be contain about 21500 barrels of crude oil, sludge and associated water. Hence, the tank bottom area includes the crude oil, sludge and associated water, so its required high concentration of treatment chemicals ranging from 600–1000 ppm that represented by biocides chemicals, and this quantity of biocides may be increased or decreased according to the indicated range. The

following equation shows the minimum calculations for the required chemical substances for treatment:

Chemical consumption =  $\frac{21500 \times 600 \times 42 \times 3.785}{1000000} = \frac{2050}{200} = 10$  drums Whereas, the circulating pump capacity = 1923 m<sup>3</sup>/hr (9615 bbls/hr)

Circulating pump capacity for 2 hours = 3846 m3/2hrs (19230 bbls/2hrs)

Hence, the amount of crude oil required to be circulated through time 2 hours equals 19230 barrels and regarded as similar with that quantity of crude oil contained in the tanks at level 1.0m height.

Consequently, the quantity of chemical treatment substance (10 drums), if its injected through 2 hours of circulation process to the tank bottom area will be of concentration about 600 ppm, because of inlet and outlet will be take place within the lower area of storage tank at level 0.5 m.

Table 5 gives the specifications of suggested treatment chemicals (biocides) to eliminate from this type of bacteria. It could be used one type or two types to kill the bacteria in the storage tanks by using at least quantity 100 drums.

	1			
Biocides	Structure	Concentration %	pН	Quantities
Jof cide 5622	Phosphonium sulfate	75%	2-3	50 Drums
Jof cide 5692	Gluteraldehyde	50%	4 – 5	50 Drums
Jof cide 5672			2-3	50 Drums

Table 5 Treatment chemicals specifications

According to this study, these suggestions can be applied on one storage tank only, and if it gives a successful results can be generalized for the other tanks at different stages and intervals or suggested another alternative treatment procedure. Also, it can be applied annually or half or quarter annually or some thing like that.

#### 11. Conclusion.

From the previous study we can concluded the following:

- **1.** The chemical results indicated that the sulphate reducing bacteria occur intensively in the lower portions of tanks and decreasing toward the top.
- 2. The bacterial activity is concentrated in the area of tanks bottom because of the presence of sludge and the remains of associated water in crude oil.
- **3.** It is noticed that the bacterial activity reach vertically to level about 1.5 meters from tanks bottom.
- 4. The chemical analysis of the collected samples from storage tanks revealed that the concentrations of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  fluctuate in the storage tanks ranging from 9.10-23.0 mg/l and 17.4-36.0 mg/l respectively, indicating that the degree of corrosion which is a function of SRB.
- **5.** Also, it can be noticed that  $S^{2-}$  exhibit a wide variation in content which attributed to SRB in tanks, whereas, the highest content recorded in Tank 02 (324 µg/l) while the lowest value in Tank 05 (54 µg/l).

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#### 12. Recommendations.

In the light of the previous study we can recommended by:

- **1.** Treatment process should applied to eliminate from SRB in the storage tanks to prevent the corrosion damage.
- **2.** Applying biocide chemicals e, g. Jof cide 5622, Jof cide 5692 and Jof cide 5672 on the storage tanks.
- **3.** The concentration of chemicals treatment varies from type to another at different pH values with quantity 50 drums.
- **4.** The treatment system and treatment program must be applied as illustrated previously.
- 5. It can be apply more than one alternative plan to eradicate the SRB.

#### **References.**

- [1] Gaines, R. H. (1910) "Bacterial activity as a corrosion influence in the soil." Journal of Engineering Industrial Chemistry.
- [2] Von Wolzogen Kuhr, C. A. H. and van der Vlugt, L. S. (1934) "Graphitization of cast iron as an electro-biochemical process in anaerobic soils. Water Services Ltd <u>www-water</u>- services - info.
- [3] Booth, G. H. and Tiller. A. K. (1962) "Polarization studies of mild steel in cultures of sulphate-reducing bacteria. Part 3. Halphilic organisms." *Transactions of the Farady Society.*
- [4] Tiller, A.K. (1988) The impact of microbial induced corrosion on engineering alloys, p. 3-9 in C. A. C. Sequeira and A.K. Tiller (ed.), Microbial Corrosion.
- [5] Videla, H. A. (1996) "Detection, identification and monitoring." Manual of Biocorrosion, Lewis Publishers, Boca Raton.
- [6] Thierry. D. and Sand, W. (2002) "Microbially influenced corrosion." Corrosion Mechanisms in Theory and Practice. Marcus.
- [7] Beech, L. B. and Gaylarde. C. C. (1999) "Recent advances in the study of biocorrosion-an overview." *Revista de Microbiologia*.
- [8] Widdel, F. (1988) "Microbiology and ecology of sulfate and sulfur-reducing bacteria." In Biology of Anaerobic Microorganisms, *Edited by A. J. B. Zehnder*. *New York: John Wiley*.
- [9] Jorgensen and N. P. Revsbech. (1983) Colorless sulfur bacteria, Beggiatoa sp. and Thiovulum sp., in 0<sub>2</sub> and H<sub>2</sub>S microgradients.
- [10] Fauque, G. D. (1995) Ecology of sulfate reducing bacteria. In L.L. Barton (ed),Biotechnology handbooks, volume 8, Sulfate – reducing bacteria. New York: Plenum Press.
- [11] Hamilton, W. A. (1985) Sulfate reducing bacteria and anaerobic corrosion. Annu. Rev. Microbiol. 39.

- [12] Von Wolzogen Kuhr, C. A. H. and van der Vlugt, L. S. (1934) "Graphitization of cast iron as an electro-biochemical process in anaerobic soils. Water Services Ltd www-water- services - info.
- [13] Flemming. H. C. (1996) "Biofouling and microbiologically influenced corrosion (M1C)- an economic and technical overview." Heitz, E.; Sand W.; Flemming, H.-C. (eds.), Microbial Deterioration of Materials, Springer, Heidelberg.
- [14] Hamilton, W.A. (1998a) Bioenergetics of sulfate-reducing bacteria in relation to their environmental impact. Biodegradation.
- [15] Hamilton, W.A. (1998b) Sulfate-reducing bacteria: physiology determines their environmental impact. Geomicrobiololoy J.