

## GEOCHEMICAL EVALUTION FOR FORMATION WATER OF SOME WELLS IN AMAL OIL FIELD, SIRT BASIN, LIBYA Asmaa D. Alnajar<sup>1</sup>, Naima. K. Elgariani<sup>2</sup>, Anwar M. Alsaiah<sup>3</sup>

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#### Abstract

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The present paper deals with classification of oilfield water of Maraghand Amal formations at Amal oil field, concession NC-12, in the eastern margin of the Sirt basin, Libya.Ten chemically analyzed water samples from different wells were used in this study; chemical analyses of the major ions of the water samples showed Total Dissolved Solids (TDS) in the ranges from 205487 to 234912mg/l.

The geochemical ratios of Na/Cl, ((Na-Cl)/SO4), and ((Cl-Na)/Mg) were calculated for formation water of ten wells classification following Sulin's (1946), whereindicate that all of these water are Cl-Ca type waters under subsurface conditions; this type reflects isolated waters with hydrostatic conditions. According to Bojarski's (1970), the chloride-calcium type of this water subdivided to chloride-calcium III, which reflects the favorable zone for the preservation of hydrocarbons, followed by chloride-calcium II in other wells. This class reflects the transition zone between active hydrodynamic and stable zones.

Graphical methods in water analysis enable efficient pattern comparison for quick identification of differences between water samples.Consequently, both the piper diagram and the stiff diagram were utilized in this study. The piper diagram in this study indicates most of the samples were classified as  $(Na^++K^+)$  and  $Ca^{2+}$  types of cations and  $Cl^-$  types of anions; then these waters consist of the alkalis that exceed alkaline earths. The Stiff Diagram polygons showed most of the samples reveals similar chemical compositions with high chlorine and sodium levels, followed by magnesium and bicarbonate, while sulfate is low. In contrast, the waters in some wells have higher magnesium concentrations.

Keywords: Geochemistry; Classification; Amal Field; Oil field Waters.



يتناول هذا البحث تصنيف مياه حقول النفط في تكويني مراغوأمال في حقلاً مال النفطي، امتياز 12-NC،فيا لهامش الشرقي لحوض سرت، ليبيا. تم استخدام عشر عينات من المياه المحللة كيميائيًا من آبار مختلفة في هذه الدراسة؛ أظهرت التحاليل الكيميائية للأيونات الرئيسية في عينات المياه أن المواد الصلبة الذائبة الكلية (TDS) تتراوح بين 205487 إلى 234912 ملغ/لتر.

تم حساب النسبالجي وكيميائية (Na/Cl) و((Na-Cl)SO4)، و((Cl-Na)/Mg) و (Cl-Na) لمياه التكوين لعشر آبار وفقًا لتصنيف سولين (1946)، حيثتشير إلى أن جميع هذه المياه من نوع -Cl Caتحتظر وفتحت السطحية؛ هذا النوع يعكس مياهًا معزولة تحتظر وفهيدروستاتيكية. ووفقً البوجارسكي (1970)، تم تقسيم الماء من نوع كلوريد-كالسيوم إلى كلوريد-كالسيوم III، الذي يعكس منطقة مواتية لحفظ الهيدروكربونات، يلي هكلوريد-كالسيوم آفي آبار أخرى. تعكس هذه الفئة منطقة انتقالية بين المناطق هيدروديناميكية نشطة ومناطق مستقرة.

تمكن الطرق البيانية في تحليل المياه من مقارنة الأنماط بكفاءة لتحديد الفرق بين عينات المياه بسرعة. وبالتالي، تم استخدام كل من مخطط بايبر ومخطط ستيف في هذه الدراسة. يوضحمخططبايبر فيهذهالدر اسةانمعظمالعيناتتمتصنيفها علدانهامننو عالكاتيونات (+K+ (Na<sup>+</sup>+K) و<sup>2</sup>-Ca<sup>2</sup> والأنيونات من نوع-C1؛ وبالتالي فإن هذه المياه تتكون من القلويات التي تفوق القلويات الأرضية. أظهرت مضلعات مخطط ستيف أن معظم العينات تكشف عن تراكيبكيميائية متشابهة بمستويات مالير من منطو من من منطق المياه من مع من من مع مع من التحديم والمن من من محمد العينات من من منطع مالعينات من المالي من من التونات من نوع-C1 وبالتالي فإن هذه المياه تتكون من القلويات التي تفوق القلويات الأرضية. أظهرت مضلعات مخطط ستيف أن معظم العينات تكشف عن تراكيبكيميائية متشابهة بمستويات عالية من الكلور والصوديوم، تليها المغنيسيوم والبيكر بونات، بينما يكون مستوى الكبريتات منخفضًا. على النقيض، تحتوي المياه في بعض الأبار على تراكيز أعلى من المغنيسيوم.

## 1. Introduction

Water geochemistry provides a series of powerful tools for solving various oilfield development and production problems. Specifically, naturally occurring chemical "tracers" in water can be used to identify the origin and track the movement of water in oil fields, as well as to predict the precipitation of scales. These naturally occurring tracers include the absolute and relative abundance of the various dissolved salts (anions and cations) as well as the isotopic composition of certain cations and the hydrogen and oxygen stable isotopic composition of the water itself. Which formation is responsible for water moving behind casing can be determined by comparing formation water geochemistry data with data from produced waters.

The produced water or petroleum- associated waters often have salinities in the range from less than 10,000 up to more than 200,000 mg/l. However, most oilfield brines have salinities much higher than seawater salinities. Hence, oilfield waters are often termed oilfield brines, especially when their total salinities are more than 100,00 mg/l (Refai, 2011).

# **1.1 Location of Study Area:**

The Amal Field is situated in Concession 12, on the eastern margin of the Sirt Basin, inCyrenacia Province, Libya. The concession lies some 275km southeast of the Mediterraneancoast and 925km ESE of Tripoli.Geographically, Concession 12 lies in desert terrain, hilly in the north and sandy in thesouth. The nearest town is Augila, which lies immediately to the south of thefield. The Amal Field is located on Amal High and Maragh Low. It lies in the northeast flank of Sirte Basin in the northern part of Concession 12, between coordinates of Latitudes 29°19' 04" and 29° 41' 47" North and Longitudes 21° 01' 05" and 21° 14' 35" East, Figure (1). (Harugecompany, 2005)



Figure (1) Illustrate Location map of the concession 12, Libya modified after Haruge company.

## **1.2 Literature review**

The name Amal Formation has recently been used for a formation in the subsurface of the Amal Field area (Roberts, 1970). Therefore, the Amal Formation is here proposed as a new formation in the subsurface of the eastern Sirt Basin, however, it is identical to therock unit used by Roberts. (1970) provides a valuable discussion of the lithology of this formation in the Amal Field, its regional structural setting, and

itsimportance as a major petroleum reservoir. The Amal Field was discovered by well B1-12, drilled in 1959, when Mobil first drilled the Amal Field.

# 2.Stratigraphy and petroleum system

## 2.1 Geological and Structural Setting

The Sirt Basin is a large sedimentary basin located in central north Libya that has produced significant oil and gas resources over several decades (Schlumberger service company, 1997). Formed during the Late Paleozoic to Mesozoic breakup of the supercontinent Pangaea, the basin transitioned from an extensional rift setting to a passive margin as the African plate migrated northwards relative to Eurasia (Jiranek, e.t., 1998). The Sirt Basin is a major intracratonic rift system in central Libya. The sedimentary succession within the basin reflects its tectonic and structural evolution, which is closely related to the opening of the Atlantic Ocean and the opening and subsequent closure of the Tethys Oceans in Mesozoic and Tertiary times (Whitbread, 1989). In general, the sedimentary sequence of the Sirt Basin overlies Precambrian igneous and metamorphic basement rocks and comprises sporadically distributed and poorly dated Lower Paleozoic clastics which are unconformably overlain by a thick Lower Cretaceous and Tertiary clastic and carbonate sequence.

# 2.2 Lithology of study area:

The stratigraphic nomenclature used is that employed by Veba Oil Operations (previously Mobil Oil Libya). The stratigraphic column in the study area comprise deposits that range from pre Cambrian to Tertiary presented in Figure (2).

## 2.2.1 Basement:

The basement has been described by Mobil (1979) as consisting of twomajor igneous centres. A widespread Cambro-Ordovician or older (500 million years) basement, consisting predominantly of granitic rocks with rhyolites and tuffs as well as trachytic volcanics. This is the type of basement penetrated by the wells in the southern part of the field. To the north, Lower Cretaceous-Jurassic (135 million years) intermediate volcanics (F1-12) are centred on the Tharwa High (North Amal).

## 2.2.2 Amal Formation:Cambro-Ordovician

The Amal Formation is predominantly a sandstone sequence. It is heterogeneous in color, grain size and sorting. The grain size ranges from very fine sand to cobbles with the medium to coarser grain sizes being more common. Accessory constituents are feldspar, mica, pyrite, hematite and various dark minerals. Clays, sericite and rarely dolomite are found as cementing materials in much of the formation. Interbedded with the sandstone, but comprising a much lesser part of the formation, are gray silty clays and gray, green and red, brittle, micaceous shales. In addition to the sedimentary rocks, volcanic rocks in the form of dikes, sills or flows are found at a number of horizons in the upper part of the formation. Contact relationships in the B1-12 well, the Amal Formation is unconformably overlain by the Maragh Formation. The base of the formation was not reached in the B1-12, but in other wells, such as B2-12, the Amal Formation unconformably overlies volcanic rocks. In the type section, the top of the Amal Formation is placed at the change from the friable dolomitic sandstone of the Maragh Formation to the more firmly cemented quartzitic Amal sandstone. Because of onlapping relationships around the Amal high, the Amal Formation can be overlain by various Rakb Group clastics or carbonates. The base of the formation, where reached, occurs at the change from sandstone to volcanic rocks. Paleontology and Age. Radiometric determinations on volcanics within and beneath the Amal Formation have given a broad and inconsistent spread of ages ranging from Cambrian to Jurassic. Regional considerations, however, suggest that the most likely age of the Amal Formation is Cambro-Ordovician. Origin of Name This formation is the principal reservoir of the Amal Field from which it derives its name, and its importance as

a major petroleum reservoir. Distribution the Amal Formation, or its equivalents, are widely spread in the eastern Sirt Basin. it may be equivalent to the Hofra Formation in the western Sirt Basin. In the Amal Field area, the Amal Formation varies greatly in thickness.

#### **2.2.3Maragh Formation: Upper Cretaceous**

The Maragh Formation lies unconformably on the Amal Formationor the Barremian Sand/ Nubian Sand, separated from the underlying formations by the Sirt Unconformity, the Maragh Formation is referred to as the Bahi Formation.

The Maragh Formation is thinning from northeast to southwest. The presence of the Maragh in this position can be explained as either transgression up the lows or a preferential preservation in the low protected areas with erosion in the higher areas. The distribution of the Maragh Formation suggests that it was once more widely distributed and that what is present now is an erosional remnant, erosion could have happened at both the Santonian and Campanian unconformities. The Maragh Formation is easily distinguished from the underlying Amal Group by its relatively soft and unconsolidated state.

The Maragh Formation was divided into three units by Geopec (1994), and this division has been followed:

- The Maragh unit X, which is represented by sequences of loosely consolidated conglomerates.
- The Maragh unit A, followed by less conglomeratic than Maragh X, is described as being friable, very fine to fine grained moderately to poorly sorted, glauconitic sublitharenite to lithic subarkose, accompanied by phosphatic and bioclastic remains, interbedded with mudstone/shale and carbonate layers.
- The Maragh unit Bis distinguished by the calcite and dolomite cemented sandstones underlying less cemented sandstones of the Maragh A and the overlying shales and limestones of the Rakb C.

The Amal Field covers anarea of about  $880 \text{km}^2$  and is situated on the Amal High, on the eastern flank of theSirt Basin, adjacent with the Rakb and Nafoora-Augila fields. The Amal Field is flanked by the Ajdabiya Trough to the west and the Maragh Low to theeast. The structure plunges to the north, into the Tharwa Low and the reservoirpinches out, up-dip, to the south. The crest of the structure lies near the southernboundary of the field at a depth of about -9,530'TVDSS. With a nominal oil watercontact of -10,260'TVDSS. The Amal Field has been subdivided into three sectors: B, N and E. Both B andE sectors are on the footwall to the major intra-field fault which separates it from the Nsector in the hanging wall. B and E sectors are separated from one another by a high-angle east-west oriented fault.Figure 3.

	Period	Sub Period	Group	Formation	Member	Lithology	Note
	Pa Mioc	ene		Garet Uedda			Loose surface sands
	Mioc	ene:	Najah	Giarabub		ceccecceccecc	Dolomites and limestones interbedded with clays
1					Arida		Sandstone and limestone Interbedded with mudstone
	Oligo	cene		Gebel	Augila		Limestone interbedded with sandy clay
		Upper		Akhdar	Rashda	0000000000000	Clay with minor inter-bedded
~			+		Smara	155555555555555555555555555555555555555	Argillaceous limestone with
rtiar	Econo			Ciele	Ruddoffer		clay
Ter	Eocene	Middle	Cyrenaica	Giaio	Buddamar	anananananan	Argillaceous limestone with clay
					Etla	Municipal and a second	Limestone with dolomite
		Lower	1	Mesdar			Limestone becoming dolomite. downwards with dolomite
			+ +	Abu Eas	+	- Angeneration	Argillaceous marts and calcareous
		Upper		Aburas			limestones.
		Opper		Upper Sabil			Limestone, chalky with hard dolomite
	Paleocene		Farigh	Sheterat	+		Rhele with argillaceous
		Lower				Contraction of the	limestone
		LU		Lower Sabil		www.everyeveryeveryeverye	Dolomite with minor interbeds of calcarenite
	1			Kalaah	+		Fine Limestone interbedded
				Kalash			calcilutites and calcarenities
				Rakb	Rakb A	CELECCEPTER C	Shale interbedded argillaceous limestones and siltatone
							Shale and limestone with minor
					Rakb B		alitatones
	Upper Cretaceous	Upper	Harash		Rakb C		Shale with interpets or innestance and dolomite. The base of the unit is often formed of sitty sandstone
					Rakb D	SECONDECCE	Shale,grey-black, interbedded sandstone, white-tan,very fine grained
			1		Maragh B		Calcite and dolomite cemented sandstone
0			1	Maragh	Maragh A		Glauconitic sandstone, fine grained interbedded with mudstone/shale.
OZO			1	000/02/10/02/02/02/02/02	Maragh X		Loosely consolidates conglomerates.
lesc	1		+		Unit 1	And they have been been been and and and and and and and and and an	Multi-colored shale with interbedded
-	Cretaceous				Unit 2		Argillaceous quartzitic sandstone with interpadded red shale and sittstone.
	1 1			Nubian	Unit 3		White guartz sandstone, fine to
	+				Unit 4		Interbeded multi-colored quartzitic
	Upper				Unit 4		sandstone, siltstone and share. White to gray sandstone interbedded
	JUIGOOIC				Unit 5		siltatone and shale.
	Lower Jurassic		Sine		Unit V		conglomeratic, feldspathic quartzitic sandatone, Interbedded are volcanics.
	Permian				Unit IV		A very fine to very coarse grainee, pour to medium sorted, grey to red feir/spathic, guartzitic sandstone.
ŝ	Carboniferous	1		Amal	Unit III		Multi-colored quartzitic sandstone, fine grained to coarse grained.
Sozo	Ordovician	1			Unit II		Coarse to fine grained sandstone interhedded with thin conglomeratic.
Pale	Cambrian	1			Unit I	······································	very coarse, grey to pink, tight,
	Cambrian	-		Bahi			Conglomerate sandstone.grey to brown
D	re Cambrian		+	Basement	-	Terreter and a second state of the	Granitic rocks with rhyolites and tuffs

Figure (2) Stratigraphic Columnar Section of Study Area(Haruge

company, 2005).



Figure (3) Structural Location of the Amal Field on The Amal High

## 3. Previous Studies:

Research on the chemical properties of formation water has concentrated on two primary aspects: the classification of formation water and its distribution characteristics. Many previous studies have explored the classification of formation water.

Liu et al. (2024) studied the geochemical characteristics and origin of the formation water of the saline lake basin: a case study of the Quaternary Qigequan formation in the sanhu depression, qaidam basin. Their findings revealed that the formation water in the study area has a high total dissolved solids (TDS) content and is mainly type IV and V of CaCl<sub>2</sub>.

Abou El Leil et al. (2022) studied classification and geological environment identification of produced water in oilfields. Moreover, they found the type of formation water is belonging to CaCl<sub>2</sub> type and deep marine environment.

Studied prediction of calcium carbonate and calcium sulfate scale deposits in Mabruk oilfield, Libya: studied by (Alnajar and Refai 2021). Naima Elgariani (2007) studied the oilfield water of the Nasser oil field; according to Sulin's, Bojarski's, and Scholler's geochemical investigation, the petroleum-associated water belongs to Cl-Ca, followed by SO<sub>4</sub>-Na, Cl-Mg, and HCO<sub>3</sub>-Na waters.

## 4. Purpose of study:

Knowledge of oilfield water type and classification, from the chemical composition of oilfield waters in Amal oilfield, Sirt basin, Libya. In other words, determine the environment of deposition.

## 5. Methods of study:

The chemical analysis of ten oilfield water samples collected from: B - 35, B - 45, B - 86, B - 100, N - 3, N - 18, N - 30, N - 50, and N - 63 wells. These samples were taken from December 2018 to November 2023 and tested in the laboratoryof the Amal labinHarouge Oil Operations (Harouge, 2005), which was distributed on the Amal oilfield in the Sirt basin, Libya. Figure (1). Table (2) summarizes the results of the analysis, which were calculated first in mg/l. This interpretation includes determination of total dissolved solids (TDS), major cations (Na<sup>+</sup>,K<sup>+</sup>,Ca<sup>2+</sup>, and Mg<sup>2+</sup>) and anions (SO4<sup>2-</sup>, Cl<sup>-</sup>, and HCO3<sup>-</sup>), type of water, as well as equivalent per million (epm) Table (3), so it can be used later on in the calculation of the percentages of the different parameters in the water type classification approach. The water type classification presented here adheres to Sulin's classification

established in 1946, with modifications introduced by Bojariski in 1970, as presented in Collins (1975). This classification was selected due to its relevance and alignment with the data under analysis.

Furthermore, the Rock Work works soft were used in ternary, and finally results of these parameters were put statistically onto specified tables.

#### 6. Geochemical Interpretations:

Geochemical interpretation was conducted using the following Formulas:

## Part per million (ppm):

A dimensionless concentration term that expresses the number of unit weights of solute per million unit weights of solution (ppm).

If the water is very fresh, the specific gravity is essentially 1.0, and ppm and mg/l are equal. However, as the TDS of the water increases, the specific gravity increases, and the units become increasingly different.

$$ppm = \frac{mg/L}{S.G}(1)$$

Where:

S.G: Specific gravity of water (relative density). Milliequivalents per Liter (meq/L):

$$meq/L = \frac{(mg/L) \times valance}{Atomic \, ormolecularwieght}$$
(2)

#### **Equivalents per Million (epm):**

This unit of concentration is calculated as follows:

$$epm = \frac{meq/L}{S.G}$$
(3)

To Classify of oilfield waters (types of waters) according to Sulin, we used the following formulas:

In this classification, the epm is the usable unit. It's based on:

- 1. Na/Cl.
- 2. (Na Cl)/SO<sub>4</sub>.
- 3. (Cl Na)/Mg.

# I- Type of Waters is Cl – Ca:

When:

$$\label{eq:na} \begin{array}{ll} Na/Cl < 1.0, \ (Na-Cl)/SO_4 < 1.0 \ and \ (Cl-Na)/Mg > 1.0. \ (4) \\ \textbf{II-} \qquad \textbf{Type of Water is } Cl-Mg: \end{array}$$

When:

Na/Cl < 1.0,  $(Na - Cl)/SO_4 < 0.0$  and (Cl - Na)/Mg < 1.0. (5) III- Type of Water is  $HCO_3 - Na$ :

When:

Na/Cl >1.0,  $(Na - Cl)/SO_4 > 1.0$  and (Cl - Na)/Mg < 0.0. (6) IV- Type of Water is SO<sub>4</sub> - Na:

When:

Na/Cl > 1.0,  $(Na - Cl)/SO_4 < 1.0$  and (Cl - Na)/Mg < 0.0. (7)

Bojarski noted considerable variation in the composition of Cl-Ca type waters and categorized these waters accordingly. Based on Bojarski's research, we utilized the following formulas:

Also, in this classification, the epm is the usable unit. It's based on the Na/Cl ratio.

a) Cl – Ca type I water: When: Na/Cl > 0.85(8) b)Cl – Ca type II water: When: Na/Cl = 0.85 - 0.75(9) c) Cl - Ca type III water: When: Na/Cl = 0.75 - 0.65 or likely 0.60 (10)d) Cl – Ca type IV water: When: Na/Cl = 0.65 - 0.50(11)e) Cl – Ca type V water: When: Na/Cl < 0.50(12)

# 7. Results and discussion:

The aqueous solubility of petroleum hydrocarbons increases with increasing temperature and pressure and decreases with increasing water salinity. Occurrences of petroleum accumulations often correlate with salinity transition zones, i.e., where the salinity ranges from 50,000 to 100,000 mg/liter (Collins 1975).

Figure (4) illustrates variation values in Total Dissolved Solids (TDS) concentrations at (mg/l) of oil field waters in Amal Oil – Field, which ranged from 205487 to 234912 mg/l. According to Gorrell's classification, all the studied samples are brine waters. Table (2).

This map showed the changes of TDS in the study area with the contour interval 5000, where TDS values increased in the east and north directions.

Finally, the TDS map illustrates water movement in East and North directions in addition, other words trending from West and South East. Where decreasing at south at (B118 and B86)wells.



Figure (4) Geochemical map showing distribution of TDS (mg/l) in Amal Oil field.

## 7.1 Classification of oil field waters:

Water analyses have generally been classified according to a system proposed by Palmer (1911, in Collins, 1975). First, the strong bases (Na<sup>+</sup>, k<sup>+</sup>) are combined with the strong acids (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) to form primary salinity (S1). Then the strong bases are combined with the weak acid (HCO<sub>3</sub><sup>-</sup>) to form primary alkalinity (A1). Next, the weak bases (Ca<sup>2+</sup>, Mg<sup>2+</sup>) are combined with the strong acid (Cl<sup>-</sup>,SO<sub>4</sub><sup>2-</sup>) to form secondary salinity (S2). Finally, the weak acids are combined with

the weak bases to form secondary alkalinity (A2). In fact, such combinations of ions do not take place, and it is hard to relate the different water classes to their history and geology. This classification was not used in this study.

The Russian hydrologist Sulin (1946) proposed a classification that is claimed to have genetic significance. This classification of the subsurface hydrochemical system is based upon various combinations of dissolved salts in the waters, which are divided according to Table (1) and equations (4) through (7). There are four major classes of waters; each one refers to different environments from natural water distribution:

- Continental (terrestrial)conditions that promote the formation of sulfate waters. Such conditions supply soluble sulfate constituents to the water, and the genetic type of such a water is "sulfate – sodium".
- 2. Continental conditions that encourage the development of sodium bicarbonate waters are characterized by the genetic type known as "bicarbonate sodium."
- 3. Marine condition and the formation of a " chloride magnesium" type of water.
- 4. The deep subsurface conditions within the Earth's crust lead to the creation of a "chloride calcium" type of water.

The first two types are indicative of meteoric and/or artesian waters, while the third pertains to marine environments and evaporite sequences. The fourth type is representative of deep stagnant conditions.

Sulin's system (1946) underwent modification by Bojarski (1970 in Collins, 1975). This modification aimed to redefine Sulin's classification of water types and provide a new interpretation of the environments linked to each type, as follows:

1. The "bicarbonate-sodium" water type is found in the upper zone of the sedimentation environment, characterized by hydrodynamic conditions that favor the preservation of petroleum and natural gas deposits.

- 2. The "sulfate-sodium" water type indicates the reaction of sodium with chloride or sulfate.
- 3. Waters of the "chloride magnesium" type are characteristic of the transition zone between hydrodynamic areas, which is becoming more hydrostatic in the deeper part of the basin.
- 4. Water of the "chloride calcium"type occurs in deeper zones that isolated from the influence of infiltration waters and are hydrostatic.

Туре	s of water	Ratio of concentrations, meq%			
		Na/Cl	(Na - Cl)/SO₄	(Cl – Na)/Mg	
Meteoric	Sulfate sodium	>1	<1	<0	
Mixed	Bicarbonate sodium	>1	>1	<0	
Connate	Chloride magnesium	<1	<0	<1	
Connate	Chloride calcium	<1	<0	>1	

Table (1) Major Classes of Water by Sulin's Classification

A significant variation in the chemical composition of the chloridecalcium type was noted, and this classification was detailed by Bojariski (1970) in Collins (1975) as follows:

a-Class, "**chloride** – **calcium I**" with a ratio of Na/Cl > 0.85 refers to an active hydrodynamic zone. It is considered a zone of little prospect for the preservation of the hydrocarbon.

b-Class, "chloride – calcium II" with a atio of Na/Cl = 0.85 - 0.75, refers to the transition zone between hydrodynamic zone and stable hydrostatic zone. It is considered a poor zone for hydrocarbon preservation.

c- Class, "**chloride** – **calcium III**" with a ratio of Na/Cl = 0.75 - 0.65, represents condition for the favorable preservation of hydrocarbon deposits. It is designated as a fairly hydrocarbon preservation environment.

d-Class, "chloride – calcium IV" with ratio of Na/Cl = 0.65 - 0.50,

represents a complete isolation environment of hydrocarbon accumulation as

well as by the presence of residual water. This class represents a good zone for hydrocarbon preservation.

e-Class, "**chloride** – **calcium V''** with ratio of Na/Cl < 0.50, refers to the presence of highly altered residual ancient seawater. This type is one of the most likely indicators for the hydrocarbon accumulation zone.

Table(2) chemical analysis of the oil – field waters from Amal Oil .Field NC-12, sirt basin Libya in mg/l

Wel	Cations(mg/l)			Anic	Anions(mg/l)			р	Sp.	
I	Na⁺	k⁺	Ca <sup>++</sup>	Mg⁺	Cl <sup>-</sup>	SO	HCO	(mg/l	Н	Gr.
No.:				+		4	3	)		
B-	591	33	196	131	1301	5	195	21075	6.	1.1
35	01	0	95	2	13			1	0	4
B-	657	95	121	292	1322	26	271	21428	6.	1.1
45	24	0	44	8	40			3	0	4
B-	599	63	177	583	1262	35	281	20548	5.	1.1
86	90	0	55		13			7	3	4
B-	611	12	109	696	1350	7	172	21547	5.	1.1
100	37	00	22	2	76			6	7	4
B-	607	10	187	960	1297	1	239	21059	5.	1.1
118	43	0	98		58			9	8	4
N-3	640	10	185	131	1364	39	239	22179	5.	1.1
	97	80	37	2	94			8	7	5
N-	659	12	110	124	1411	12	166	22212	5.	1.1
18	70	40	2	17	03	4		2	5	5
N-	639	12	219	222	1453	5	134	23491	4.	1.1
30	49	60	84	3	57			2	8	5
N-	593	11	236	131	1382	20	122	22382	5.	1.1
50	33	20	47	2	67			1	8	5
N-	668	12	125	342	1364	14	137	22081	5.	1.1
63	88	00	25	6	94	0		0	4	5

7.2Classification of study area:

According to sulin, based on the previous formulas from ten samples, all of the waters were Cl - Ca type waters; these results are represented in Table (4). This was done using equations (4) through (7).

In addition, Cl – Ca waters reflect the fact that these waters are associated with oil in a deep subsurface environment. So we can determine water flow directions in oil fields by tracing such types of waters, especially if we have already Cl – Ca waters in any studied field. The analyzed water was classified based on Na/Cl ratios according to the Bojarski (1970) classification modified from the sulin classificationThis was done using equations (8) through (12). The results, as shown in Table (5), showed that in the two wells (B – 45, N – 63) the Na/Cl ratios were 0.77 and 0.76, respectively. This means that the water is of the second type of chloride calcium (Cl – Ca II), which indicates that the transitional zone between an active hydrodynamic zone and a more stable hydrostatic zone of the sedimentation basin is considered a poor zone for preserving hydrocarbons.

Regarding the wells (B -35, B -86, B -100, B -118, N -3, N -18, N -30, and N -50), the water is identified as type III calcium chloride. This region exhibits favorable conditions for the preservation of hydrocarbon deposits, suggesting that the environment is somewhat conducive to hydrocarbon preservation.

Well		,		epm	1		
No.:	Na⁺	k⁺	Ca++	Mg <sup>++</sup>	Cl-	SO4 	HCO 3 <sup>-</sup>
B-35	2251. 1	7.4	860.6	94.5	3213.7	0.1	2.8
B-45	2505. 6	21.3	531.1	211. 2	3269.1	0.5	3.9
B-86	2289. 0	14.1	777.2	42.1	3122.8	0.6	4.0
B-100	2326. 6	26.9	476.8	501. 2	3333.3	0.1	2.5
B-118	2315. 7	2.2	822.1	69.2	3207.7	0.0	3.4

Table(3) chemical analysis of the oil – field waters from Amal Oil Field NC-12, sirt basin Libya in epm.

N-3	2435. 0	24.1	807.9	94.3	3362.4	0.7	3.4
N-18	2504. 0	27.7	48.0	891. 6	3473.0	2.3	2.4
N-30	2412. 5	28.0	951.4	158. 7	3555.9	0.1	1.9
N-50	2252. 0	25.0	1029. 7	94.2	3403.1	0.4	1.7
N-63	2538. 8	26.8	545.4	246. 0	3359.5	2.5	2.0

Table (4) Classification of the oil – field waters from Amal Oil Field NC-12, Sirt Basin Libya, According to Sulin's (1946).

Well No.:	Na+\ Cl <sup>-</sup> epm	(Na⁺ - Cl⁻)∖ SO₄ epm	(Cl⁻ - Na⁺)∖ Mg++	Type of water
	-		epm	
B-35	0.70	-10559.24	10.18	CI-Ca
B-45	0.77	-1609.28	3.62	CI-Ca
<b>B-86</b>	0.73	-1304.45	19.81	CI-Ca
B-	0.70	-7895.17	2.01	CI-Ca
100				
В-	0.72	-48884.93	12.88	Cl-Ca
118				
N-3	0.72	-1307.78	9.84	CI-Ca
N-18	0.72	-430.12	1.09	CI-Ca
N-30	0.68	-12663.88	7.21	CI-Ca
N-50	0.66	-3167.90	12.22	CI-Ca
N-63	0.76	-322.66	3.34	CI-Ca

Libya, According to Bojarski (1970).

Well No.:	Na+ \ Cl <sup>-</sup> epm	Type of water	Class
B-35	0.70	Cl-Ca	-
B-45	0.77	Cl-Ca	II
B-86	0.73	Cl-Ca	III

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B-100	0.70	Cl-Ca	III
B-118	0.72	CI-Ca	III
N-3	0.72	CI-Ca	
N-18	0.72	CI-Ca	III
N-30	0.68	CI-Ca	
N-50	0.66	CI-Ca	III
N-63	0.76	CI-Ca	II

We observed a notable decrease in sulfate concentrations in the study area, as shown in Table (2). The sulin classification (1946) highlights groups with highly mineralized chloride-calcium or bicarbonatesodium water types, which contain reduced forms of sulfur. These are significant indirect indicators of oil presence. A low sulfate content is essential to suggest interaction with bituminous components and/or sulfate-reducing bacteria.

#### 8. Graphic representation:

Water analyses are often expressed graphically. The diagram, or pattern, obtained by graphically plotting the results of a water analysis will often highlight important points about the analysis that might be missed by simply reading the report. Pattern comparison is also an easy way to quickly spot differences in two or more waters (Patton, 1986). There are many different water analysis diagrams in way Two such

There are many different water analysis diagrams in use. Two such diagrams are:

## 8.1 Piper Diagram:

A piper diagram is a graphical representation of the chemistry of a water sample or samples. It shows the relative concentrations of six to seven ions in solutions, in this case, the cations  $Ca^{2+}$ , Mg, and  $Na^++K^+$ , and the anions  $Cl^-$ ,  $SO^{2-}_4$ , and  $HCO_3^-$ . In most natural waters, these ions make up 95 to 100% of the ions in solution.

The Piper diagram includes two trilinear diagrams, one for anions (on the lower right) and one for cations (on the lower left). For each sample, the information from each trilinear diagram is projected up into the central quadrilateral. Therefore, each sample will plot in each frame of the piper, once representing cations, once representing anions, and once representing the combination.

For each constituent, the concentration (in mg/l) is converted to chemical equivalents (meq/l) based on the valence and atomic weight. Then the percentages of each ion relative to the total are calculated and

plotted on the piper diagram. Each trilinear diagram shows the relative percentages of the three ions. Each corner on the triangles represents 100% of the ion shown at that corner. (C. Sadashivaiah et al. 2008).

Chemical data of representative samples from the study areais presented by plotting them on a Piper-tri-linear diagram for these wells, as shownin Figure (5),by the geochemical software RockWorks.

The piper diagram in the study area indicates most of the samples were classified as  $(Na^++K^+)$  and  $Ca^{2+}$  types of cations and  $Cl^-$  types of anions. Water in the Amaloil field consists of alkalis that exceed alkaline earths. The dominant cation found in the water is  $(Na^++K^+)$  followed by  $Ca^{2+}$  and the dominant anions are  $Cl^-$  followed by  $HCO_3^-$ .



Figure (5) Piper diagram showing proportion of major ions in Amal Oil Field.

## 8.2 Stiff Diagram:

It is also called a **Butterfly Diagram**. It is a graphical representation of chemical analyses, first developed by H.A. Stiff in 1951. It is widely used by hydrogeologists and geochemists to display the major ion composition of a water sample. A polygonal shape is created from four parallel horizontal axes extending on either side of a vertical zero axes. Cations are plotted in meq/l on the left side of the zero axes, one to each horizontal axis, and anions are plotted on the right side. Stiff patterns

are useful in making a rapid visual comparison between water from different sources, i.e., connate injection waters.

This diagram is the most widely used in the graphic representation of oil-field water analysis. The scale may be either arithmetic or logarithmic. See also Figures6.a and 6.b(Patton, 1986).

Figures 6.a and 6.b show the stiff diagram for some wells in the Amal oil field; Figure 6a shows the similarity in chemical composition of these waters from the study area. The concentration of chlorine and sodium is high in all wells, followed by magnesium, bicarbonate, and very low amounts of sulfate concentrations; this is because bacteria reduce sulfate to sulfide in a confined environment, reducing the sulfate and bicarbonate contents in the formation waters (Lie et all., 2024).

While we observe that wells B-45 and B-100 have higher concentrations of magnesium and lower concentrations of calcium relative to other wells depicted in the same figure.

As for Figure (6b), we notice that the water in wells N-3, N-30, N-50, and N-63 has almost the same composition, as it contains high concentrations of chlorine and sodium, followed by calcium and then magnesium, which indicate the same origin and source of water. In well N-18, we see a noticeable decrease in calcium concentrations with an increase in magnesium concentrations compared to the rest of the wells in the same figure.



Figure (6.a) Stiff diagram showing the major ion composition of water in the Amal Oil Field.





## 9. Conclusion

This study presents the results of the geochemical classification of some wells in Amal Oil Field in the Sirt Basin,Libya. These wells are: (B - 35, B - 45, B - 86, B - 100, B - 118, N - 3, N - 18, N - 30, N - 50, and N - 63).

From geochemical calculations and interpretations of the studied oil – field water samples, the following conclusions are illustrated:

Cations in oil – field waters are: Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>. Anions are: Cl<sup>-</sup>, HCO<sup>-</sup><sub>3</sub>, and SO4<sup>2-</sup>.

Total Dissolved Solids (TDS) range from 205487 to 234912 mg/l. According to Gorrell's classification, all the studied samples are Brine waters.

According to Sulin's classification, all studied wells are: CI - Ca type waters (Connate); CI - Ca waters reflect that these water are associated with oil ina deep subsurface environment andalso reflect isolated waters with hydrostatic conditions. These waters were also classified according to the Bojarski, and the results showed that the majority of waters were classified as CI - Ca type III. This type describes conditions that are conducive to the preservation of hydrocarbon deposits. It is identified as a relatively favorable environment for the preservation of hydrocarbons. Followed by CI - Ca type II This area represents the transitional zone between an active hydrodynamic zone and a more stable hydrostatic zone within a sedimentation basin, which is regarded as a less favorable environment for hydrocarbon preservation.

Chemical data of representative samples from the study oil field were presented by plotting them onPiper and Stiff diagrams as follows: In the piper diagram, most of the samples were classified as  $(Na^++K^+)$ and  $Ca^{2+}$  types of cations and  $Cl^{-}$  types of anions. Water in the Amal oil field consists of alkalis that exceed alkaline earths, and strong acids exceed weak acids. The dominant cation found in the water is  $(Na^++K^+)$ followed by  $Ca^{2+}$  and the dominant anions are Cl<sup>-</sup> followed by HCO<sup>-</sup><sub>3</sub>. Stiff diagrams show increasing concentrations of Na<sup>+</sup>, Ca<sup>2+</sup>, and Cl<sup>-</sup>and decreasing concentrations of Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>.In most wells, which indicate the same origin and source of water, other samples showhigher concentrations of  $Mg^{2+}$  and lower concentrations of  $Ca^{2+}$ . and we note a decrease in  $SO_4^{2-}$  concentrations in all wells. These are significant indirect indicators of oil presence. A low sulfate content is essential to suggest interaction with bituminous components and/or sulfatereducing bacteria. While the increase in magnesium concentration in some wells in the study area is due to the rock description of the formations forming that area, which is represented by the presence of interferences of volcanic rocks with sandstone rocks, as well as perhaps the mineral composition of the reservoir rock, as it was previously indicated that it contains clay and mica minerals.

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- Abou El Leil, I.M., and et al., 2022, Classification And Geological Environment Identification Of Produced Water In Oilfields. ISTJ International Science and Technology Journal, vol 30: p.1-20, (2022).
- Barkham S., Habesch S., Libya Concession 12 Amal Field Geological Studies, December 2005, Haruge Unpublished report.
- Barr,F.T. and Weagar, A.A., 1972, Stratigraphic nomenclature of the Formation in Sirt Basin: Petroleum Exploration Society of Libya.
- Collins, A.G., 1975, Geochemistry of oil –field waters, Amsterdam, Netherlands: Elsevier scientific Publishing.
- Dicky, P.A., 1986, Petroleum Development geology: penn well publishing company, Tusa, oklahomausa. Third edition.
- Elgariani. N, 2007, Role of Oil Field water geochemistry in hydrocarbon Expolration and production in Nasser field, NC-6, Libya: Unpolished M.SC. Thesis, University Tripoli, Libya.
- Geopec, 1994, Amal Field, Final Report.

- Jiranek, J., Cartwright, J. and Vejmelek, L., 1998, Fault sealing analysis of a segment of the Outer Moroccan Rifian Fold Belt, northwest Africa. Marine and Petroleum Geology, vol.15(7), pp. 635-649, (1998).
- Liu, X., and et al., 2024, Geochemical characteristics and origin of the formation water of the Saline Lake Basin:a case study of the Quaternary Qigequan Formation in the Sanhu Depression, Qaidam Basin: Geoscience Letters., DOI 10.1186/s40562-024-00332-y,(In press).
- Mobil, 1979, Amal Field Study Geological Report.
- Patton, C. C., 1986, Applied water technology: Campbell petroleum series norman, Oklahoma. Second Edition.
- Qader, F.M., and et al., 2021, Geochemical Evaluation Of Formation Water, Mauddud Reservoir, Khabbaz Oilfield, Kirkuk Area, Northern Iraq. UKH Journal of Science and Engineering, vol. 2(5): pp.28 -35, (2021).
- Refai, T.R., 2011, produced water management in Libyan oil fields: unpublished report Geological Engineering Department.
- Roberts, J. (1970). Amal Field. In: Geology of Giant Oil Fields (ed Halbouty, M.T.). Mem. Am. Assoc. Petrol. Geol., 14, 438-448.
- Schlumberger service company,1997. Unpublished Technical Report.
- Whitbread, M.H., 1989, Mesozoic rift-drift sequence of northern Africa and eastern South America.