

Physico-chemical Characterization and Salinity Distribution of the Oilfield Water in the Upper Member of Zubair Sandstones in Rumaila North Oilfield, Southern Iraq

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Received: March 16, 2017; *revised:* June 29, 2017; *accepted:* July 11, 2017

Abstract

The oilfield water in the upper member of Zubair reservoir (Barriemian-Hauterivian) in Rumaila North oil field is investigated for the interpretation of salinity and geochemical evolution of brine compositions. The interaction of the oilfield water with reservoir rocks resulted in a brine water, which is derived from the marine water and is partially mixed with meteoric water; the composition of the water is similar to that of formation water from the offshore/onshore Mesozoic reservoirs of the Gulf of Mexico. The high average of total dissolved solid (TDS) (215625 mg/l) is consistent with the average electrical conductivity (351024 μ s), and is predominantly represented by Cl (123679 mg/l), Na (29200 mg/l), and Ca (14674 mg/l). The main contributing cations (epm%) are Na (70.2), Ca (18.9), Mg (8.1), and K (1.7). The main anions include Cl (99.7), SO₄ (0.25), HCO₃ (0.07), and CO₃ (0.005). The sodium content is six times greater than that of seawater; calcium and magnesium contents are three times greater, and chloride is 6.5 times greater. The sulfate is depleted to one sixth, due to a sulfur release from sulfates into the hydrocarbon phase. Zubair oilfield water is characterized by an acidic pH (pH=5.2- 5.77), high specific gravity (1.228), high fluid pressure (4866 psi), hydrocarbon saturation of 43%, water saturation of 57%, and porosity of 12.7%. The mineral saturation model indicates that Zubair oilfield water is unsaturated water with respect to all the suggested minerals at a pH of 5.45, but at a simulated pH of 9.12, brucite is at equilibrium; brucite and portlandite are supersaturated at a pH of 11.9. The mineral solubility responses to the changes in temperature, pressure, pH, oxidation potential (Eh), and ionic strength, thereby proportionally developing formation damages.

Keywords: Oilfield Water, Specific Gravity, TDS, Water Resistivity, Saturation Index, Salinity

1. Introduction

Rumaila North Oilfield (RNOF) is located in southeastern Iraq, 45 km west of Basra town, where several oilfields are present (Figure 1). Zubair formation, which is of Barremian age of Lower Cretaceous, has a significant oil reservoir in southern Iraq (Buday, 1908). It is composed of dominantly sandstone succession with some shale intercalations and minor limestone (Khaled et al., 2013) of variable thickness increasing towards the northeastern, while decreasing towards the west and northwestern, ranging from 280 to 400 m at the type section and from 350 to 450 m in northern

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Kuwait (Khaled et al., 2013). Zubair formation is of poor to fair potential source rock due to the shale units, so some oil could have been generated. Low to mid-maturity, 0.2–2.6 wt.% TOC, and a T_{max} ranging from 420 to 440 °C characterize the formation (Al-Ameri et al., 2011). The kerogen of the Jurassic-Lower Cretaceous source rocks mainly of Upper Jurassic-Lower Cretaceous Sulaiy formation has transformed into oil and gas. It has migrated and accumulated in different Cretaceous reservoir traps with further migration to the Tertiary traps (Al-Ameri et al., 2011). In RNOF, it emplaces conformably over Ratawi formation, and gradually beneath the Shuaiba formation (Owen and Naser, 1958). As it has a deltaic environment, the controlling factor of the reservoir characterizations is where sands have been deposited (Nath et al., 2015).

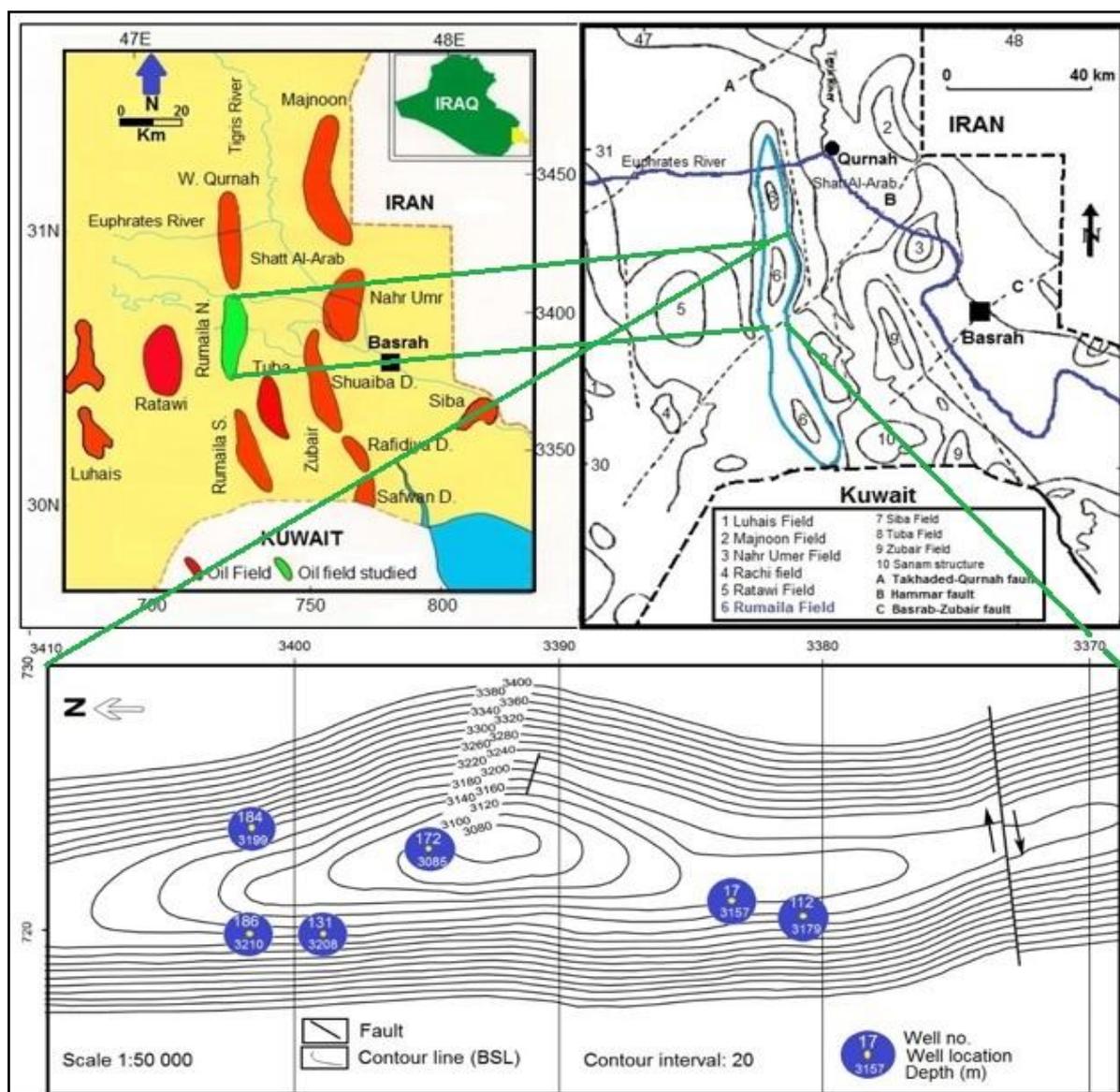


Figure 1

Top: location map (left); a subsurface structural map of Rumaila oilfield and adjacent oilfields (right) (Al-Mutury and Alasdi, 2008); bottom: a detailed structural contour map of Zubair reservoir in RNOF with the location of the studied oil wells.

Zubair reservoir has been studied by many researchers, but all these studies have not addressed the subject of the oilfield water, its chemical and physical properties, and its interactions that may impact the physical properties of the reservoir. Most of these studies have focused on the petroleum system

and organic chemistry of crude oil and have neglected the water role and inorganic geochemistry. Understanding the chemistry of oilfield water and salinity distribution throughout the reservoir can be employed to predict the best drilling sites and understand the oil production heterogeneity. The fluid flow direction which is an essential parameter for hydrocarbons can be suggested by hydrochemistry (Brouwer and Jansen, 2004). The ratio of $(\text{HCO}_3 + \text{CO}_3)/\text{SO}_4$ in the developed oilfield provides an excellent evidence for determining oil-water and oil-gas contacts in an undeveloped oil field, and also can be used for exploring whether hydrocarbons are present or absent. This study aims (1) to determine the origin and type of the oilfield water; (2) to discuss the salinity distribution and ionic abundance in the reservoir, based on the brine chemical composition and physical reservoir properties; and (3) to build up a simulation model of the mineral saturation at different pH values.

2. Subsurface geology

The productive reservoir is composed of sandstone layers with intervening shale beds, restricted in an N-trending doubly plunging asymmetrical anticline (Al-Fadel and Al-Ansari, 1992). The dimensions of RNOF are 43 km long and 14 km wide (Figure 1). Subsurface depth from the sea level to the top of the reservoir ranges from 3200 to 3270 m. The subsurface structural contour map was drawn using six oil wells (Figure 1). The structural setting could potentially influence the fluid flow within the reservoir. Zubair reservoir is successively characterized by four interbedded shale and sand members as a deltaic sedimentary environment (Abbo and Saffar, 1967; Al-Siddiki, 1978). A detailed stratigraphic section of Zubair reservoir in RNOF is integrated with self-potential (SP) and resistivity logs (Figure 2).

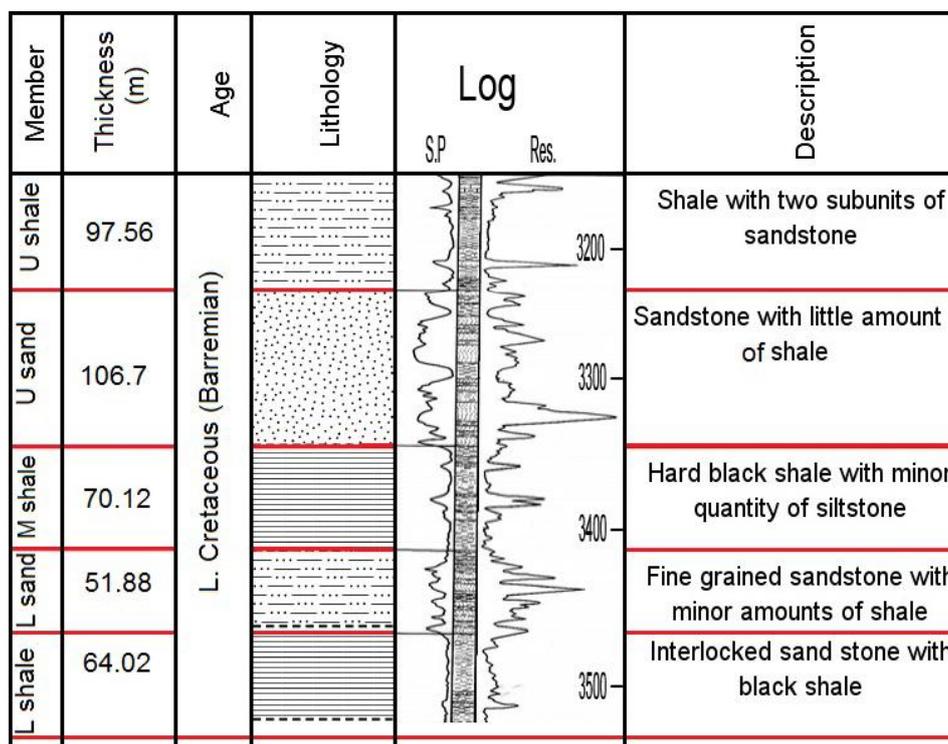


Figure 2

A stratigraphic section of Zubair reservoir associated with the well logs after Al-Naqib, 1967.

3. Sampling and methods

Oilfield waters from Zubair reservoir in RNOF were collected by the South Oil Company (SOC) at various depths (Table 1). The samples were filtered to $<0.45 \mu\text{m}$ and acidified with ultrapure

concentrated nitric acid (HNO_3) for the ions reservation. Major cations and anions were analyzed by analytical methods proposed by the SOC. The structural contour map of Zubair reservoir in RNOF was drawn using the data provided by the SOC. Temperature ($^{\circ}\text{C}$), apparent water salinity (AWS), salinity ($\%$), water saturation (S_w), hydrocarbon saturation (S_H), fluid pressure (P_f), resistivity of water (RW at 25°C and at a certain temperature), and porosity were calculated by using specific equations shown in the results section. Total dissolved solid (TDS) and electrical conductivity (EC) were determined in situ. The mineral saturated index and mineral precipitation model was simulated using the PHREEQC software program. AquaChem and Aqion software programs were used for performing the piper, stiff, and Schoeller diagrams. Hydrochemical parameters were calculated and used for the determination of the origin and type of oilfield water origin.

4. Results and discussion

4.1. Physicochemical reservoir properties

Physical properties of Zubair reservoir in RNOF is presented in Table 1. The pH probably changes due to the chemical equilibrium shifting as new ions are combined with H^+ or OH^- (Collins, 1975), where it plays an important role in controlling the salt solubility in solutions. The high TDS (207350-230100; average 215625 mg/l), predominantly by Na and Cl (29200 and 123679 mg/l respectively) as the anions and Ca (14674 mg/l) as the cation is consistent with the electrical conductivity (340362-372762; average 351024 μs). The recorded high specific gravity (SG) in Zubair reservoir (ranging from 1.1315 to 1.415 with an average of 1.228) is greater than that of some Iraqi oilfields such as Mishrif (1.1502) and Yamama (1.1387) reservoirs, and larger than that of some global oilfields such as Stephens (1.1350) and Wesson (1.1490) reservoirs.

Table 1

Physico-chemical properties of the oilfield water in Zubair reservoir at NROF; SG: specific gravity measured at 15°C ; RW = water resistivity; $P_f = 0.465$ psi/ft.; T ($^{\circ}\text{C}$) calculated as $0.67/\text{ft.}$; AWS: apparent water salinity; S_w : water saturation; S_H : hydrocarbon saturation; and P_f : fluid pressure.

| Parameters | FW-17 | FW-112 | FW-131 | FW-172 | FW-184 | FW-186 | Av. |
|--------------------------------|--------|--------|--------|--------|--------|--------|--------|
| Depth (m) | 3157 | 3179 | 3208 | 3085 | 3199 | 3210 | ---- |
| pH | 5.5 | 5.45 | 5.77 | 5.70 | 5.10 | 5.2 | 5.45 |
| T ($^{\circ}\text{C}$) | 69.4 | 69.9 | 70.5 | 67.8 | 70.3 | 72.7 | 70.1 |
| EC ($\mu\text{s}/\text{cm}$) | 346633 | 372762 | 352275 | 347840 | 346274 | 340362 | 351024 |
| TDS (mg/l) | 215300 | 230100 | 213500 | 217400 | 210100 | 207350 | 215625 |
| AWS (mg/l) | 125500 | 126050 | 129575 | 120300 | 120450 | 120200 | 123679 |
| Salinity ($\%$) | 227 | 228 | 234 | 217 | 218 | 217 | 223 |
| SW | 0.58 | 0.55 | 0.60 | 0.55 | 0.57 | 0.59 | 0.57 |
| SH | 0.42 | 0.45 | 0.40 | 0.45 | 0.43 | 0.41 | 0.43 |
| SG | 1.1405 | 1.1315 | 1.1407 | 1.400 | 1.1410 | 1.4150 | 1.2280 |
| RW (25°C) | 0.028 | 0.027 | 0.028 | 0.029 | 0.029 | 0.029 | 0.028 |
| RW (T) | 0.014 | 0.013 | 0.013 | 0.014 | 0.013 | 0.013 | 0.013 |
| P_f (psi) | 4816 | 4849 | 4894 | 4706 | 4880 | 5049 | 4866 |
| Porosity ($\%$) | 11.9 | 11.2 | 13.7 | 11.3 | 13.9 | 14.2 | 12.7 |

Resistivity is a reflection of a liquid pressure and is inversely proportional to both TDS and EC. Empirical equations set out below (Equations 1 and 2) have been used to compute the water resistivity (RW) based on total dissolved solid (TDS and EC); the results turned out to be close because of the harmonic relation between TDS and EC.

$$\log RW = 2.841 - 0.788 \log (TDS) \text{ at } 25^\circ\text{C} \quad (1)$$

$$RW = 10000 / EC \text{ at } 77^\circ\text{F or } 25^\circ\text{C } (\Omega\text{cm}) \quad (2)$$

where, TDS is measured in mg/L, and the water resistivity (RW) is expressed in Ohm. Water resistivity (RW) was computed in six oil wells at 25°C by using Equation 2, and at a certain temperature using Equation 3:

$$RW(T) = \frac{1.5(RW(25))^{0.987}}{(1.017)^T} \quad (3)$$

where, $RW(T)$ is water resistivity at temperature T ($^\circ\text{C}$), and $RW(25)$ is water resistivity at 25°C . If TDS is known, the resistivity at a given temperature can be calculated by using Equation 4:

$$RW(T) = \frac{957}{((TDS)^{0.778} \times (1.017)^T)} \quad (4)$$

The outcome is that RW is reversely correlated to TDS with correlation factor of 0.65 and is defined by:

$$Y = -0.0753X - 1.4835 \quad (5)$$

The relationship is shown in Figure 3. Water saturation (SW) in Zubair reservoir was calculated by using Equation 6, and the results are listed in Table 1:

$$SW(\%) = \frac{AWS}{TDS} \quad (6)$$

where, AWS is apparent water salinity. The chloride value can generally be used to quantify the reservoir-water salinity (Tiab and Donaldson, 2004). Zubair reservoir has an RW of 0.57%.

Hydrocarbon saturation (SH) was also computed by Equation 7 stated by Afizu (2013):

$$(SH) = (1 - SW)\% \quad (7)$$

Consequently, the average SH in Zubair reservoir is 0.43% (Table 1). As it is well known, the logging tools are widely used in determining RW . In this study, the salinity of water was reversely used as a function to estimate water resistivity and reservoir temperature. As shown in Figure 3, a proportional correlation between salinity and water resistivity is documented. The Gen-9 chart of Schlumberger was used to clarify the resistivity versus the equivalent NaCl concentration. The resistivity and temperature values at which the value was determined are used to approximate the NaCl ppm. In Zubair oilfield water, the salinity indicates that the water resistivity is 0.02 at 66°C (Figure 4). Basically, the formation resistivity shows a positive correlation with the hydrocarbon saturation, but it

is negatively correlated to the water saturation. The salinity (S‰) value (Table 1) was calculated at a well temperature based on Equation 8 stated by Lewis and Perkin (1979).

$$S (\%) = 1.805 \text{ Cl} (\%) \quad (8)$$

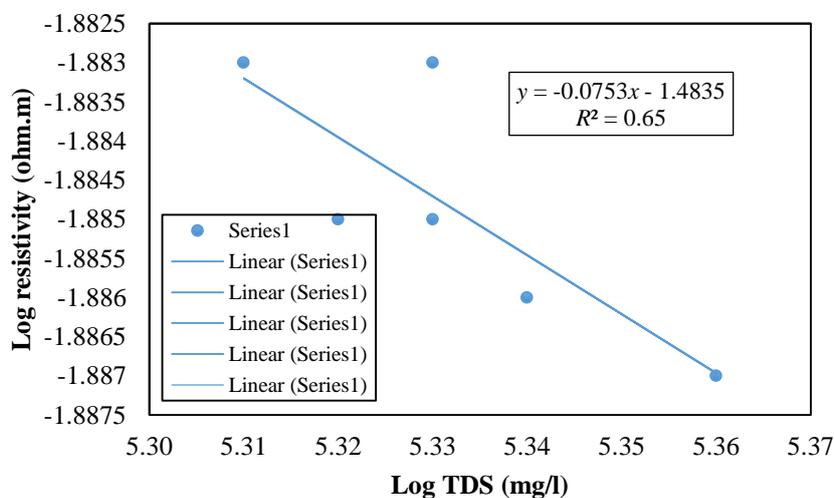


Figure 3
Relationship between *RW* and TDS in Zubair reservoir.

4.2. Brine composition and reservoir pressure

The concentration of the ions (Na, K, Ca, Mg, Cl, SO₄, CO₃, and HCO₃) are presented and listed in Table 2. The oil field water in Zubair reservoir at the NROF is characterized by predominant sodium (57550-60500 mg/l), which is six times greater than that of seawater, so a closed system of fossil water is indicated (Collins, 1975). Sodium is a dominant cation (Na⁺ > Ca²⁺ > Mg²⁺ > K⁺). The interaction of the oilfield water with reservoir rock resulted in high salinity. The normal content of Na in rainwater and seawater is respectively about 0.2 and 10556 mg/l; it is around 42803 to 74500 mg/l in the waters of several oilfields in the world (Table 2). In the United States (Kansa oil field), the content of Na⁺ and Ca²⁺ increases by increasing salinity (Collins, 1975) and varies from 42803 to 74500 mg/l in the waters of several oilfields in the world. Most oilfield waters contain more Na than any other cations, and it is believed to be of marine origin (Collins, 1975). The halite, feldspar, and clay minerals are the main source of sodium (Todd, 2005). As Zubair formation is of deltaic environment originated by acidic igneous rocks, the feldspar and eventually clay minerals are evident sources of Na along with the primary marine sea water as the main source. In the natural water system, calcium is dominant: 400 mg/l in sea water, 2000-3000 mg/l in the subsurface brines with some as high as 30000 mg/l (Collins, 1975); in some global oil fields, it reaches more than 20000 mg/l (Al-Yasiri, 2000). Carbonates and sulfates are expressed as the main sources of Ca. The solubility is proportionally correlated with CO₂ partial pressure and temperature but negatively correlated with pH. The amount of Ca released from sulfates depends on their solubility which decreases with increasing temperature. The role of CO₂ is described in reducing the pH value toward acidity which accelerates the dissolution of carbonates and provision of Ca ions. Calcium content in Zubair reservoir oilfield water (13600-15990 ppm) is the third highest concentration after chloride and sodium; the calcium content of Zubair reservoir oilfield water is three times larger than that of the seawater.

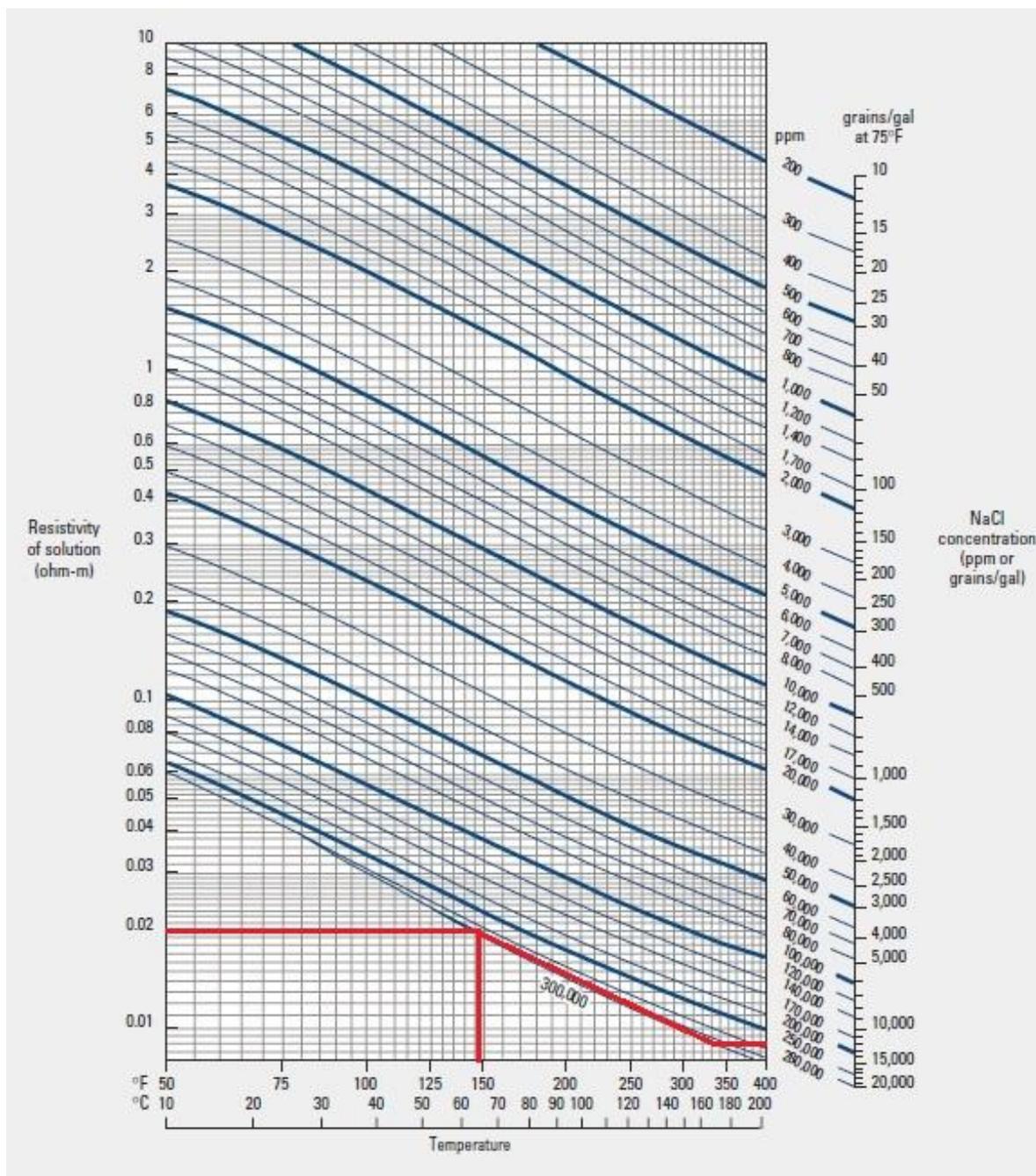


Figure 4
Salinity of water as a function of water resistivity and temperature.

The weight ratio of Mg to Ca in seawater is about 3. The Mg content (3200-4150; average 3542 mg/l) of Zubair reservoir is three times as large as that of the seawater (1272 mg/l). Subsurface brines and world's oil fields have a wide range of Mg content varied from less than 100 mg/l to more than 30000 mg/l, but compared to sea water, many subsurface types of brine are mostly depleted in Mg. During the preliminary prediction, K concentration was expected to be present at a low concentration in solution due to the low solubility of K-containing minerals and the high affinity of K to adsorb onto clay surfaces. The range (1900-3350 mg/l) and average amount (2400 mg/l) of K in Zubair reservoir are almost six times greater than those of K concentration in seawater.

Table 2

Ionic concentrations in Zubair reservoir at NROF compared to some USA reservoirs (Collins, 1975), Iraq oil fields, and sea water; C/S: (HCO₃+CO₃)/SO₄; DB: difference balance.

| Wells | Type | Depth (m) | Unit | Ca ²⁺ | Mg ²⁺ | Na ⁺ | K ⁺ | Cl ⁻ | SO ₄ ²⁻ | HCO ₃ ⁻ | CO ₃ ⁻ | C/S | DB | TDS |
|----------|---------------|-----------|-------|------------------|------------------|-----------------|----------------|-----------------|-------------------------------|-------------------------------|------------------------------|------|--------|--------|
| FW-17 | | 3157 | ppm | 15500 | 3200 | 60500 | 2100 | 125500 | 450 | 100 | nil | 0.22 | 183 | 215300 |
| | | | epm | 775 | 267 | 2630 | 56 | 3535 | 9.4 | 1.6 | nil | | | |
| | | | epm% | 20.78 | 7.15 | 70.55 | 1.51 | 99.7 | 0.26 | 0.05 | nil | | | |
| FW-112 | | 3179 | ppm | 13900 | 4150 | 60400 | 2200 | 126050 | 270 | 170 | 15 | 0.68 | 163 | 230100 |
| | | | epm | 695 | 346 | 2626 | 56.4 | 3551 | 5.6 | 2.8 | 0.5 | | | |
| | | | epm% | 18.7 | 9.3 | 70.5 | 1.5 | 99.7 | 0.16 | 0.08 | 0.01 | | | |
| FW-131 | | 3208 | ppm | 14150 | 3700 | 60200 | 2150 | 129575 | 470 | 153 | nil | 0.32 | 26 | 213500 |
| | | | epm | 707 | 308 | 2617 | 55.13 | 3650 | 9.8 | 2.5 | nil | | | |
| | | | epm% | 19.2 | 8.4 | 70.9 | 1.5 | 99.7 | 0.3 | 0.07 | nil | | | |
| FW-172 | Present study | 3085 | ppm | 14901 | 3400 | 57550 | 2700 | 120300 | 530 | 150 | nil | 0.28 | 198 | 217400 |
| | | | epm | 745 | 383.3 | 2502 | 69.2 | 3389 | 11 | 2.5 | nil | | | |
| | | | epm% | 20.7 | 7.9 | 69.5 | 1.9 | 99.6 | 0.32 | 0.07 | nil | | | |
| FW-184 | | 3199 | ppm | 13600 | 3300 | 58300 | 1900 | 120450 | 390 | 110 | nil | 0.28 | 135 | 210100 |
| | | | epm | 680 | 275 | 2535 | 48.7 | 3393 | 8.1 | 1.8 | nil | | | |
| | | | epm% | 12.2 | 7.8 | 71.6 | 1.4 | 99.7 | 0.24 | 0.05 | nil | | | |
| FW-186 | | 3210 | ppm | 15990 | 3500 | 58250 | 3350 | 120200 | 390 | 140 | 20 | 0.41 | 313 | 207350 |
| | | | epm | 799 | 292 | 2533 | 85.9 | 3386 | 8.1 | 2.3 | 0.67 | | | |
| | | | epm% | 21.6 | 7.9 | 68.3 | 2.3 | 99.7 | 0.24 | 0.07 | 0.02 | | | |
| Min. | | | 13600 | 3200 | 57550 | 1900 | 120200 | 270 | 100 | 15 | | | 207350 | |
| Av. | | | 14674 | 3542 | 59200 | 2400 | 123679 | 417 | 137 | 18 | | | 215625 | |
| Max. | | | 15990 | 4150 | 60500 | 3350 | 129575 | 530 | 170 | 20 | | | 230100 | |
| St.Dev | | | 947.9 | 344.1 | 1308.8 | 535.7 | 3940.8 | 89.1 | 26.9 | 3.5 | | | 7954 | |
| Av. | | | epm% | 18.9 | 8.0 | 70.2 | 1.7 | 99.7 | 0.25 | 0.07 | 0.005 | | | |
| *Oh | | | | 9100 | 2432 | 54395 | 0 | 106216 | 768 | 450 | 106216 | | | 279577 |
| Texas | USA | | | 21680 | 2638 | 42803 | 166 | 111860 | 130 | 330 | 111860 | | | 291467 |
| *LA | | | 20000 | 523 | 48737 | 1040 | 80336 | 0 | 0 | 80336 | | | 230972 | |
| Kansas | | | 48800 | 2000 | 74500 | 650 | 188900 | 432 | 0 | 188900 | | | 504182 | |
| Mishrif | | | | 11020 | 2632 | 73572 | 1610 | 141953 | 501 | 233 | 141953 | | | 373474 |
| *NU | Iraq | | | 13913 | 2423 | 69768 | 1790 | 140229 | 512 | 248 | 140229 | | | 369130 |
| Yamama | | | | 14259 | 2169 | 59583 | 640 | 123591 | 825 | 446 | 123591 | | | 325104 |
| Seawater | | | | 400 | 1272 | 10556 | 380 | 18980 | 2700 | 140 | 18980 | | | 35357 |

*LA: Los Anglos; Oh: Oklahoma; NU: Nahr Umer.

The average concentration of Cl exceeds the salinity of seawater by about 6.5 times. It was recorded as 123679 mg/l varying within a range restricted between (120200 and 129575) mg/l. Sulfate concentration is six times less than the sulfates concentration in seawater (2700 mg/l) ranging from 270 to 530 mg/l with an average of 417 mg/l. Carbonates (HCO_3 and CO_3) are sources of alkalinity. As they can form insoluble compounds, they can cause negative effects on the reservoir quality. Accordingly, the investigation of their concentration in the oilfield water is of great significance. These anions are available in natural water (Davis and Dewiest, 1966); HCO_3 concentration (140 mg/l) is much less than CO_3 (18980 mg/l) in seawater. In the current study, a small amount of HCO_3 (137 mg/l) and CO_3 (18 mg/l) were detected. As chloride increases (123679 mg/l) in the strong brines, carbonates are present only in very small amounts (Collins, 1975). The amount of bicarbonates in Zubair reservoir seems similar to the bicarbonate concentrations in seawater, while CO_3 content is much less in Zubair reservoir compared to seawater. Carbon dioxide forms bicarbonate at a high pressure and at a low temperature, but a part of HCO_3 is reversely converted into CO_2 by a slight increase in temperature or a decrease in pressure. The long residence times, the dissolution of reservoir lithology, and the ion exchanges with clay minerals are the main sources of reservoir salinity. Compaction is one of the main reasons and controlling factors causes abnormal high pressures in a reservoir. Some parameters such as ratio of shale to sand thickness, mean reservoir permeability, elapsed time since deposition, the rate of deposition, and the overburden thickness are interrelated in compaction (Harkins and Baugher, 1969). Fluid pressures are approximately hydrostatic, and the sand permeability is enough to dissipate the expelled water from the compacting shale units. The sandstone unit in Zubair reservoir is restricted by the shale units, so the expelled water yielded from the compacted shale is dissipated within the pore spaces of the sandstone. The dissolving of salt tends to increase with depth; Ca and Cl ion concentrations increase against depth (Figure 5). Calcium increases with depth, and the calcium content of Zubair reservoir samples would be more than 13.5 g/l at a depth shallower than 3500 m. Chloride in the samples of water from abnormally pressured sands is below the average concentration line, while, regarding their depth burial, the samples of Zubair reservoir are more concentrated than they should be. A reverse relation was detected with bicarbonates denoting a decrease in bicarbonate with depth. The waters from the zones of abnormal pressures have more bicarbonate considering their depth of burial. The water samples of Zubair reservoir have less bicarbonate than what is expected based on their burial depth. The highest fluid pressures (P_f) (4706 and 5049 psi) were found at wells FW-172 and FW-186 respectively, where the salinity and SG are higher. Consequently, the relatively high pressure detected near the anticline axis causes the fluid to flow towards the low-pressure locations.

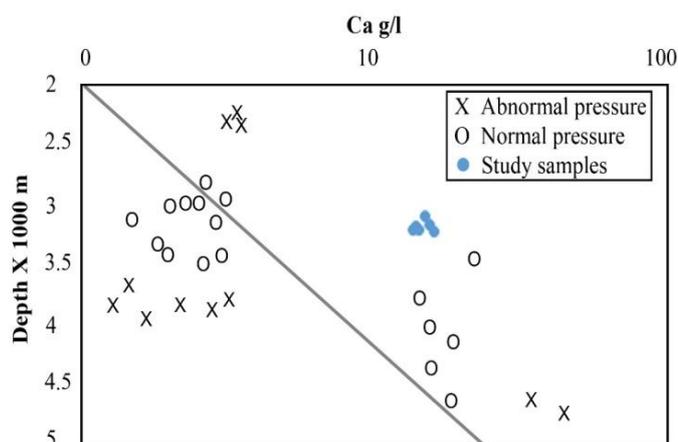
4.3. Oilfield water origin and classification

The infiltrated meteoric water and marine origin water are two main types of the oil field water (Ivanov et al., 1968). The ratios $r(\text{Na}+\text{K})/r\text{Cl}$ and $r\text{Ca}/r\text{Cl}$ are used as hydrochemical parameters for determining the origin of oilfield water. Such parameters are characteristics of marine origin when they being less than one; however, if they are larger than one, they indicate a meteoric origin (Table 3). The ratios ($r\text{Na}+r\text{K}/r\text{Cl}$) in all the water sample of Zubair oilfield are less than one, and the negative values of the ratio $r\text{Na} - r\text{Cl} / r\text{SO}_4$ indicate an original marine water. The low ratio of $r\text{Mg}/r\text{Cl}$ may attribute to form MgCl_2 which is a good indicator for hydrocarbon accumulation; it may also indicate a diagenesis processes. The ratio of $r\text{SO}_4/r(\text{CO}_3+\text{HCO}_3)$ points out some chemical reactions that occur only near hydrocarbon accumulations; thus, this ratio may be used as an indication of the position of the water with respect to hydrocarbons (Collins, 1975). The very low amount of $r\text{SO}_4/r\text{Cl}$ indicates the low circulation of deep water, where sulfate is reduced.

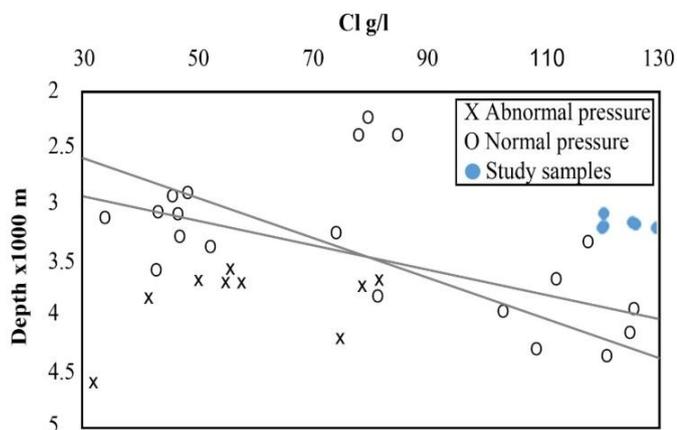
Table 3
Hydrochemical function ratios of oil field waters in Zubair reservoir.

| Ratios | Range | | Average |
|------------------------|---------|---------|---------|
| | Minimum | Maximum | |
| $(rNa+rK)/rCl$ | 0.70 | 0.73 | 0.71 |
| rCa/rCl | 0.12 | 0.21 | 0.18 |
| rMg/rCl | 0.07 | 0.09 | 0.08 |
| rSO_4/rCl | 0.002 | 0.003 | 0.0025 |
| $rSO_4/(rSO_4+rCl)$ | 0.001 | 0.003 | 0.002 |
| $rSO_4/(rCO_3+rHCO_3)$ | 1.60 | 5.90 | 3.10 |
| $rNa - rCl / rSO_4$ | -165.2 | -90.6 | -111.5 |

a)



b)



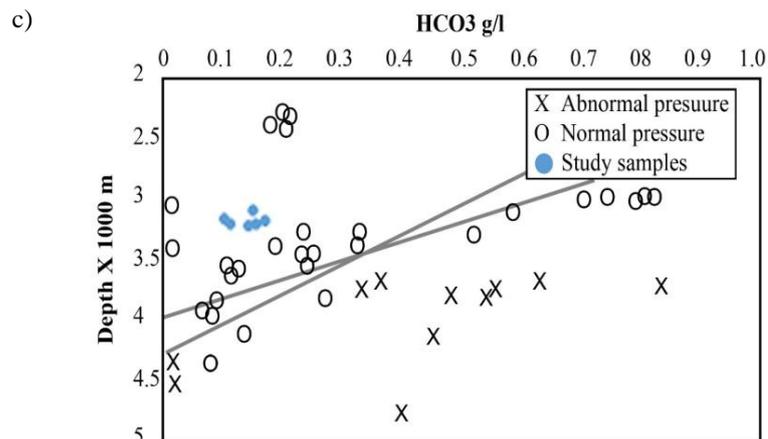


Figure 5

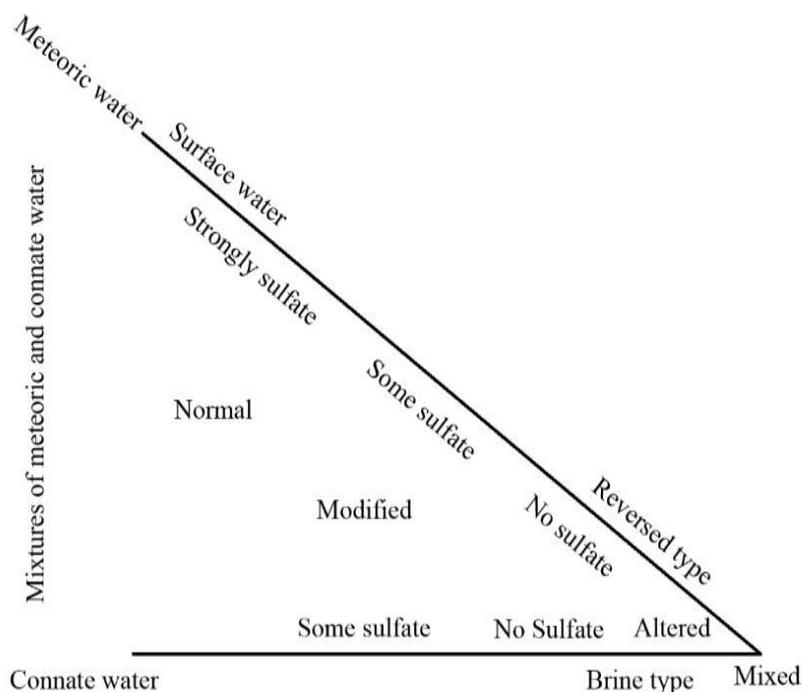
The concentration of ions (Ca, Cl, and HCO_3) versus well depth in Zubair reservoir oilfield water samples (blue solid circles) compared with a global data (symbol X and O) sourced from Collins (1975).

The general characteristic categories of oilfield water types that can be generated from different mixtures of meteoric and connate water are presented in Table 4. Basically, meteoric water affects diluting the salinity of the connate water. Mixed water has a wide range of salinity; it may be normal, modified, or altered (Figure 6). A normal group is characterized by the dominance of alkaline earth metals and a high sulfate concentration; thus, the ratio of carbonate to sulfate is less than one. A case of mainly meteoric origin is characterized by the ratio of carbonate to sulfate as high as 1-15, and sulfate salinity more than 15% of the total salinity. If it is mainly of connate origin, then sulfate salinity will be more than 1% of the total salinity, and alkaline earth metals will be less than 10% of the total ions. Altered group (reversed type) is characterized by primary alkalinity greater than 50%, sulfate and salinity less than 15% of the total salinity, the ratio of carbonate to sulfate generally greater than 15, and alkaline earth generally less than 8% of the total reacting value. An altered group of brine type includes sulfate salinity less than 0.5% of the total salinity and alkaline earth cations varying between 2-10%. Mixed type has a primary alkalinity less than 50%, sulfate salinity less than 1% of the total salinity, and alkaline earth cations varying from 1 to 2. The original composition of marine waters at the time of deposition along with other factors such as dissolution processes, long residence times, ionic exchanges with clay minerals, and lithology type is an essential factor controlling the salinity of oilfield water. The water in Zubair reservoir is classified as a brine type (Figure 6).

Table 4

General characterization of different mixtures generated from mixing meteoric with connate water.

| Water type | Sulfate | Carbonate /SO ₄ | Alkalinity Earths (%) | Alkalinity | Sulfate salinity (%) |
|------------|-----------------|----------------------------|-----------------------|--------------------|----------------------|
| Normal | High sulfate | < 1 | Dominant | | |
| Modified | Mainly meteoric | 1-15 | | Primary alkalinity | >15 |
| | Mainly connate | 1-15 | <10 | Secondary Salinity | >1-<15 |
| Altered | Reversed | >15 | <8 | >50 | <15 |
| | Brine | No sulfate | | Secondary salinity | <0.5 |
| Mixed | | | 1-2 | <50 | <1 |
| Zubair | | 2.7 | 8.9 | 0.2 | <1 |

**Figure 6**

Alteration of meteoric and connate water mixtures (after Rogers, 1917).

4.4. Ionic abundance and water type

Ionic balance, Stiff diagram, hydrochemical formula, and Schoeller diagram clearly present the chemical facies of Zubair oilfield water. Chloride is almost equivalent to the total of Na, Ca, and Mg, whilst sulfate, carbonate, and potassium are rare (Figure 7a). It is evident that the reservoir brine is relatively poor in carbonates, bicarbonates, and sulfates, while it is comparatively rich in chloride and sodium (Figure 7b). A semi-chemical homogeneity in the oilfield water of Zubair reservoir was identified with anions $rCl > rSO_4 > HCO_3$, cations chemical facies of $rNa > Ca > Mg > K$, Na-Cl family, and Cl group (Table 5 and Figure 7b). The high variation was detected in the HCO_3 and CO_3 due to the differential carbonate dissolution throughout the reservoir. The sulfate content shows a little variation in the reservoir, which is attributed to the variation in the depth of oil-water contact throughout the studied wells. As the water semi-homogeneity demonstrated above, a Stiff diagram of FW-186 is presented as an example. As shown, chloride is the predominant anion followed by common cations (Na and Ca) (Figure 7c).

Table 5

The dominant cations and anions and water type in Zubair reservoir.

| Well No. | Water type | | | |
|----------|-----------------------|---------------------|--------|-------|
| | Anions | Cations | Family | Group |
| FW-172 | $rCl > rSO_4 > HCO_3$ | $rNa > Ca > Mg > K$ | Na-Cl | Cl |
| FW-17 | $rCl > SO_4 > HCO_3$ | $rNa > Ca > Mg > K$ | Na-Cl | Cl |
| FW-112 | $rCl > SO_4 > HCO_3$ | $rNa > Ca > Mg > K$ | Na-Cl | Cl |
| FW-18 | $rCl > SO_4 > HCO_3$ | $rNa > Ca > Mg > K$ | Na-Cl | Cl |
| FW-131 | $rCl > SO_4 > HCO_3$ | $rNa > Ca > Mg > K$ | Na-Cl | Cl |
| FW-186 | $rCl > SO_4 > HCO_3$ | $rNa > Ca > Mg > K$ | Na-Cl | Cl |

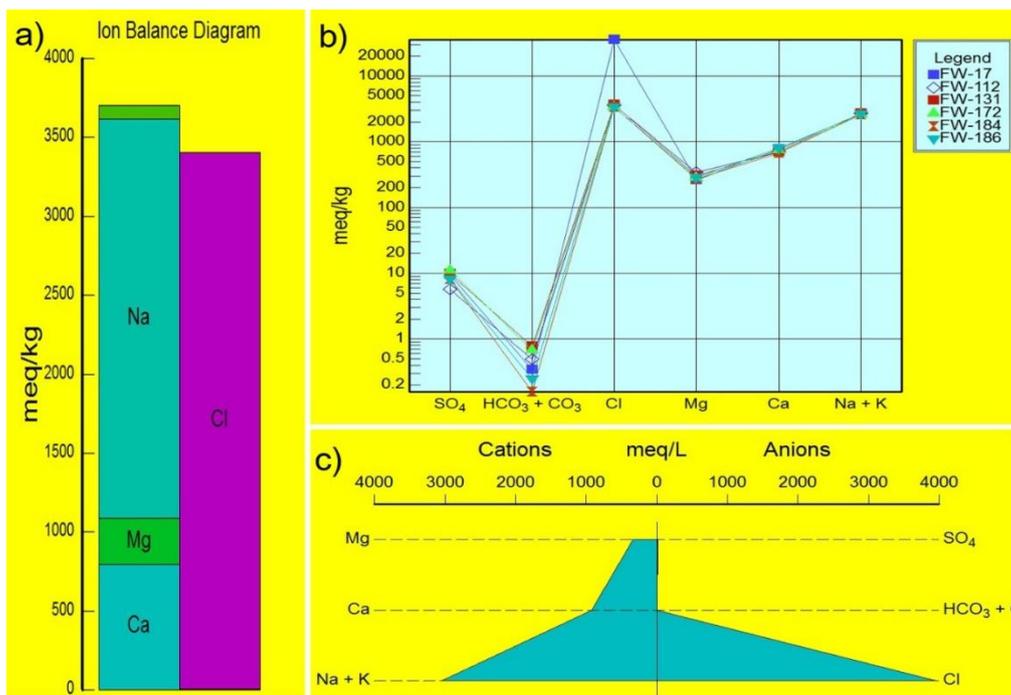
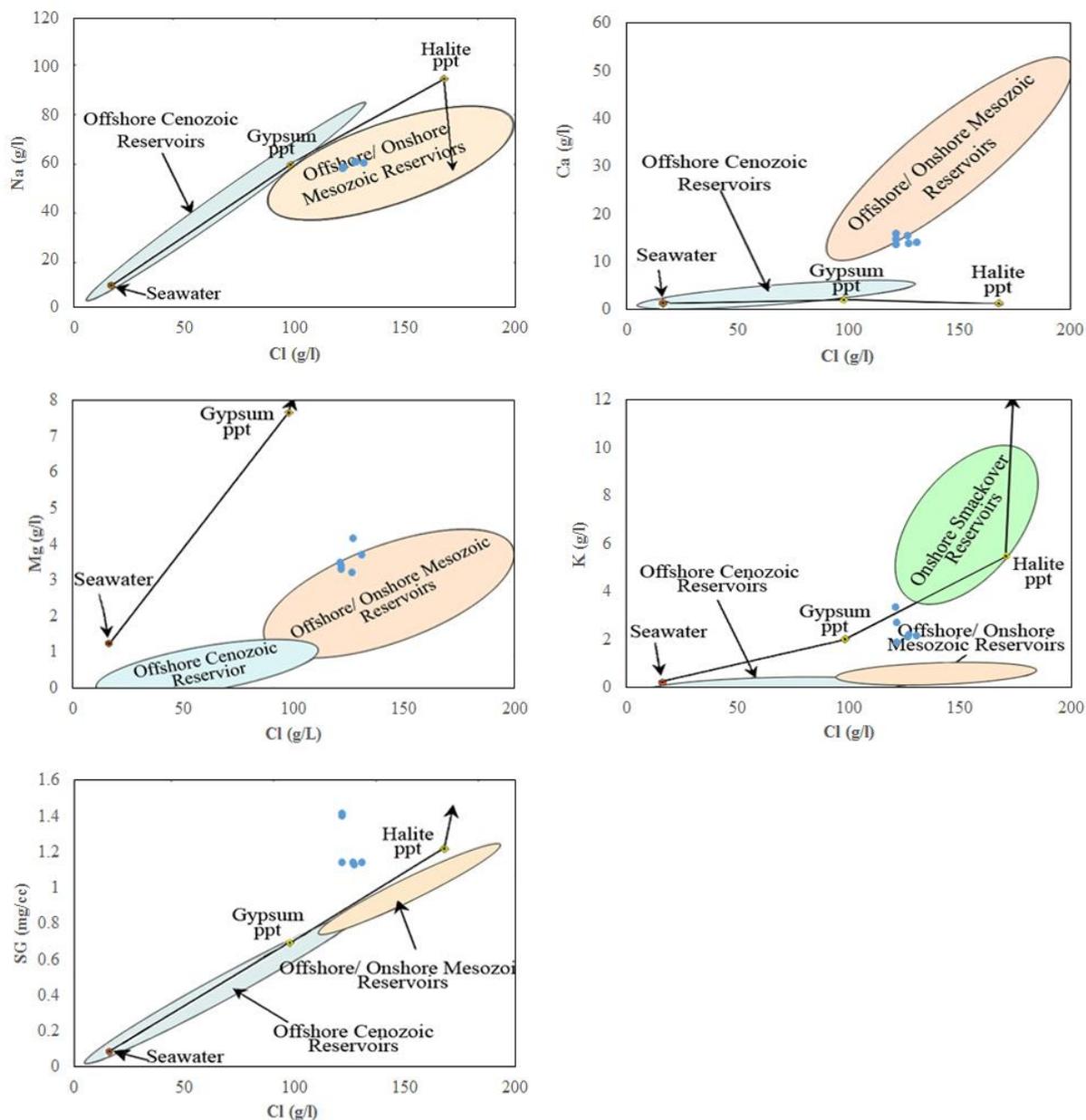


Figure 7

Ionic balance: a) Schoeller diagram, b) Stiff diagram of well FW-186, and c) Stiff diagram of the oilfield water in Zubair reservoir in RNOF.

4.5. Ionic relationships

Chloride concentrations versus Na, Ca, Mg, K, and specific gravity (SG) in Zubair reservoir are plotted on a cross plot shown in Figure 8. A trajectory of sea water gypsum evaporation and halite precipitation proposed by McCaffrey et al. (1987) and Carpenter (1978) is used for the comparison. Sodium and Cl concentrations appear less than what is defined by the evaporation trajectory due to dilution with fresher water during the initial evaporation stage or shortly after burial. Hence, the composition of the formation water of Zubair reservoir seems to be similar to the compositional ranges of the formation water of the Gulf of Mexico offshore/onshore Mesozoic reservoirs. Calcium-Cl cross plot displays the low concentration of Ca, so the compositional brine of Zubair reservoir in all wells occupies the lower edge of the offshore/onshore Mesozoic reservoirs. The Mg-Cl cross plot clearly indicates a low Mg concentration, and they are located on the upper edge of the offshore/onshore Mesozoic reservoirs edge, which may be due to the exhaustion of Mg via dolomitization. If kaolinite and/or illite are formed, the range of K concentrations in the brine will be plotted below the evaporation trajectory reflecting a potassium removal from solution. A cross plot of Cl-K shows that in the Gulf Coast Cenozoic and Mesozoic reservoirs, K occupies a field below the evaporation trajectory due to potassium removal during the formation of kaolinite and/or illite. All the points that represent a brine of Zubair oilfield are almost plotted on the trajectory of gypsum halite precipitation reflecting soluble K ions with deficiency of sorption process on clay mineral surfaces due to the little amount of clay minerals in the Upper Sandstone Unit. A significant note has been recorded from the cross plot of specific gravity versus chloride, as brine in Zubair reservoir has a high specific gravity higher than those of the global oil fields.

**Figure 8**

Cross plot of chloride versus sodium, calcium, magnesium, potassium, and specific gravity (SG) in Zubair oilfield water (blue solid circles); sodium and magnesium are located below the sea water-gypsum trajectory occupying almost the offshore/onshore Mesozoic reservoirs; potassium is located below the sea water-gypsum trajectory but above the upper limit of the offshore/onshore Mesozoic reservoir; specific gravity (SG) displays Zubair oilfield water as concentrated brine.

4.6. Mineral saturation model

Mineral saturation index is a chemical expression which provides good information about the solution chemistry. This concept was applied to understanding whether the total dissolved solids will remain dissolved or precipitate a particular mineral. The zero value of the mineral saturation index indicates a chemical equilibrium, but negative and positive values mean mineral dissolved and precipitated respectively. It can be summarized as: $SI > 0$ means supersaturated; $SI = 0$ means equilibrium; $SI < 0$ denotes undersaturated. The saturation index (SI) is calculated by the following expression:

$$SI = \log \left(\frac{IAP}{K_{sp}} \right) \quad (9)$$

where, *IAP* is an ion activity product representing the chemical activities of the dissolved ions of the mineral. *K_{sp}* represents the solubility product. Mineral saturation index at actual pH and simulated pH values were calculated by PHREEQC software program to predict the nature of the oilfield water and to understand which mineral can precipitate. In addition to the chemical composition of the oil field water, the reservoir temperature and pressure must be known as the input into the geochemical modeling program. Reservoir temperatures were estimated using a geothermal gradient of 0.67 °C per 100 feet (Pollack and Watts 1 976). Fluid pressures at each well were calculated based on a hydraulic potential gradient of 0.465 psi per foot as listed in Table 1.

Table 6

Mineral species that have the potential for formation damage and the saturation index (SI) calculated at different pH values.

| Mineral | Composition | *SI (kcal/mole) at pH | | |
|--------------|--|-----------------------|--------|--------|
| | | 5.45 | 9.12 | 11.9 |
| Anhydrite | CaSO ₄ | -0.516 | -0.483 | -0.498 |
| Antarcticite | CaCl ₂ .6H ₂ O | -4.45 | -4.55 | -4.61 |
| Arcanite | K ₂ SO ₄ | -5.24 | -5.18 | -5.15 |
| Bischofite | MgCl ₂ .6H ₂ O | -5.03 | -5.41 | -5.17 |
| Brucite | Mg(OH) ₂ | -6.96 | 0.0 | 5.34 |
| Glaserite | Na ₂ K ₆ (SO ₄) ₂ | -16.9 | -16.7 | -16.6 |
| Glauberite | Na ₂ Ca(SO ₄) ₂ | -2.7 | -2.63 | -2.62 |
| Gypsum | CaSO ₄ .2H ₂ O | -0.4 | -0.365 | -0.382 |
| Halite | NaCl | -0.85 | -0.865 | -0.868 |
| Hydrophilite | CaCl ₂ | -11.9 | -11.9 | -11.9 |
| Mirabilite | Na ₂ SO ₄ .10H ₂ O | -2.65 | -2.61 | -2.59 |
| Portlandite | Ca(OH) ₂ | -12.7 | -5.41 | 0.188 |
| Sulfur | S | --- | -94.5 | --- |
| Sylvite | KCl | -1.99 | -2.0 | -2.0 |
| Syngenite | K ₂ Ca(SO ₄) ₂ .H ₂ O | -4.41 | -4.32 | -4.3 |
| Thenardite | Na ₂ SO ₄ | -2.93 | -2.9 | -2.87 |

* SI>0 means supersaturated; SI=0 means equilibrium; SI<0 means undersaturated.

The saturation indices in Table 6 suggest that most water samples are unsaturated with respect to all suggested minerals. The model suggested brucite will be in equilibrium at a simulated of pH 9.12, but supersaturated at a pH value of 11.9 with respect to brucite and portlandite.

The geochemical model with respect to thermodynamic potential showed that in a case of changing the temperature, pressure, pH, Eh, and ionic strength, the solubility will be changed resulting in precipitation some minerals causing formation damage. The model investigated the pH and Eh of formation waters as important parameters influencing the mineral solubility. The lower pH caused by injection of CO₂ or acid led to dissolving calcite, thereby enhancing porosity and permeability in reservoirs. Consequently, clay minerals available as a substantial amount within calcite will be

released and occlude pore throats, causing a reduction in permeability. The average of fluid pressure in Zubair reservoir is 48656 psi. The decreasing reservoir pressure could trigger anhydrite precipitation (Collins and Kayser, 1985) and can lead to a decrease in the solubility of anhydrite during normal primary production.

The amounts of dissolved constituents in the oilfield water can reach more than 350,000 mg/l. This salinity distribution depends on hydraulic gradients, depth, mobility, solubility, the exchange reactions, mineral formation, sulfate reduction, and ultrafiltration through clay-shale membranes (Collins, 1975). During high salinity, the fine grains are adsorbed onto the matrix and do not migrate due to the attraction between dipole fines and environment. By contrast, in the low-salinity oilfield waters, the fines are desorbed from the matrix and migrate (Zhang et al., 2007). The predominance of sodium in Zubair oilfield water at the NROF (six times more than that of seawater) indicates a closed system of fossil water. Sodium was not adsorbed reversely onto clay mineral surfaces again, which is due to having much weaker interaction than the divalent cations; as Na is a highly soluble element, its dominance does not mean that an alkali scale will be precipitated. The divalent cations are easily exchanged and replaced with monovalent ions (Hem, 1985). Calcium deposition negatively influences the petrophysical characteristics of the reservoir. The high concentration of calcium confirmed soluble carbonates from the shale member due to the interaction between water and reservoir rocks. Calcium ions at western limb trap tend to be greater than the eastern limb. The high content of Mg ion in Zubair reservoir may reflect the paucity of dolomite scale to be formed, where depletion of Mg ion can probably be attributed to the replacement reaction forming dolomite. The potassium content in Zubair reservoir is six times more than the K concentration in seawater, reflecting that the pH values which are suitable for dissolving clay minerals and feldspar from the shale units exist in the reservoir. The dissolution processes enhance the reservoir quality and assist in determining the highly permeable sites and permeability barriers. The K-rich minerals (mica and illite) are available in the shaly unit of Zubair reservoir; therefore, to keep clay mineral stable, cares must be taken during secondary injection (Awadh et al., 2014). Therefore, K^+ must be available in the injected waters to prevent K releasing from clay minerals. The highest concentration was detected at the well FW-131 within the west limb of the anticline trap. The ratios of rCl/rNa and $rCl/rNa+rK$ in all the studied wells are more than one, which indicates a marine origin. The decrease of sulfate from oil field water is believed either to be linked with cations (Ca, Sr, and Ba) to form gypsum, celestite, and barite respectively, to be connected with the chemical reaction with hydrocarbons, where it is probably reduced to sulfide, hydrogen sulfide, or to be linked with the oxidation to free sulfur. The percentage of sulfur in the Upper Sandstone Member in Zubair reservoir is restricted between 1.97 and 2.46 with an API of 29° (Al-Azawi, 2012), and limited to 2 in the Raudhatain field in Kuwait (Adasani, 1967); so this member is of medium oil quality. Mineral precipitation leads to negative effects on the reservoir characterizations as it plugs pores. The most probable expectation is the link of sulfates with hydrocarbon, forming free sulfur and H_2S gas. The sulfate is highly reduced to sulfide and converted into H_2S ; on the other hand, an equivalent portion of the oil is oxidized to carbon dioxide and carbonate. The C/S ratio (0.22-0.68) indicates the heterogeneity of the reduction in Zubair reservoir, which may be due to the potential energy and hydrostatic environment. A ratio of sulfate to chloride and carbonate higher than 1 leads to a considerable admixture of upper water. The acidic tendency of pH (5.2- 5.77) reflects a positive role in the reservoir quality through preventing the further reduction of the porosity and permeability due to mineral deposition. The acidity of pH may be attributed to H_2CO_3 and H_2S in the fluid system; Morad (1998) mentioned that such components (H_2CO_3 and H_2S) are a controlling system of pH. In Zubair reservoir, silica is still stable due to acidic pH since it is dissolved at a pH of 9; hence, quartz is a stable phase in the sandstone unit. The basic source of bicarbonates is from the dissolution of carbonates at acidic pH values between 5 and 7 (Taylor, 1958).

The decreasing in bicarbonate amount in the brine water indicates a neutral pH and no high carbonate dissolution with the normal pressure. The high SG is a reflection of high salinity indicating dissolution processes. The highest fluid pressure (P_f) near the anticline axis suggests the fluid flows towards anticline limbs.

6. Conclusions

The chemistry of the oilfield water in the Upper Sandstone Member in RNOF is affected by the reservoir lithology, geological formations, through which the water passes, meteoric water, and the hydrocarbons. It has high average salinity (223‰) predominated by cations (epm%), including Na (70.2), Ca (18.9), Mg (8.1), and K (1.7); and anion comprising of Cl (99.7), SO_4 (0.25), HCO_3 (0.07), and CO_3 (0.005). Compared to seawater, sodium and Cl contents are 6 and 6.5 times greater respectively; Ca and Mg are three times greater; the sulfate is less depleted. Possibly, shale member responded to compaction more than sandstones, leading to the release of water molecules due to the temperature increase. This process supplied fresh water to the adjacent sandstone unit lowering its salinity, while increasing salinity within the shale itself.

Dissolution processes are dominant due to low pH values, resulting in high salinity with a high SG. SG of Zubair reservoir is greater than that of some Iraq oilfields. The differential dissolution has led to the heterogeneity of salinity distribution within the reservoir. The high SG recorded in Zubair reservoir (at an average of 1.228) is greater than that of some Iraq oilfields such as Mishrif (1.1502) and Yamama (1.1387) reservoirs and global oilfields such as Stephens (1.1350) and Wesson (1.1490) reservoirs. Therefore, the sites of high salinity should be carefully taken into consideration during the well drilling in order to avoid the high pressure sites. The formation resistivity is directly proportional to hydrocarbon saturation, but inversely proportional to water saturation. An inverse response function to TDS is established ($R^2=0.656$), which is expressed by equation $Y=-0.0753X - 1.4835$. Water is the main driven force for oil in the Upper Sandstone Member which is a pay zone in RNOF. Hence, the oil mobility in this part is relatively high due to high water saturation. The high pressure values found at well Fw-186 (5049 psi) and Fw-184 (4880 psi) may be attributed to the high accumulation of bitumen at the eastern flank of the anticlinal trap due to the low salinity resulted in a decrease of the permeability.

7. Acknowledgments

Author is very grateful to the South Oil Company (SOC) for providing samples and some necessary information, without which the research could not be completed.

Nomenclature

| | |
|-------------|---------------------------|
| <i>AWS</i> | : Apparent water salinity |
| <i>DB</i> | : Difference balance |
| <i>EC</i> | : Electrical conductivity |
| <i>Eh</i> | : Oxidation potential |
| <i>IAP</i> | : Ion activity product |
| <i>kcal</i> | : Kilo calorie |
| <i>Ksp</i> | : Solubility product |
| P_f | : Formation pressure |
| <i>Res</i> | : Resistivity |

| | |
|------------|--------------------------|
| <i>RW</i> | : Water resistivity |
| <i>S</i> | : Salinity |
| <i>SP</i> | : Spontaneous potential |
| <i>SG</i> | : Specific gravity |
| <i>SH</i> | : Hydrocarbon saturation |
| <i>SI</i> | : Saturation index |
| <i>SW</i> | : Water saturation |
| <i>TDS</i> | : Total dissolved solid |

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