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Hydrogeochemistry of oilfield water and formation damage of Zubair reservoir in North Rumaila Field - Southern Iraq

A Thesis

Submitted to the College of Science University of Baghdad in Partial Fulfillment of the Requirements for the Degree of Master of Science in Geology (Geochemistry)

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DEDICATION

To my precious home, Iraq

To Supervisor Dr. Salih Muhammad Awadh

To my love: my father, mother and brothers

To my beloved wife "Zainab" that encouraged me

and endured troubles...

To my kids ...

I dedicate this work with my love

Ali Ramthan

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Abstract

The Zubair Formation (Lower Cretaceous) is one of the important oil reservoirs in southern Iraq. The upper sandstone member of this formation in the North Rumaila oilfield is the main reservoir of oil production. Reservoir pressure was decreased in conjunction with the production process over time, so the style of water injection became necessary to raise the pressure and maintain the reservoir properties. The South Oil Company may become accustomed to the use of The Qarma water for injections, it is also hoped to use the Main Outfall Drain (MOD). For this reason, this study highlights the hydrogeochemistry of the oilfield water and the expected damage as a result of MOD injection to the Zubair reservoir.

This study addresses the physical and chemical properties of the oilfield water collected from 6 wells within the North Rumaila filed along with the 2 samples from MOD. The oilfield water is classified as brine water has TDS of 123679 mg/l, and specific gravity of 1.22811 at 15°C, of marine origin of weak acidic pH (5.1-5.7). Its type is Na-Ca-chloride and anions are ordered as rCl > SO₄ > HCO₃, whereas cations ordered as rNa > Ca > Mg > K. The water of The Main Outfall Drain (MOD) is a very saline surface water, but with high TDS (26790 mg/l) of weak alkaline pH (7.6- 7.55) containing bacteria colonies of Escherichia coli (E. coli), Coliform, F. Streptococcus that may participate in formation damage.

Clay minerals are diagnosed in 16 core samples collected from wells. The XRD and SEM tests show that most abundant mineral is quartz with a small amount of kaolinite altered by the chemical weathering of feldspar. Bitumen occurs filling the interstitial pores, fractures and dissolution cavities, where kaolinite participates to close the pores when driven with the solutions causing reduced permeability. Some petrophysical tests are made to determine the permeability.

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The present study demonstrates that the mixing of formation water with the MOD water form a salt crust (Scale) consisting of anhydrite, barite, celstite and calcite reducing the permeability of the reservoir where they precipitate in closing the pores causing blockage and damage to the reservoir petrophysical properties. A laboratory experiments are achieved on mixing ratio of the oilfield water with both of MOD water and the sea water as well as the simulation geochemical model using PHREEQC software. The best ratio of mixing oilfield water to MOD water is 90%:10%, oilfield water to sea water is 60%:40%, 70%:30%, 80%:20% and 90%:10% where the mixture was under saturation and no chance to precipitate any salt (Scale).

A set of laboratory experiments are conducted on changing the pH values of the solutions injected in the core samples. The gradual change in the value of pH from acidic to alkaline (3, 5, 7 and 9) cause a decrease in permeability from 104, 103, 97 and 90 MD respectively, and formation damage (18-25%) in the cores samples. The sudden change of pH from 3 to 11 causes a significant reduction in permeability from 72 to 39 MD and formation damage amounts to 44%. The main reason for this damage is a dispersion of kaolinite and accumulation in the necks of pores.

The core samples are subjected to the injection with NaCl solution in two stages (gradual and sudden decrease of concentration) to ensure the damage causes. In the case of gradual reduction of the salt concentration from 20% to 15%, 10%, 5% and then to 2%, it is observed that permeability decrease to 155, 150, 148, 147 and 140 MD respectively of the core samples and a formation damage is obtained ranging from 9 to 14.4%. But in the case of sudden change of NaCl concentration from 20% to 2%, a decrease in permeability from 200 to 193 MD is observed and formation damage ranges from 10.7 to 12.2. Accordingly, the low salinity leads to formation damage due to decrease the permeability. Finally, the high pH and low salinity leads to a formation damage and a decrease in the amount of reservoir permeability.

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Chapter One

Introduction

1- Introduction

1-1 Preface

Many researchers are interested in oilfield water (Collins, 1975). It became important in recent years, where it has a role in determining the depositional conditions and also helps in the study of oil migration and accumulation in the geological layers. Oilfield water has become a vital issue in scientific studies of oil, starting from exploration, drilling, field development and production. It characterizes by special specification greatly differ in terms of chemical composition from surface water (rivers – sea – lakes). Oil production as it is also known in the initial stages depends on the natural pressure of the reservoir, and when production progress is less than this pressure it becomes necessary to use additional water to release oil to enhance production. This method is called the secondary production.

The South Oil Company uses the waters of the Shatt AL-Arab River after chemical treatments for injection purposes and raise the reservoir pressure of the Zubair formation. It is hoped to use the Main Outfall Drain (MOD) water for injection purposes. Accordingly, this study investigates a chemical compatibility between oilfield water from the Zubair Formation and Main Outfall Drain (MOD) to diagnose the damage cause in the reservoir due to the mixture. The added water will change the chemical environment of the oil reservoir. It will affect on the geometric situation of the reservoir and the petrophysical properties (permeability–porosity). Hydrogeochemistry and formation damage will be the major topics in this study, as an attempt to design the compatible water using experimental tests.

1-2 Location of the study area

The study area includes the North Rumaila Field which lies approximately 54 km west of Basra town. This oil field is 40 km long and 13.5 km wide. It is double plunging anticline, slightly asymmetrical, with the long axis trending N-S. Eight oilfield wells (R-172, R-17, R-112, R-184, R-131, R-186, R-136 and R-120) are selected for collecting the oilfield water and core samples (Figure 1-1). Sampling method will be described in chapter two.

The Main Outfall Drain (MOD) is selected to collect water samples that require for water compatibility. The MOD passes northwest of the North Rumaila field (Figure 1-1). The work on MOD was started in 1953 and it was intended to carry saline water that had been used for irrigation of farmlands in the central and southern regions of Iraq. It was completed in December 1993, it is 565 km long, from Baghdad at Ishaqi, to its mouth in the Khor Al-Zubair River. It passes around the southwestern edge of the Hammar marsh, and joins Shatt Al-Basra canal which discharges into the Arabian Gulf (Khthi et al, 2010).



Figure 1-1: Location Map shows the study area (North Rumaila field).

1-3 Objectives of the study

This study aims at:

- 1- Assessing the chemical and physical specifications of the oilfield water in the Zubair formation within the North Rumaila field.
- 2- Determining the formation damage that may be caused by water injection into the reservoir for the purpose of continuing the process of oil production.
- 3- Diagnosing the mechanism of formation damage by knowing the types of clay minerals and their impact on the reservoir.
- 4- Determining the precipitated scale that produced from mixing the proposed surface water with formation water and determine the saturation index.

1-4 Previous Studies

Studying oilfield water is considered as one of the basics to evaluate of oil reservoirs performance, and plays an important role in the oil basins. Globally, the researchers Angino and Billings (1969); Hitchon (1969); Hitchon and Friedman (1969); Hitchon et al. (1971), Hitchon and Hays (1971) conducted geochemical studies on the oilfield water and sub-surface geology particularly, geochemical and hydrodynamic oilfield water in the Western Canada Basin and the Surat Basin in Australia.

Chebotarev (1955) found a relationship between water quality and hydrocarbons gatherings, by collecting samples of oilfield water from different fields in the world. He also found that the proportion of 72.7% of the

reservoir water is a type calcium chloride, 23% of type bicarbonates, and 3.3% of sulfate type. It was concluded that this water sulfates and bicarbonates is water mixed with surface water and modern carried to great depths.

Gray and Rex (1966) discussed formation damage in sandstone caused by clay dispersion and migration, and they suggested that dispersion of mica needles and small kaolinite crystals is the principal cause of clay migration damage in the suite of sandstones studied.

Hubbert (1967) stated that the hydraulic slopes occur as a result of two main reasons, these are variations in topographical and the presence of anomaly pressures underground resulting from the of sedimentary compaction and other reasons.

Billings et al. (1969) found five types of oilfield water in Western Canada sedimentary basin and postulated the origin of two of the types. One type of water was formed by selective membrane filtration which produced waters containing high concentration of dissolved solids. A second type was a mixture of membrane-concentrated formation water and bitterns formed after the precipitation of halite but before the precipitation of sylvite.

Bajorski (1970) studied hydrochemistry of water reservoir for a number of oil fields in the world. It was concluded that calcium chloride water are always accompanied by the accumulation of hydrocarbons, especially those containing a high proportion of mineralized chloride and a low concentration of sulphate.

Morris and Hepperd (1982) explained the behavior of clay minerals in the Bridport Sands. Comprise mainly kaolinite and mixed-layer clays of both the illite - chlorite and illite – smectite types, where the blockage pores result (i)

adsorption of water and expansion of poorly and (ii) the physical movement of authigenic kaolinite crystal aggregates.

Pittman and King (1985) noted formation sensitivity tests showed that the kaolinite-rich sandstone was stable at 2% NaCI water, but introduction of fresh water caused permeability impairment. Acid treatment to remove damage produced sporadic results. Injection of HCI raised the permeability temporarily.

Bennion and Thomas (1992) gave a description of the damage mechanism, which can occur during a thermal stimulation operation; these processes would include (i) Mineral transformations (ii) Mineral solubilization / dissolution (iii) Wettability alterations (iiii) In-situ emulsion formation.

Chang (1992) worked modeling of formation damage due physical and chemical interactions between fluids and reservoir rocks. It was concluded that Formation sensitivity to the invading fluids that triggers clay swelling and clay fines migration is model by considering hydrodynamic effect and change of pore fluid composition, salinity, and pH conditions. Geochemical reactions involving dissolution-precipitation of minerals and ion exchange are modeled through a kinetic approach.

There are recent studies related to formation damage including a study of Lanson et al. (1998). It was found that the transformation of kaolinite to dickite in sandstone reservoirs has major geochemical and thermodynamical implications. Because they display a continuous sequence of kaolinite-todickite transformation over great depths, diagenetic kaolins occurring in the pores of reservoir sandstones constitute the best means of reliable investigation of the structural relationships between kaolinite and dickite in a nearly closed system.

After it has been reviewing the most important global studies related to the hydrochemistry of the oilfield water and formation damage, it is necessary to highlight the Iraqi Studies as follows:

Al-Ameri et al. (1995) determined four palynofacies types indicating of island barrier at the upper part of Zubair Formation. These palynofacies are found to coincide with the environments of swampy delta-plain, delta front, prodelta, and Shelf Sea.

Al-Abbasy (1999) studied the hydrogeochemical and hydrodynamic for the Upper Cretaceous age of East Baghdad field, and mentioned that the total dissolved solids of the oilfield water are directly related to the ions Na^+ , Ca^{2+} , Mg^{2+} , K^+ and Cl^- and inversely related to the ions SO_4^{2-} , Fe^{2+} .

Al-Atroshy (1999) shows the acidity of Zubair oilfield water led to dissolve of calcareous cementing material in shales causing fractures allowing hydrocarbons to migrate vertically upward to sandstone member in the Zubair Formation. He also mentioned that first structural closure was formed in Zubair formation during Early Cenomanian, and it has stable during Late Cenomanian.

Al-Yasiri (2000) studied the hydrogeochemistry of the Zubair Formation in South Rumaila Field of Southern Iraq. He confirmed that oilfield water characterized by their acidity, high salinity, and among the clay minerals, kaolinite represents the main mineral occurred in the present rocks and its has a great negative effect on the properties of the reservoir when the chemical properties of the formation water altered (low salinity, high pH).

Jafar (2001) diagnosed the oil migration timing of Zubair Formation which was generated from the shales in the formation itself, West Qurna, North Rumaila and South Rumaila fields are considered within the maximum

maturation for oil generation, after Maastrichtian period and the following period. During the period of deposition of Umm-Er-Radhuma Formation.

Razoian (2002) the has study includes improving enhanced recovery of the Mishrif reservoir in the fields of North of Rumaila, West of Qurna and Zubair reservoir in South Rumaila field, and the manufacture of crude oil emulsion in water and finding a new technology to develop oil fields.

Abbas (2002) determined the origin of oilfield water in some wells studied in the East Baghdad field (Khasib reservoir) in terms of hydrochemistry as old isolated marine water not mixed with meteoric water.

Khafaji (2003) explain respects the hydrogeochemical and hydrodynamic of oilfield water in four Cretaceous reservoirs in the southern Iraq. The oilfield waters are marine origin, old, isolated and have not been mixed with recent continental waters. As each reservoirs a closed hydrogeological system and represents a unique hydrochemical system having a similar chemical composition, high salinity (ranging between 125 –254 gm/l) and they are all of chloride – calcium water type.

AL-Atabi (2009) his study deals with the general physical and chemical characteristics of Yamama Formation water in selected oil fields - southern Iraq. The study confirms the occurrences of two types of formation water; the first one is the connate water, which is brine, hypersaline, and marine in nature reflects the possibility of hydrocarbon accumulations, and the second is mixing water reflects the mixing of original marine water with percolating meteoric water for various degree. Al-Jubory (2005) studied reservoir properties of the sand member of Zubair Formation in the Southern Rumaila Oil Field and determined the porosity, permeability and sedimentary facies (channel, swamp, marshes, distributary mouth bar and prodelta facies).

Al-Haidary (2009) studied the biomarkers of Zubair Formation oil and its sources in Basra. Modeled transformation ratios indicate that 53-75% of its generation potential has been reached. In contrast, younger source rocks are immature to early mature (<20% generation), whereas older source rocks are mature to over mature with 100% generation.

1-5-Geologic Description

1-5-1 Zubair Formation

The Zubair Formation was first described by Jones (1948) and later was defined by Owen and Nasr (1958). They noted that it is comprises 389 m of sandstone, siltstone, and shales, it is overlain conformably and gradationally by the Aptian Shuaiba Formation and underlain conformably and gradationally by shales and limestone of the Valanginian-Hauterivian Ratawi Formation (Fadel and Ansari, 1992).

The age of the formation was studied by many researchers, Al-Naqib (1967), Bellen et al (1959), Abbo and Safer (1967), Castro (1976), Ibrahim (1983), Al-fars (1998) and AL-Husseinni (2000). The age of the formation was primarily assigned by Owen and Nasr (1958) to be Early Aptian – Barremian (Al-Azzawi, 2012). While Boudy 1980 pointed out that this Formation consists of detrital clastics, and belongs to the Lower Cretaceous cycle (Late Beriassian–Albain).

There are no exposures of the Zubair Formation, neither was it encountered in bore holes around the Rutba-Hail arch. It is presumable that the formation is cut out at the regional erosional unconformity of Late Aptian/or Alpian (Bellen et al., 1959). Zubair Formation has a broad extension in Iraq (Figure 1-2), and adjacent countries. Where in Arabic Saudi is equivalent to Biyadh Formation. The deposition of the Zubair and Biyadh in the context of the history of the Arabian plate, reflect a major geodynamic phase in the evolution of the African system. This phase is termed continentlization (Mashadani, 1984). In Iran will be equivalent to Jdvan Formation (mud and shale), whereas in Syria be equivalent to Lower Sarmord Formation (sandy and marly limestone) (Buday, 1980). It consists in south Iraq from mutually sequences of sandstone, shale and secondary proportion of limestone (Buday, 1980).

Depositional environment of Zubair is deltaic facies, and evidence come from cores in the Rumaila, Zubair, west Qurna, and the top part of the Zubair section in Luhais oil fields and no cores of the westerly situated wells were examined (Al-Fadel and Ansari, 1992).

The thickness of this formation at the type locality is about (389.2m) increasing towards Afaq area (Aq-1) about (500m), and decreasing towards the west to (200m) or less (Ali and Nasser, 1989). Khafaji (2003) mentioned that the increase in thickness with the increasing sandstone towards the southwest, indicates that the sandstones are the foundation component of this Formation in southwest Iraq (Figure 1-2). The lower and upper contacts of the Formation are mostly gradational and conformable in the central part of the basin. But towards the west in the Salman Zone the lower boundary of the Formation is unconformable, and the upper boundary with the overlying Albian sequences is unconformable (Jassim and Goff, 2006). It represent as repetitive succession of sandstone and shale with small amount of silt (Nasr and Hedson, 1953 in Bellen et al., 1959).



Figure 1-2: Isopachmap of the Zubair Formation in Iraq (Jassim and Goff, 2006).

The Zubair Formation is the most prolific reservoir in the south of Iraq, especially in the Zubair and Rumaila oil fields. The most important occurrences of oil in the Zubair Formation are in the southern Iraq oil fields of Zubair, Rumaila, Ratawi, Tuba and Luhais. Oil has also been discovered in the Zubair Formation further east in the Majnoon, Halfaya and Huwaiza fields (Jassim and Goff, 2006).

The Zubair Formation is assumed to represent a prograding delta originating from the Arabian Shield. The sand isolith of the formation in central and southern Iraq suggest influx of clastics from the northwest in Central Iraq and probably from the southwest in south Iraq (Jassim and Goff, 2006). In some wells on the west side of the Mesopotamian Zone and the Salman Zone in southern Iraq, the Zubair Formation passes laterally into Ratawi and Yamama Formations (Buday, 1980).

The upper sandstone member of the Zubair Formation is considered as the main pay zone in this oilfield. Along one there are three subsurface structural features, previously thought as a single structure is West Qurna, North Rumaila and South Rumaila Field. Oil was first discovered in Rumaila North oilfield in 1959. The field was first developed in 1970. However, on the surface there are no geological characteristics marks showing the separation of the three fields. The study area, like the rest of the desert areas to west of Basra, covered by sand and gravel of the Dibdibba Formation (Pleiestocene). Hammar Marsh covers the northern half of the field.

1-5-2 Lithostratigraphy in the North Rumaila Field

The structural map of the Rumaila structure was interpreted in the past as a continuous single anticline. But in fact. It comprises a series of three subtle domal structures. These are north, south Rumaila and west Qurna fields. The southern half of the structure –the area known as Rumaila– is largely open, uninhabited desert (Figure 1-1).

Zubair Formation is divided into five members in North Rumaila field. These were informally named top to bottom (Fadel and Ansari, 1992):

- Upper Shale Member
- Upper Sandstone Member
- Middle Shale Member
- Lower Sandstone Member
- Lower Shale Member

The subdivisions are based on the dominance of sand on shale in the lithofacies of the members. The current study is interested with the Upper Sandstone member, generally composed of clean friable porous sandstone, intercalated with few thin shales and fewer siltstone layers, and believed it have been deposited in a moderate fluvial dominated deltaic environment. Digenetic processes (mainly cementation) partially lithified the clastic sediments giving the rock its friable nature. (Ali and Nasser, 1989) mentioned that the reservoir sandstone layers of the Zubair Formation are fundamentally made of quartz particles (95-99%) weakly cemented with silica (0.2%), carbonates (0.3%) and iron oxides (0.1%). The sandstone layers have a high porosity (19%) and (500 md) permeability. Clay minerals are present in two forms, (i) as segregated secondary layers with limited distribution interbedded with the sandstone layers, and (ii) dispersed clay particles within the interparticle pore-space of the clastics (argillaceous sandstone facies). Sandstone layering within the Upper Sandstone Member in North Rumaila Field is related to syndepositional processes acting within tidal embayment and channels within a tidal dominated delta with associated long shore bars created by long shore winds. Within the Upper Sandstone Member of the North Rumaila Field, the five lithological units, these units are found to be persistent and well defined over North Rumaila field and extending into West Qurna culmination. They are considered to represent different phases in the sedimentary history of the field (Mustafa, 1973). These units are, from top to bottom, as follows (Figure 1-3):

- 1- Unit AB the predominant lithology is sandstone.
- 2- Unit C the predominant lithology is shale.
- 3- Unit DJ the predominant lithology is sandstone.
- 4- Unit K the predominant lithology is shale.
- 5- Unit LN the predominant lithology is sandstone.

Unit AB: is characterized by shale, silty sandstone top gradationally underlying the upper shale member, and having a sharp contact with shale of layer C below it. The net sandstone varies from 11.9 m at R-37 to 3.4 m at R-4. The sandstone percentage varies from 100% at R-14 to 64% at R-4, and thin layer of siltstone, less frequently, shale occur in this unit (Mustafa, 1973). Often these are at or near the top, generally they are of one meter or less in thickness and are not extensive over the field. Porosity ranges of this layer are 8-21.3%.

<u>Unit C:</u> it is placed at the bottom of AB sandstone and at the top of the persistent shale bed. This consists predominantly of shale and considered non-reservoir layer.

Unit DJ: it consists of sandstone with thin layers and lenses of siltstone, silty shale and shale. The total thickness of this unit is varies from 61 m at R-8 to 53.9 m at R-19. The sandstone percentage varies from 96% at R-37 to 62% at R-19. This major sandstone unit has a great importance from the reservoir point of view since it forms a large part of the main pay of North Rumaila field.

Unit K: it is identified at the base of the thick DJ sandstone and at the top of a continuous and prominent shale bed. This shale bed is absent in some wells and instead unit K starts with a siltstone bed. This unit is consists of shale which becomes silty or sandy near the base. The unit varies in thickness from 3.5 m at R-17 to 7m at R-37.this unit is considered as an effective barrier

between the sandstone units DJ and LN due to the thickness of this unit and the continuous shale distribution northwards and down the flanks of North Rumaila Field.

Unit LN: this unit is composed predominantly of sandstone of thin beds and layers of siltstone, silty shale and shale. The upper contact is well defined expect at R-17 and R-37 and is taken at the base of shale or less frequently siltstone and at the top of sandstone of unit LN. the lower contact marks the boundary between the upper sandstone and the middle shale members(Mustafa, 1973).

The five members subdivisions of formation within the field, reflects cycle variation in the rate of sediments supply, and is due to cyclic variation in the epirogenic movements in the source area. These units were further found to be divisible to 12 layers. These units and layers were recognized as prominent variation in the sedimentary phases of the delta construction.



Figure 1-3: Stratigraphic column of South Iraq, Basrah region (Rumaila and Zubair oil fields), shows the five lithological units of Upper Sandstone Member. (Modified after Al-Ameri et al, 2011).

Many other lithological elements were found to be of localized extent, representing minor and local variation in the sedimentary environment. These are beds, or a number of beds within the dominant lithology of the unit that are essentially extensive. They are generally separated from each other by the occurrence of minor shale beds (in case of sandstone layers, however, in many wells these shale partings do not exist and the layer boundaries become subjective.

The following is a brief explanation of each of these layers (Table 1-1):

Layer D: It is made of laterally overlapping sandstone bodies of tidal inlet fills interbedded with thin shale partings with limited lateral extent.

Layer F: Predominantly, it consists of shaly sandstone with increase shaliness toward the top. The layer is not persistent and in areas it was difficult to pick from the underlying layer (G).

Layer G: Good sandstone development was noted within this layer with thin shale partings in certain areas. It has much in common with the underlying layer H. porosity ranges are (11.6-22.8%).

Layer H: Very much similar to the layer above it with multiple laterally overlapping channel fills. Porosity is comparable to layer G. Llayer H is separated from the underlying layer J by thin shale which is not believed to be an impediment to fluid flow.

Layer J: It is made of coarsening upward sandstone bodies overlapping each other laterally, the lower part of the layer shows a distinct increase in shaliness and contact, in a number of areas of the field, with the underlying layer K, is gradational.

Layer L: It is dominantly an accumulation of laterally overlapping sandstone bodies of tidal inlet fills interbedded with thin shale partings. Shale development is erratic and in certain areas it resulted in local permeability barriers inhibiting communication within the sublayers.

Layer M: Relatively, it is a thin sandstone accumulation with a noted increase in shaliness, especially toward the base.

Layer N: It is the bottom most layer of the Upper Sandstone Member and with less developed sandstone than in the layers above it. It grades downwards into the Middle Shale Member. However, porosity ranges are 9.5 - 23.2%. There are three non-reservoir layers C, E, K, made of shale, silt and thin sandstone, are laterally pervasive covering the area of the oil pool and will impede vertical migration of reservoir of fluids (Fadel and Ansari, 1992).

Z/2 Marker (Top)	Units	Zone	Layers	Notes		
	AB		AB			
	С		С	non-reservoir		
		DJ1	D			
Ummon			E	non-reservoir		
Sandstone	DJ		F			
Member			DI2	G		
				0,12	Н	
						J
	K		K	non-reservoir		
		LN1	L			
	LN		Μ			
Z/4 Marker		LN2	N			
Bottom						

Table 1-1: The main units, zones and layers of the Zubair Reservoir.

1-5-3 Tectonic framework and basin evolution:

The area of study lies in the Mesopotamian Zone of the Unstable shelf. (Buday and Jassim, 1984) divided the Mesopotamian Zone into three subzone, Zubair, Euphrates and Tigress subzone (Figure 1-4). Zubair Subzone is characterized by many of elongated folds of N-S to NW-SE direction representing by the giant oilfields in Basra province. These folds, which finally enclosure in Late Cretaceous, characterized by linear and narrow anticlines with a little appearance to faulted basement rock (Buday and Jassim, 1984).

The Mesopotamian Basin is of NW-trending foredeep to the Zagros fold and thrust belt that formed in response to the continental collision of the Arabian and Eurasian plates. Collision started during the Late Cretaceous and increased in intensity during the Paleogene/Neogene (Beydoun et al., 1992). The Mesopotamian Basin is relatively unaffected. Deformation increases in intensity from west to east towards the Zagros Mountains. The fields in the Basra occur along N-S trending folds in the southern part of the basin. N-S striking, basement-cored anticlines in this part of the basin began forming in the Paleozoic, with continued but with more limited growth throughout the Mesozoic and Early Cenozoic (Al-Ameri, 2011).

The Zagros foothills and foreland basin hold the greatest concentration of oil in the world. The structures in the foreland have a north /south trend, at a high angle to the Zagros. These are old structures that date back to at least the Late Cretaceous. Because they are largely buried with little to no surface expression, these structures were found many years after the first oil in the Middle East as seismic data was required for their discovery (Jassim and Goff, 2006).


Figure 1-4: The tectonical map of Iraq, illustrating the tectonic divisions (Jassim and Goff, 2006).

The Rumaila oil field is one of these old structures with both sandstone and carbonate reservoirs, looked at as a single structure. Beydon (1991) referred that the petroleum structures created due to one or more than process, as follows:

- 1- The relative movement of the deep basement faults caused some closures due to the different compressibility of the positive structures that overlaying the basement.
- 2- The flowage of Harmoz series salts (salt domes) upwards as a result of differential sedimentary loading.
- 3- The presence of north-north eastern anticline due to the Arabian-Iranian plates conduction during (Late Cretaceous) and (Late Tertiary), while the Alpine Orogeny of Zagros- Tourous that caused differentiation in Hormuz salts distribution and the upper evaporitic deposits.
- 4- The superposition that formed between Zagros series (NE-SE) and Tourous series (E-W) that affected the Arabian anticline is of (N-S) direction (AL-Humood, 2002).

Generally, the region is characterized by the existence of structures in the form of folds of different sizes, such as Rumaila, Zubair, Nahr Umar, Allhis, and Rashi, with a general trend of north - south.

There geological and geophysical evidence confirms the existence of tectonic saline movements. Jabal Sanam and Nahr Umr are attributed to the movement of huge salt blocks and evaporites of the Cambrian Era (Hormuz Formation) and have similar domes in Iran, Saudi Arabia and the Arabian Gulf. Buday (1980) suggested the presence of numerous fault zones and major joints within the sediments of the Mesozoic with directions NNW - SSE and (NE-SW). These structures confirm that the main folding movement occurred during the Cretaceous period, and that these movements have nothing to do with the movement of the Zagros. For this, the Zubair Formation might be affected by the emergence of structures in the sedimentary basin.

<u>Chapter Two</u>

Materials and

Methods

2-1 Preface

This chapter deals with material and methods that have been used in this study. It includes field and laboratory works. Field work plan was drawn for sampling the Zubair Formation at North Rumaila Field as well as the Main Outfall Drain (MOD) which is an artificial river. The Zubair Formation was the sampling target to collect oilfield water and core samples as well, whereas the MOD was selected to be as alternative source for injection water for the secondary oil production. Water samples are subjected to hydrochemical analyses and compatible tests, whilst the core samples subjected to petrophysics analyses, XRD and SEM. Clay minerals are identified to follow up and study the formation damage in the Zubair reservoir. The detail field and laboratory works are described below.

2-2 Field Work

Eight wells in North Rumaila Field are selected. These wells are R-172, R-17, R-112, R-184, R-131, R-186, R-136, and R-120. The minimum and maximum depths are 3045 and 3253m respectively (Table 2-1). Oilfield water samples along with the core samples are collected. Oilfield water samples are collected from these wells which penetrated the Zubair Formation (Cretaceous reservoir), which represents the main reservoir in the field. It is composed of clastic rocks. Plastic bottles are then tightly closed after collecting water. All samples are transferred to the laboratory for analyzing. Many parameters are on-site measured such as pH, electrical conductivity (EC) and total dissolved solids (TDS). For the purpose of obtaining accurate results and avoid the error, a specific device is calibrated and used in the measurements of these parameters.

Sixteen core samples are collected from the same wells at different depths belonging to the Cretaceous. These core samples have been stored in the Nahr-Umr store which represents one of the South Oil Company site stores. Some of these core samples are displayed in plate 2-1. Two surface water samples from Main Outfall Drain (MOD) are collected (Figure 2-1). The first sample is collected from site 200 m away from regulater gate, while the second is collected from area under the Zubair Bridge. Plastic bottles are used for collecting these samples.

Table 2-1: Number and depth of core samples (RC), oilfield water samples(FW) of Zubair Formation (North Rumaila Field) and water samples (MW) of
Main outfall drain (MOD).

Well No.	Depths (m)	Number and type of samples			
		Oilfield Water (FW)	Core Sample (RC)		
R-186	3210	1	1		
	3253	-	1		
R-184	3199	1	1		
	3185	-	1		
R-131	3208	1	1		
	3085	1	1		
R-172	3050	-	1		
K-172	3045	-	1		
R-136	3178	-	1		
R-120	3192	-	1		
	3157	1	1		
D 17	3230	-	1		
N-1 /	3120	-	1		
	3125	-	1		
D 110	3179	1	1		
R-112	3155	-	1		
Water		Main Outfall Drain (M	(OD)		
Samples					
MW1	surface	1	-		
MW2	surface	1	-		
]	Total	(6) \overline{FW} + (2) MOD	16		



Plate 2-1: Core Sample (RC-17, Depth = 3157m), (RC-184, Depth = 3199m) and (RC-131, Depth = 3208m) collected from the Zubair Formation in North Rumaila Field.



Figure 2-1: The location of sampling (oilfield water of North Rumaila field and surface water of MOD)

2-3 Laboratory work

Laboratory work includes analysis of oilfield water, surface water and core samples. Water samples are prepared before analyses and then subjected to physico-chemical analyses and chemical compatibility which are done in the Central Laboratories of South Oil Company in Iraq, while the bacterial tests done in the Bacteriological laboratory of the Ministry of Science and Technology. Core samples are also subjected to XRD in the Iraq Geological Survey laboratory. Scanning electron microscope (SEM), Petrophysical analysis and core flooding are prepared at the Central Laboratories of South Oil Company. Polarized microscope tests of some cores are prepared at the workshop of the Department of Geology.

2-3-1 Chemical Analysis

Cations (Na⁺, K⁺, Mg²⁺ and Ca²⁺) and anions (Cl⁻, HCO₃⁻, SO₄²⁻ and CO_3^{2-}) in the oilfield water along with water samples are determined by many methods (Table 2-2) as follows:

Table 2-2: The methods used in water samples analyzing.

Element	Analysis method
Na^+, K^+	Flame photometer
$Ca^{2+}, Mg^{2+},$	Gravimetric, Titration with 0.2 EDTA – Na salt using
SO_4^-	Erich chrome
$Cl^{-}, HCO_{3}^{-},$	Titration with $0.2 \text{ N H}_2 \text{SO}_4$ and phenoephthaline
CO_{3}^{2}	indicator

2-3-2 Physical Properties

These properties are measured on-site directly to prevent changes over time. These measurements include the hydrogen number (pH), total dissolved solid (TDS) and electrical conductivity (EC).

2-3-2-1 Hydrogen Number (pH)

It is defined as the negative common logarithm of the concentration of hydrogen ions $[H^+]$ in moles/liter as PH = $-\log_{10}$ $[H^+]$. It is a measure of alkaline and acidic, and influenced by ions concentrations carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻) (Hem, 1985). It measured by device pH meter type (Model pH A943TTT2).

2-3-2-2 Total Dissolved Solids (TDS)

This includes anything present in water other than the pure water molecule (H_2O) and suspended solids, Basically, the total dissolved solids is the sum of the cations and anions in the water. TDS is sometimes inferred from electrical conductivity and is reported in units of parts per million or mg/l (Davis and Dewiest, 1966). Quality and quantity of dissolved salts in water is varies depending on the water source, physical and chemical conditions of formation, digenesis processes and various weathering processes (Tood, 1980). Two methods are used to determine the TDS. These are evaporation method and chlorinity.

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2-3-2-3 Electrical conductivity (EC)

It means the ability of 1 cm³ of water to pass electrical current at 25 °C, it is generally use a measure of purity of water or the concentration of ionized chemicals in water (Todd, 2005). The variation of conductivity provides important information for assessing the water quality, and is directly proportional to the amount of the TDS. The EC of rain water ranges between 2 and 100 μ s/cm but for ground water is between 50 and 50000 μ s/cm and for sea water it reaches 50000 μ s/cm (Hem, 1985).

2-3-3 Bacterial tests

Two water samples are collected from Main Outfall Drain (MOD) in sterilized of 1L bottles. The samples are sent to the Bacteriological laboratory of the Ministry of Science and Technology. Volume 1-10 ml from each water sample is taken for each test. Sample is transferred into Petri dish, or gas positive tube according to the type isolation. A set of plates of bacteria are incubated for more than day at $37C^{\circ}$ (Benson, 2001 and Tortora et al., 2000). The suitable Agar with sterilized conditions and special temperature is poured (Table 2-3).

Microorganism types	Type of Agar	Incubation (hours)	T°C
Escherichia coli (E. coli)	MacConky Broth	24	44
Coliform	Azide dextrose broth	72	44
F. Streptococus	Azide dextrose broth	72	37

 Table 2-3: Methods of test samples for Microbial Identification

2-3-4 Accuracy of water samples

Many types of errors may be resulted from several reasons, mainly from devices itself and unstable laboratory conditions in addition to the personal errors coming from person analyst. Consequently, and to avoid such these errors the method of (Hem, 1989) and (Mazor, 1990) are used. The analytical accuracy of the water samples is indicated from the results of reaction error test uncertainty (U) or relative difference (R.D) by calculating absolute difference between total cations and anions concentration on the total of concentrations in epm unit as percentage according to the following equation.

R.D % =
$$\frac{r \Sigma Cations - r \Sigma Anions}{r \Sigma Cations + r \Sigma Anions} \times 100$$

A%=100-R.D

Where R.D% relative difference

A is accuracy or certainty

When (R.D < 5%) the results could be accepted for interpretation, but if 5% < R.D < 10% then the results are accepted with risk. If the value (R.D% >10%) the results could not be depended upon (Hem, 1989). In this study, R.D% value range between (0.25-2.71 %) for oilfield water and between (0.25 - ⁻³.44 %) for MOD (Table 2-4). Accordingly, the results of the analyses appear to be acceptable and can be depended in the hydrochemical interpretation.

Oilfield water samples				W	ater samp	les (M	OD)
Sample NO.	R.D%	A%	Decision	Sample NO.	R.D%	A%	Notes
FW-186	2.44	97	Accepted	MW1	0.25	99	Accepted
FW-184	1.85	98	Accepted	MW2	3.44	97	Accepted
FW-131	0.24	99	Accepted				
FW-172	2.71	97	Accepted				
FW-17	2.37	97	Accepted				
FW-112	2.13	97	Accepted				

 Table 2-4: Analytical accuracy of the results of oilfield water and water samples.

2-3-5 Polarized microscope

The core samples are collected from selected depths of the Zubair Formation. All cores are well dried under sun. Thereafter, two thin sections for each core are prepared at the workshop of the Department of Geology. Mineralogical identification, texture and micro images are done using a polarized microscope at the laboratory of Geochemistry, Department of Geology, University of Baghdad

2-3-6 X-Ray Diffraction (XRD)

A total of three samples are selected from wells no. RC-131, RC-184 and RC-17, for the XRD test in order to identify the mineralogical composition

(Table 2-5) and the type of clay minerals in rocks. Rock components are examined by bulk sample method, whereas clay minerals are studied according to the procedure of (Thorez, 1976) and (Grim, 1968). The procedure for the different treatments (Normal, Heating and Ethyl Glycolation) to diagnose the mineral clay type existing in these samples are used as follows:

- 1- grinding rock samples is made by grinding machine to get powder , distilled water is added to the powder and then some drops of H_2O_2 (30%) to discard organic matter from clay minerals (Folk, 1974).
- 2- One gram of the scattered matter Na-hexametaphosphate id added to make clay grains scatter in the solution. The solution is agitated and then 2 ml of the upper part of the suspension are transferred to the another beaker. This method is repeated many times and then the suspension is left to become denser.
- 3- The suspended dense clay are dropped by pipette on the glass slides with three slides for each sample and let to dry at room temperature.
- 4- Samples are studied by X-Ray diffraction technique as follows:

A-Normal (untreated) samples are scanned at range of $2\Theta = 5^{\circ}-50^{\circ}$.

B-Ethyl Glycolated samples are scanned at range of $2\Theta = 5^{\circ} - 20^{\circ}$.

C-Heated samples (at 550 C for 2h) are scanned at range of $2\Theta = 5^{\circ}-20^{\circ}$.

5- Bulk sample method without washing, the powder of the sample is put in the metallic pit and then pressed by glass slide to orient it, and then the samples are examined at range of $2\Theta = 10^{\circ} - 40^{\circ}$. X-Ray diffraction is performed in the Iraq Geological Survey laboratories. The analyses conditions are listed in (Table 2-6).

Well No.	Core samples						
	Petrophysical tests	XRD tests	SEM tests				
RC-186	2	-	-				
RC-184	2	1	1				
RC-136	1	-	-				
RC-131	1	1	-				
RC-172	3		-				
RC-17	4	1	1				
RC-120	1	-	-				
RC-112	2	-	_				
Sum	16	3	2				

Table 2-5: Techniques used in analyzing the core samples.

 Table 2-6:
 The conditions of XRD analyses.

X-Ray	Slit	Measure
Target: Cu K-Alpha Wave: 1.54060 Voltage: 40 KV Current: 30 Ma	Divergence: 1.0 deg Scatter: 1.0 deg Receiving: 0.15 mm	Axis: Theta- 2 Theta Scan mode: Continuous Scan Range: 5.0- 50.0 deg Step: 0.05 deg Speed: 5.0 deg/min

2-3-7 Scanning Electron Microscope (SEM)

Core samples are examined by SEM for the identification of the clay minerals and their presence in the pore spaces of the sandstone. Many images are taken under different zoom to display the distribution patterns of clay minerals in the core sample.

2-3-8 Petrophysical analysis

Sixteen core samples (plugs) each 3 inch long and of diameter 1.50 inch are cut into two pieces for each well. The cores are cleaned from Hydrocarbon by a sox let extraction using a toluene as organic solvent. To ensure good cleaning, a Hexane material as another organic solvent is used then the core samples are dried in an oven at 60° C for 6h.

Water sensitivity of cores was determined by first measuring permeability to air, concentrated artificial brine, and finally to successively more dilute brines, then eventually ending with fresh water. In some cases switching directly from concentrated brine to fresh water was used as a test for water sensitivity (Gray and Rex, 1966). (Jones, 1964) maintained that this procedure is a more severe test for testing water sensitivity.

Susceptibility to induced water sensitivity is determined by comparing permeability of cores to fresh water before and after saturation with monovalent cation brine. Usually a brine of NaC1 which is used for initial saturation and flooding tests. Petrophysical analyses included measuring the porosity, air permeability and liquid permeability as following:

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2-3-8-1 Porosity

Porosity is measured by using Helium Porsometer according to the following formula:

$$Q = \frac{VP}{VP + VG} \times 100$$

Where:

Q = Porosity VP = Vacuum Pore (cm^3) VG = Grains Size (cm^3)

2-3-8-2 Air Permeability

Permeability is measured by using Micropermeameter and Darcy law enforcement in accordance with the following equation:

$$\mathbf{Ka} = \frac{\mathbf{CLQ}}{\mathbf{A}}$$

Where:

Ka = Air Permeability (Mille Darcy)

A = Sample section area (cm^2)

C = The device represents conversion Factor

L = The sample length (cm)

Q = Flow rate (cm³/s)

2-3-8-3 Liquid Permeability

It means the saturation of the core sample (Plugs) in brine concentration 20% of NaCl, according to the following steps:

- 1- Rock sample is placed in a cylindrical a bowl airtightsize 1000 ml, filled with a solution of NaCl and usually for 24 h.
- 2- Pull the amount of air from brine and rock samples by vacuum process.

3- Permeability of liquid is measured by core holder Hassler Permeameter (Figure 2-2). It is calculated in accordance with the Law of Darcy:

$$KL = \frac{245 V \eta L}{Apt}$$

Where:

KL = permeability of the liquid (Milli Darcy)

 $\dot{\eta}$ = the viscosity of the liquid (cp).

V= Sample size (Ml).

L = Sample length (cm).

A = Sample section space (cm^2) .

P= Pressure on the sample (PSI).

T= Fluid flow time (Min).



Figure 2-2: Chart shows the core holder Hassler Permeameter.

2-3-9 Formation Damage ratio

The indicators of formation damage are includes permeability impairment, skin damage and decrease of well performance. Formation damage which resulted by clays can be classified as that caused by swelling clays or non-swelling clays (Mohan et al, 1993). Smectite and mixed layer clays swell with changing ionic conditions, then eventually disperse and migrate with the flowing fluid. Swelling alone reduces the effective area for flow and causes reduction in permeability. Kaolinites and illites are non-swelling clays that tend to detach from the rock surface and migrate when the colloidal conditions are conducive for release. The migrating particles can get trapped in pore throats, thus causing a reduction in permeability. However, damage ratio is calculated according to the following equation:

$$\mathbf{Dr} = \mathbf{100} - \frac{\mathrm{KL}_{\mathrm{f}} \times \mathbf{100}}{\mathrm{KL}_{\mathrm{I}}}$$

Where the:-

Dr = Damage ratio.

KL_I = Initial permeability.

 KL_f = Final permeability.

A saline solution of sodium chloride is prepared in the laboratory and in different concentrations and variable pH (strong acid 3- strong alkaline, 11) to inject into plug samples for the purpose of calculating the damage in permeability as a result of these solutions injection. The pH value is controlled by adding the HCl and NaOH.

2-3-10 Chemical Compatibility

An oil production is needs to adding water through well. This added water must be of specific characteristics. For this reason, chemical compatibility should be tested to know a water type suitable for adding to the oilfield or no. This study selected the Main Outfall Drain (MOD) as a source for supplying surface water, and therefore the samples of these waters are subjected to the chemical compatibility. Chemical compatibility is conducted between the Main Outfall Drain (MOD) water and oilfield water of the North Rumaila field in addition to sea water. Chemical compatibility is computed by two methods for knowing the type and amount of the scale (salty crust) which is formed during the mixing between two different solutions (water added during oil production). These methods are explained below:

2-3-10-1 Laboratory model for chemical compatibility

This method is conducted by set of experiments in the laboratories of the South Oil Company (SOC) using the procedure according of the American Petroleum Institute (API). This procedure includes preparing two groups of water (the oilfield water from the Zubair Formation and the MOD water) to be mixed together. One liter of each is used in every test. The mixing percentages are (10-90%), (20-80%), (30-70%), (40-60%), (50-50%), (60-40%), (70-30%), (80-20%), (90-10%). A small sample from these solutions are placed in test tubes 100 ml on a water bath at 60 ° C for 21 days. The process is periodically monitored to see cases in which made up precipitation. The results are recorded after 24h, a week later, after two weeks and three weeks later.

2-3-10-2 Mathematical chemical compatibility model

PHREEQC software program, version 2 is a computer program for simulating chemical reactions and transport processes in natural or polluted water. The program is based on equilibrium chemistry of aqueous solutions interacting with minerals, gases, solid solutions, exchangers, and sorption surfaces, but also includes the capability to model kinetic reactions with rate equations that are completely user-specified in the form of basic statements. PHREEQC was capable of simulating a variety of geochemical reactions for a system including:

- Mixing of waters,
- Addition of net irreversible reactions to solution,

• Dissolving and precipitating phases to achieve equilibrium with the aqueous phase, and effects of changing temperature.

The purpose of this program is to identify the type of scale (salt crust) formed during mixing two types of water.

2-4 Office work

As usual, the office work is complementary to all the work to reach the desired end. It includes reviewing the references, previous studies, reports and collecting the geological information on the study area. Several programs are used such as PHREEQC version 2, AquaSalchem-2012, and Rock Ware Aq.QA version 1.1.1, 2008 to draw Schoeller and Stiff diagrams to assess the water type.

Chapter Three

Hydrogeochemistry

3-1Preface

Oilfield water was defined by (Collins, 1975) as natural water present in pores and holes of the reservoir rocks before subsurface injection process. Therefore, this water is called sometime a (formation water) or (reservoir water). This chapter deals with the physical and chemical parameters: pH, TDS, EC, specific gravity, major cations and anions and set of laboratory experiments related to chemical compatibility to determine the MOD compatible water with the oilfield water of Zubair reservoir and to find the saturation index in compatible water. Hydrochemistry is useful for understanding the nature of reservoir and characteristics of oils, where the chemical composition of these waters demonstrates several factors, including the origin of this water (Al-Yasiri, 2000). The water quality is described using hydrochemical formula, Stiff diagram and Scholler Classification. Chemical compatibility between oilfield water of Zubair Formation and MOD were done using laboratory methods and mathematical model using the PHREEQC software program. For mathematical model also the sea water is studied as a compatible water. The Main Outfall Drain (MOD) which is a proposed source of water for injection. The mixing ratios of MOD to the oilfield water [(10-90%), (20-80%), (30-70%), (40-60%), (50-50%), (60-40%), (70-30%), (80-20%) and (90-10%)] are tested. Most common oilfield scales represented by barium sulfate, calcium carbonate, strontium sulfate and calcium sulfate in terms of saturation index are carefully studied. Each scale compound is determined. In each test, the amount of soluble and precipitate is determined to find the saturation index.

3-2 Physical Properties of oilfield water

3-2-1 Hydrogen Number (pH)

The pH is a measure of the hydrogen ion concentration in water. The pH of pure water at 25° C is 7.0, which means that there is 10^7 mole per liter of H⁺ in solution. Other constituents are soluble by water. The pH probably will change because the chemical equilibrium shifts as a new ions combine with H⁺ or OH⁻(Collins, 1975). The pH of oilfield waters is usually controlled by the CO₂ and HCO₃ system and often acidic because they contain H₂CO₃ and H₂S (Morad, 1998). (Komatina, 2004) Classified water according to the pH value (Table 3-1).

Value of pH	Water Quality
<3.5	Strongly acid
3.5-<5.5	Moderate acidic
5.5-<6.8	Weakly acidic
6.8-<7.2	Neutral
7.2-<8.5	Weakly alkaline
8.5 and more	Alkaline

Table 3-1: Classification of water quality depending on the value of the pH,(after Komatina, 2004).

(Hem, 1985) mentioned that the amount of pH in the groundwater ranged between 6.5 and 8.5 with the possibility of having the values of less than 6.5. pH have an important role in the solution because it controls the solubility of many salts. In the Rumaila oilfield (Zubair Formation) the pH values seem homogenize and ranged between 5.2 to 5.77 (Table 3-2). When discuss the results with classification of (Komatina, 2004), the oilfield water in the Rumaila field appears a weakly acidic. Thus, it has a positive role on the reservoir. In general, alkaline water have a negatively role on the reservoir, where they lead to deposition components of the carbonate and thus lead to reduce the porosity and permeability.

Table 3-2: Physical properties of oilfield water in North Rumaila field,

		Oilfield Water of North Rumaila Field							
Parameter	ter FW-186 FW-184 FW-131 FW-172 FW-17								
PH	5.2	5.10	5.77	5.70	5.5	5.45			
EC (µs/cm)	346274	340362	352275	347840	346633	372762			
TDS (ppm)	207350	210100	213500	217400	215300	230100			
Sp.Gr (15°C)	1.415	1.1410	1.1407	1.400	1.1405	1.1315			

Sp.Gr $(15^{\circ}C)$ = specific gravity at $15^{\circ}C$.

3-2-2 Total Dissolved Solids (TDS)

The TDS includes all the solid material in solution which is ionized or which is not ionized, but do not include suspended material, colloids, or gases (Davis and Dewiest, 1966). Dissolved salts in the water are an indicator of the amount of salinity and water quality.

(Collins, 1975) concluded through his study of the oilfield water in the fields (Kansa) in the United States, that the Na⁺ and Ca²⁺ concentrations increase with increase the salinity. A TDS value of Rumaila ranged from 207,350 to 230,100 ppm (Table 3-2). The TDS a value for Zubair reservoir is approximates the TDS value of fields southeastern New Mexico (SENM), which is 270,000 ppm (LeBas et al, 2013). On depending on (TDS), water in this field has classified as highly saline water (Brine) according to the classification (Hem, 1970) (Table 3-3). Because the water of oilfield has high salinity, and chloride is dominant. It is possible to calculate the salinity from

the chloride content (Cl⁻) or the so-called "Chlorinity", according to the equation placed by (Kudsen, 1901) in (Abbas, 2002) (Table 3-4):

S%= 300+ 1.805 Cl⁻ (ppm)

The high salinity resulting from the exchange of sodium ions between the oil and oilfield water, as well as between them and the reservoir rock (Al-Atabi, 2009). If water contains a small amount of TDS it is considered as mixed with surface water, or if it contains a high concentration of TDS it is considered either ancient water or connate water, due to friction and interaction with reservoir rocks through the geological time.

Table 3-3: Classification of water based on TDS (Hem, 1970).

Water class	Concentration of TDS in ppm
Fresh	< 1000
Moderately Saline	1000-10000
V. Saline	10000-35000
Brine	Over 35000

Table 3-4: Salinity values calculated (laboratory + Chlorinity) FormationZubair wells in the North Rumaila field.

Well No.	TDS (ppm) calculated laboratory	TDS (ppm) calculated as a chlorinity	$\Delta \mathbf{S}^{*}$
FW-186	207350	217261	9911
FW-184	210100	217712	7612
FW-131	213500	234182	20682
FW-172	217400	217441	41
FW-17	215300	226827	11527
FW-112	230100	227820	2279

(*): decimals have been omitted.

3-2-3 Electrical Conductivity

Electrical conductivity or conductance is the ability of a substance to conduct an electric current. It is the inverse of water resistivity. Under the International System of Units (SI), it has been proposed that the unit of conductivity by renamed the "Siemens." The microsiemens (μS) is numerically the same as the micromho (Hem, 1985). Distilled water does not contain dissolved salts and, as a result, it does not conduct electricity and has an electrical conductivity of zero. Conductivity probes are of value in exploring wells to determine differences in water quality with depth. The response of the conductance value to temperature changes is somewhat different for different salts and different concentrations, but in diluted solutions for most ions increase of 1°C increases conductance by about 2% (Hem, 1985). Electrical conductivity closely related to TDS because it is a function of the concentrations of all ionic solutes. It is ranged from a few tens of μ S for low-TDS groundwater up to thousands of μ S for brines. The average EC value of oilfield water in the North Rumaila field is about (200,000) µS. The correlations between (EC) and (TDS) for water in North Rumaila Field as shown in Figure 3-1.



Figure 3-1: Variation between TDS and EC in oilfield water in North Rumaila field.

3-2-4 Specific Gravity

The values of specific gravity in the waters of the Rumaila field are ranges from 1.1315 to 1.1407 and average 1.22811 (Table 3-2). When comparing these values of oilfield water in north Rumaila field with Iraq and global oil fields, it founds that the Zubair reservoir in North Rumaila Field has a greater specific gravity; this may be due high salinity (Table 3-5).

Table 3-5: Compared the Specific gravity values to formations global oil fields.

Physical properties	Zubair	Mishrif	Yamama	Stephens	Wesson
	Reservoir	Reservoir	Reservoir	Reservoir	Reservoir
Sp. Gravity	1.22811	1.1502*	1.1387*	1.1350**	1.1490**

*Al-Khafaji (2003), ** Collins (1975)

3-3 Chemical components of oilfield water in Zubair Formation

They include major cations (Na⁺, K⁺, Ca²⁺ and Mg²⁺) and major anions (Cl⁻, $SO_4^{2^-}$, $CO_3^{2^-}$ and HCO_3^{-}).

3-3-1 Major Cations

3-3-1-1 Sodium (Na⁺)

Sodium is one of the most abundant ions in natural waters. Actual concentrations range from about 0.2 mg/L in some rain and snow to more than 100000 mg/L in brine (Goldschmidt, 1958). It concentration in seawater is about 11000 ppm, and more than 140000 ppm in the waters of several Formations to oil fields in the world (Table 3-6). Most oilfield waters are contains more sodium than any other cation and it was believeds to be of marine origin (Collins, 1975). The Halite, feldspar, and generally, the clay minerals are also a source of Na⁺ ion (Todd, 1980).

The table (3-6) of the oilfield water of Zubair Reservoir in the North Rumaila field, the concentration of sodium ranges between (57550-60500) ppm with average 58683 ppm. These values are considered high in comparison with sea water. The sodium content is six times its content in seawater. This refers to enrichment sodium indicating a very ancient water reserved a closed system (Collins, 1975). A direct proportion between sodium and TDS are detected (Figure 3-2).

Sodium retained by adsorption on mineral surfaces, especially by minerals having high cation- exchange capacities such as clays. However, the interaction between surface sites and sodium and with monovalent ions generally, is much weaker than the interactions with divalent ions. Cation-

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exchange processes in freshwater systems tend to extract divalent ions from solution and to replace them with monovalent ions (Hem, 1985).

Table 3-6: Chemical components in the Zubair reservoir water (Rumailafield) and compared with seawater and some of the world's oil fields.

Cations and	S. no.	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	HCO ₃	CO_3^{2-}	SO ₄ ²⁻	
anions			(ppm)							
	FW-186	15990	3500	58250	3350	120200	140	20	390	
	FW-184	13600	3300	58300	1900	120450	110	Nil	390	
North	FW-131	14150	3700	60200	2150	129575	153	Nil	470	
Rumalia Field	FW-172	14901	3400	57550	2700	120300	150	Nil	530	
Ticiu	FW-17	15500	3200	60500	2100	125500	100	Nil	450	
	FW-112	13900	4150	60400	2200	126050	170	15	270	
Range		13600- 15900	3200- 4150	57550- 60500	1900- 3350	120200- 129575	100- 170	15 - 20	270 - 530	
Average		14673	3542	58683	2400	123679	137	17.5	416	
*Sea water		400	1272	10556	380	18980	140	-	2649	
*Oklahoma		9100	2432	54395	-	106216	450	-	768	
*Texas		21680	2638	42803	166	111860	330	-	130	
*Los Anglos		20000	523	48737	1040	80336	-	-	-	
**Mishrif Fiel	ld	11020	2632	73572	1610	141953	233	-	501	
**Nahar Ben Ui	ner Field	13913	2423	69786	1790	140229	248	-	512	
**Yamama Fie	eld	14259	2169	59583	640	123591	446	-	825	
Collins, 1975		48800	2000	74500	650	188900	0	-	432	

*Al-Atabi (2009)

**Khafaji (2003)

Chapter Three



Figure 3-2: Relationship between each of the Na and TDS.

3-3-1-2 Calcium (Ca²⁺)

Calcium is considered one of the most important cation, where its concentration in natural waters ranges between 0.1 and 100 ppm, while in drinking water ranges from 75 to 200 ppm (Davis and Dewiest, 1966). Sea water contains 400 mg/l and subsurface brines often contain 2000-3000 mg/l, with some as high as 30000 mg/l (Collins, 1975). Precipitation of calcium carbonate in the sea is the prime mode of the origin of limestone, the solubility of calcium carbonate in sea water increases with salinity and increasing partial pressure of carbon dioxide, but it decreases with increasing pH, calcium content, and temperature (Collins, 1975). Calcium dissolves as bicarbonate as a result of chemical weathering of calcium-bearing minerals. Slight changes in the pH of waters containing calcium bicarbonate will cause

calcium carbonate to precipitate, and calcium carbonate is one of the most common deposits found in plugged oilfield lines, equipment, and reservoirs (Clemmit et al, 1985). The solubility of calcium sulfate decreases with increasing temperature. Calcium concentration reach in some oil fields of the world to more than 20000 ppm (Table 3-6). The concentration of calcium in the oilfield of Zubair reservoir is the third largest concentrations after elements of chloride and sodium, and its content ranged between 13600-15900 ppm with an average 14673 ppm. This element is have great significance in studying the oilfield water, because when chemical conditions of the reservoir (pH -Temperture) changes, the calcium will contribute to be precipitated causing a negative impact on the the petrophysical properties of the reservoir (Al-Yasiri, 2000). It combines with carbonate and sulfate ions, and fill in the spaces in the rocks reducing porosity and permeability. Therefore it will affect the movement of fluids such as oil and gas. These high values of calcium confirm that carbonate are dissolved in the Upper Sandstone Member of Zubair formation. The lack of carbonate cement currently in the samples studied also confirm that. It is worth mentioning that the current calcium concentration is the final output of each diagenesis process, and certainly for a change in the chemical and physical conditions (Temperature and pH).

In comparison the concentration of calcium with the fields of the world's which vary between 9100 to 20000 (Table 3-6), it appears to lie within the actual limits. But when it is compared with seawater, a clear increase of (twenty times) is observe so that it is a very ancient water. Generally, CO_2 plays an important role in reducing the pH, which accelerates the melting of mineral carbonats, thereby it increases the concentration of calcium as bicarbonate according to the following equation:

$CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2$

3-3-1-3 Magnesium (Mg²⁺)

Magnesium is dissolved during chemical weathering. Ferromagnesian minerals in igneous rocks and magnesium carbonate in carbonate rocks are generally considered to be the principal sources of magnesium in natural waters. Apparently the Mg and the Cl are most likely to remain in true ionic solution; however, several other variables occur during diagenesis which lead to depletion of magnesium in waters. Shales, sandstones, and limestone contain 15000, 7000 and 47000 ppm of magnesium, respectively. Subsurface brines contain from less than 100 mg/l to more than 30000 mg/l, however, many subsurface brines are depleted in magnesium if compared to a marine evaporite sequence (Mason, 1966). Concentration of Mg in oilfield water ranges from (3200-4150) ppm, with average 4150 ppm (Table 3-6). The average Mg concentration in seawater is 1300 ppm, while in the world's ranges between 100 and 30000 ppm. This means that it is within the normal limits of oilfield water (Table 3-6). Depletion of Mg in some waters probably is a result of the replacement reaction to form dolomite, CaMg (CO₃). The large differences in the ionic radii of Ca (0.99 A) and Mg (0.65 A) are the reason for this diadochy. The concentration of Mg in the present study is less than Ca (13200) ppm. The reason is probably due to that the process of decomposition of dolomite is slow in comparison with limestone cement (Al-Yasiri, 2000).

3-3-1-4 Potassium (K⁺)

It is considered as alkaline ions similar of sodium ion in many of the chemical properties. The range of K in the oilfield water of the Rumaila field varies between 1900 and 3350 ppm (Table 3-6). The current concentration of potassium is less than sodium, and this is due to the low solubility of minerals

containing K-feldspar and resistant to weathering than minerals containing sodium, in addition to the adsorption of potassium ion by clay minerals which is more than sodium. It value is more than 2-4 times than seawater. It is appears to lie within the ordinary limits when compared with oil fields of the Iraq that contain 1610-1790 ppm.

3-3-2 Major Anions

3-3-2-1 Chloride (Cl⁻)

Chloride is present in all types water, whether surface or groundwater, and because of its abundance and rapidly of solubility in water. So it is present in all water in nature, even rivers contain a proportion of it (up to 3 mg/L) (Hem, 1970). Todd (1980) explained that the source of this ion is the result of dissolve mineral halite in salt and sediment layers. It is considers one of the major ions in seawater reaching to 18980 ppm (Table 3-6). Chloride is the dominant ion having highest concentration ranging from 120200-129575ppm, with average of 123679 ppm. This high percentage of chloride is due to the ease of solubility and difficulty in adsorption on clay minerals (Mason and Moor, 1982). Chloride is higher than the Na and Ca Such relationship occurs in marine water (Figure 3-3). During its incursion to the bottom through geological formations, amounts of Na is lost more than Cl because of ionic exchange on clay mineral surfaces compared to chloride (Figure 3-4).



Figure 3-3: The concentration of Cl, Ca and Na in the north Rumaila field of Zubair Formation.



Figure 3-4: The relationship between Na and Cl in Zubair Formation (North Rumaila Field).

3-3-2-2 Sulfates (SO₄²⁻)

Sulfates in oil reservoirs have gained greater importance, resulting in the possibility it linked with other ions such as strontium and barium composed of sulfate precipitate is insoluble such as Stronitianite and Barite, and lead to negative effects on the reservoir as it plugs pores and thus prevent the passage of the liquid (Al-Atabi, 2009). The presence of sulfates both help directly on the emergence and activity types of Sulfate Reducing Bacteria, which cause oxidation of oils and convert them to heavy crudes (Collins, 1975). The average of SO₄²⁻ in oilfield water is 416.7 ppm; it is varies between 270 and 530 ppm (Table 3-6).

When these values are compared with seawater (900 ppm), oilfield water of the world's (10 to 3000 ppm), it is found that the sulfate concentrations are within the actual limits. Sulfate may be reduced in response to the possibility of bio-influenced activity due to time between sampling and laboratory tests. (Collins, 1975) had directly mentioned to the decrease sulfate in comparison with chloride in oilfield water.

3-3-2-3 Bicarbonate (HCO₃⁻) and Carbonate (CO₃²⁻)

These anions are found in all types of water and their concentration ranges in natural waters between 50–400 ppm (Davis and Dewiest, 1966). The presence of these ions in the oilfield water acquires a special significance, they occur as scales and insoluble and have negative effects on the behavior of the reservoir, where it would impede the movement of fluids in the oil reservoirs. These ions are considered the source of alkalinity in water, which means that its total bicarbonate, carbonate and hydroxide ions. If the pH of the water is less than 4.5, the water possesses what is called "mineral-acid acidity". The acidity of petroleum-associated water may indicate the presence of various dissolved gases and salts. Most petroleum-associated waters contain little or no acidity. If water contains acid, it does not contain alkalines (Collins, 1975), as explained in chapter four. Bicarbonate combines with Ca and Mg. The source of bicarbonate in ground water is from the dissolution of carbonate rocks and from carbonate species with pH usually between 5 and 7 (Taylor, 1958). Their concentrations ranges in natural waters between 50-400 ppm (Davis and Dewiest, 1966). The average of bicarbonate in the current study is 137 ppm, ranging from 100 to 170 ppm. They seem to have ordinary values in comparison with the other oilfields (Table 3-6). The carbonate ion is found in two wells only are (R-112 and R-186), the concentrations were low an average of 15 ppm and it is absent in remnant wells. This may be attributed to the decomposition of HCO_3^{-} . Which later inverts into CO_2 dissolved in the water. Finally, and after reviewing the results of chemical components of the oilfield in North Rumaila Field, it can be inferred that the major cations are ordered as Na⁺> Ca²⁺> Mg²⁺> K⁺, whereas the major anions order is Cl⁻ $>SO4^{2}>HCO_{3}$) (Figure 3-5).



Figure 3-5: Bar shape displays the concentrations cations and anions in oilfield water in Zubair Formation (North Rumaila Field).
3-4 Water Quality

3-4-1 Hydrochemical Formula

Hydrochemical formula can be determined according to (Ivanov, 1968) by the formula below:

TDS gm/l Anion epm % decreasing order pH Cation epm % decreasing order

Cation and anion unit is in epm % decreasing in order, TDS in gm/l. Values (epm %) less than 15% are ignored from the formula. According to the chemical formula, it is simple to classify the oilfield water type. Tables 3-7 describes water type. The chemical formula is similar for all samples of the studied wells, therefore the oilfield water of Zubair Formation in North Rumaila field Water-type sodium - calcium – chloride.

3-4-2 Origin of the oilfield water

There is consensus among geologists is that oilfield water originated from prehistoric seas (Obire, 2003). Generally, the water is divided according to their origin into two main types (Ivanov et al., 1968) namely:

- 1- Infiltrating meteoric water.
- 2- Marine origin water.

The water of the oil fields differs widely from one to another in both content of chloride and total load of dissolved mineral matter. It is thoughts that these variations are caused by such physical factors as the geologic structure, the lenticularity of the beds, and the amount of rainfall. The hydrochemical ratio (rNa+rk)/rCl is used as a function for knowing the

origin of the water, where the water of marine origin, the value of the ratio is less than one, and if it is greater than one, the water is off meteoric origin (Table 3-8). The value of (rNa+rK/rCl) in all of the oilfield are listed in Table 3-8 indication a marine origin, because is less than one.

Table 3-7: Hydrochemical formula of the oilfield water in north Rumailafield, TDS (gm/l).

Sample No.	Chemical Formula	Water type
FW-186	$TDS_{(207.35)} \frac{Cl_{(99.6)} SO_{4(0.2)} HCO_{3(0.07)} CO_{3(0.02)}}{Na_{(67.1)} Ca_{(22.4)} Mg_{(8.2)} K_{(2.4)}} pH_{(5.2)}$	Na-Ca-Chloride
FW-184	$TDS_{(210.1)} \frac{Cl_{(99,7)} SO_{4(0,3)} HCO_{3(0.05)}}{Na_{(71.7)} Ca_{(19.3)} Mg_{(7.8)} K_{(1.4)}} pH_{(5.1)}$	Na-Ca-Chloride
FW-131	$TDS_{(213.5)} \frac{Cl_{(99.7)} SO_{4(0.3)} HCO_{3(0.05)}}{Na_{(71)} Ca_{(19.2)} Mg_{(8.36)} K_{(1.5)}} pH_{(5.77)}$	Na-Ca-Chloride
FW-172	$TDS_{(217.4)} \xrightarrow{Cl_{(99.7)} SO_{4(0.4)} HCO_{3(0.1)}}{Na_{(69.1)} Ca_{(20.7)} Mg_{(7.9)} K_{(1.9)}} pH_{(5.7)}$	Na-Ca-Chloride
FW-17	$TDS_{(215.3)} \xrightarrow{Cl_{(99.7)} SO_{4_{(0.3)}} HCO_{3_{(0.1)}}}{Na_{(70.6)} Ca_{(20.8)} Mg_{(7.2)} K_{(1.5)}} pH_{(5.5)}$	Na-Ca-Chloride
FW-112	$TDS_{(230.1)} \frac{Cl_{(99.8)} SO_{4(0.2)} HCO_{3(0.1)} CO_{3(0.01)}}{Na_{(70.5)} Ca_{(18.7)} Mg_{(9.3)} K_{(1.6)}} pH_{(5.45)}$	Na-Ca-Chloride

	Ra	inge		
Ratios	Minimum Maximum		Average	Origin
(rNa+rK)/rCl	0.73	0.76	0.75	Marine
rCa/rCl	0.19	0.24	0.21	Marine
rMg/rCl	0.08	0.10	0.08	Marine
rSO₄/rCl	0.0015	0.0032	0.0024	Marine
rNa – rCl/ rSO4	-164.37	-80.28	-112.31	Marine

Table 3-8: Hydrochemical ratios of the oilfield water in the Zubair Reservoir (North Rumaila Field).

As long as the ratios of the hydrochemical function (rNa+rK)/rCl, rCa/rCl, and rSO_4/rCl are less than 1, and the ratio of rNa - rCl / rSO4 is negative so it is of marine origin (Table 3-8).

3-4-3 Classification of oilfield water

3-4-3-1 Schoeller classification

(Schoeller, 1955) classified waters on the basis of their dissolved constituents and in the following order of importance: (1) chloride; (2) sulfate; (3) bicarbonate plus carbonate; (4) index of base exchange (IBE); and (5) relationships of anions to cations. The classification uses semi logarithmic graph to plot the concentrations of the anions and cations. The concentrations are plotted in meq/l. This type of diagrams allows making a visual comparison in different water in descending order (Shoeller, 1972).

Figure 3-6 illustrates the pattern of oilfield water on Schoeller diagram that appears to be fitted with the hydrochemical formula. The water type, water family and water group of oilfield water are listed in Table 3-9. Consequently, the oilfield water in Zubair reservoir (North Rumaila Field) is Chapter Three

classified according to Schoeller classification to be described of chloride group Na-Cl family.

Table 3-9: The oilfield water of Zubair reservoir classification based on
Schoeller classification.

Comula No	Ту			
Sample No	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 3-6: Schoeller diagram of the oilfield water to Zubair Formation.

3-4-3-2 Stiff diagram

Stiff diagram is used for presenting cations and anions data (epm) graphically. Cations are represented on the left side, whereas the anions on the right side of the diagram. The end of points is then connected by a straight lines to form a closed diagram, sometimes called a "butterfly" diagram (Collins, 1975). Generally, oilfield water of North Rumaila Field is with one hydrochemical system, due to the similarity of all studied wells in Stiff diagram (Figure 3-7).

3-5 Physical and chemical parameters of the MOD

Two surface water samples are collected from the main outfall drain (MOD) in southern Iraq (Table 3-10). It is tested for chemical compatibility by mixing it with oilfield water of Zubair Formation, to decide it is useful and can be used as water injection in oil production. For this reason, physical and chemical properties are studied.

Table 3-10: Locations of surface water samples collected from the MOD,
southern Iraq for chemical compatibility.

G 1	Water	Coord	ination	The nearest	Date of
sample no.	type	Latitude	Longitude	marker	analysis
MW1	surface	N 30° 24.391	E 47° 46.627	Near the regulator	27/11/2012
				gate	
MW2	surface	N 30° 26.266	E 47° 45.738	Zubair Bridge	27/11/2012

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Figure 3-7: Water analysis data display by Stiff diagram for oilfield water in North Rumaila Field.

3-5-1 Physical properties of MOD

The MOD water is surface water resulting from washing farmland, industrial and municipal sources come from sub paracentesis stretching along its course from Baghdad down to its mouth in the Khor Al-Zubair in Basra.

The physical properties include the hydrogen number (pH), electrical conductivity (EC), total dissolved solids (TDS) and specific gravity (SP). The results are listed in Table 3-11. The average of pH is 7.5 referring to neutral to slightly alkaline water. The surface water in Iraq is mainly alkaline (AI-Lamie, 1998). The pH values of MOD may be increased by one degree during the winter reaching 8.5, due to the lack of phytoplankton, low temperature and rainfall that contain carbon dioxide (AI-Monshed, 1998). A high average of EC value (30950 μ S/cm) is recorded (Table 3-11) indicating a high amount of salt dissolved in water. (Richard, 1954) confirmed that the water of MOD is an agricultural, industrial paracentesis water of high salinity. The EC value increases towards the Arabian Gulf due to increased water drainage.

The average of TDS is 26790 ppm, which is considered high compared with the Tigris and Euphrates River. Towards the south, a natural hydrological processes, municipality, untreated industrial waste, and irrigation water increase the average of MOD as well as the evaporation (Abdul Ameer and Sdjan, 2011). However, the specific gravity is expected to lie within the limits of natural water which is 1.0202.

Sample No.	pН	EC (µS/cm)	SP. gravity	TDS (ppm)
MW1	7.55	31900	1.0205	26480
MW2	7.6	30000	1.0200	27100
Average	7.5	30950	1.02025	26790

Table 3-11: Some physical properties of the Main Outfall Drain (MOD).

3-5-3 Chemical properties of MOD

The chemical results of the MOD are presented in Table 3-12. The average concentration of Na is 6400 ppm. The high value of sodium is compared with the local and global rivers (Table 3-12). The high rate of evaporation resulted from higher temperatures plays an important role in concentration the dissolved ions, in addition to high salinity content in the Iraqi soil in central and southern regions of iraq (Khathi et al, 2010).

Potassium in average is 117.5 ppm (Table 3-12). Its origin mostly comes from chemical fertilizers used for farmland. Relatively, high concentration of Ca (666 ppm) is recorded due to the high temperature resulting in high concentrations of carbon dioxide that forms carbonic acid that reacts to form soluble calcium bicarbonate. In addition to the calcium concentration in natural waters depends on the nature of the soils and areas, which passes the in it MOD. The average concentration of Mg is 1505 ppm; it appears twice more than Ca.

The chloride ion has 10775 ppm in average due to the washing the saline soil and Sabkhas. Sulfate has 7050 ppm in average attributed to the discharge water rich in Na₂SO₄, MgSO₄, CaSO₄ and gypsum (Kinghorn, 1983). The average of bicarbonates is 281ppm, but the carbonate has lacked.

Generally, Stiff diagram of the MOD is illustrated in Figure (3-8), the Na and K are the predominant cations, whilst the Cl is the predominant anions.

Table 3-12: Chemical properties of Main Outfall Drain (MOD) compared
with the results published in (Al-Marsoumi et al, 2006 and Faur, 1998) for
local and global Rivers.

Sample No.	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl	SO ₄ ²⁻	CO ₃ ²⁻	HCO ₃
				(p	pm)			
MW1	6375	125	712	1560	10650	6600	Nil	281
MW2	6425	110	620	1450	10900	7500	Nil	-
Average	6400	117.5	666	1505	10775	7050	-	281
*Tigris	51.11	2.98	56.5	30.8	86.6	158.9	-	150
*Euphrates	97.7	5.5	98.2	37.9	142.4	561	-	151
**Mississippi	11	2.8	34.0	8.9	10.3	25.5	-	116
**Colorado	95	5.0	83.0	24	87.0	270	-	135
**Amazon	1.5	0.8	5.2	1	1.1	1.7	_	20
**Nile	1.7	1	25	7	3.9	13	_	131

* Al-Marsoumi et al (2006).

** Faur (1998).





3-6 Chemical Compatibility and saturation index

Mineral saturation index is an index showing whether a water will tend to dissolve or precipitate a particular mineral. Its value is negative when the mineral dissolves, positive when it may precipitate, and zero when the water and mineral are at chemical equilibrium. The saturation index (SI) is calculated by comparing the chemical activities of the dissolved ions of the mineral (ion activity product, IAP) with their solubility product (K_{sp}). In equation form, SI = $log(IAP/K_{sp})$. It is calculated by PHREEQC software program. Saturation index is very important for calculating the chemical compatibility. Chemical compatibility is a holding group laboratory experiments through which the river water mixing with the oil field water at different rates. Thereafter, the properties of the new water are tested to be sure whether compatible or incompatible as injection water for the oil produced. The MOD water is selected as a surface water to mix by different ratios with the oilfield water of Zubair Formation in the North Rumaila Field. Waters that can be mixed without a precipitate called compatible, if they can be mixed without producing chemical reaction between the dissolved solids in the waters and thus precipitating insoluble compounds (Henkel, 1953). Water used for the injection usually contain a number of inorganic salts and sometimes-organic salts in solution, it is a common practice to test the compatibility of the injection water and water in the formation before starting injection operation (Collins and Bryant, 1985). Generally, scale (salt crust) precipitated as result of mixing is one of the most important problems that inflict damage at the injection systems and the main oil reservoir. It can also plug production lines, equipment and impaired fluid flow (Merdhah, 2007). In the case of injection systems, scale formed may cause a plug in the pores of the Formation and thus a decrease in permeability and cause obstruction to the flow of fluids with time (Collins and Wright, 1982). One of the most important and hazardous kinds of these phenomena is mineral scale deposition due to the incompatibility between injected and formation waters and changes in temperature, pressure, gas dissolution and pH. On the other hand, this is a process of deposition of scales from aqueous solutions of minerals, referred to brines, when they become supersaturated solutions as the result of changes in the state of their thermodynamic and chemical equilibrium (Fakhri, 2011). The most important ions present in oilfield water and cause scale precipitation are: Ca²⁺, Sr²⁺, Ba²⁺, Fe²⁺, HCO⁻ and CO₃²⁻ (Oddo et al., 1982). Scale deposition can occur from one type of water because of supersaturation with scale-forming salts attributable to changes in the physical conditions under which the water exists (Yuan and Todd, 1991). Scale also can deposit when two incompatible waters are mixed and supersaturation is reached. The main source of oilfield scale is mixing of incompatible waters that are called incompatible if they interact chemically and precipitate minerals when mixed (Merdhah, 2007). The most common types of scales known in the oil reservoirs are listed in Table 3-13. The most common scales encountered in oil field operations are sulfates such as calcium sulfate (anhydrite, gypsum), barium sulfate (barite), and strontium sulfate (celestite) and calcium carbonate (calcite).

			Solubility		
Compound Name	Formula	Specific gravity	Cold water (mg/l)	Other	
Barium sulfate	BaSO ₄	4.50	2.20	60 mg/l in 3%HCl	
Calcium carbonate	CaCO ₃	2.71	14.0	Acid soluble	
Strontium sulfate	SrSO ₄	3.96	113.0	Slightly acid soluble	
Calcium sulfate	CaSO ₄	2.96	2.09	Acid soluble	
Calcium sulfate	CaSO ₄ .2H ₂ O	2.32	2.41	Acid soluble	
Sodium chloride	NaCl	2.16	357.0	Insoluble in HCl	

 Table 3-13: Most common oilfield scales (Mackay et al, 2003).

3-6-1 Laboratory model of chemical compatibility

In accordance with the reservoir conditions at various temperatures (50 - 70°C) and differential pressures (6.894 – 13.789 bar), laboratory mixing for all of the waters of oilfield and MOD are done in the laboratories of the South Oil Company. The mixing ratios of oilfield water to MOD water are as follows (90%-10%), (80%-20%), (70%-30%), (60%-40%),(50%-50%), (40%-60%), (30%-70%), (20%-80%), (10%-90%), (0%-100%) and (100%-0%) equivalent to 100 ml and monitoring if precipitation occurs during 24h, a week later, after two weeks, three weeks later. Basic turbidity (bottle tests) is a good preliminary indicator of fluid incompatibility (Benion, 1991). Table 3-14 lists the results that represent the amount of scale formed as a result of mixing processes of the total volume (%).

Test	Mixing ratios (volume %)/ 100ml			The quantity of precipitate (volume %)			
Test No.	MOD water	Oilfield water of Zubair Formation	After 24 hours	After a week	After two weeks	After three weeks	
1	10	90	0.15	0.15	0.15	0.15	
2	20	80	0.15	0.15	0.15	0.15	
3	30	70	0.30	0.30	0.30	0.30	
4	40	60	0.40	0.40	0.40	0.40	
5	50	50	0.45	0.45	0.45	0.45	
6	60	40	0.50	0.50	0.50	0.50	
7	70	30	0.50	0.50	0.50	0.50	
8	80	20	0.50	0.50	0.50	0.50	
9	90	10	0.20	0.20	0.20	0.20	
10	100	0	Nil	Nil	Nil	Nil	
11	0	100	0.20	0.20	0.20	0.20	

Table 3-14: Results of compatibility tests between designed mixture of theoilfield water and MOD water at 50 - 70°C.

During all the tests, it is observed that an amount of precipitate is formed with exceptional of test no.10 where no precipitate occurs due to no mixing, because the water of the MOD alone without mixing (Table 3-14).This indicates a chemical reaction between the ions in the mixed solution. The largest amount of precipitate (0.5% of the total volume) formed during mixing the solutions (MOD water to oilfield water) with ratios of 60%-40%, 70%-30% and 80%-20% with total volume of 100ml (Table 3-14). The smallest amount of precipitate (0.15% of the total volume) formed during mixing the solutions (MOD water to oilfield water) with ratios of 10%-90% and 20%-80% with total volume of 100ml.These tests practically confirms that the mixture of oilfield water with Zubair Formation and MOD water is incompatible due to formation of precipitates. A significant result of the time factor also was detected. There is no effect of time on the reaction. The reaction in the mixed solution occurs at the preliminary time, where the mixed solution becomes supersaturation and eventually during 24 h reaction becomes completed (Figure 3-9).



Figure 3-9: Compatibility curve between the oilfield and MOD waters displays mixing ratios (volume % of 100ml) and the amount of precipitate at mixture.

3-6-2 Mathematical model of chemical compatibility

This model is designed to know the type of scale formed and calculate the saturation index during mixing two types of water different in components chemical and physical properties.

At the first, the saturation index (SI) indicates if a solution is in equilibrium undersaturated or supersaturation condition with regard to a solid phase. A value of 1 signifies a ten fold supersaturation, a value of (-2) a hundred fold under saturation in relation to a certain mineral phase. Equilibrium can be assumed for a range of (-0.5) to (+0.5). If the SI value is below (-0.5), the solution is undersaturated with regard to the corresponding mineral, if the SI exceeds (+0.5) the water is supersaturated with respect to this mineral (Hussein et al., 2011). Thermodynamic modeling uses standard software, which was performed to assess the compatibility of various injection water sources with oilfield water. Therefore, PHREEQC version-2 is used in this study because it is able to simulate the interactions that take place during the mixing and mineral types precipitated.

3-6-2-1 Chemical compatibility of sample MW1

Saturation index (kcal/mole) is calculated for the mixture resulted from the oilfield water of Zubair Formation and MOD in the sample MW1 at reservoir conditions. Table 3-15 lists the saturation indices for the anhydrite, barite, celestite and calcite minerals. The SI of anhydrite (-1.39) - (-0.51), barite (-0.167) - (0.2), celestite (-1.29) - (-0.87) and calcite (-1.55) - (+1.37) (Table 3-15). These values of SI refer to that the anhydrite, barite and celestite are undersaturated, whereas calcite is saturated. This case causes the lack of precipitation of anhydrite, barite and celestite and precipitate calcite (Figure 3-10). The incompatibility happens in cases of mix oilfield water with a MW1 sample of MOD with ratios of 0%-100%, 10%-90%, 20%-80%, 30%-70% 40%-60% (Table 3-15).

The major ions dissolved in the mixture are SO_4 , Ba and Sr because anhydrite; barite and celestite are unsaturated and under the equilibrium state. It is important in these mixtures will precipitate of calcite scale will form because it has a positive saturation index more than +0.5, therefore, calcite appears to occupy the precipitation zone in Figure 3-10. However, this water is incompatible, because the scale formed during mixing (Collins, 1982).

Table 3-15: Saturation index of the mixture designed for the oilfield water ofZubair Formation and MOD (sample MW1) at the reservoir conditions.

Mixing Ratios (volume %)		Saturation Index (SI) (kcal/mole)				
Oilfield water %	MW1 of MOD %	Anhydrite	Barite	Celestite	Calcite	Result
0	100	-1.39	-1.67	-1.29	0.86	incompatible
10	90	-0.64	-0.37	-0.89	1.37	incompatible
20	80	-0.52	-0.23	-0.87	1.26	incompatible
30	70	-0.51	-0.20	-0.98	1.01	incompatible
40	60	-0.52	-0.20	-1.09	0.71	incompatible
50	50	-0.58	-0.23	-1.13	0.37	compatible
60	40	-0.64	-0.29	-1.14	0.02	compatible
70	30	-0.75	-0.36	-1.23	-0.35	compatible
80	20	-0.87	-0.46	-1.39	-0.72	compatible
90	10	-1.05	-0.61	-1.19	-1.13	compatible
100	0	-1.30	-0.83	-1.21	-1.55	compatible



Figure 3-10: Saturation index of the mixture of oilfield water from Zubair reservoir and MOD (sample MW1) at the reservoir conditions.

The mixtures formed from mixing the oilfield water with the MW1 of MOD in ratios of 50%-50%, 60%-40%, 70%-30%, 80%- 20%, 90%-10% and 100%- 0% are compatible because they have SI are less the +0.5 (Table 3-15). Therefore, these mixtures can be used for injection to the oilfield of Zubair reservoir and no scale will precipitate. Figure 3-10 clarifies this case and displays that there is no precipitation for anhydrite, barite, celestite and calcite because all curves occupied the undersaturation zone for the mixture mentioned above.

3-6-2-2 Chemical compatibility of sample MW2

Saturation index (kcal/mole) of the mixture of the oilfield water of Zubair Formation and sample MW2 collected from MOD under reservoir condition is calculated through 11 mixtures. Table 3-16 presents results of the saturation index of anhydrite, barite celestite and calcite. According to the SI value, in a solution of 100% MW2, calcite is precipitated (Table 3-16). In mixtures of 10%, 20%, 30% and 40% oilfield water by 90%, 80%, 70% and 60% MW2 respectively, anhydrite, barite and calcite are precipitated. In mixture of 20% oilfield water and 80% MW2, anhydrite, barite and calcite are precipitated. Only barite is precipitated from mixtures of 50% to 50%, 60% to 40% and 70% to 30% of oilfield water to MW2 (Table 3-16). All the mixtures mentioned above are incompatible, because the scale of minerals precipitated is formed. The mixture formed from oilfield water to MW2with ratios 80% to 20%, 90% to 10% and 100% to 0% are compatible waters due to no minerals precipitate and eventually no scale formed (Table 3-16). Collins (1975) supported this conclusion. Figure 3-11 illustrates the minerals that are precipitated. Celestite is not precipitate from any mixture of the oilfield with MW2 waters; therefore, it is representing by a curve occupying the equilibrium and undersaturated zones. Anhyrite is precipitated in case the mixing ratios between the oilfield water with MW2water are 10%-90%, 20%-80% 30%-70% and 40%-60%, therefore, this mineral occupies the precipitation zone at these mixing ratios (Figure 3-11). Barite is precipitated from the mixtures designed for the oilfield water and MW2water with ratios of 10%-90%, 20%-80% 30%-70%, 40%-60% 50%-50%, 60%-40% and 70%-30%. Consequently, the barite curve occupies the precipitation zone at these ratios. Calcite is precipitated from these mixtures of ratios 0%-100%, 10%-90%, 20%-80% 30%-70% and 40%-60%, accordingly, the calcite curve occupied the precipitation zone at these ratios (Figure 3-11).

Mixing Ratios (volume %)		Saturation Index (SI) (kcal/mole)				
Oilfield water %	MW2 of MOD %	Anhydrite	Barite	Celestite	Calcite	Result
0	100	0.25	-0.40	-0.27	1.12	incompatible
10	90	0.60	0.81	0.19	1.23	incompatible
20	80	0.64	0.91	0.29	1.06	incompatible
30	70	0.62	0.91	0.23	0.82	incompatible
40	60	0.56	0.87	0.02	0.54	incompatible
50	50	0.48	0.81	-0.01	0.23	incompatible
60	40	0.36	0.71	-0.23	-0.08	incompatible
70	30	0.19	0.57	-0.67	-0.42	incompatible
80	20	-0.05	0.36	-0.50	-0.77	compatible
90	10	-0.42	0.01	-1.01	-1.15	compatible
100	0	-1.30	-0.83	-1.67	-1.55	compatible

Table 3-16: Saturation index of the mixture designed for the oilfield water ofZubair Formation and MOD (sample MW2) at the reservoir conditions.



Figure 3-11: Saturation index of the mixture of oilfield water from Zubair reservoir and MOD (sample MW2) at the reservoir conditions.

3-6-2-3 Chemical compatibility of seawater

To find the chemical compatibility of seawater with the oilfield water of Zubair reservoir, saturation indices (kcal/mole) are calculated for 11 mixtures at the reservoir conditions. Table 3-17 shows the results of saturation indices of anhydrite, barite, and celestite are negative indicating that these minerals are in equilibrium or undersaturated state and no mineral precipitate. Therefore, all these minerals occupied the undersaturated zone (Figure 3-12). The SI of calcite is more than 0.5 for the mixture of oilfield and seawaters of ratios of 0%-100%, 10%-90%, 80%-20%, 70%-30, 60%-40% and 50%-50% (Table 3-17). Consequently, these mixtures occupied the precipitation zone (Figure 3-12), and eventually they represent incompatible water. But, when they mixed in ratios 60%-40%, 70%-30%, 80%-20%, 90%-10% and 100%-0%, they appear a compatible water, because all SI of minerals (anhydrite, barite, celestite and calcite) are less than +0.5, and therefore the curves of these minerals occupied the undersaturated zone indicating that there is no scale formed (Figure 3-12).

Mixing Ratios (volume %)		Saturation Index (SI) (kcal/mole)				
Oilfield water (%)	Seawater (%)	Anhydrite	Barite	Celestite	Calcite	Result
0	100	-0.29	_	_	1.84	incompatible
10	90	-0.18	-0.05	-1.35	1.76	incompatible
20	80	-0.18	-0.05	-0.93	1.57	incompatible
30	70	-0.22	-0.01	-0.65	1.32	incompatible
40	60	-0.27	-0.01	-0.76	1.04	incompatible
50	50	-0.35	-0.05	-0.84	0.71	incompatible
60	40	-0.44	-0.11	-0.98	0.36	compatible
70	30	-0.57	-0.20	-1.13	-0.05	compatible
80	20	-0.73	-0.33	-1.29	-0.47	compatible
90	10	-0.96	-0.52	-1.38	-0.97	compatible
100	0	-1.30	-0.83	-1.49	-1.55	compatible

Table 3-17: Saturation index of the mixture designed from the oilfield water ofZubair Formation and seawater at the reservoir conditions.





With reference to have been dependent on the analysis of the South Oil Company to seawater.

3-6-3- Quantity of mineral scale

3-6-3-1Calcium Carbonate (CaCO₃) scale

As previously mentioned, that to know the quantity and quality of the scale formed the value of saturation index is needed. Supersaturation state is the most important factor for precipitation. Table 3-18 shows the amount of calcium carbonate scale formed by mixing of oilfield water with the MOD and seawater in a unit g/m^3 . The most frequent scaling problem comes from calcium carbonate (CaCO₃) because it precipitates fast. According to Clemmit et al. (1985), calcium carbonate is formed through different mechanisms, the water containing the carbonate ion a few percentages could decompose and

become calcium carbonate. This decomposition is caused by pressure dropping which release carbon dioxide and thus change the equilibrium by increase of pH and the solution becomes acidic. Therefore, the calcium carbonate scale is most common in the oil fields, its crystals are large. When scale is found together with impurities in the form of finely divided crystals, then the scale appears uniform. Deposition of CaCO₃ scale results from precipitation of calcium carbonate as the following equation (Merdhah, 2007):

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$$

Reason for this scale is the interaction between calcium and bicarbonate ions. This reaction is the major cause of calcium carbonate scale deposition in oilfield operations. The solubility of $CaCO_3$ depends on pH, the equilibrium can be shifted to the right side to convert $CaCO_3$ to soluble $Ca(HCO_3)_2$ by adding an acid (lowering pH), as shown in the following equation (Larson and Buswell, 1942):

$$CaCO_3 + H \leftrightarrow Ca^{2+} + HCO_3^{-1}$$

Mixing Ratios		Amount of CaCO ₃	Mixing Ratios		Amount of CaCO ₃	Mixing Ratios		Amount of CaCO ₃
FW (%	SW (%)	(g/m ³)	% FW	% MW1	(g/m ³)	% FW	% MW2	(g/m ³)
0	100	167	0	100	66	0	100	76
10	90	135	10	90	90	10	90	80
30	70	106	30	70	61	30	70	51
50	50	50	50	50	20	50	50	13
70	30	0	70	30	0	70	30	0

Table 3-18: Amount of calcium carbonate precipitable from mixturesbetween FW and SW, MW1, MW2 water at reservoir conditions.

Results in Table 3-18 show when less oilfield water ratio at 70%, leads to an increase for CaCO₃. Figure 3-13 displays the best mixing ratio of the MOD water and seawater is (70% -30%), because there is not observed any precipitation at this point, and may be the solution is at this point be equilibrium to undersaturation.



Figure 3-13: Amount of calcium carbonate (g/m³) precipitable from mixtures between FW and SW, MW1, MW2 water at reservoir conditions.

3-6-3-2 Calcium and barium sulphate scales

(Collins, 1975) mentioned that the mixing of surface and oilfield waters results in solutions either saturated or undersaturated with relatively insoluble compounds such as calcium carbonate, calcium sulfate, strontium sulfate, and barium sulfate. Calcium sulfate (CaSO₄) is more soluble than barium sulfate (BaSO₄). However, calcium ion (Ca²⁺) is present in natural water sources

more abundantly than Ba^{2+} and thus $CaSO_4$ will cause more scaling problem than $BaSO_4$. On the other hand, $BaSO_4$ are difficult to re-dissolve once precipitated (Neuman, 1933 in Collins, 1975).

Calcium sulfate is important in studies of petroleum, because it is complex and may crystallize in the solution in three forms: gypsum (CaSO₄.2H₂O), hemihydrite (CaSO₄.1/2H₂O) and anhydrite (CaSO₄). These compounds are stable depending on temperature and ionic strength and they have decreasing solubilities with increasing temperatures above 40°C (Merdhah, 2007).

Barium sulfate is most insoluble scale that can be precipitated from oilfield waters. It forms a hard scale which is extremely difficult to remove. The solubility of barium sulfate is about a thousand times less than that of calcium sulfate, at surface conditions. Generally, the solubility of barium sulfate goes up with increasing temperature, pressure and salt content of the brine. Thus the prediction of barium sulfate scale has been much easier than the others since a pressure, temperature or salt content drop will increase precipitation (Connell, 1983). In mixture designed from the oilfield and MW2 with a ratio of 90%-10%, there is no scale of CaSO₄ and BaSO₄, while in mixture of 80%-20% there is no scale of CaSO₄, but 3.4 g/m³ of BaSO₄ scale is precipitated (Table 3-19). A different weight of CaSO₄ and BaSO₄ scales are precipitated from the mixture of 70%-30%, 50%-50%, 40%-60%, 30%-70%, 10%-90%. 441 g/m³ of CaSO4 is formed a scale precipitated from 100% of MW2 (Table 3-19), but no BaSO4 scale precipitated. The scale amounts of CaSO4 and BaSO4are plotted in Figures 3-14 and 3-15 respectively.

Table 3-19: Amount of calcium and barium sulphate precipitable from
mixtures between FW and MOD in sample MW2 water at reservoir
conditions.

Mixin	g Ratios	Scale			
FW (%)	MOD (MW2%)	Amount of CaSO ₄ (g/m ³)	Amount of BaSO ₄ (g/m ³)		
0	100	441	0		
10	90	3134	0.7		
30	70	3462	2.1		
50	50	2500	3.3		
70	30	627	3.7		
80	20	0	3.4		
90	10	0	0		







Figure 3-15: Amount of Barium sulfate (g/m³) precipitable from mixtures between FW and MOD water in sample MW2 at reservoir conditions.

Chapter Four

Formation



4-1 Preface

Permeability is a measure of rocks ability to conduct fluids. It is considered one of the most important reservoir specifications which controls oil production. The formation damage that occurs in the reservoir leads to a decrease in permeability. Reductions of permeability have been observed in many global oil reservoirs. The sandstone reservoirs are shown to be more permeable to brines than to fresh water (Baptist and Sweeney, 1955). The ability of some petroleum reservoir sands to pass oil decreases by the interaction of the porous rock with water (Dodd et al, 1954). Several sources are recognized as possibly contributing to this problem such as mineral scale deposition, solid invasion, clay swelling and rock-fluid incompatibility (Fakhri, 2011).

The presence of clay minerals is one of the reasons affecting the permeability, these minerals are exposed to swelling or dispersion, in case of a change of the chemical environment of the reservoir as a result of water injection with chemical specifications that are different from the specifications of the oilfield water in the reservoir, and thus influence the reservoir performance and production rate.

Water injection is a common method in oil fields, for the purpose of pressure maintenance and enhanced oil recovery. During secondary recovery by this method, reductions of permeability have been observed in many reservoirs (Fakhri, 2011). For this purpose, a series of experimental works has been conducted to study the formation damage and decline in permeability resulting from clay minerals of the Zubair reservoir by a change in brine concentration and change in hydrogen number (pH), if using an injection system without treatment.

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4-2 Petrography of sandstone

Fluid moving in the depths governed by the laws of restricted. This movement is based on the available pores within the reservoir. Permeability and porosity in the reservoir depend on the fabric, texture and processes affecting the rocks. Sandstone consists primarily of quartz, feldspar and rock fragments. The process of transferring clastic from the source to the sedimentation basin, works on the maturation of components. The main source of sandstone is granite rocks that supply feldspar as well as quartz. Feldspars are unstable in comparison to quartz-resistant weathering conditions. The final product of chemical weathering of feldspar is clay minerals such as kaolinite.

Petrographic study has been made in thin sections prepared from the hard sandstones collected from different depths of North Rumaila Field. In sandstone cores of the Zubair reservoir, quartz is the most abundant grain. Two patterns of bitumen in the hand specimen cores are observed by naked eye. Figure 4-1a displays bitumen filled fractures, and Figure 4-1b show impregnated samples with bitumen indicating high porous.



Figure 4-1: Core samples display bitumen features in the sandstone of the Zubair reservoir. Sample no (a is R-131C) and (b is R-184C).

Thin sections of sandstone cores are examined by polarized microscope to show the oil path through the reservoir. Several paths of crude oil are can pass through inside the reservoir. Fissures and fractures are a large path that permit oil to move. Movement of crude oil is a little faster when they are interconnected. Figure 4-2 presents fissures and pores filled with bitumen.



Figure 4-2: Bitumen fill fissure and the pores of sandstone; a=5X (-); b=5X (+), sample no R-17C ; depth 3157m

Bitumen fills interstitial pores and fractures. The grains are predominantly formed from quartz which have highly pits and scratches, moderate to not well sort, rounded to sub-rounded indicating a turbulent transportation from close supplying source (Folk, 1974). The important diagenetic changes which have been observed grain compaction that leading to effects of pressure solution. Authigenic development of minerals is precipitation of cement that formed from silica and clay in most the cement does not cover the whole sample, but there are sites have high porosity and little cement, it developed of intergranular fractures due to differential compaction (Figure 4-3).



Figure 4-3: Enlarged dissolution opening fractures fill with bitumen among quartz and very little grains of feldspar due to develop the intergranular fracture, a=5X(-); b=5X(+); sample R-17C; depth 3157m

Dissolution in reservoir condition of acidic nature is almost dominant and contributes to enlarge the gaps, voids, cracks, fissures and fractures (Figure 4-3). Sometime very fine particles move and transport by oilfield water or crude oil itself from place to another. Transmitted grains cause the closure of the openings leading to reduced permeability.

When increase permeability, fluid moves faster, and this causes dissolving of granules leading to enlarged voids and interstitial pores (Figure 4-4). At the same time, some small grains are mechanically transported, which may not find enough slots to pass, causing accumulation and reduction of reservoir permeability. Partial dissolution and replacement of quartz, feldspar and mica grains of the cementing material enhance the porosity and permeability in sandstone.



Figure 4-4: Bitumen fills voids and interstatial spaces among sandstone grains, a=10X(-); b=10X(+); sample no R-17C; depth 3157m

4-3 Clay minerals induced Formation damage

Formation damage is impairment of reservoir permeability by adverse processes (Civan, 2000). The productivity of oil and gas wells are depends upon the effective permeability of reservoir sands to those fluids, and anything that decreases the permeability of sands will decrease the rate of oil and gas production. Most reservoir sands contain both interstitial water and clay minerals (Baptist and Sweeney, 1955). Clay minerals are considered one of the main reasons which effect on the reservoir properties, which cause the formation damage and reduce the permeability of the rocks. Because these minerals can be a negative effect on the reservoir from through dispersion or swelling, when changes the chemical specifications of water the surrounding with it.

Many researchers have studied the relationship between the permeability of the rocks and the change in the water chemistry of the surrounding, such as: Almon (1982); Mangan (1965); Bennion et al. (1991); Harper and Buller (1986); Bennion et al. (1997); Civan (2007); Mohan et al. (1993); Gray and Rex (1966); Pittman and King (1985). They explained that these rocks are influenced by the change of water specifications in the reservoir that have been named the water sensitivity. Mohan et al. (1993) mentioned that the phenomenon of water sensitivity in reservoirs sandstone which contains mainly non-swelling clays. His study demonstrated that the role of pH, ion exchange, and brine concentration on the release or detachment of migrating clays from pore surfaces and subsequent permeability loss of the porous medium. The importance thing to understand the formation damage is to study clay minerals as an influential factor on the permeability in sandstone reservoirs through three main aspects, the amount of clays, quality and its location within the rocks (Al-Yasiri, 2000).

Clay minerals occupy a large fraction of sedimentary formations which are extremely small, mostly platy-shaped materials that may be present in sedimentary rocks as packs of crystals (Civan, 2000). Neasham (1977) divided clay particles in sandstones into three general types: (i) discrete particles, (ii) pore-lining clays and (iii) pore bridging clays. Clay site within the pores of the rocks large role in decrease permeability, because of the larger surface area of exposure to these minerals to water, and thus leads to the dispersion or swelling (Al-Yasiri, 2000).

The clay minerals can be classified into three main groups (1) Kaolinite group, (2) Smectite (or Montmorillonite) group, and (3) Illite group. In addition, there are mixed-layer clay minerals formed from several of these three basic groups (Civan, 2000). The sensitivity of clay minerals of water and their impact on permeability rocks different from one mineral to another, depending on basic silica structure. Aylmor (1982) said that the clay minerals of the semectite and kaolinite groups is one of the most prominent groups that cause highest ratios of damage in the permeability of the rock. Allen and Riley (1964) classify sandstone into two types depending on the amount of clay minerals present (i) Clean sandstone if the proportion of clay minerals less than 5%, and (ii) Dirty sandstone which contains more than 5%.

Generally, clay minerals irrespective of it quantity have danger and threat to oil reservoirs.

4-4 Mineralogy of clay minerals using XRD and SEM

Because of the small particle size of clay minerals and the fact that most of the clay minerals are a complex mixture, they are difficult to distinguish in ordinary microscope (Millot, 1970 in Al-Azzawi, 1996).

Core samples collected from the Zubair reservoir in the North Rumaila Field subjected to diagnosis by XRD and Scanning Electron Microscope (SEM). XRD test shows that the clay minerals are represented by kaolinite (Figures 4-5, 6, and 7).

Kaolinite is formed mainly by decomposition of K-feldspars, granite, and aluminum silicates. It is widespread in sedimentary rocks, originated from false hexagonal blocks, thus exist as mineral fills the blanks, it has a negative impact on porosity of the reservoir oil (Seemann, 1979). The crystalline structure consists of 1:1, one layer of the mineral consisting of an alumina octahedral sheet and a silica tetrahedral sheet that share a common plane of oxygen atoms and repeating layers of the mineral of hydrogen bonded together (Bear, 1965). As a consequence of this structure, the silica/oxygen and alumina/hydroxyl sheets are exposed and interact with different components in the solution (Grim, 1968).

The core samples of the wells R-17C, R-131C and R-184C are separated into clay minerals and non-clay minerals. These two fractions are identified by XRD. Clay minerals are prepared and tested as (i) Normal (untreated), (ii) Ethylene Glycolated, (iii) Heated to 550°C for 2h. The non-clay minerals fraction which is the main fraction of the core sample is also subjected to the XRD technique as bulk sample. XED test for the bulk samples reveals that the samples are composed mainly of quartz, while the clay fraction is formed of kaolinite (Figures 4-5, 6 and 7).



Figure 4-5: X-Ray diffractogram of sandstone sample (well no R-17C; depth 3157m).



Figure 4-6: X-Ray diffractogram of sandstone sample (well no R-131C; depth 3208m).



Figure 4-7: X-Ray diffractogram of sandstone sample (well no. R-184C; depth: 3199 m).
Kaolinite is one of the clay minerals the charge balancer or charge container very few, this charge is centered on the outer surface of the mineral and is affected by pH, and created as a result of hydration the bonds which linking Si-O, Al-OH formed hydroxyl ion (OH⁻) on the mineral surface (Drever, 1982).

Typically, kaolinite has a cation exchange capacity (CEC) of 3 to 15 meq/100 g (Grim, 1968), while values quoted for the specific surface area of kaolinite are from 10 to 20 m²/g (Coles and Yong, 2002). The cation exchange capacity (CEC) of kaolinite strongly depends on the particle size (both thickness and diameter in the 00l plane), and pH value. Particle size is more important than crystallanity in affecting kaolinite CEC. It is commonly believed that cation exchange occurs due to the broken bonds around the crystal edges, the substitutions within the lattice, and the hydrogen of exposed surface hydroxyls that may be exchanged (Ma and Eggleton, 1999).

Based on the above, Drever (1982) said that when the pH value of the solution is smaller than zero point charge (ZPC) of kaolinite, mineral surface will be rich in hydrogen ion (H^+) with a positive charge, and thus the surface of the mineral will charge positive as well. But if the value of pH is greater than the value of ZPC of Kaolinite, the mineral surface is rich in hydroxyl ion (OH⁻) with a negative charge. When the pH value is equal to the value of ZPC, the surface of the mineral charge will be positive, because the amount of ZPC to Kaolinite is within the limits of the acid. Generally, value of the ZPC of the kaolinite ranging from 2 - 4.6.

The SEM study reveals that many of the clay mineral grains have undergone partial pressure resulting in the formation of deteriorate the reservoir quality. SEM study shows the commonly occurring clay mineral in the sandstone of Zubair reservoir is kaolinite which is wide occurrences in

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stacking of book pattern around inter-granular pore, this leads to narrowing these pores. Authigenic growth of kaolinites reduces the permeability/porosity ratio (Figure 4-8).



Figure 4-8: SEM image display how kaolinite stacking around inter-granular pores. Sample no R-17C; depth 3157m

Also kaolinite occurs around quartz grain, because authentically generated from feldspar transformation and from very fine grains of kaolinite. It is migrates from its original place to another place and accumulated in large quantities reducing permeability (Figure 4-9). This case is named Fines invasion and migration. Clay migration can cause a severe permeability reduction even in so-called "clean" sandstones. This type of damage can drop

a very permeable sandstone to less than 1% of its original permeability in a few hours.



Figure 4-9: SEM image display quartz grain buried by accumulated kaolinite (sample noR-17C; depth 3157m).

4-5 Permeability induced Formation Damage

For the purpose of knowing the formation damage in permeability of the Zubair reservoir, specific brine solution similar to the formation water in terms of the (salinity and pH) has been attended. The core samples used in the tests are sandstone of Zubair Formation are 3 inch length and of diameter 1.50

inch. The average porosity of these cores is 17% and the initial permeability varied from 70 to 250 M.D of all samples. All of cores are cleaned using methanol in Soxhlet extractor and dried in oven at 100°C for an overnight before the use. This process was done in the South Company Laboratories (SOC). After that, the cores are subjected to two tests. The first, these cores (plugs) are injected with solutions of a variable hydrogen number (pH) from strong acidic pH=3 to strong alkaline pH=11. Secondly, injection of sodium chloride solutions (NaCl) with different concentrations in the cores. 16 tests were conducted through this method, the final permeability and formation damage are measured at each stage.

4-5-1 Salinity induced formation damage

The core samples are saturated with sodium chloride solution to determine the formation damage in terms of permeability using injection methods that are carried out by gradual and sudden reduction salts as follows: **First:** gradual reduction of salt (NaCl) from 20% -15% -10% -5% then to 2%. **Secondly:** sudden reduction of salt (NaCl) from 20% to 2% directly.

The initial and final permeability at different concentration of NaCl (20, 15, 10, 5 and 2%) is listed in Table 4-1. Formation damage is computed based on initial and final permeability in each stage; the results are presented in Table 4-1. The following equation is used for computing the formation damage (Dr %):

$$Dr = 100 - \frac{KLf \times 100}{KLI}$$

Where (KL_I) is initial permeability; and (KL_f) is final permeability.

The reduction of NaCl concentration during each experiment was a simulation to salinity reduction in the oilfield. The results in Table 4-1 show that permeability is directly proportional to the concentration of the solution. As an example, core no. R-186C when salt concentration was 20%, the permeability is 155, but with reduction the concentration of the solution gradually down to 2%, permeability has positively responded and becomes 140 M.D (Figure 4-10) with formation damage 17.6 (Table 4-1). The formation damage is closely linked with permeability.

Table 4-1: Formation damage during the gradual reduction salt (NaCl) and values of the initial and final permeability of the core samples of Zubair reservoir (North Rumaila Field).

				Concentration of NaCl				l		
Core No	Depth		KL_{I}	20%	15%	10%	5%	2%	Δ P	∆Р%
INU.	(111)	(%)	(M.D)	KL _f (M.D)						
R-186C	3210	22	170	155	150	148	147	140	30	10.5
Form	ation dat	nage (Di	r %)	8.8	11.7	12.9	13.5	17.6		
R-184C	3199	19	200	177	175	170	170	168	32	11.1
Form	ation dat	nage (Di	r %)	11.5	12.5	15	15	16.0		
R-131C	3208	29	250	190	189	185	189	190	60	21
Formation damage (Dr %)				24	24.4	23.3	24.4	24.0		
R-136C	3178	20	150	142	140	140	140	130	20	7
Form	ation dat	nage (Di	r %)	5.3	6.6	6.6	6.6	13.3		
R-17C	3157	17	135	120	110	110	110	102	33	11.5
Form	ation dat	nage (Di	r %)	11.1	18.5	18.5	18.5	24.4		
R-120C	3192	14	100	80	77	77	77	77	23	8
Formation damage (Dr %)				20	23.0	23.0	23.0	23.0		
R-112C	3179	18	180	166	160	160	155	155	25	27.7
Formation damage (Dr %)				7.7	11.11	11.11	13.8	13.8		
R-172C	3085	110	110	102	102	100	100	100	10	3.5
Formation damage (Dr %)				7.2	7.2	9	9	9		

M.D=Milli Darcy; Ø=Porosity; P=Permeability

Permeability follows a path of positive relationship with the salt concentration, it is very clear in all wells except for the sample R-131C (Figure 4-10). Highest permeability has been recorded at a salt concentration of 20%, while the lowest permeability has been recorded at a salt concentration of 2% of all wells, except for the sample R-131C. For example, the value of the initial permeability of the sample R-17C is 135 M.D, when decrease the NaCl concentration to 2%, the value of permeability has also decreased to 102 M.D with formation damage is 24.4%.

Figure 4-10 presents permeability change in response to the concentration of salts. The general trend is positive with the emergence of some anomalous. From the laboratory experiments, it is proven that the formation damage increases with reduction the salt concentration in the solution, which shows an inverse relationship between them. The highest damage is recorded 24.4% in the well R-17C, while less damage (9%) was found in the sample R-172 (Table 4-1) and (Figure 4-11). All shapes in Figure 4-11 display an inverse relationship in general statistical format, with the exception of one shape, which represents sample R-131C as display a consistent relationship with permeability shown in Figure 3-10.

Chapter Four



Figure 4-10: Permeability relationship with gradual reducing of NaCl concentration in 8 samples collected from 8 wells (one sample for each) of the Zubair reservoir (North Rumaila Field).

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Figure 4-11: Formation damage relationship with gradual reducing of NaCl concentration in 8 samples collected from 8 wells (one sample for each) of the Zubair reservoir (North Rumaila Field).

During the period of initial flow, the permeability declines sharply after the water enter in the pores. Permeability declines was slowed gradually where decrease of salts concentration. This phenomenon was observed in all the core tests in which the damage was severe. This means that the cores of the Zubair Formation are produce dispersions of the native clay during core flood tests, therefore, the permeability declining was observed (Gray and Rex, 1966). This declining in permeability may be due to the kaolinite during change the concentration of NaCl, and it is subjected to the phenomenon of dispersion and led to partially fill of the pores (Rolfe at.al, 1960, Schofild and Samson, 1952).

Al-Yasiri (2000) mentioned that the damage in permeability during the injection of sodium chloride solution can be explained through the relationship between reduced concentration and increase of pH the solution. It can be explained gets absorption of sodium ion on the surface kaolinite, it will get ionic exchange between the sodium and hydrogen ions (H⁺) in the solution, this leads to increase concentration of (OH⁻) in solution and thus increases the value of pH.

Table 4-1 shows the damage in the core of Zubair Formation as a result of changing the chemical specifications of the solution; it was observed the damage value rise with low NaCl concentration. Hewitt (1963) has emphasized the possibility of damage from migrating clays and the degree of damage is believed to be a function of the amount of clay minerals (Gray and Rex, 1966).

The presence of small crystals of the kaolinite (Figures 4-8 and 9) may be the reason of damage and water sensitivity in current sandstone rocks. The damage of Zubair Formation happens with clay dispersion and decline permeability. This is considered to be the best available evidence of clay migration damage as opposed to clay swelling damage, because of the Kaolinite is the only clay mineral dominant. The second test on permeability is done by the sudden reduction of salt concentration from 20% to 2% directly. Then, formation damage is computed in case of sudden reduction salt (NaCl) from 20% to 2%. The results are presented in Table 4-2.

Table 4-2: Results of permeability and formation damage under the suddenreduction of NaCl of samples collected from 2 wells of the Zubair reservoir(North Rumaila Field).

				Concentratio			
Core No	Depth (m)	Ø (%)	KL _I (M D)	20%	2%	ΔΡ	∆ P%
110.		(70)	(111.12)	KL _f (N			
R-186C	3253	15	140	128	125	15	35 7
Forma	tion dam	age (D	r %)	9	10.7	13	55.7
R-17C	3230	23	220	200	193	27	64.2
Forma	tion dam	age (D	r %)	9	12.2	21	04.2

M.D=Milli Darcy; Ø= Porosity; **P**=permeability

This test shows that there is a sharp decline in permeability. It is declined of the sample R-186C from 128 M.D to 125M.D with formation damage 10.7%, whilst in the sample R-17, it decreased from 200 M.D to 193 M.D with formation damage 12.2% (Figure 4-12 and 4-13).

Generally, the effect of gradual reduction of NaCl produces a decline in permeability varies between (7-27%) (Table 4-1), whereas during sudden reduction in NaCl, the permeability declined between (35.7-64.2%) (Table 4-2). Accordingly, the sudden reduction causes more damage than the gradual reduction of the Zubair reservoir rock.



Figure 4-12: Decline the permeability in response to the sudden reducing of NaCl concentration. Well: R-186C and Well: R-17C.



Figure 4-13: Decline the permeability in response to the sudden reducing of NaCl concentration. Well: R-186C and Well: R-17C.

4-5-2 pH induced formation damage

A set of laboratory experiments was designed to determine the effect of the pH on permeability. For this reason, four samples are collected from the oilfield water and tested with acidic pH (3 and 5), neutral pH (7) and alkaline pH (9 and 11). Thereafter the final permeability and formation damage are computed for each case. The results are listed in Table 4-3.

It was recorded a clear reduction in permeability during the gradual increase in the pH value from acidic (3) to 5 an neutral (7) and then to alkali of 7 and eventually to 9. In all these experiments, the permeability is declined when the solution goes towards alkaline (Figure 4-14). Formation damage in each case is computed ranging from 18.7% to 25%, and the negative values are means improving the permeability (Table 4-3).

Table 4-3: Results of permeability and formation damage under acidic,natural and alkaline pH of samples collected from 4 wells of the Zubairreservoir (North Rumaila Field).

Core No	Depth	Ø	KLI	pH=3	pH=5	pH=7	pH=9	pH=11	۸D	
	(m)	(%)	(M.D)		KL _f (M.D)					Δ Γ %
R-184C	3185	14	105	104	103	97	90	80	25	25
Format	tion dam	age (E	Dr %)	0.96	1.9	7.62	14.3	23.8	25	25
R-17C	3120	14	100	102	100	90	77	75	25	25
Formation damage (Dr %)			-2.0	0.0	10.0	23.0	25.0	23	23	
R-112C	3155	10	90	100	90	82	70	70	20	20
Formation damage (Dr %)			-11.0	0.0	8.88	22.2	22.2	20	20	
R-172C	3050	20	160	160	160	140	135	130	30	30
Formation damage (Dr %)				0.0	0.0	12.5	15.6	18.7	50	50

M.D= Milli Darcy; Ø= Porosity; P=permeability

These results indicate that any increase in solution alkalinity followed by an increase in the formation damage (Figure 4-15).



Figure 4-14: The negative relationship between permeability and pH for 4 samples collected from 4 wells of the Zubair reservoir (North Rumaila Field).



Figure 4-15: Formation damage relationship with pH in 4 samples collected from 4 wells (one sample for each) of the Zubair reservoir (North Rumaila Field).

In the case of sudden reduction of pH, permeability declined in sample R-17C from 70 M.D to 39 M.D with formation damage 44.28%, whilst in sample R-172, it declined from 165 M.D to 100 M.D with formation damage 39.3% (Figure 4-16) and (Figure 4-17).

Table 4-4: Results of permeability and formation damage under the sudden rising of pH
from acidic to alkaline of samples collected from 2 wells of the Zubair reservoir (North
Rumaila Field).

Core No	Depth	Ø	KL _I (M.D)	р Н=3	pH=11		
	(m)	(%)		KL _f (M.D)		Δ P	ΔΡ %
R-17C	3125	8	70	72	39	21	20
Form	nation dam	age (Dr	%)	-2 44.28		51	32
R-172C	3045	18	165	165	100	(5	(9
Form	nation dam	age (Dr	0	39.3	00	08	

M.D=Milli Darcy; Ø= Porosity; **P**=permeability



Figure 4-16 The negative relationship between permeability and suden reducing pH from acidic to alkaline of samples collected from 2 wells of the Zubair reservoir (North Rumaila Field).



Figure 4-17: Formation damage relationship with pH in 2 samples collected from 2 wells (one sample for each) of the Zubair reservoir (North Rumaila Field).

The results show that these core samples were damaged substantially as a result of changing the value of the pH .The effluent pH reaches a maximum of about 11 in all the experiments. Van Der Waals attractive forces and electrostatic repulsive forces between the surface and the clay particles Mohan et al, (1993) .The concentration of solution and pH value affect the repulsive forces. The surface potential of kaolinite influences by the type of cation and pH value.

Overall, the gradual increase in the value of the pH has resulted in a decrease in permeability ranged from 30 to 20% (Table 4-3), while during the sudden increase in the pH values, the permeability declined 68 to 32% (Table 4-4). From here, it is clear that the sudden increase in the pH value is more dangerous than the gradual increase on the Zubair reservoir characterization.

4-5-3 Biologically induced formation damage

Bacteria can be introduced into the formation at any time during drilling, completion, stimulation or work over operations when aqueous phase fluids are utilized. Bacteria which can be problematic in oil reservoirs fall into two types, classified as aerobic and anaerobic: Aerobic bacteria require a constant source of dissolved oxygen to survive and are usually only problematic in long-term water injection operations. Anaerobic bacteria require no dissolved oxygen and tend to be more widespread and problematic in a number of different scenarios (Bennion et al., 1992).

In the MOD, the surface water suggested to be as injection water to the Zubair oilfiled, the average of total counts of bacteria is 5.75×10^4 represented by Escherichia coli 14.5 cell/100ml, Coliform 19.5 cell/100ml and *F*. *Streptococus* 5.5×10^4 (Table 4-5).

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Table 4-5: Results of bacterial test on the MOD water suggested as injectionwater to the oilfield of the Zubair reservoir for oil production.

Sample no.	Total plate count	Escherichia coli (E. coli)	Coliform	F. Streptococus					
	Cell/100ml								
MW1	5.5 X 10 ⁴	15	20	4.5 X 10 ⁴					
MW2	6 X 10 ⁴	14	19	4.6 X 10 ⁴					
Average	5.75 X 10 ⁴	14.5	19.5	5.5 X10 ⁴					

Total coliform counts give a general indication of the sanitary condition of a water supply. It includes bacteria that are found in the soil, in water that has been influenced by surface water, and in human or animal waste. Fecal coliforms are the group of the total coliforms that are considered to be present specifically in the gut and feces of warm-blooded animals. Because the origins of fecal coliform is more specific than the origins of the more general total coliform group of bacteria, fecal coliforms are considered a more accurate indication of animal or human waste than the total coliforms. Escherichia coli (E. coli) is the major species in the fecal coliform group. E. coli is considered to be the species of coliform bacteria that is the best indicator of fecal pollution and the possible presence of pathogens. Streptococcus is a genus of spherical Gram-positive bacteria belonging to the phylum Firmicutes. Arcobacter, Halanaerobium, Marinobacter, Propionibacterium, Streptomyces, Leuconostoc, Acinetobacter, Bacillus and Streptococcus are bacterial communities in oil reservoirs counted from southern offshore Brazilian basin (Sette et al., 2007). Bacteria thrive best at a temperature range between approximately 40°C to approximately 70-800°C but can actively propagate at temperatures as low as 200°C and at temperatures of up to 135°C for very hardy strains. There are three major problems associated with the introduction and propagation of bacteria in porous media in the reservoir. These are:

It builds polymer as a biofuel upon the surface of the formation to protect themselves from fluid shear. The physical adsorption of this biofilm can cause a significant reduction in injection or productivity of a given well over an extended period of time. Oxidants such as bleach or peroxide are commonly used to both reduce and desorb the polymer and kill colonies of growing bacteria (Bennion et al., 1992). Bacteria cause corrosion problems, when colonized on metal Surface's produces H₂S. Sulfate reducing bacteria causes toxicity, a particularly the anaerobic bacteria. Metabolize elemental sulfate which may be present in naturally occurring formation water or injection waters and create toxic H₂S gas as a by-product. This H₂S gas is highly soluble in oil or water and can be potentially toxic or lethal to human beings in concentrations of greater than approximately 1000 ppm.

4-6 Mechanism of dispersion of clay particles

The dispersion term is considered for dissolved species, and it is created as a result of clay-water reaction, which yields clay hydration and swelling, or clay particle dispersion and pore plugging by movemnet with the produced or injected water. It is one of the problems facing the oil reservoirs. Bennion (1999), Bishop (1997), Thomas (1994) identified the common formation damage mechanisms in order of significance and summarized the seven formation damage mechanisms as follows:

- 1- Fluid-fluid incompatibilities.
- 2- Rock-fluid incompatibilities.
- 3- Solids invasion.

- 4- Phase trapping/blocking.
- 5- Chemical adsorption/wettability alteration.
- 6- Fines migration.
- 7- Biological activity.

What concerns us in this chapter is rock-fluid incompatibilities for example contact of potentially swelling smectite clay or deflocculatable kaolinite clay by non-equilibrium water based fluids with the potential to severely reduce permeability (Civan, 2000).

The core samples of Zubair Formation produces dispersions of native clay during core flood tests, while permeability declines. The mechanism most reasonable to clay dispersion is the growth of the small kaolinite crystals on the surfaces of other minerals such as quartz (Gray and Rex, 1966). The reason is weak the weak Van Der Waal forces in addition to the attract ion forces in solution.

Since the Zubair Formation is of Late Cretaceous and consists mainly of sandstone, siltstone, and shales, the authigenic clay (present kaolinite) is the most abundant. So, the phenomenon of dispersion of clay is clear evidence of the damage in this reservoir. Fraser (1964) described the electrical polarization measurements of Berea sandstone that provides a strong support to the concept of clay dispersion as a consequence of selective water composition changes. Electrical polarization measurements reflect the relative degree of dispersion or flocculation in clay water systems. Berea sandstone saturated with sodium chloride displays an abrupt and pronounced polarization as the salinity of the pore water is reduced to a critical concentration and severe permeability decrease for Berea sandstone occurs precisely in this concentration range (Gray and Rex, 1966). Similar effect may be present in the Zubair Formation.

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4-7 Discussion

The common formation damage mechanism that includes Fluid-fluid incompatibility, rock-fluid incompatibility, fines invasion and migration are described by Bennion (1999; Bennion and Thomas (1991) and Bishop (1997). Johnston and Beeson (1945) and Moore (1960) were among the first to investigate and report large decreases in permeability of clay-containing sandstones with decreasing salinity of the pore water. The concensus is that water sensitivity or loss of permeability of sandstones can be attributed either to clay swelling in the rock pores and clay particle migration. The degree of damage is believed to be a function of the amount of swelling montmorillonite and mixed layer clay present. Formation damage triggered by swelling of montmorillonite is now a widely recognized phenomenon by the oil industry, and is routinely considered in evaluating "problem" wells by some oil companies. In Zubair reservoir there is no swelling minerals like montmorillonite, this was revealed by the XRD and SEM.

Kaolinite group breaks apart into fine particles. The results of the present study suggest that only the finest size crystals of authigenic kaolinite are mobile. kaolinite crystals grow on the surfaces of other minerals such as quartz. These clay crystals would be held in place only by weak Van Der Waal forces and the attraction of bonds shared by doubly charged ions such as calcium. The replacement of divalent ions with monovalent ions does not cause clay dispersion until pore water salinity is reduced.

Another potentially significant damaging mechanism of permeability impairment in sandstonere reservoirs containing oils is that of clay deflocculation. Clay deflocculation represents a disruption of electrostatic bonds which are holding the clays together in a bound or flocculated state. Significantly, the principal patterns in clay migration damage have been identified by X-ray diffraction and electron microscopy as tiny hexagonal

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kaolinite crystals invaded the intergranular pores and stacked around quartz grain. These hexagons are dislodged from the pore walls in sandstones and are trapped in pore throats where they build up an internal filter cake within the sandstone. Bacteria can act to close and reduce reservoir permeability. Oxidants such as bleach or peroxide are commonly used to both reduce and desorb the polymer and kill colonies of growing bacteria that build polymer as a biofilm upon the surface of the formation to protect themselves from fluid shear (Bennion et al., 1992).

Chapter Five

Conclusions and Recommendations

5. Conclusions and recommendations

5.1 Conclusions

- 1. The Zubair Formation which is an upper sandstone member in the North Rumaila oilfield consists mainly of porous quartz filled with bitumen, and it has a small quantity of kaolinite. Regardless of the quantity of kaolinite, it has negative effects on the petrophysical specifications of the oil reservoir in case of changing the chemical environment during the process of injecting water that differs in its chemical and physical specifications from the nature of formation water. Ionic exchange occurs during the mixing MOD water or sea water with formation water of the Zubair reservoir, and thus a scale will be created that have a negative effects on the movement of fluids. Interaction between mixtures formed inside the reservoir and the surrounding rocks leads to disperse minerals. This dispersion participated in formation damage. The Zubair reservoir water has acidic pH (5.1 - 5.7). This range fits the reservoir and have a positive role on petrophysical specifications (porosity and permeability). Thus any changing in the pH value towards the alkaline state creates problems leading to poor oil production, because alkaline water precipitates the dissolved carbonates in the pores and interstitial spaces reducing the porosity and permeability.
- 2. The formation water of the Zubair reservoir is of marine origin of very high salinity, where the average of TDS is 215300 mg/l containing high concentrations of dissolved ions. Chloride is the predominant (123679 mg/l), sodium (59200 mg/l), The anions are range rCl> rSO₄> HCO₃ and the cations as rNa> Ca> Mg> K. The water type is Na-Ca- chloride. A positive correlation between chloride and each of sodium and calcium are recorded.

- 3. Water of MOD has weak alkaline pH (7.55 and 7.6) with high salinity (TDS= 26790 mg/l) compared to natural rivers due to the natural and anthropogenic sources. Chloride is also the predominant ion.
- 4. The formation water of the Zubair reservoir is incompatible with the MOD water. A scale is deposited during mixing together. The amount of precipitated salts varies depending on the mixing ratios. The precipitated salts lead to many problems in the oil reservoirs. They prevent the movement of fluid in the reservoir due to locking the pore spaces and fractures.
- 5. When mixing the water formation of the Zubair reservoir with the MW1 sample collected from the MOD, with ratio of 20 to 40% MOD, a scale of anhydrite, barite, celstite and calcite is formed with saturation index of +1.26. A scale of calcite is 20 to 90 gm/m³. When increase the quantity of the water sample (MW1) to a range of 50 to 90%, this solution (mixture) becomes compatible to the formation water of the Zubair reservoir with saturation index of -1.3 to +0.37. This range of the saturation index indicates that the mixture is in equilibrium and under saturation.
- 6. When mixing the water formation of the Zubair reservoir with the MW2 sample collected from the MOD in ratios ranging from 10 to 70% to the total volume of the mixture, a scale of the calcite, anhydrite, barite is formed with saturation index higher than +0.5. This indicates that mixture is saturated and incompatible to the Zubair formation water. The amount of precipitated calcite scale varies between 13 to 80 gm/m³, the anhydrite varies between 441 to 3462 gm/m³, the barite varies between 0.7 to 3.7 gm/m³. For obtaining a compatible water, the mixture must be formed by mixing MW1 in ratios that varies from 80 to 100%.

- 7. When mixing formation water of the Zubair reservoir with the sea water in ratios 10-90%, 20-80%, 30-70%, 40-60%, 50-50%, the mixtures are incompatible. A salt scale consists mainly of calcite (50-176 gm/m³) is formed due to the high saturation index (+1.84) which is a function of precipitation. For the purpose of obtaining compatible water, the ratio of formation water must be increase to range from 60 to 90% from the total volume of the mixture. The saturation index of these mixtures ranges between -1.55 to -0.11 indicating unsaturated solution and eventually, there is no precipitation.
- 8. The permeability declines and damage occurs due to kaolinite movement influenced by the chemical change of the properties of the solution (salinity and pH) during the use of injected mixture (solution) to the reservoir.
- 9. The gradual reduction of the concentrations of the injected mixture (solution) consisting of sodium chloride, leads to a clear reduction in the reservoir permeability and came formation damage ranging from 9 to 14.4%.
- 10. The sudden reduction of the concentration of the injected mixture (solution) leads to decline permeability and get formation damage ranged from 10.7 to 12.2.
- 11. The effect of gradual reduction of NaCl produced a decline in permeability reach to (7-27%), whereas during sudden reduction in NaCl the permeability declined with average from (35.7-64.2%). Therefore, the sudden reduction is more damage from gradual reduction of the Zubair reservoir rock.

- 12. Generally, at higher pH of the solutions injected, the amount of formation damage increases, When gradual changing of the pH value from pH = 3 to pH = 11, permeability decreases clearly, and the formation damage ranges from 18.7 to 25. During the sudden change in the pH of the solution injected, the permeability decreases sharply, and the damage reached to end by 44.28%.
- 13. The effect of gradual increase of pH produced a decline in permeability reach to (20-30%). whereas during sudden increase in pH the permeability declined with average from (32- 68%). Therefore, the sudden increase is more damage from gradual increase of the Zubair reservoir rock.
 - 14. The pH and concentration of injected solutions consisting of sodium chloride affect the permeability, but the pH effect is more pronounced and causes formation damage.
 - 15. The presence of certain bacterial species (Escherichia coli (E. coli), Coliform, F. Streptococus) in the MOD water may contribute to increased the formation damage and reduce the permeability.

5-2 Recommendations

In case of water injection, this study is recommends avoiding the use of alkaline water for secondary oil production to avoid the deposition of salts (scales), and eventually to prevent the reduction of reservoir permeability. At the same time, the water of MOD is permissible to use as injected water in specific ratio, but a little risk may be occurred.

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المستخلص

يمثل تكوين الزبير (الكريتاسي الاسفل) احد المكامن النفطية المهمة في جنوب العراق. حيث يمثل العضو الرملي الاعلى التابع لهذا التكوين في حقل الرميلة الشمالي المكمن الرئيس لأنتاج النفط. لقد تناقصت الضغوط المكمنية بتزامن مع عملية الانتاج عبر الزمن، فاصبح أسلوب حقن الماء ضروريا لغرض رفع الضغط والمحافظة على مواصفات المكمن. إعتادت شركة نفط الجنوب على استخدام مياه الكرمة لغرض عمليات الحقن، ومن المؤمل ان تستخدم مياه مجرى المصب العام. لهذا السبب، فان هذه الدراسة سلطت الضوء على هيدروجيوكيمياء المياه المصاحبة للنفط، والاضرار المتوقعة جراء حقن مياه المصب العام في مكمن الزبير.

تناولت هذه الدراسة الخصائص الفيزيائية والكيميائية للمياه المصاحبة للنفط التي تم جمعها من 6 آبار ضمن حقل الرميلة الشمالية، جنبا إلى جنب مع 2 عينة من مجرى المصب العام. صنفت المياه المصاحبة للنفط في مكمن الزبير كمياه شديدة الملوحة، تحوي 123679 ملغم/لتر من الاملاح حاصلية الذائبة الكلية، ووزن نوعي 112281 مقاس عند 15 درجة مئوية، بحرية الأصل ذات داله حامضية ضعيفة (5.1 -5.7). نوع المياه هو صوديوم- كالسيوم- كلورايد، اذا تترتب الايونات السالبة كما ياتي: كلور> كبريتات> كربونات، وتترتب الأيونات الموجبة كما ياتي: صوديوم السالبة كما ياتي المورة مين الذائبة الكلية عالية (2670). >كالسيوم > مغنيسيوم > بوتاسيوم. أما مياه مجرى المصب العام فهي مياه سطحية تكون فيها كمية الاملاح الصلبة الذائبة الكلية عالية (2670) ج.م. م. وذات داله قاعدية ضعيفة (5.5 -7.6) ، وبكتريا المكورات العقدية، والتي يمكن ان تشارك في التضرر الطبقي.

تم تشخيص المعادن الطينية في 16 عينة لبابية جمعت من الابار. أظهرت فحوصات الاشعة السينية والمجهر الالكتروني الماسح أن المعدن الاكثر وفرة هو الكوارتز، مع كمية قليلة من الكاؤلينايت المتغير عن التجوية الكيميائية لمعادن الفلدسبار. يوجد البتيومين مالئا للفراغات البينية والكسور وتكهفات الاذابة، حيث يساهم الكاؤلينايت في غلق الفتحات اثناء تحركه مع المحاليل مسببا تناقص النفاذية. وتم اجراء بعض الفحوصات البتروفيزيائية لتحديد النفاذية.

أثبتت الدراسة الحالية ان خلط المياه المكمنية مع مياه المصب العام يؤدي الى تكوين قشرة ملحية مكونة من الانهايدرايت، والبايرايت، والسلستايت والكالسايت تسبب تقليل نفاذية الصخور المكمنية، اذ تترسب في المسامات الصخرية، وتعمل على انسدادها مسببة اضرارا على المواصفات البتروفيزيائية للمكمن، حيث تمنع مرور السائل تم انجاز تجارب مختبرية على نسب خلط المياه المصاحبة للنفط مع كل من مياه مجرى المصب العام ومياه البحر، مع موديل محاكاة جيوكيميائي باستخدام البرنامج الحاسوبي فريك. لقد وجد ان افضل نسبة خلط بين المياه المصاحبة للنفط و مياه مجرى المصب هي 90 : 10%، وبين المياه المصاحبة للنفط ومياه البحر هي 60 : 40% و 30 :07% و 80 :20% و 10 :01% حيث يكون الخليط في كل نسبة تحت الإشباع وفي هذه الحالة لا توجد فرصة لترسيب الإملاح (القشرة الملحية).

تم إجراء مجموعة من التجارب المختبرية على تغيير قيم الدالة الحامضية للمحلول المحقون في العينات اللبابية. إن التغيير التدريجي في قيمة الدالة الحامضية من حامضية نحو القلوية (3، 5، 7، 9) سبب انخفاض النفاذية من 104، 103، 97، 90 ملي دارسي على التوالي، وتضرر طبقي بمقدار (18-25%) في العينات اللبابية. أما التغيير المفاجئ في الدالة الحامضية من 3 الى 11، فقد سبب انخفاض كبير في النفاذية من 72 الى 39 ملي دارسي، وبلغت نسبة التضرر الطبقي 44٪. السبب الرئيسي لهذا الضرر هو تشتت معدن الكاؤلينايت وحركته وتراكمه في أعناق المسامات.

وبغية التأكد من اسباب التضرر، خضعت العينات اللبابية الى اسلوب حقن محلول ملحي لكلوريد الصوديوم بمرحلتين ايضاً هما التخفيض التدريجي والمفاجئ لتركيز الاملاح. في حالة التخفيض التدريجي لتركيز الاملاح من 20% الى 15% الى 10% الى 5% الى 2%، لوحظ حدوث انخفاض في النفاذية من 155 الى 150 الى 148 الى 147 الى 140 ملي دارسي لعينات اللباب، وحصول تضرر طبقي تراوح ما بين 9 الى 14.4%. لكن في حال التغير المفاجئ لتركيز كلوريد الصوديوم من 20% الى 2%، فقد لوحظ حدوث انخفاض في النفاذية من 200 الى 193 ملي دارسي، والتضرر الطبقي تراوح من 10.7 الى 2.21%. تبعا لذلك، فأن الملوحة القليلة تؤدي الى حدوث تضرر بسبب نقصان النفاذية، وكلما زاد مقدار الملوحة زادت نفاذية الصخور. تبين ان الدالة الحامضية العالي (القاعدية) والملوحة القليلة تؤدي الى حدوث تضرر طبقي ونقصان في نفاذية المكمن النفطي.



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هيدروجيوكيميائية المياه المصاحبة للنفط والتضرر الطبقي لمكمن الزبير في حقل الرميلة الشمالي – جنوبي العراق

رسالة مقدمة الى كلية العلوم، جامعة بغداد وهي جزء من متطلبات نيل درجة ماجستير علوم في علم الأرض - جيوكيمياء

من

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2005

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