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Produced Water Geochemistry from an Upstream Oil Operation

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Abstract

Oil and gas industries generate a significant amount of water during the production. The composition of this water varies with the geologic age, depth, and geochemistry of the region along with the chemicals added during the process. Geochemistry of formation water is used for aquifer identification, pollution problems, water compatibility studies, corrosion monitoring, water-quality control, water flooding, exploration, and to diagnose wellbore integrity issues. The current study investigates the spatial and temporal variation of produced water geochemistry from one of the largest conventional oil field, Ghawar field, Saudi Arabia. Produced water from different wellheads were collected and analyzed for different geochemical characteristics. Sixteen wells from ABQQ, nineteen wells from ANDR and twenty wells from SDGM area were selected for the current study. Sampling and analysis were performed as per the standard procedures. Results indicated that the pH of the sample varied from 6.0 to 7.4, and Electrical conductivity from 94200 to 102690 μS/cm. The spatial variation of major cations and anions were also recorded and represented by graphical plots. Metal analysis indicated the highest concentration for boron, which is 20.5 mg/L at ABQQ area, whereas all other metals are very low in concentration. Temporal variation of a single well at SDGM area indicated drastic change in the ionic concentration, whereas the geochemistry remains same as indicated by Tickler plot. The water type of the respective area was studied by tickler plots, which indicated same source of formation water in different wells at ABQQ, ANDR and SDGM areas. The ionic concentration is also used to predict corrosion and scaling issues. By Langelier Saturation Index (LSI) and Ryznar Stability Index (RSI), the sample from all the wells showed higher scaling potential. The study concludes that the water type in different areas under Ghawar field remains same regardless of drastic changes in the ionic concentration, which can be used to diagnose wellbore integrity issues.

Keywords

Formation Water, Petroleum Reservoirs, Groundwater, Ghawar Field, Tickler Plot

1. Introduction

Oil and natural gas are described as one of the most important industrial activities in the twenty-first century and play an influential role in the global economy as the major source of energy and revenue for many countries. The processes and systems involved in producing and distributing oil and gas are highly complex, capital-intensive, and require state-of-the-art technology. The upstream segment of the oil and gas industry contains exploration activities, which include creating geological surveys and obtaining land rights, and production activities. Fracking, or hydraulic fracturing, is a technique using a high-pressure liquid to extract oil or gas from geologic formations. This major upstream production activity generates enormous quantity of water, which requires proper treatment and management strategy.

Produced water (PW) is a term used in the oil industry to describe water that is produced as a byproduct during the extraction of oil and gas. It is the water trapped in reservoir (or below oil zone) and brought to surface along with oil and gas production. Fresh water, brine/seawater, and production chemicals sometimes are injected into a reservoir to enhance both recovery rates and the safety of operations and these surface waters and chemicals sometimes penetrate to the production zone and are recovered with oil and gas during production. The PW may include water from a reservoir, water previously injected into the formation, and any chemicals added during the drilling and production processes. Quantities of produced water increase as oil-producing field matures. Produced water represents the largest volume waste stream in oil and gas production operations on most offshore platforms.

Produced water is not a single product, it has a simple to complex composition that is variable, and it is considered as a mixture of dissolved and particulate organic and inorganic chemicals. Chemical and physical properties of produced water vary considerably which depends on several factors including, geographic location of the field, age and depth of the geological formation, hydrocarbon-bearing formation geochemistry, extraction method, type of the produced hydrocarbon, as well as its chemical composition in the reservoir. This is a complex mixture of organic and inorganic compounds and the largest volume of by-product generated during oil and gas recovery operations. It usually contains oil (dispersed and dissolved), metals (heavy metals), NORM, salt, chemical additives used during drilling, suspended solids, etc.

The Kingdom of Saudi Arabia possesses around 17 per cent of the world's proven petroleum reserves. Most are located in the Eastern Province, including the largest onshore field in Ghawar. The full picture of the produced water and its impact on the environment is yet to be fully realized due to the lack of produced water characteristic data. Geochemical properties of formation water reflect the sedimentary environments and the sealing conditions of the formation, which are of great significance for oil and gas exploration. Formation water can evaluate the petroleum preservation conditions and thus can be used to identify hydrocarbon reservoirs. Geochemical water analysis is used to diagnose major wellbore integrity issues during production stage. Geochemistry of extraneous water in the water-bearing horizon could be used to identify the well casing or cementing. Also, formation water geochemistry is utilized to identify the source of produced water and monitor events, including reservoir communication, water breakthrough and issues such microbiologically induced corrosion and scaling. So specific studies for each region should be done as its characteristics varies from region to region and such studies will also help in identify and solve many problems in the oil and gas industry. Hence, the objective of the current paper is to understand the full geochemical composition of produced water, which will be utilized to resolve many major well integrity issues raised from upstream oil operation at Ghawar oil field. The results from the current study will also be utilized as baseline data for any future research.

2. Literature Review

Al-Ghouti et al. (2019) reviewed produced water volumes across different countries, its general characteristics, different treatment methods including physical, chemical, and biological techniques, and reuse of produced water after treatment for different purposes. Produced water properties and volume can even be varying throughout the life time of the reservoir as it depends on location and the technology used for extraction (Ahmadun et al., 2009). Produced water composition, fates and disposal methods are described by Neff et al. (2011). The environmental impacts of produced water discharge to the ocean from offshore facilities were also discussed. Due to the ageing of wells, it is also expected that the water to oil ratio will be averaging 12 (v/v) for crude oil resources by 2025 (Dickhout et al., 2017). Thus, the market growth for the management and reuse of produced water is expected to grow further.

Produced water contains the same salts as seawater, with sodium and chloride the most abundant ions. The most abundant inorganic ions in high-salinity produced water are, in order of relative abundance in produced water, sodium, chloride, calcium, magnesium, potassium, sulfate, bromide, bicarbonate, and iodide. Concentration ratios of many of these ions are different in seawater and produced water, possibly contributing to the aquatic toxicity of produced water (Pillard et al., 1996). The organic and inorganic components of produced water discharged from offshore wells can be in a variety of physical states including solution, suspension, emulsion, adsorbed particles, and particulates (Tibbetts et al., 1992). A geochemical characterization of produced waters from Kuwait are studied by Alfarhan & Duane (2011). The objective of their study was to harmonize the database of brine waters in terms of regional identity by comparison with oilfield brines elsewhere, identify water-rock interaction, and statistically treat daily recordings from the pits in order to identify injection peaks and troughs. Laboratory analyses of major and minor cations and anions from the Rawdatayn samples and from the Sabriyah oilfield samples are shown in Environmental isotopic studies were used to determine the geochemistry of groundwater from different formations of Saudi Arabia (Carrigan, 1993). Hydrochemical studies on formation water by Birkle et al. (2013) from Unayzah and Khuff petroleum reservoirs of Saudi Arabia suggest the presence of evaporated seawater and meteoric water in different proportions throughout the reservoir. In their study, chemical and isotopic fingerprinting techniques were used to support for tracing the origin and evolution of formation waters taken during downhole and drill stem tests from exploration wells in Saudi Arabian oil and gas fields. Concentration level of different pollutants especially heavy metals in drilling wastes are described by Nasir et al. (2021).

3. Materials and Method

The Kingdom of Saudi Arabia possesses around 17 per cent of the world's proven petroleum reserves. Most are located in the Eastern Province, including the largest onshore field in Ghawar. The Ghawar Oil Field is by far the largest conventional oil field in the world and accounts for more than half of the cumulative oil production of Saudi Arabia. The field measures approximately 280 km-long and up to 36 km-wide (Saner et al., 2005). It is divided into six areas. From north to south, they are Fazran, Ain Dar, Shedgum, Uthmaniyah, Haradh and Hawiyah. Although Arab-C, Hanifa and Fadhili reservoirs are also present in parts of the field, the Arab-D reservoir accounts for nearly all of the reserves and production (**Figure 1**). Current study discusses the geochemistry of produced water from some of the fields under Ghawar.

The current study focused on 16 wells from ABQQ, 19 wells from ANDR and 20 wells from SDGM area. Sampling was performed during different months of 2022. The field service team collected samples from different wellheads in one-liter glass bottles and transported to laboratory by following the required preservation methods. Samples received by the lab are checked for the integrity and logged into the Laboratory Information Management System (LIMS). The respective chemist performed phase separation analysis and recorded the volume of water in percentage. The water separated is then distributed to respective lab sections and performed the geochemical and trace metal analysis. Necessary quality control samples were also run to ensure the accuracy and precision of the data. Lab is equipped with different quality assurance programs including running Certified Reference Materials (CRMs), Lab Control Samples (LCS), Unknown QA and Spike. The data obtained are then reviewed by senior lab chemist and authorized in the system. Graphical representations were also utilized in the current study to interpret the data. Geochemical water analysis can identify the water composition of a well, with diagrams being commonly used to identify such

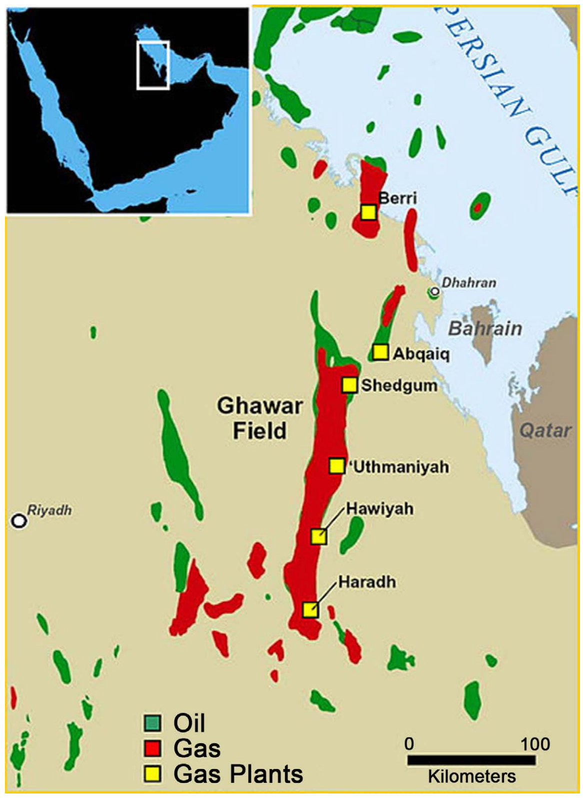

Figure 1. Map of Ghawar Field comprising of major production areas.

composition. One of these diagrams is the Tickler diagram, which is plotted to provide information on the source and type of formation water.

4. Results and Discussion

Produced water is not a single product, it has a simple to complex composition that is variable and the geochemical analyses are used by the petroleum industry in studies related to subsurface formation identification, pollution problems, water compatibilities, corrosion, water-quality control, water flooding, and exploration.

Geochemical analysis was performed for water samples collected from 16 wells of ABQQ, 19 wells of ANDR and 20 wells of SDGM locations. Maximum, Minimum and Average values for each parameter were calculated for three locations and tabulated in Table 1.

In the oilfield, one of the prime uses of these analyses is to determine the source of extraneous water in an oil or gas horizon. In some wells, a leak may develop in the casing or cement, and water analyses are used to identify the water-bearing horizon so that leaking area can be repaired. With the present emphasis on water pollution prevention, it is very important to locate the source of polluting brine so that remedial action can be taken. Also, formation water geochemical analysis data utilized to identify the source of produced water and monitor events, including reservoir communication and water breakthrough.

Table 1. Geochemistry of water wells from different locations.

Area	ABQQ			ANDR			SDGM		
Parameters	Max	Av.	Min	Max	Av.	Min	Max	Av.	Min
pH	8.1	7.2	6.5	8.0	7.2	3.7	7.8	7.4	6.0
EC µS/cm	215000	113543.8	26500	177500	101148.9	930	118600	102690	94200
Sp. Gravity	1.1471	1.0666	1.0015	1.1084	1.0552	1.0003	1.0637	1.0534	1.0337
Ca mg/L	31500.0	9911.9	1420.0	15500.0	6747.2	56.0	9900.0	8626.0	5400.0
Mg mg/L	3570.0	1249.8	216.0	2080.0	993.9	5.4	1270.0	1134.4	998.0
Na mg/L	56000.0	23281.3	4100.0	40000.0	19783.3	83.0	19000.0	18100.0	18000.0
K mg/L	2300.0	965.9	174.0	1877.0	821.4	4.2	998.0	887.7	780.0
Sr mg/L	1500.0	505.8	1.8	740.0	315.7	1.5	520.0	413.5	250.0
Ba mg/L	17.1	1.9	0.1	0.6	0.3	0.1	0.6	0.3	0.1
Alkalinity as $CaCo_3$ mg/L	666.0	338.6	95.0	650.0	290.5	0.0	405.0	311.4	114.0
Cl mg/L	130000.0	56317.1	8689.0	85709.0	44903.0	241.0	53183.0	44729.1	38524.0
SO_4 mg/L	1030.0	582.5	193.0	1320.0	626.0	50.0	701.0	478.7	310.0

4.1. pH, Electrical Conductivity & Specific Gravity

pH of the formation water gives preliminary indication of any activities happened to a system. All the natural waters have a normal neutral pH ranging from 6 - 8. The pH of water becomes more acidic when H_2S and CO_2 gases dissolve in it. The degree of ionization is reflected by pH and the concentration of other gases partially ionized when they dissolve. If the pH goes more alkaline, the system obstructs the solubility of ions, which finally promotes scaling. Similarly, if the pH goes more acidic, then the water becomes more corrosive and promotes corrosion. The current study shows pH ranging from 6.45 - 8.11, 3.66 - 8.03 and 6.00 - 7.82 for samples from Abqq, Andr and Sdgm respectively.

Electrical Conductivity gives you a preliminary indication of how much of ion is dissolved in the system. Total dissolved solids (TDS) gives an idea about the scaling tendency of water. Normally EC, Sp. Gravity and TDS all are indication of level of ions in water. The conductivity of produced water can vary widely from low level to very high concentrated brine characteristics. The present study shows the electrical conductivity ranging from 26500 - 215000, 930 - 177500 & 94200 - 118600 µS/cm, for samples from Abqq, Andr and Sdgm respectively. Higher conductivity results are mainly due to the presence of dissolved cations and anions. Sp. gravity gives an indication of thickness of the water and the average value ranges from 1.0666, 1.0552, 1.0534 respectively for ABQQ, ANDR and SDGM stations. Most formation water have high dissolved solid; the density of these waters is usually higher than pure water. One of the advantages of Sp. Gravity is to check the accuracy of analytical data. The total dissolved solids measured by ionic concentration should match with value produced by sp.

Gravity.

4.2. Inorganic Ions

Chloride and sodium are considered as the most abundant salt ions found in produced water; however, the higher concentration of those ions normally doesn't make any issues except precipitation of sodium chloride in extremely salty brines. In produced water from both conventional and unconventional wells; sodium is considered as the dominant cation with 81% in conventional wells and more that 90% in unconventional wells. Additionally, the chloride ion is the major parameters contribute to conductivity and increase in corrosiveness of water. The present study shows the chloride ranging from 8689 - 130000, 241 - 85709 & 38524 - 53183 mg/L, for samples from Abqq, Andr and Sdgm respectively. The other major cation in the formation water is Calcium ion. The concentration of calcium reaches up to 31500 mg/L. The tendency of calcium is to combine with bicarbonate, carbonate and sulphate ions and precipitates to form adherent scale or suspended solid, which makes the calcium as one of the most important parameters in the geochemical water analysis

Magnesium concentration is normally lower than sodium and calcium ions. Most of the calcium carbonate scales contain magnesium due to the tendency of magnesium to participate as co-precipitation product with calcium scale. Magnesium ion might work as a scale inhibitor by decreasing the amount of scale produced, which might be formed by sulphate. The average concentrations of magnesium from different locations are 1249.8 mg/L, 993.9 mg/L and 1134.4 mg/L respectively. Sulphate is normally combined with calcium, barium and strontium to form a scale; while magnesium is combined with sulphate to form compounds that remain in the solution. Most of sulphate ions will be linked to magnesium; thus, there is no remaining sulphate ion to form a scale with the other ions.

The presence of sulfate and sulfide ions in produced water can leads to insoluble sulfate and sulfide at high concentrations in produced water. Moreover, the presence of bacteria in the anoxic produced water, causes the reduction of sulfate and in turn leads to the presence of sulfides (polysulfide and hydrogen sulfide) in the produced water. The major problem of high sulfate is the formation of insoluble sulfate scale by reacting to calcium, barium and strontium. In the current paper, the level of sulfate varies from 193 - 1030, 50 - 1320 & 310 - 701 mg/L for Abqq, Andr and Sdgm samples.

Barium and strontium are considered as an important ion due to the capability of them to form sulphate scale, which is insoluble. A small amount of barium sulphate scale can cause a serious problem. Strontium sulphate scale is more soluble than barium sulphate and normally the scale found is a mixture of barium and strontium sulphate

The bicarbonate ion can form an insoluble carbonate scale by reacting to calcium, magnesium, iron, barium and strontium ions. Practically, all the waters will contain bicarbonate ions, which is called methyl orange alkalinity. As for carbonate ion, it can form insoluble scales by reacting to calcium, magnesium, iron, barium and strontium. Due to the low pH of produced water, carbonate ion is rarely present in it. It is called phenolphthalein alkalinity. However, the concentration of these anions and cations varies from location and their ranges are presented in **Table 1**.

4.3. Metals

Produced water may contain certain metals like Fe, Cr, Ba, Ni, Zn and others. However, differences in the type, concentration, and chemical content of the metals are influenced by the geological age and features, injected water volume and chemical composition (Collins, 1975). Commonly, mercury, zinc, barium, manganese, and iron are found in produced water at higher concentration than the seawater concentration (Neff, 1987). For instance, Hibernia produced water have high concentrations of barium, iron, and manganese as compared to seawater. In addition, it was also reported that the barium, sodium, iron, magnesium, potassium and strontium in produced water from natural gas production field are present at higher concentrations (Johnson et al., 2008). The geology of formation and age of wells are major factors that determine heavy metals concentrations in produced water. These heavy metals should be properly managed when the produced water is spilled on ground surface or discharged into water bodies because they damaged the ecosystem (Udeagbara et al., 2020). In the current study, all the metals analyzed showed very low concentration. **Table 2** shows types of metals analyzed and the concentration from Abqq, Andr and Sdgm fields.

Table 2. Metal levels in samples from different field.

Metals	Unit	Field		
		Abqaiq	Aindar	Shedgum
Boron	mg/l	20.5	3.7	14.0
Iron	mg/l	0.02	0.02	0.04
Copper	mg/l	0.04	0.01	0.03
Lead	mg/l	<0.01	<0.01	<0.01
Zinc	mg/l	0.01	<0.01	<0.01
Manganese	mg/l	0.14	0.46	0.03
Nickel	mg/l	<0.01	<0.01	<0.01
Chromium	mg/l	<0.01	<0.01	<0.01
Aluminum	mg/l	0.05	0.07	0.06
Barium	mg/l	3.4	0.3	0.03
Silver	mg/l	<0.01	<0.01	<0.01
Cobalt	mg/l	<0.01	<0.01	0.01
Cadmium	mg/l	<0.01	<0.01	<0.01

4.4. Graphical Plots

An important task of water investigation is the compilation and presentation of chemical data in a convenient manner for visual inspection. Graphs are used in comparing the similarities and differences in the concentration of the chemical constituents in each water sample analyzed. Graphs are also used in detecting mixing of water of different composition and identifying chemical processes occurring as water passed through the aquifer system. The graphical presentation is an aid to rapid identification of a water, and classification as to its type. For this purpose, a variety of data presentation techniques have been developed for showing the major chemical constituents over the year and these include: Bar Charts, Pie Charts, Stiff Diagrams, Scattered Plots, Schoeller Diagrams, Piper Diagram etc are used in water industry. Figures 2-5 represents spatial distribution of major ions in ABQQ, ANDR and SDGM locations.

4.5. Tickler Diagram

The Tickler diagram was developed using a 6-axes system or stat diagram. There would be percentage reaction values if the ions are plotted on the axes. The percentage values are calculated by summing the epm's, and multiplying them by

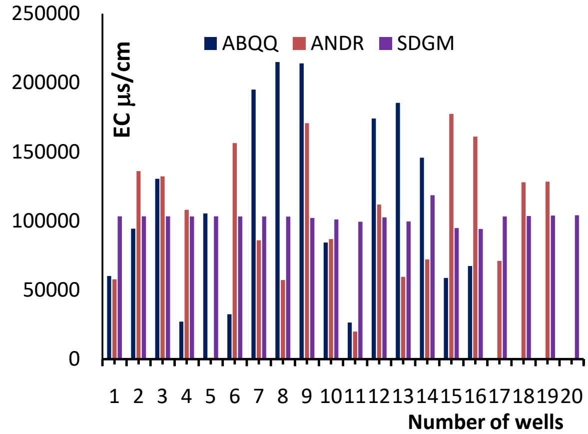

Figure 2. Spatial variation of electric conductivity.

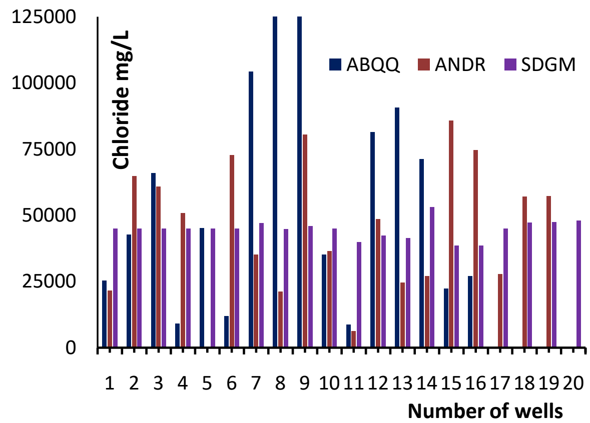

Figure 3. Spatial variation of Chloride ion.

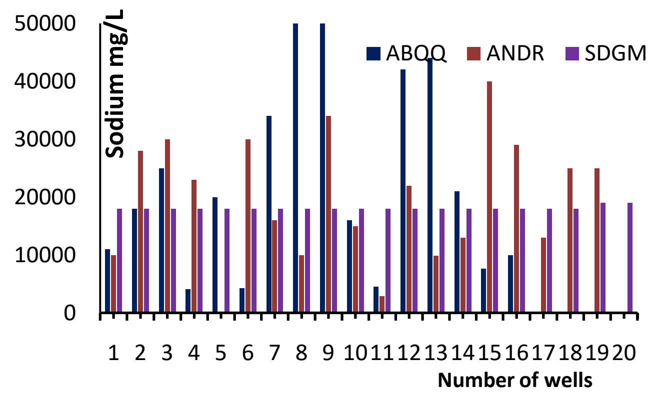

Figure 4. Spatial variation of Sodium.

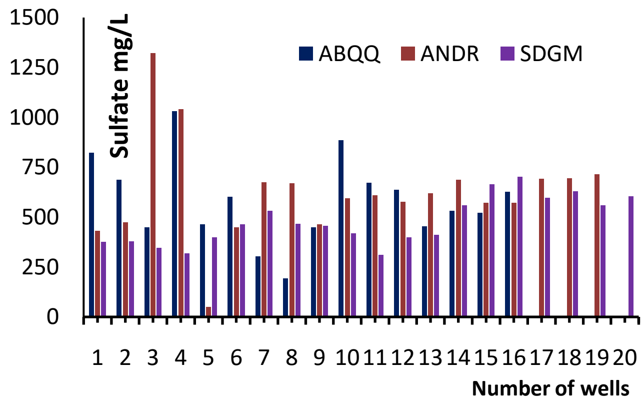

Figure 5. Spatial variation of sulfate.

100. The Tickler diagram is used to identify the source of water by comparing it with other Tickler diagrams in the nearest wells. Comparison of Tickler diagrams for samples with different geochemical characteristics are used to identify the source of samples. **Figures 6-8** represents the tickler diagram for formation water from abqaib, andr and sdgm areas. In each plot it is confirmed that even though the geochemical characteristics differs a lot, all samples are following the same pattern of Arab-D formation in the Tickler diagram. So, the present study confirms the same source of formation water in different wells at ABQQ, ANDR and SDGM areas.

Temporal variation of geochemical data

Spatial and temporal variation of produced water occurs due to different geological pattern and natural processes occurring in the system by time. Formation water quality also changes due to manual addition of many types of drilling fluids and chemicals and processes such as sea water injection to increase the productivity. In this study, we will compare the formation water quality of single well for two years period. Below graph represents the temporal variation of major ions and tickler diagram for sample from a single well at SDGM area (**Figure 9**). From the data, it is confirmed that even though the ionic concentration has changed during the investigation period, the geochemistry of the aquifer remains same as is indicated from the Tickler diagram (**Figure 10**).

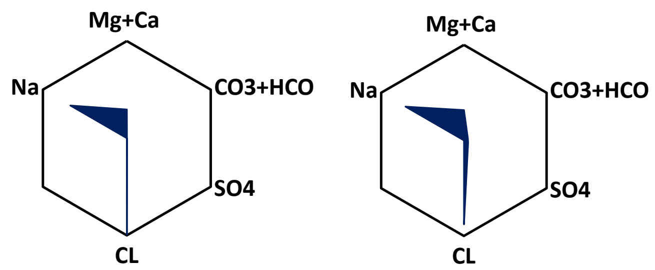

Figure 6. Spatial variation of Tickler plot for ABQQ with TDS 205694 mg/L & 16327 mg/L.

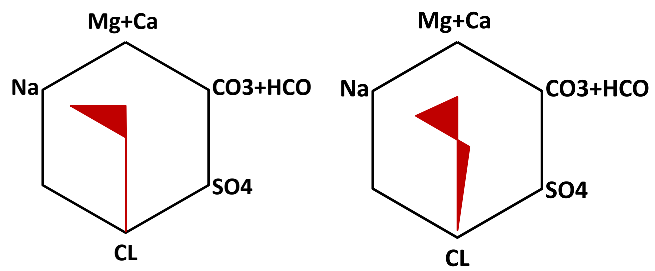

Figure 7. Spatial variation of Tickler plot for ANDR with TDS 136992 mg/L & 435 mg/L.

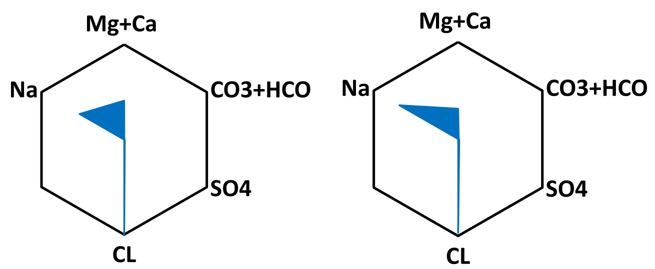

Figure 8. Spatial variation of Tickler plot for SDGM with TDS 83017 mg/L & 64098 mg/L.

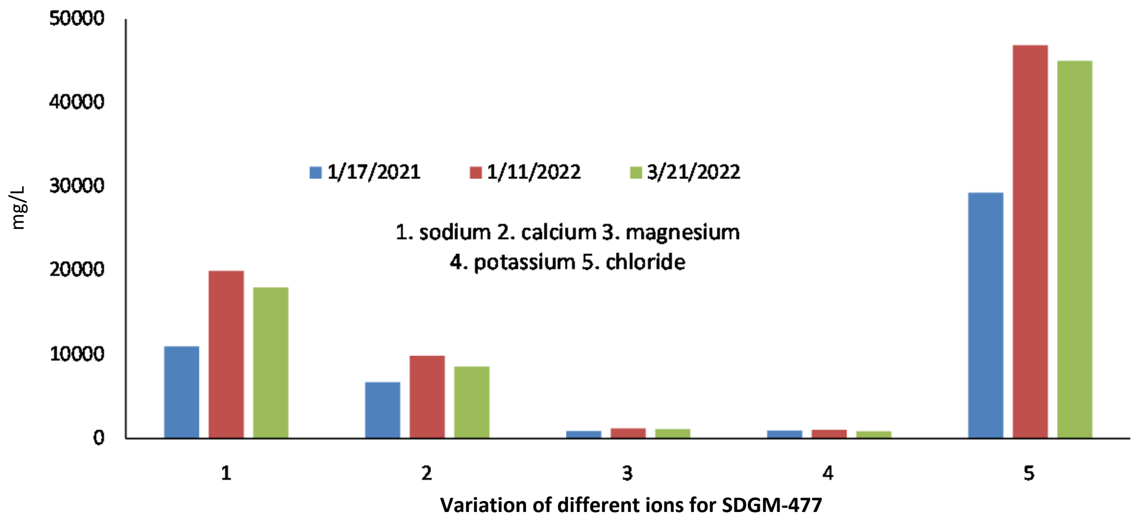

Figure 9. Temp.

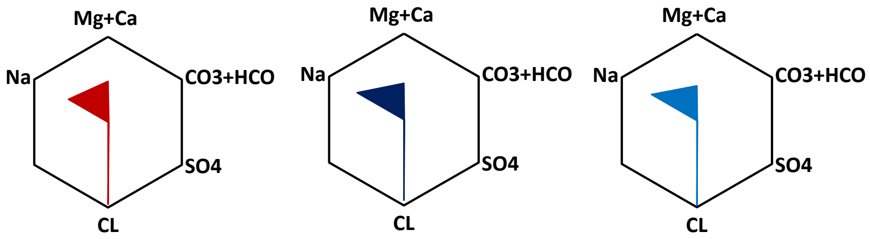

Figure 10. Tickler diagram of SDGM-477 with respect to Temporal variation.

4.6. Prediction of Corrosion and Scaling

The scale formation and corrosivity is qualitatively predicted using various indices. The Langelier Saturation Index (LSI) is an indicator of water scaling potential. Ryznar Stability Index (RSI) can predict the corrosion and scaling in water samples with different hardness. In the current study water samples were collected from different wellheads were tested for geochemical and microbial parameters. Geochemical test indicated scaling potential in all the samples. Different indices calculated based on geochemical data indicated scaling potential in all the samples. At the same time higher concentration of SRBs in few samples indicated corrosion threat to the system as well. The prediction concluded the importance of different scale inhibition mechanism and corrosion control in Oil and Gas industry.

5. Conclusion

The current study reviews the characteristics of formation water from different locations of Ghawar Oil Field, the largest conventional oil field in the world located in Saudi Arabia. The cycle of the study includes research review and investigation, field sampling, laboratory experiment and mathematical analysis of the generated data. Physical analysis of the sample indicated that the pH of all the samples were in the neutral range, neither acidic nor alkaline. Geochemical characterization indicated varying ionic composition with salinity ranging from 94.2 mS/cm to 102.69 mS/cm. Even though all the samples showed temporal and spatial variation based on different ionic concentrations, tickler diagram indicated same origin for all the formation water. Differences in the concentration could be due to production enhancement through sea water injection or other geochemical activities. The concentration of different metals were very low except for Boron, which is found to be 20.5mg/L. Evaluation of the geochemical data based on developed indices indicated tendency for scaling in all the samples. The study concludes that the water type in different areas under Ghawar field remains same regardless of drastic changes in the ionic concentration, which can be used to diagnose wellbore integrity issues. Limitations of the study include a lack of field data to interpret major issues such as corrosion and scaling in oil and gas operation. We recommend the future researchers to utilize the current data in breaking the hidden truths beneath the formation water.

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Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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