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EVALUATING THE CHARACTERISTICS OF OFFSHORE OILFIELD PRODUCED WATER

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Abstract

Large volumes of produced water are associated with the production of oil and gas in onshore and offshore oilfields. Produced water is separated from the oil and gas and either reinjected into the reservoir or discharged to the environment. Therefore, evaluation of produced water characteristics is very important and essential for both environmental and reservoir management. Produced water is a very complex mixture and contains different compounds that can have negative impact on the environment and economical problems associated with oil and gas production. This study has evaluated the characteristics of water produced from an offshore oilfield. Many samples of the oilfield produced water during eleven years of the production and at different depths were analyzed. The evaluation included the analysis of pH, specific gravity, salinity, total dissolved solids (TDS), cations and anions constituents and compared with the standards characteristics of seawater. The values of specific gravity, salinity, TDS, and some ions such as sodium and chloride of oilfield produced waters are increased with increasing the oilfield depth. The minimum and maximum of their values are more higher than the standards characteristics of seawater. However, sulfate concentration is inversely proportional with the oilfield depth. pH value was lowered with increase the production year and varied between 4.2 and 6.8.

Keywords: Offshore oilfield; Produced water; Salinity; Cations; Anions; Seawater.

1. Introduction

Oilfield wastewater known as produced water is generated in large 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. Currently, it has been well known that the oil industry has to handle more produced water than oil which makes the oil industry looks more like a "water industry" [1]. In the United States, oil wells produce about 7 to 10 barrels of water for each barrel of oil [2]. Moreover, produced water represents approximately 98 % of the total volume of production waste generated by the oil and gas industry [3]. It was estimated that, about 210 million bbl of water was produced each day in 1999 worldwide [1,4]. This volume represents about 77 billion bbl of produced water for the entire year. Sources of this water may include flow from above or below or within the hydrocarbon zone, or flow from injected fluids and additives resulting from production activities [3,5]. Produced water discharged to surrounding environment or other times the water may be used for water flooding or reservoir pressure maintenance [2-3].

The quality of produced water vary considerably depending on the geographic location of the reservoir oilfield, the geochemistry of the producing formation, the type of hydrocarbon product being produced and the characteristics and type of the producing well (oil or gas) [3,6-7]. Produced water characteristics and volume can vary throughout the lifetime of a well [6]. Produced water is usually very salty and may contain suspended and dissolved solids, residual hydrocarbons, numerous organic species, heavy metals, naturally occurring radioactive and chemicals used in hydrocarbon extraction [2,5,7]. Major components of produced water vary according to the type of production activity associated with these types which includes oil production and gas production [5]. Normally, the waters derived from gas wells contain several times greater concentration of metals than that derived from oil wells [7].

Water evaluation is important for petroleum industry both in upstream and downstream. In upstream, it is very crucial in designing and choosing, drilling program (drilling fluids), the well integrity (casing materials,), the MWD/LWD (measurements while drilling and logging while drilling) programs and even the artificial lift methods needed for the production. In downstream, the designing of the surface facilities, till disposing the water are directly affected by such compositions. Furthermore, the importance of oilfield produced water analyses is to supply reliable information about: source and characterization of the water produced with oil, quality check of injection water, prediction of corrosion rate, prediction of scale formation rate, prediction of the environment and natural resources; monitoring of chemicals used for the water treatment, analytical backup for projects in oil industry and ecological demands [8].

Because many produced waters contain elevated levels of dissolved ions (salts), hydrocarbons, and trace elements, untreated produced water discharges may be harmful to the surrounding environment [2]. In recent years, oilfield produced water has been regarded as a major pollutant of the environment in many countries [9]. Several environmental impacts have been caused by discharging produced water without previous treatment. The most commonly environmental concerns are as the followings [2-3,5]:

- Aqua-toxicological effects, which is deleterious to aquatic life.
- Reduced oxygen level enough to damage aquatic species.
- Excess sodicity which cause clay deflection (degradation of soils).
- Excess soluble salts which can cause plants to dehydrate and die.
- Injection formation plugging due to suspended solids, which results in injection pressure.
- Scale problem which causes well bore clogging and fluid flow prevention.
- Environmental impact due to chemical additive like corrosion inhibitor and H_2S scavenger.

Produced water can have different potential impacts depending on where it is discharged. For example, discharges to small streams are likely to have a larger environmental impact than discharges made to the open ocean by virtue of the dilution that takes place following discharge [10]. Many studies represent the effect of dilution. The produced water discharges in near shore shallow environment can lead to the accumulation of hydrocarbons and micro-organisms up to 500 m from discharge points [11]. Furthermore, dilution of the produced water was predicted to occur by a factor of 1000 at 500 m from the discharge site [12]. The ecological health of many river systems is threatened by the discharge of toxic compounds and the accumulation of these contaminants in these aquatic environments. Many freshwater river systems have been classified as unfit for human consumption by the Federal Environmental Protection Agency [9]. It was concluded that fresh water dilution of produced waters from oilfield before disposal could be very effective [6].

Several studies investigated the characteristics of produced water and its impact on the surrounding environmental. Neff described produced water for ocean discharge as containing up to 48 ppm of oil [13]. Besides, most produced waters are more saline than seawater [6,13]. Produced waters may contain concentrations of chloride 150 to 180 g/L (sea water contains an average of 35 g/L) [15]. With these levels of salts the water becomes toxic for many forms of life [15]. Produced waters may also contain chemical additives used in drilling and producing operations [16] and in the oil/water separation process. These chemicals can affect the oil/water partition coefficient, toxicity, bioavailability, and biodegradability [6]. Smith has also confirmed the negative effects of produced waters on the Indonesian environment [17]. Oboh noted that the discharged of oilfield produced waters had high metal ions and total hydrocarbon concentrations [18].

This study is aimed to evaluate the characteristics of water produced from offshore oilfield at Arabian Gulf. The evaluation includes the analysis of many different samples of produced water during eleven years of the oil production and at different oilfield depths. The evaluation includes the produced water analysis for pH, specific gravity (Sp. Gr.), salinity, total dissolved solids (TDS), cations and anions constituents. In addition, comparison of these characteristics with the standards characteristics of seawater was investigated.

2. Materials and Methods

2.1. Sampling

The evaluated produced water in this study was generated in the offshore oilfield in Arabian Gulf. Different samples were collected during the eleven years of the production. 22 samples from the oilfield were collected at different depths. All the collected samples were preserved in accordance with guidelines and International Standards. Measurement of temperature and pH were done at the sampling point due to sensitivity of their values, while the analyses of other parameters were done in the laboratory.

2.2. Analyses

All samples were filtered through a 0.45 μm regenerated cellulose membrane filter. The produced water samples were analyzed for specific gravity (Sp. Gr.), salinity, total dissolved solids (TDS), anion and cation constituents. The characteristic of produced water was evaluated according to ASTM standard tests. Table 1 represents the analysis procedures.

Table 1. Methods of produced water analysis.

Parameter	Method of analysis
Temperature	Mercury thermometer
pH	Glass electrode
Sp. Gr.	Hydrometer
Salinity	Titration
TDS	Titration
Ca	EDTA titration
Mg	EDTA titration
SO_4	Barium sulfate turbidity
HCO_3	Sulfuric acid titration
Cl	Silver sulfate
Na	EDTA titration

3. Results

Results of the analysis of the offshore oilfield produced water samples at different depths and during eleven years of production are described and compared with standard characteristics of seawater.

3.1. Physical characteristics

Physical characteristics of oilfield produced waters such as temperature, pH, specific gravity, salinity and total dissolved solid at various oilfield depths and production years were analyzed. The temperature values of all samples were in the range from 48ºC to 61ºC. Table 2 illustrated the minimum and maximum values of the produced waters characteristics during the studying period. The result of physical characteristics of the oilfield produced water is shown in Figure 1.

pH value

The pH of the water is not used for water identification or correlation purposes, but it will indicate possible scale forming or corrosion tendencies of a water. The pH also may indicate the pressure of drilling mud filtrate or well treatment chemicals. The pH measurement should be made in the field if a close to natural conditions value is desired. The pH values of the oilfield produced waters for the different years of production and oilfield depths are shown in the Figure 1. The value of pH was varied between 6 and 6.8 during the 1st and 2nd years of the production. During the following nine years of the production, pH lowered and varied between 5.9 and 4.2. There is no clear relationship between pH value and the oilfield depth, and the ranges of pH in the different oilfield depths overlap considerably. For example, the pH value was 4.2 and 5.8 at 10275 and 10266 ft depths, respectively. However, the pH value was 6.1 at the different depths of 9325 and 10392 ft. As shown in Figure 1and Table 2, the pH values of all the oilfield produced waters were lower than the allowable limit of the seawater. The allowable pH values are in the range 7.7 - 8.3 in the seawater.

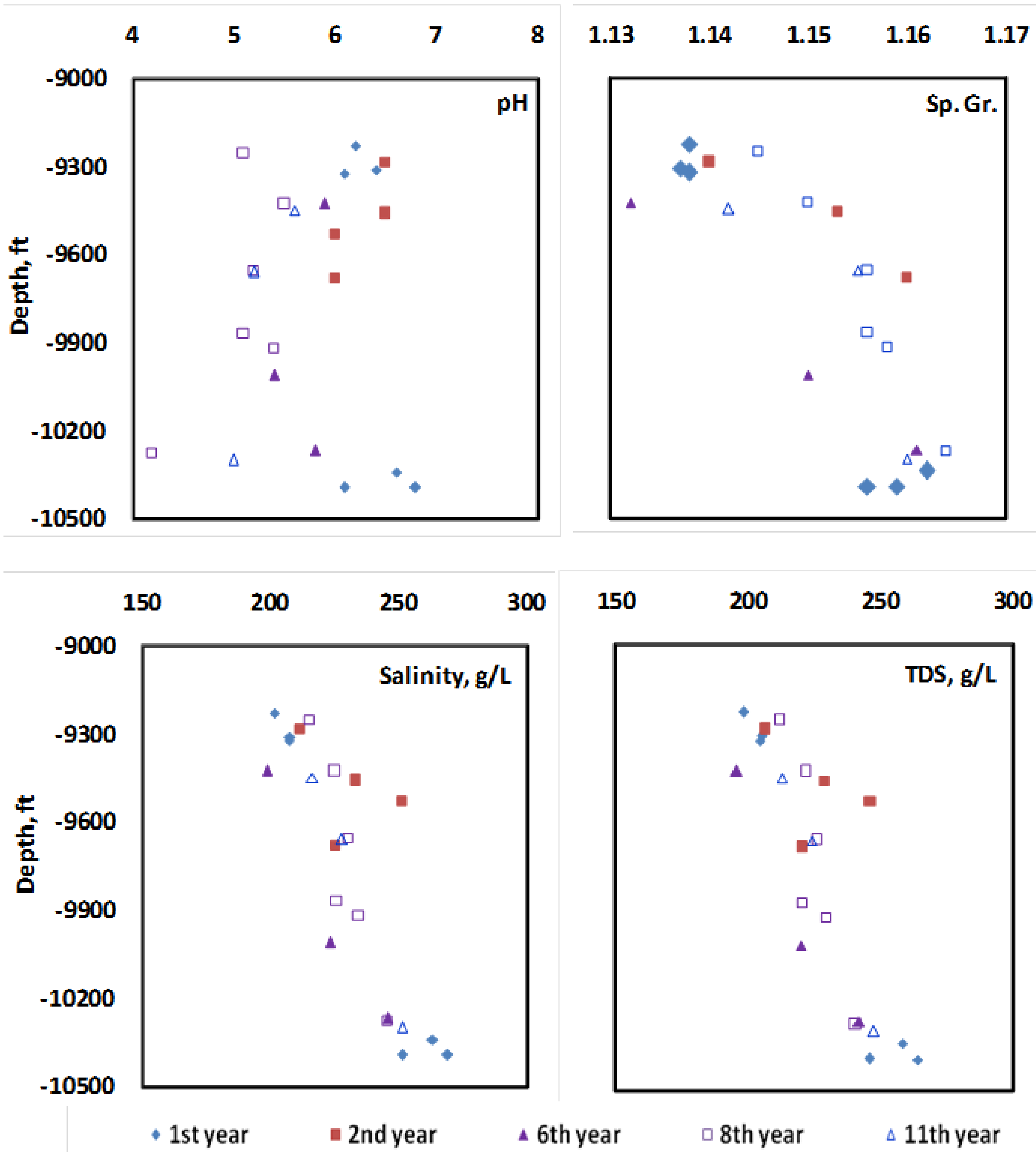

Figure 1. Physical characteristics of oilfield produced water at various oil production years and depths.

Table 2. Characteristics of oilfield produced water in g/L (except pH and Sp. Gr.)

Parameter	1st year		2nd year		6th year		8th year		11th year		Seawater
	min	max	min	max	min	max	min	max	min	max	
pH	6.1	6.8	6.0	6.5	5.4	5.9	4.2	5.5	5.0	5.6	7.7-8.3
Sp. Gr.	1.137	1.162	1.140	1.16	1.132	1.161	1.145	1.164	1.142	1.16	1.026
Salinity	201.81	269.09	211.76	251.54	198.89	245.69	215.27	245.68	216.44	251.54	35.00
TDS	198.16	263.98	206.52	246.26	195.93	242.01	212.27	240.52	213.11	247.62	-
Mg	2.07	3.65	1.56	2.72	1.46	1.77	1.46	2.19	0.61	0.97	1.29
Ca	14.43	20.44	15.87	23.57	15.71	21.64	17.39	25.65	19.44	25.05	0.41
Na	56.14	77.19	60.96	66.98	57.14	69.30	59.37	65.34	61.16	69.16	10.76
Cl	122.31	163.08	128.34	152.45	120.54	148.90	130.47	148.90	131.18	152.75	19.37
HCO_3	0.21	0.49	0.21	0.42	0.39	0.56	0.21	0.31	0.23	0.31	0.014
SO_4	0.16	0.73	0.26	0.61	0.21	0.38	0.20	0.55	0.17	0.23	2.71

Specific gravity

Results of the produced water analysis in Figure 1 show that the specific gravity values are increased with increasing the oilfield depth. The specific gravity minimum and maximum values are in the range 1.132 - 1.164 (Table 2). There is no clear relationship between the specific gravity and production year and the values of it in the different production years overlap considerably. For example, the maximum value of specific gravity was about 1.16 during the 1st, 2nd, 6th and 11th years. As shown in Figure 1 and Table 2, the specific gravity of all oilfield produced water samples are more than the specific gravity of seawater (1.023).

Salinity and TDS

Produced water contains a mixture of different compounds. Salinity is a general attribute of produced water. The properties of produced water vary depending on the geographic location of the oilfield, the geological host formation, and the type of hydrocarbon product being produced [3]. Table 2 illustrated that, oilfield produced waters have salinities of 199 g/L to more than 269 g/L, comparing with 35 g/L of seawater salinity. This means that the average salinity from the oilfield produced waters is as much as six times of the seawater. As shown in Figure 1, the salinity of produced waters generally increases with oilfield depth. For example, the salinity was varied between 199 and 245.7 g/L during the 6th production year with increasing the depth from 9428 to 10266 ft, respectively. However, there is no clear relationship between salinity value and the year of production, and the ranges of salinity in the different production years overlap considerably. In addition, salinity can described as total dissolved solid (TDS). TDS is a reflection of suspended and dissolved ions inherent in the produced water. It is an important indicator of the usefulness of water for various applications [10]. TDS obtained from the produced waters in the range 196 to 264 g/L.

3.2. Cation constituents

Major cation constituents identified in oilfield produced water include sodium, calcium, and magnesium. Their concentrations from the oilfield produced waters versus the different years of production and oilfield depth are shown in the Figure 2.

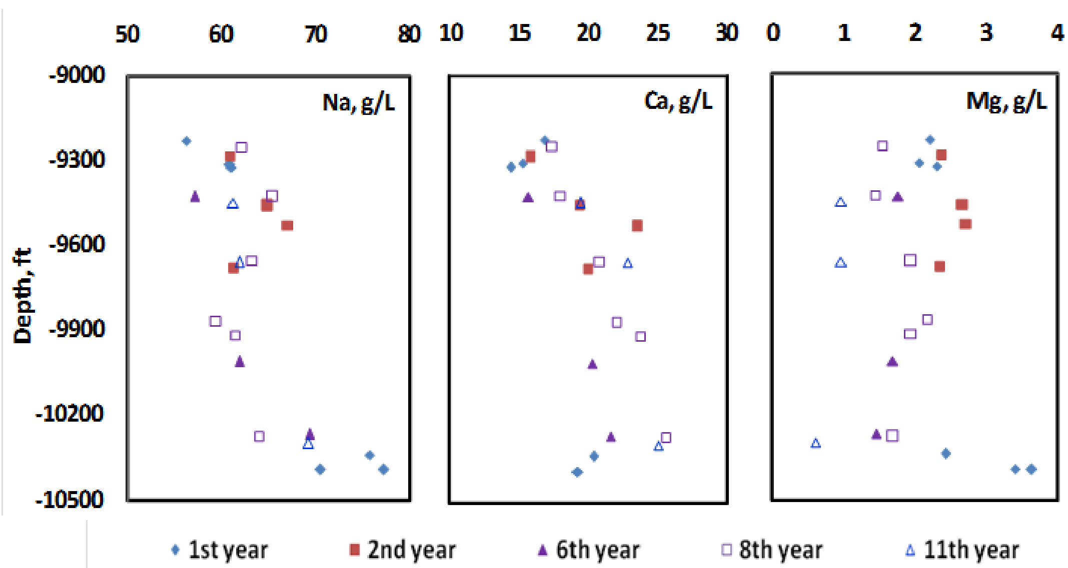

Figure 2. Cation constituents of oilfield produced water at various oil production years and depth

Sodium is the most commonly occurring dominant cation in the oilfield produced waters. Once sodium is in solution, it has a tendency to stay in solution. It is not easily precipitated with an anion, and it is not as easily adsorbed by clay as potassium, barium and magnesium. From Figure 2, sodium concentration of produced waters generally increases with oilfield depth. The concentration was increased from 56.14 g/L to 70.5 g/L with increasing the depth from 9230 ft to 10392 ft, respectively. However, no significant differences are shown in the results of sodium concentration and the year of production. The ranges of sodium concentration are in the different production years overlap considerably. From Table 2, the average minimum and maximum values of sodium during the oil production period are 66.6, 63.97, 63.22, 62.3 and 65.16 g/L for 1st, 2nd, 6th, 8th and 11th year, respectively. These values are as much as six times of the seawater (10.76 g/L).

The concentration of calcium in the oilfield produced waters is a function of origin of the water, the ages of the water and the enclosing rocks, type of rock, and type of clay in the rock. Reactions, such as ion exchange, formation of dolomite, formation of chlorite, etc. affect the concentrations of calcium in oilfield produced waters. As shown in the Figure 2, calcium concentration was in the range from less than 14.5 g/L to more than 25 g/L. The same trend of the calcium concentration and the relation with oilfield depth as sodium concentrationhas been noticed. Also, no significant differences are shown in the results of calcium concentration and the year of production (see Figure 2) and the ranges of calcium concentration in the different production years overlap considerably. However, from Table 2, the average minimum and maximum values of calcium during the oil production period are 17.43, 19.72, 18.53, 21.52 and 22.25 g/L for 1st, 2nd, 6th, 8th and 11th year, respectively. These values are more higher thanthe calcium of seawater (0.41 g/L).

Magnesium concentrations in the oilfield produced waters, like calcium concentrations, are dependent upon origin of the water, rock, etc. Perhaps the prime reaction that affects the magnesium concentration in oilfield produced waters is the formation of dolomite. In general, the reaction depletes the concentration of magnesium and increases the concentration of calcium. As shown in Figure 2, neither the different oilfield depth nor the period of oil production up to 8th yearhas influenced the concentration of magnesium. Table 2 illustrated that magnesium concentration is approximately inversely proportional with the calcium concentration. The average minimum and maximum values of magnesium during the oil production period are 2.86, 2.14, 1.62, 1.81 and 0.79 g/L for 1st, 2nd, 6th, 8th and 11th year, respectively. The magnesium concentration during the 11th oil production year is lower than the permissible limit of the seawater (1.29 g/L).

3.3. Anion constituents

Produced water from the oilfield is rich in many anions such as chloride, bicarbonate, and sulfate. The anions concentration inthe oilfield produced waters for the different years of production and oilfield depths are shown in Figure 3.

The major anion in the most oilfield produced water is chloride. Chloride is often accounting for more than 90% of the anion content of produced waters [19]. Also, it is the predominant anion in seawater, and it is very mobile in the total hydrosphere. The chloride ion does not form low solubility salts: it is not easily adsorbed on clays or other mineral surfaces. Chloride does not play a significant role in most of the oxidation and reduction reactions in produced waters. It also does not form important solute complexes. The concentration of chloride in oilfield produced waters ranges from less than 19 g/L to more than 200 g/L (Figure 3). Depth of the oilfield influences the chloride concentrations. The chloride concentration increased from more than 122 g/L to 163 g/L with increasing the oilfield depth from 9230 ft to 10393 ft, respectively. However, chloride concentrations are independent of the production year of the oilfield. These results are compatible with the average minimum and maximum values of chloride (Table 2) during the oil production period and these values are as much as seven times of the seawater (19.37 g/L).

Bicarbonates usually are present in produced waters. From Figure 3, the produced waters contain from 0.21 to 0.56 g/L of bicarbonate. The same trend of the bicarbonates concentration and the relation with depth and the production year as chloride concentration. The bicarbonate concentration increased from more than 0.21 g/L to 0.49 g/L with increasing the oilfield depth from 9230 ft to 10393 ft, respectively.

These results are also compatible with the average minimum and maximum values of bicarbonates (Table 2) during the oil production period and these values are very much more than the bicarbonates of seawater (0.014 g/L).

Figure 3 shows that, oilfield produced waters contain from 0.16 up to 0.73 g/L of sulfate. However, seawater contains about 2.71 g/L of sulfate. Sulfate concentration is inversely proportional with the oilfield depth. It is concentration decreased from 0.55 g/L to 0.21 g/L with increased the oilfield depth from 9255 ft to 10275 ft. In addition, sulfate concentrations are independent of the production year of the oilfield as shown in Figure 3. However, Table 2 illustrated that, the average minimum and maximum values of sulfate during the oil production period are 0.44, 0.31, 0.29 and 0.2 g/L for 1st, 2nd, 6th and 11th year, respectively. Excepting this value of sulfate concentration during the 8th oil production year is 0.38 g/L.

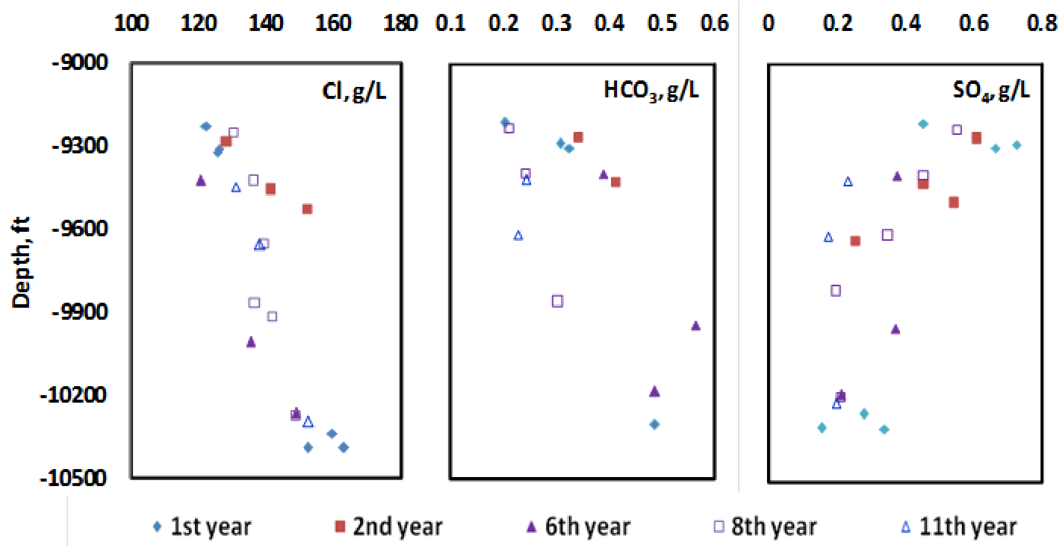

Figure 3. Anion constituents of oilfield produced water at various oil production years and depths.

4. Discussion

The pH of produced water has been generally reported in the literature to be in the ranges of 8.1 - 8.6 [5]. According to the investigated results in this study, pH values of the oilfield produced waters in the range 4.2 to 6.8, are lower than the allowable range of seawater (7.7 to 8.3). A change in the pH of water can have a number of consequences. In the environment, many plants and animals are harmed, or even killed, as a result of acidification. Many varieties of fish and aquatic life are extremely sensitive to changes in water pH. Generally, as the pH decreases and the acidity increases, fewer and fewer organisms can survive. Furthermore, acidic water can also cause problems for human consumption. It can be quite dangerous when combined with other compounds. Water with a pH that is less than 6.5 can leach metal ions, including iron, manganese, copper, lead and zinc from plumbing fixtures and pipes. In return, can be quite dangerous. On the other hand, the oilfield produced water is more corrosive at lower pH which can causes well casing and well integrity become corroded specially in mature oil fields which are producing since long time of more than 50 years such as those in Arab Gulf area. In such fields, many wells are suffering from many well integrity problems such as fluid flow behind casing causing unwanted water and or/gas production. Another problems have been included during reinjection of such water into other reservoirs or fields which could be incompatible and create scaling precipitations and a lot of other related problems.

The specific gravity of oilfield produced water are higher (1.132 - 1.164) than specific gravity of seawater (1.0263). The increase of specific gravity is according to the increasing of the salts dissolved into water. Thus, specific gravity increases linearly with a salinity increase. As a result, specific gravity increases as water becomes more saline and lower temperature. As oilfield depth increases, the specific gravity increases and produced water becomes more saline and more denser making low well efficiency to flow naturally and need more lifting power of gas lift and/or electric submersible pumps (ESP).

Salinity in oilfield produced waters is due mainly to dissolved sodium and chloride, with fewer contributions from calcium and magnesium [2]. Oilfield produced waters contain high salinity, as much as six times of the seawater. With these levels of salinity the water is toxic for many forms of life. The toxicity of produce water was tested on fish, bacteria and fungi in the aquarium environment [20]. About 100 % mortality occurred at 60 % concentration of produce water within 24 hours. Mortality ranged between 50 % and 80 % when the same organism was exposed to 40 % concentration for 96 hours [19]. For crop plants the irrigation water is considered saline when TDS is more than 2 g/L [15-16]. In addition, it was concluded that, a 1000 ppm change in the salinity can be tolerated by most organisms, however, a given volume of 70,000 ppm brine would require 34 volumes of seawater [21].

Oilfield produced water is typically rich in many cations such as sodium, calcium, and magnesium and anions such as chloride, sulfate and bicarbonate. Figures 2 and 3 and Table 2 illustrate that, the sodium and chloride concentrations from oilfield produced waters were in the range more than their concentration in the seawater and comprise about 90 % of the TDS of produced water (Figure 1). Besides, TDS of produced waters in the United States can range from about 3 to more than 350 g/l, with sodium and chloride generally comprising 70 - 90 % of the TDS [22]. Mostly, produced water derived from deep oilfield is characterized by Na/Cl ratios of less than 1, (Ca+Mg)/SO_4 ratio of greater than 1. This differentiation worked especially well at concentrations of greater than 10 g/L of TDS. So, it is not a surprise that the toxicity from high level of salt (Na + Cl) is probably the greatest environmental threat posed by produced water.

On the other hand, high sodium levels compete with calcium and magnesium for uptake by plant roots; therefore, excess sodium can prompt deficiencies of other cations. Elevated levels of sodium satisfies charge sites in soil minerals, particularly clays, leading to a net loss of attraction between soil particles and also can cause poor soil structure and inhibit water infiltration in soils [2], with the effect of increasing erosion and stream turbidity [23]. Infiltration into shallow ground water sources is also a concern when water is applied for irrigation use. Mineral accumulation due to subsurface ion exchange can change the water quality of shallow, underlying aquifers [2]. In addition, excess sodium with chloride toxicity, are major limiting factors in the use of untreated or insufficiently treated oilfield produced water for agricultural purposes.

The concentration of sulfate in the oilfield produced water is influenced by bacterial activity and by the concentration of calcium. Compared to seawater the oilfield produced waters show a major decreasein sulfate (as shown in Figure 3) and a higher increase in calcium (average concentration of calcium is five times that of the seawater). Because, calcium is present in relatively high concentration, the concentration of sulfate present will be low. In general, waters associated with limestone, dolomite, gypsum, or gypsiferous shale will contain more calcium than waters associated with sandstone.

Some oilfield produced waters containing high concentrations of magnesium and low concentrations of the other alkaline earth metals may contain concentrations of sulfate. The magnesium, can also pose significant threats in places, because the analysis of oilfield produced waters contain average concentration of magnesium two times the seawater.

The $CaCO_3$ formation rates increase with increasing the HCO_3^- content in the oilfield produced water. $CaCO_3$ scale formation occur simultaneously from the thermal decomposition of bicarbonate ions according to the following equation:

$$Ca^{2+} + 2\,HCO_3^- \leftrightarrow CaCO_3 \downarrow + CO_2 \uparrow + H_2O$$

From the above results, except pH value, all produced water characteristics are independent of the production year of the oilfield. On the contrary, it was concluded that, produced water characteristics can vary throughout the production period of a well for lift optimization and reinjection [6]. Additionally, because the oilfield produced waters contain elevated levels of salinity, cations and anions, untreated produced water discharges may be harmful to the surrounding environment.

5. Conclusion

Water analysis is very important for petroleum engineering industry from both upstream and downstream activities. Produced water represents the largest waste stream associated with oil and gas production in the studied oilfield. The results of the evaluation of the offshore oilfield produced water at Arabian Gulf illustrated the following:

- Most produced water characteristics independent of the production year of the oilfield. Excepting, pH value was lowered with increase the production year.
- Many characteristics of the produced water such as specific gravity, salinity, TDS, sodium and chloride are increased with increasing the oilfield depth.

- Generally, oilfield produced waters contain elevated levels of specific gravity, salinity, TDs, cations and anions more than the standards characteristics of seawater. Excepting, sulfate concentration is lower than the standards characteristics of seawater.
- It can be concluded that, untreated produced water discharges may be harmful to the surrounding environment.

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