

العدد التاسع و الستون / يونيو / 2023

## CHARACTERIZATIONS AND CLASSIFICATION OF FORMATION WATER PRODUCED IN OILFIELDS

Dr. Abdulkhalik Y. Khatab  
Petroleum Engineering Department, Faculty of Engineering,  
Tobruk University<sup>1</sup>  
Chemistry Department, Faculty of Science, Tobruk University<sup>2</sup>  
Chemical Engineering Department, Faculty of Engineering,  
Tobruk University<sup>3</sup>  
[almabroukhalhasy@gmail.com](mailto:almabroukhalhasy@gmail.com)



## CHARACTERIZATIONS AND CLASSIFICATION OF FORMATION WATER PRODUCED IN OILFIELDS

### Abstract:

Formation water known as oilfield wastewater, produced water, associated water and brine; which generated in great volumes in onshore and offshore oil and gas production. As more and more world major oilfields mature, more water begins to be produced from oil producers because of aquifer encroachment and/or water injection. The evaluated characteristics of offshore oilfield produced water in oilfields is very important for petroleum engineering industry from both upstream and downstream activities, as well as is essential for both environmental assessment and reservoir management. This study has been conducted on two oilfields namely Sarir and Nafora for oil producing wells to distinguish the characterizations of the produced water. Also, the water characteristics are investigated in five gathering centers in Sarir oilfield. The study included the analysis of sixty water samples to determine the physiochemical characterizations. The data obtained from the chemical analysis were used to classify formation water and to determine the environmental deposition using Sulin's system. The results revealed that the type of formation water in both two fields are belonging to  $\text{CaCl}_2$  type and deep marine environment. The Stiff diagrams of the studied formation water of Sarir field were constructed for five gathering centers and compared with different patterns of Stiff diagrams. Most of the studied water exhibits a similarity of these patterns, but some of them show slightly deviation, this may be attributed to the type of formation and the source of brine.

**Index Terms:** Oilfield, formation water, produced water, salinity, cations, anions, concentration.

## العدد التاسع و الستون / يونيو / 2023

### خصائص وتصنيف مياه التكوين المنتجة في حقول النفط

د. عبد الخالق خطاب أحمد بنونس

#### الملخص :

يُعرف الماء المنتج المصاحب للنفط بالماء الطبقي أو الماء الأجاج، والذي يكون بكميات كبيرة في كلٍ من حقول النفط والغاز البرية والبحرية المنتجة على حدٍ سواءٍ. وهناك الكثير من الحقول العالمية الرئيسية التي أوشكت على النضوب مما شكل زيادة كبيرة في حجم الماء المصاحب نظراً لتداخل خزانات المياه الجوفية محل الهيدروكربونات المنتجة في الأماكن أو نتيجة الحقن المائي بهدف الحفاظ على ضغط المكمن. وتُعد عملية تقييم المياه المنتجة في الحقول النفطية غاية في الأهمية لكلٍ من الصناعة النفطية خلال الأنشطة المكمية أو الأنشطة السطحية، فضلاً عن كونها عملية أساسية في التقييم البيئي وإدارة المكمن. لقد أجريت هذه الدراسة على حقلين نفطيين هما حقل السرير وحقل النافورة المنتجين للمياه المصاحبة للنفط بغرض تبيان مواصفات وخصائص هذه المياه. من جانبٍ آخر فقد تم دراسة خمسة مراكز تجميع بحقل السرير حيث تضمنت الدراسة تحليل 60 عينة من المياه لتعيين المواصفات الفيزيوكيميائية. وقد أستخدمت النتائج المتحصل عليها من التحليل الكيميائي في تصنيف الماء الطبقي وتحديد البيئة الترسيبية باستخدام نظام سولين *Sulin's system*. حيث أظهرت النتائج أن نوع الماء الطبقي في كلا الحقلين يندرج ضمن النوع كلوريد الكالسيوم  $CaCl_2$  وأن البيئة الترسيبية التي تشكل فيها هي بيئة بحرية عميقة. من جهةٍ أخرى تم دراسة الخصائص باستخدام مخططات ستيف للماء الطبقي بحقل السرير وتمت مقارنتها بأتماط مخططات ستيف لمراكز التجميع الخمسة، حيث أسفرت معظم المياه المدروسة عن وجود تماثل مع هذه المخططات عدا القليل منها الذي أظهر حيوداً طفيفاً والذي يعزو بطبيعة الحال إلى نوع التكوينات الصخرية ومصدر الماء الطبقي.

**المصطلحات الدالة:** حقول النفط، الماء الطبقي، الماء المنتج، الملوحة، الكاتيونات، الأنيونات، التركيز.

## 1. Introduction

A basic knowledge of the physics and chemistry of subsurface waters and petroleum is essential for petroleum engineers because many problems associated with exploration, formation damage or production problems, enhanced oil recovery, wettability, and others are directly associated with the physical and chemical behavior of subsurface waters and petroleum as a whole, or as groups of constituents.

Water produced during oil and gas extraction operations may be called formation water, oilfield water and brine, and constitutes the industry's most important waste stream on the basis of volume. Today, nearly 115 billion barrels per year (bbl/y) of water are produced worldwide as a by-product of oil and gas [1,2]. In average, for every barrel of oil, three barrels of water are produced from oil wells. As the well ages, this ratio dramatically increases, sometimes rising as high as 50 barrels of water per barrel of oil produced [3]. The water varies greatly in quality and quantity and in some cases the water can be a useful by-product or even a salable commodity. Produced water is most often considered a waste, but the industry is beginning to consider this material as a potential profit stream. Whether waste or commodity, produced water has management costs that need to be kept in-line with each specific production project and region or it could adversely affect the life of the well, thereby leaving substantial recoverable reserves in the ground. Produced water handling practices must also be environmentally protective or the operator could face regulatory action. Produced water handling methodology depends on the composition of produced water, location, quantity and the availability of resources [4,5].

## 2. Location of Study

The Sarir "C" field, which is 35 miles (56 km) long and 25 miles (40 km) wide covering approximately 146 square miles (378 km<sup>2</sup>), is located in a tectonically relaxed region of South Eastern Libya. Nafora oilfield was located in the south of Libya at Oasis area (Figure 1).

This study was carried out on the produced water of Sarir and Nafora oilfields for oil producing wells to distinguish the characterizations of the water production. Also, the water characteristics are investigated in five gathering centers of Sarir field.

### 3. Constituents of Produced Waters from Oil and Gas Fields

Organic constituents are normally dispersed or dissolved in produced water and include oil and grease and a number of dissolved compounds. All formation waters contain dissolved solids, primarily sodium chloride. The water sometimes is called brine or salt water. However, oilfield brines bear no relationship to seawater, either in the concentration of solids in the distribution of the ions present [7]. Generally, oilfield waters contain much higher concentrations of solids than seawater does. Formation waters have been reported with total solid concentrations ranging from as little as 200 ppm to saturation, which is approximately 300,000 ppm. Seawater contains about 35,000 ppm total solids. The dissolved cations commonly found in oilfield waters are  $\text{Na}^+$ ,  $\text{Ca}^{++}$ , and  $\text{Mg}^{++}$  occasionally  $\text{K}^+$ ,  $\text{Ba}^{++}$ ,  $\text{Li}^+$ ,  $\text{Fe}^{++}$ , and  $\text{Sr}^{++}$  are present. The most common anions are  $\text{Cl}^-$ ,  $\text{SO}_4^{--}$  and  $\text{HCO}_3$ . Also  $\text{CO}_3$ ,  $\text{NO}_3$ , Br, I,  $\text{Bo}_3$ , and S are often present [8].

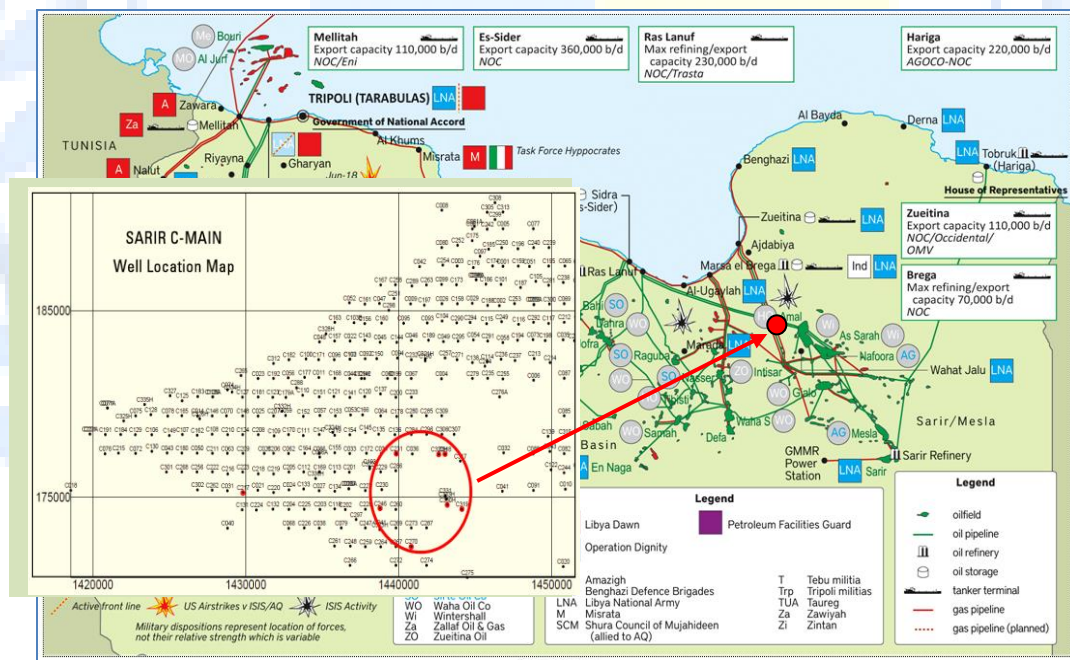


Fig. 1 A map showing wells locations of Sarir and Nafora oilfields [6]

## 4. Materials and Methods

### 4.1. Sampling

Sixty water samples were collected from the investigated wells and gathering centers. All the collected samples were preserved in accordance with guidelines and International Standards and analyzed in the field laboratory using XRF analytical technique.

### 4.2. Study Objectives

The main objective of this study is to recognize the large amounts of produced water that associated to the petroleum industry and investigate the characterization properties and classification of formation water produced in both Sarir and Nafora oilfields.

## 5. Oilfield Waters

The genesis of petroleum is intimately associated with shallow marine environments; hence, it is not surprising that water found associated with **oil** generally contains dissolved salts, especially sodium and calcium chlorides. Petroleum source rocks originally formed in lakes or streams, and the porous sediments that became today's petroleum reservoirs could have acquired saline waters by later exposure to marine waters. Thus, the original waters present in the sediments when they were developed may have been either fresh water or saline marine water. After the original deposition, however, the oilfield sedimentary formations have histories of subsidence, uplift, reburial, erosion, etc. Therefore, the chemistry of the original water may have been altered by meteoric water, marine water infiltration at a later time, changes of salt types and concentrations due to solution of minerals as subsurface waters moved in response to tectonic events, and precipitation of some salts that may have exceeded equilibrium concentration limits [9].

The origin of deep saline subsurface waters has not been completely explained. The most plausible explanation is that they were originally derived from seawater. If seawater is trapped in an enclosed basin, it will undergo evaporation, resulting in precipitation of the dissolved salts. The least soluble salts will precipitate first, leaving a concentrated brine deficient in some cations and anions when compared to seawater. The common order of evaporative deposition from seawater in a closed basin is: calcium carbonate (limestone) > calcium-magnesium carbonate (dolomite) > calcium sulfate (gypsum) > sodium chloride

## العدد التاسع و الستون / يونيو / 2023

(halite) > potassium chloride (sylvite). Dolomite begins to precipitate when the removal of calcium from solution increases the Mg/Ca ratio. The residual brines (containing unprecipitated salts at any period) may migrate away from the basin and leave the evaporites behind, or they may become the interstitial water of sediments that are rapidly filling the basin [10]. In accumulating marine clastic sediments, aerobic bacteria consume the free oxygen in the interstitial waters and create an anaerobic environment in which the anaerobes become active and attack the sulfate ion, which is the second-most important anion in seawater. The sulfate is reduced by the bacteria to sulfide, which is liberated as hydrogen sulfide (marsh gas) [10]. Thus, the composition of saline oilfield waters, or brines, is quite different from the average composition of seawater (Table 1). The ions in the brine are enriched with respect to seawater. Several mechanisms of enrichment are possible: (1) the original seawater may have evaporated if it was trapped in a closed basin; (2) movement of the waters through beds of clay may have concentrated cations by acting like a semipermeable membrane allowing water to pass through, but excluding or retarding the passage of dissolved salts; and (3) mixing with other subsurface waters containing high salt concentrations. The content of alkali cations is many times greater in the oilfield brines than in the water that owes its salinity to the dissolution of salts from the earth, or to the infiltration of high-salinity waters from other sources.

**Table 1 Oilfield brine, average composition of seawater compared to Sarir, Nafora and Smackover, Arkansas [10]**

Constituent	Seawater (mg/L)	Sarir (Libya) (mg/L)	Nafora (Libya) (mg/L)	Smackover brine (mg/L)
Lithium	0.2	-	-	174
Sodium	10,600	17000	897	67,000
Potassium	380			2,800
Calcium	400	1813	500	35,000
Magnesium	1,300	1387	280	3,500
Strontium	8	-	-	1,900
Barium	0.03	-	-	23

العدد التاسع و الستون / يونيو / 2023

Boron	5	-	-	130
Copper	0.003	-	-	1
Iron	0.01	-	-	41
Manganese	0.002	-	-	30
Chloride	19,000	15953	1367	172,000
Bromide	65	-	-	3,100
Iodide	0.05	-	-	25
Sulphate	2,690	365	210	45

There are many reactions between the ions that can occur as the environmental conditions change with burial. Consequently, the composition of oilfield waters varies greatly from one reservoir to another. Commonly, the salinity (total amount of dissolved salts, or TDS) of petroleum-associated waters increases with depth (there are a few exceptions to this). The principal anions change in a characteristic manner as depth increases: (1) sulfate is the major anion in the near-surface waters; (2) below about 500 meters, bicarbonate may become the principal anion; and (3) in brines from deeper formations, chloride is the principal anion. The ratios of the cations also change with respect to depth. The Ca/Na ratio increases, whereas the Mg/Na ratio decreases [10].

The concentrations of salts in formation waters are expressed as weight percent (wt%): milligrams per liter (mg/L) or parts per million (ppm). The quantities are related as follows: 1% = 10,000 ppm and mg/L = ppm/density .

Where ionic reactions are involved, the contents of ions are expressed as milliequivalents per liter (meq/L). One meq of a cation reacts quantitatively with exactly one meq of an anion:

$$\text{meq/L} = (\text{meq/L}) \times (\text{valence/molecular weight})$$

The calcium and magnesium cation concentrations of subsurface waters are probably functions of the origin of the specific oilfield water as well as its history of contact with infiltrating waters. These cations undergo reactions forming dolomite and enter into ion exchange reactions; consequently, they are normally found in lower concentrations than sodium cations. Other cations are present in concentrations less than 100 mg/L [11].



## العدد التاسع و الستون / يونيو / 2023

Oilfield waters are frequently referred to as connate or interstitial water, which is found in small pores and between fine grains in water-wet rocks. As defined by Collins, the two terms are synonymous and they are indistinguishable as used in the petroleum literature [12]. “Connate” implies that the water is the original fossil water present in the rocks from the time of original deposition. One cannot be certain of this because the original water may have been displaced or mixed with other waters during the geologic history of the sedimentary formation. Collins considers connate water as fossil water that has not been in contact with water from other sources for a large part of its geologic history.

### 6. Chemical Composition and Classification of Formation Water

#### 6.1. Chemical Composition

Because of long-time contact with the reservoir rocks and crude oil, the formation water contains a considerable deal of metallic salts, such as sodium salt, potassium salt, calcium salt, and magnesium salt, and for this reason, the formation water is also called brine. Formation water has competitively higher salt concentration that makes the formation water distinguished from the land-surface water. The total salt concentration in formation water is called salinity.

Positive ions commonly encountered in formation water include  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ , and some other positive ions such as  $\text{Ba}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Li}^+$  also take a little share; the commonly encountered negative ions include  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{Br}^-$ , as well as some trace ions.

Usually, in the formation water, there also exist diverse microorganisms, among which the most common one is the anaerobic sulfate-reducing bacterium which is rather stubborn to be eliminated. The microorganisms cause the corrosion of casings and build-up in pores of the formation. However, the origin of them is still rather vague for us. It is guessed that they may originally exist in the trapped and closed reservoirs or, perhaps, are brought to the underground formations during drilling operations.

## 6.2. Salinity and the milligram-equivalent concentration of the ions

Salinity is the total concentration of the mineral salts in water and is expressed with the unit mg/L or ppm (one millionth). It is the total concentration of both the positive and negative ions in it. Salinity varies within a wide range from several thousand to hundreds of thousand (unit mg/L) in different oil field. A high salinity, which sometimes can be up to  $3 \times 10^5$  ml/L, is a typical value for formation water [13].

Under original reservoir conditions, the formation water is in a state of saturated solution, but when it flows up to the land surface, due to the pressure and temperature drop, the salts will fall of the solution. In severe cases, the wellbores can be salt-crusted and the production will be brought into trouble.

Because the positive and negative ions react with each other in equivalent amounts, the salt concentration in formation water is usually expressed by milligram-equivalent concentration which equals the ratio of a certain ion's concentration to its equivalent value. The compounded equivalent values of some common ions in oil formations are shown in Table 2. For example, the concentration of chloride ion ( $\text{Cl}^-$ ) is 7896 mg/L, and the compounded equivalent value is 35.3; then, the milligram-equivalent concentration of the chloride ion can be obtained as follows:  $7896/35.3 = 225.6$  mg/L.

**Table 2 Compounded equivalent values of common ions in oil formations**

No.	Positive ion	Compounded equivalent values	No.	Negative ion	Compounded equivalent values
1	$\text{Ba}^{2+}$	68.7	1	$\text{CO}_3^{2-}$	30.0
2	$\text{Ca}^{2+}$	20.0	2	$\text{HCO}_3^-$	61.0
3	$\text{H}^+$	1.0	3	$\text{Cl}^-$	35.3
4	$\text{Fe}^{3+}$	27.9	4	$\text{OH}^-$	17.0
5	$\text{Fe}^{2+}$	18.6	5	$\text{O}^{2-}$	8.0
6	$\text{Mg}^{2+}$	12.2	6	$\text{SO}_4^{2-}$	48.0
7	$\text{Na}^+$	23	7	$\text{S}^{2-}$	16.0
8	$\text{Sr}^{2+}$	43.8	8	$\text{SO}_3^{2-}$	40.0

### 6.3. Water hardness

Hardness of water is a term used to indicate its content of calcium and magnesium ions. In the chemical flooding (e.g., injection of polymers or active agents), high water hardness tends to worsen the effect of the stimulations by causing precipitation of the chemical agents. Therefore, clear and detailed knowledge about it is indispensable during the production.

In addition to the formation water's total salinity and water hardness, it is also necessary to know quantitatively the species and individual concentration of the ions, upon which the water type and the depositional environment it represents can be determined [13].

### 7. The Classification of Formation Water

Roughly, the total concentration of the formation water can be known in accordance with its total salinity. For further grasp of the individual concentration of every ion, either positive or negative, and their corresponding proportions, the formation water is classified to different types. Water type is named according to the tendency of a certain compound's appearance in the water. For example, the bicarbonate-sodium water refers to the water in which the bicarbonate-sodium is in a tendency to appear.

#### 7.1. Classification of Water—Sulin's System

According to the chemical components in water or, in other words, their milligram-equivalent concentration:

$$\frac{Na^+}{Cl^-}, \frac{Na^+ - Cl^-}{SO_4^{2-}}, \frac{Cl^- - Na^+}{Mg^{2+}}, \frac{SO_4^{2-}}{Cl^-} \text{ and } \frac{Ca^{2+}}{Mg^{2+}}$$

and water is classified to four types.

(1) *Sulfate-sodium (Na<sub>2</sub>SO<sub>4</sub>) type*: It represents an environment of continental washing. Generally speaking, this type reflects a weak enclosed condition on which the oil and gas could not be gathered or stored easily. Most of the land-surface water belongs to this type.

(2) *Bicarbonate-sodium (NaHCO<sub>3</sub>) type*: It represents an environment of continental deposit. This type is widely distributed in oil fields and can be utilized as a sign of a good oil and gas bearing.

## العدد التاسع و الستون / يونيو / 2023

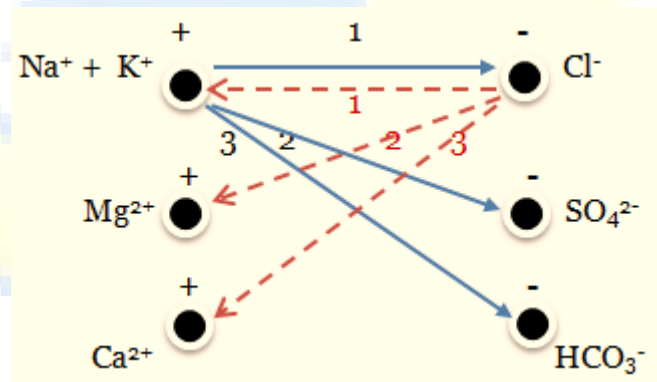
(3) *Chloride-magnesium ( $MgCl_2$ ) type*: It represents an environment of marine deposit. This type usually exists in the interior of the oil and gas fields.

(4) *Chloride-calcium ( $CaCl_2$ ) type*: It represents an environment of deep enclosed construction. This type reflects a good enclosed condition on which the oil and gas can be gathered and stored easily. This is also a sign of fine oil and gas bearing.

This method discussed above is called Sulin's water classification system. Representing each geologic environment with a special water type, it has associated the chemical components in formation water with their corresponding forming conditions [13].

### 7.2. Determination of Water Types

As illustrated in Figure 2, the order in which the positive and negative ions combine with each other is in accordance with the ions' affinity for their opposite ones. Moreover, this also offers the principle on which the water types are determined:



**Fig. 2 Diagram of the order in which the ions combine with each other [13]**

(1) When  $\frac{Na^+}{Cl^-} > 1$ , the redundant  $Na^+$  will combine with the  $SO_4^{2-}$  or  $HCO_3^-$  ions and forms  $Na_2SO_4$  type or  $NaHCO_3$  type. Further judgment can be continued as follows:

(a) When  $\frac{Na^+ - Cl^-}{SO_4^{2-}} < 1$ , it suggests that after balancing the  $Cl^-$ , the redundant  $Na^+$  will combine with the  $SO_4^{2-}$ , and since the ratio is less than 1, there will be no  $Na^+$  left for  $HCO_3^-$ . As a result, when the whole combination reaction ends what is formed finally is  $Na_2SO_4$  and that is why this kind of water belongs to the  $Na_2SO_4$  type.

العدد التاسع و الستون / يونيو / 2023

(b) When  $\text{Na} \frac{\text{Cl}^- - \text{Na}^+}{\text{Mg}^{2+}} > 1$ , it suggests that after balancing the  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , the redundant  $\text{Na}^+$  will combine with the  $\text{HCO}_3^-$  to form  $\text{NaHCO}_3$ , whereupon the water is named  $\text{NaHCO}_3$  type.

(2) When  $\text{Na}^+/\text{Cl}^- < 1$ , the redundant  $\text{Cl}^-$  will combine with the  $\text{Mg}^{2+}$  or ions and forms  $\text{MgCl}_2$  type or  $\text{CaCl}_2$  type. Further judgment is as follows:

(a) When  $\frac{\text{Cl}^- - \text{Na}^+}{\text{Mg}^{2+}} < 1$ , it suggests that after balancing the  $\text{Na}^+$ , the redundant  $\text{Cl}^-$  will combine with the  $\text{Mg}^{2+}$ , and since the ratio is less than 1, there will be no  $\text{Cl}^-$  left for  $\text{Ca}^{2+}$ . As a result, the  $\text{MgCl}_2$  type is formed.

(b) When  $\frac{\text{Cl}^- - \text{Na}^+}{\text{Mg}^{2+}} < 1$ , it suggests that after balancing the  $\text{Na}^+$  and  $\text{Mg}^{2+}$ , the redundant  $\text{Cl}^-$  will combine with the  $\text{Ca}^{2+}$  and forms  $\text{CaCl}_2$ , upon which the water is named  $\text{CaCl}_2$  type.

The procedure for water-type determination is summarized in Table 3.

**Table 3 Sulin's system of water classification [13]**

Equivalent Proportion	Parameter for judgment	Water type	Environment
$\frac{\text{Na}^+}{\text{Cl}^-} > 1$	$\frac{\text{Na}^+ - \text{Cl}^-}{\text{SO}_4^{2-}} < 1$	$\text{Na}_2\text{SO}_4$ type	Continental washing (land, surface water)
	$\frac{\text{Na}^+ - \text{Cl}^-}{\text{SO}_4^{2-}} > 1$	$\text{NaHCO}_3$ type	Continental deposit (water in oil and gas field)
$\frac{\text{Na}^+}{\text{Cl}^-} < 1$	$\frac{\text{Cl}^- - \text{Na}^+}{\text{Mg}^{2+}} < 1$	$\text{MgCl}_2$ type	Marine deposit (water in oil and gas field)
	$\frac{\text{Cl}^- - \text{Na}^+}{\text{Mg}^{2+}} > 1$	$\text{CaCl}_2$ type	Deep enclosed construction (gas field water)

### 8. Results and Discussion

The obtained results of chemical analysis were presented in Table 4. Whereas, the various cations and anions in addition to the total salinity of the investigated formation water for both Sarir and Nafora oil fields were determined and compared with other world oilfields as reported in Table 4.

**Table 4 Chemical composition and water type of the formation water in oil fields[13]**

Oil field	Total salinity (mg/L)	Na <sup>+</sup> (K <sup>+</sup> )	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub>	CO <sub>3</sub> <sup>2-</sup>	Water type
Daqang (China)	16,316	5917	11	95	7896	18	2334	45	CaCl <sub>2</sub>
Gudao (China)	3,228	1038	13	25	1036	0	1116	0	NaHCO <sub>3</sub>
Shengli (China)	17,960	4952	836	620	10,402	961	187	0	CaCl <sub>2</sub>
Renqiu (China)	178	21	9	20	43	18	67	0	CaCl <sub>2</sub>
East Texas (America)	64,725	23,029	536	1360	39,000	216	578	0	CaCl <sub>2</sub>
Gachsaran (Iran)	95,313	33,600	30	1470	55,000	4920	-	293	CaCl <sub>2</sub>
Furrial-Musipan (Venezuela)	5643	1739	59	54	1780	-	2001	-	MaCl <sub>2</sub>
Sarir (Libya)	26325	17000	1387	1813	15953	365	268.4	260	CaCl <sub>2</sub>
Nafora (Libya)	29250	897	280	500	1367	210	320	315	CaCl <sub>2</sub>

### 8.1. Formation Water Type

To determine the investigated formation water type, we use the chemical composition of the formation water of oil fields as following procedure.

1. Judge the equivalent proportion of the ions whose valence is 1:

$$\frac{Na^{+} + K^{+}}{Cl^{-}} = < 1, \text{ As initial judgment, the water can be } MgCl_2 \text{ or } CaCl_2 \text{ typed.}$$

2. Because that  $\frac{Cl^{-} - Na^{+}}{Mg^{2+}} = > 1$ , the given water belongs to the CaCl<sub>2</sub> type.

Table 4 shows the chemical compounds and types of the formation water exist in some oil fields comparing with Sarir and Nafora brine. The obtained results revealed that the investigated formation water of both Sarir and Nafora oil fields were belonging to the CaCl<sub>2</sub> type. This is clearly similar with that compared oilfields as shown in Table 4.

On the other hand, Figures 3 & 4 are depicted a comprehensive comparison among the formation waters characteristics; whereas, this comparison revealed the variance of total salinity, cations and anions in the studied formation waters in these oilfields.

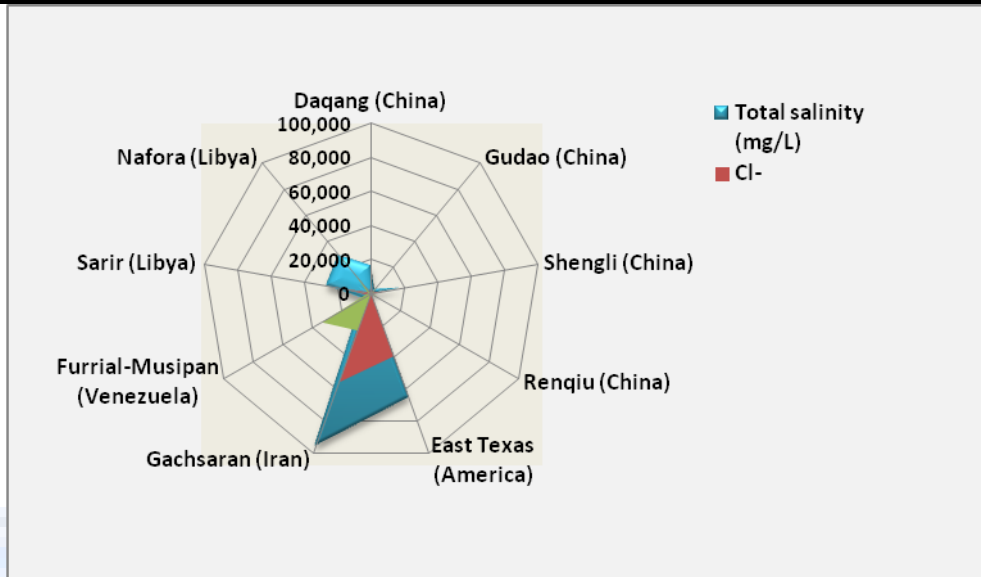


Fig. 3 Radar charts comparing the total salinity and Cl<sup>-</sup> of formation waters

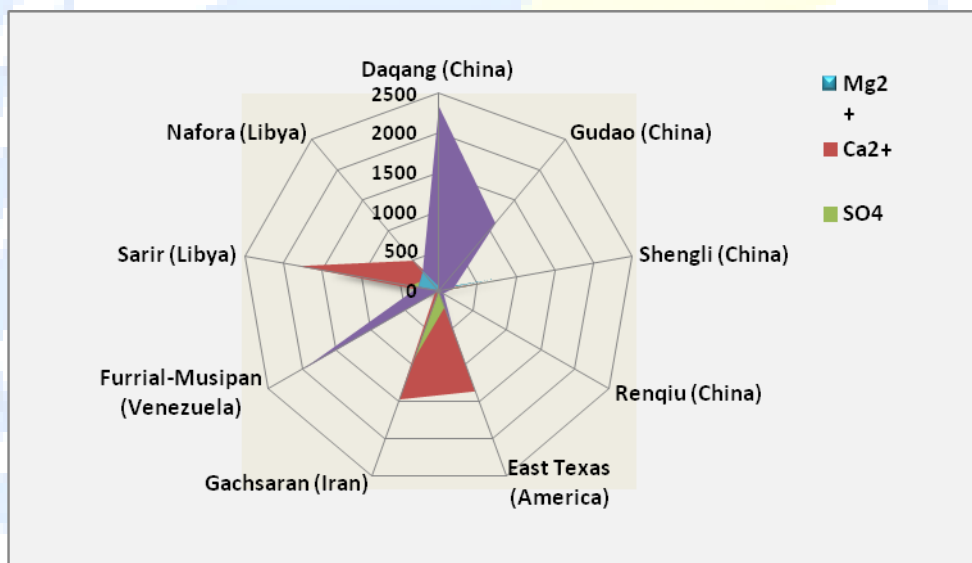


Fig. 4 Radar charts comparing the cations and anions of formation waters

## 8.2. Stiff Diagrams

The chemical analysis of formation water involved a range from 6 to 10 of numbers that representing the different composition of ions. So, the best way to represent the data was developed in patterns, these patterns called Stiff diagrams (Figure 5) . From these patterns we can distinguish easy the difference between brines.

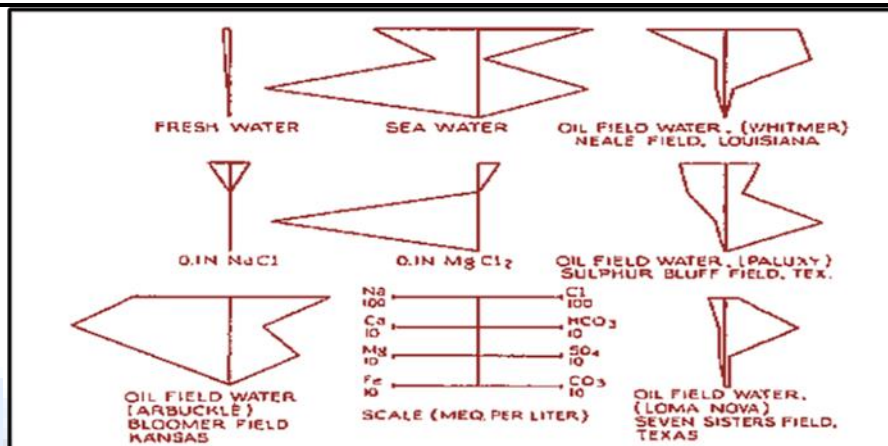


Fig. 5 Stiff patterns of formation water [14]

To construct Stiff diagrams for formation water, five gathering centers were investigated (Table 5), and we must be applied the following procedure:

Table 5 Determination of brine density

Gathering center No.	Unit	GC1	GC2	GC3	GC4	GC5
Parameter						
Total dissolved solids, TDS	ppm	68200	11800	220718	163545	24600
Total dissolved solids, TDS	%	6.82	1.18	22.07	16.4	2.5
Brine density	lb/cu ft	65.20	62.50	72.40	69.70	63.30
$\rho_w$	g/cc	1.044	1.001	1.159	1.116	1.014

### 8.3. Conversion the Concentrations from ppm to mg/l

1. Conversion the total dissolved solids, TDS from ppm into percentage (%) by dividing to  $10^6$ .
2. Brine density ( $\text{lb/ft}^3$ ) can be determine from the chart of density using the obtained TDS in percentage (%).
3. Conversion the brine density ( $\text{lb/ft}^3$ ) into g/cc.
4. Multiply the concentrations of cations and anions of brine in ppm by brine density to obtain the concentrations in mg/l.



العدد التاسع و الستون / يونيو / 2023

5. The results obtained are presented in Table 6.

**Table 6 Conversion the concentrations to mg/L**

Chemical properties	Concentration (mg/L)				
	GC1	GC2	GC3	GC4	GC5
Calcium	28188	1892	17582	38455	43605
Magnesium	12047	1448	34572.9	932	10748
Salinity, NaCl	214020	27483	240017	206181	17238
Chloride, Cl <sup>-</sup>	179568	16655	145446	125118	10444
Total iron, Fe	91	15.0	80.8	217.6	76.6
Sulphate, SO <sub>4</sub>	302	125	423	595.0	266.7
Alkalinity, HCO <sub>3</sub>	146.2	268.7	85.5	100.4	152

**8.4. Conversion the Concentrations from mg/L into meq/L**

To convert from mg/L to meq/L for cations and anions follow the following steps:

The atomic weight of Ca is 40.08 g/g mole, valence is 2 eq wt/g mole, then the equivalent weight is:

$$\text{For Ca, } \frac{40.08 \frac{g}{g \text{ mole}}}{2 \frac{eq \text{ wt}}{g \text{ mole}}} = 20.04 \text{ g/eq wt} = 20.04 \text{ mg/meq.}$$

and the milliequivalent is:

$$\frac{28188 \frac{mg}{l}}{20.04 \frac{mg}{meq}} = 1406.6 \text{ meq/L}$$

$$\text{For Na, } \frac{22.99 \frac{g}{g \text{ mole}}}{1 \frac{eq \text{ wt}}{g \text{ mole}}} = 22.99 \text{ g/eq wt.} = 22.99 \text{ mg/meq.}$$

$$\frac{214020 \frac{mg/liter}}{22.99 \frac{mg}{meq}} = 9309.3 \text{ meq/L}$$

$$\text{For Mg, } \frac{24 \frac{g}{g \text{ mole}}}{2 \frac{eq \text{ wt}}{g \text{ mole}}} = 12 \text{ g/eq wt.} = 12 \text{ mg/meq.}$$

$$\frac{12047 \frac{mg/liter}}{12 \frac{mg}{meq}} = 1003.9 \text{ meq/L}$$

العدد التاسع و الستون / يونيو / 2023

$$\text{For Cl}^-, \frac{35.5 \frac{\text{g}}{\text{g mole}}}{1 \frac{\text{g mole}}{\text{g mole}}} = 35.5 \text{ g/eq wt.} = 35.5 \text{ mg/meq.}$$

$$\frac{179568 \frac{\text{mg/liter}}{\text{g mole}}}{35.5 \frac{\text{mg}}{\text{mg/meq}}} = 5058.3 \text{ meq/L}$$

$$\text{For Fe, } \frac{56 \frac{\text{g}}{\text{g mole}}}{3 \frac{\text{g mole}}{\text{g mole}}} = 18.7 \text{ g/eq wt.} = 18.7 \text{ mg/meq.}$$

$$\frac{91 \frac{\text{mg/liter}}{\text{g mole}}}{18.7 \frac{\text{mg}}{\text{mg/meq}}} = 4.87 \text{ meq/L}$$

$$\text{For SO}_4, \frac{96 \frac{\text{g}}{\text{g mole}}}{2 \frac{\text{g mole}}{\text{g mole}}} = 48 \text{ g/eq wt.} = 48 \text{ mg/meq.}$$

$$\frac{302 \frac{\text{mg/liter}}{\text{g mole}}}{48 \frac{\text{mg}}{\text{mg/meq}}} = 6.29 \text{ meq/L}$$

$$\text{For HCO}_3, \frac{61 \frac{\text{g}}{\text{g mole}}}{2 \frac{\text{g mole}}{\text{g mole}}} = 30.5 \text{ g/eq wt.} = 30.5 \text{ mg/meq.}$$

$$\frac{1462 \frac{\text{mg/liter}}{\text{g mole}}}{30.5 \frac{\text{mg}}{\text{mg/meq}}} = 47.9 \text{ meq/L}$$

The other calculations can be carried out as the above procedure. The results are presented in Table 7.

**Table 7 Conversion from mg/l to meq/l for cations and anions**

Chemical properties (Cations and anions)	Ion concentration (meq/L)				
	GC1	GC2	GC3	GC4	GC5
Calcium, Ca <sup>++</sup>	1406.6	94.41	877.4	1918.9	2175.9
Magnesium, Mg <sup>++</sup>	1003.9	120.7	2896.1	77.7	895.7
Sodium, Na <sup>+</sup>	9309.3	1200.1	10481.1	9003.5	752.8
Chloride, Cl <sup>-</sup>	5058.3	469.2	4097.1	3524.5	294.2
Total iron, Fe	4.87	0.80	4.3	11.6	4.10
Sulphate, SO <sub>4</sub>	6.29	2.60	8.81	12.40	556
Alkalinity, HCO <sub>3</sub>	47.9	8.8	2.8	3.29	4.98
Carbonate, CO <sub>3</sub>	0.0	0.0	0.0	0.0	0.0

## العدد التاسع و الستون / يونيو / 2023

The Stiff diagrams of the studied formation water were constructed for the different gathering centers as shown in Figures 6 through Figure 10 and compared with different patterns of Stiff diagrams. Most of the studied water exhibit a similarity of these patterns, but some of them show slightly deviation, this may be attributed to the type of formation and the source of brine.

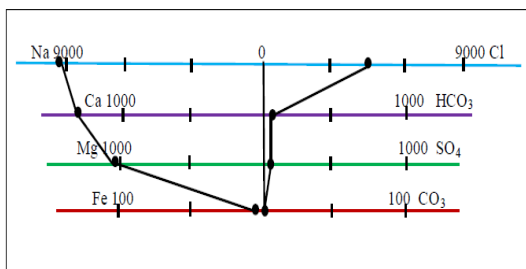


Fig. 6 Stiff diagram for GC1

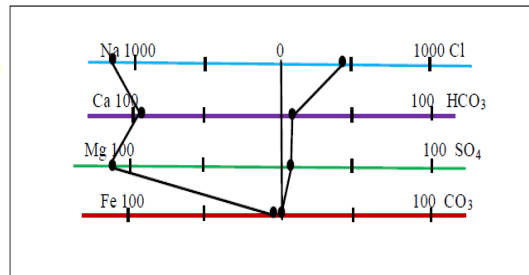


Fig. 7 Stiff diagram for GC2

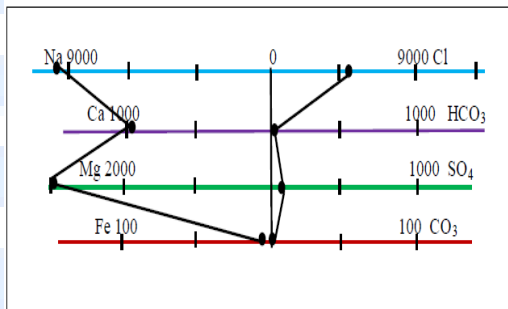


Fig. 8 Stiff diagram for GC3

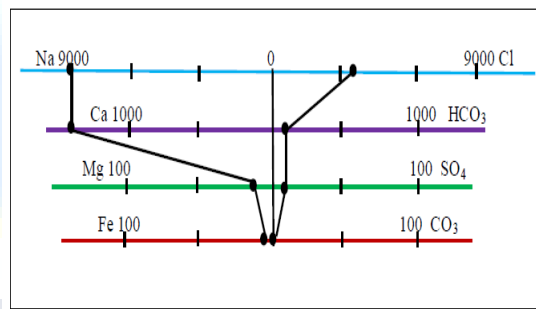


Fig. 9 Stiff diagram for GC4

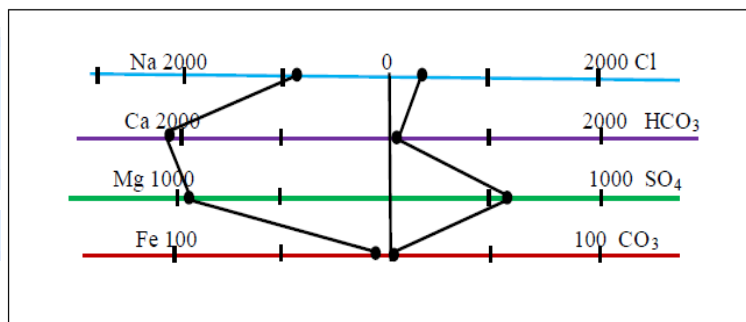


Fig. 10 Stiff diagram for GC5

## 9. Conclusion

Water analysis is very important for petroleum engineering industry from both upstream and downstream activities. The characteristics of Sarir and Nafora oil fields produced water revealed the following:

1. Oilfield produced waters contain elevated levels of salinity, TDS, cations and anions more than the standards characteristics of seawater.
2. Many characteristics of the formation water such as salinity, TDS, Na and Cl exhibit variable values, this may due to nature of reservoir formations.
3. According to the Sulin's system of water classification; the obtained results revealed that the investigated formation water of both Sarir and Nafora oil fields were belonging to the  $\text{CaCl}_2$  type and deep marine environmental deposition.
4. The comparing between the constructed Stiff diagrams for the studied formation water of gathering centers with Stiff diagrams patterns exhibit similarity, but some of them show slightly deviation, this may be attributed to the type of formation and the source of brine.

### References

- [1] Reynolds Rodney R.: "Produced Water and Associated Issues" *a manual for independent operator, Petroleum Technology Transfer Council 13*, (2003), 23-32.
- [2] Veil J.A., Puder M.G., Elcock D., and Redweik R. Jr. J. "A White Paper Describing Produced Water from Production of Crude Oil, Natural Gas, and Coal Bed Methane," (2004) ,*US DOE W-31-109-Eng-38*.
- [3] Joel, O. F., Amajuoyi, C.A. and Nwokoye, C. U., "Characterization of formation water constituents and the effect of fresh water dilution from land rig location of the Niger Delta, Nigeria", *Journal Applied Sci. Environ. Management*, 14 (2) (2010): 37 – 41.
- [4] Guerra, K., Dahm, K. and Dunderf , S., "Oil and gas produced water management and beneficial use in the Western United States", U.S. Department of the Interior Bureau of Reclamation, *Science and Technology Program Report No. 157, Technical Service Center* (2011).
- [5] Chukunedum, O. M. and Ijeoma, A. U., "Evaluation and management of produced water from selected oil fields in Niger Delta, Nigeria", *Archives of Applied Science Research*, 4 (1) (2012):39-47.
- [6] Arab Petroleum Investments Corporation, APICORP (2018) Apicorp Energy Research, Vol. 03 No. 14 | November 2018.
- [7] Frost, TK; Johnsen, S; Utvik, TI, Environmental Effects of Produced Water Discharges to the Marine Environment, OLF, Norway (1998).
- [8] Tibbetts, PJC; Buchanan, IT; Gawel, LJ; Large, R., A Comprehensive Determination of Produced Water Composition, In: Produced Water, J.P. Ray and F.R. Englehart (eds.), *Plenum Press, New York* (1992).
- [9] Collins, A. G. and Wright, C. C. "Enhanced Oil Recovery Injection Waters." Chap. 6 in: Donaldson, E. C., Chilingarian, G. V. and Yen, T. F. (Eds.) *Enhanced Oil Recovery*. Elsevier Science Pub., New York, Amsterdam, 1985, pp. 151-217.

العدد التاسع و الستون / يونيو / 2023

- [10] Collins, A. G. *Geochemistry of Some Petroleum-associated Waters from Louisiana*. US Bureau of Mines RI 7326, Natl. Tech Inf. Sv. Dept. Commerce, Springfield, VA, 1970, 31 pp.
- [11] Dickey, P. E. *Petroleum Development Geology*, 2nd ed. Penn Well Books, Tulsa, OK, 1979, 424 pp.
- [12] Collins, A. G. *Geochemistry of Oilfield Waters*. Elsevier Science Pub., New York, Amsterdam, 1975, 496 pp.
- [13] Shenglai Yang, *Fundamentals of Petrophysics*. Department of Petroleum Engineering, China University of Petroleum, Beijing, China, (2017).
- [14]. Stiff, H. A., Jr. (1951) The Interpretation of Chemical Water Analysis by Means of Patterns, *Trans., AIME*, 192, 376-379.