SCALING AND WATER PROBLEMS IN OIL AND GAS FIELDS AND REMEDIAL ACTIONS

A THESIS SUBMITTED TO THE GRADUATE
SCHOOL OF APPLIED SCIENCES
OF
NEAR EAST UNIVERSITY

By
AHMED SAMIR ABDELRAOUF ABDELAAL

In Partial Fulfillment of the Requirements for
the Degree of Masters of Science
in
Petroleum and Natural Gas Engineering

NICOSIA, 2019

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Approval of Director of Graduate School of
Applied Sciences

Prof.Dr.Nadire CAVUS

We certify this thesis is satisfactory for the award of the degree of Masters of Science in Petroleum and Natural Gas Engineering

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Finally, with all the love and respect, I would like to send special thanks to my family and friends, who have supported me all along the way, and made me the man I am today, thank you.

To my parents…

ABSTRACT

This study shows the importance of water control in oil and gas fields, discussing the problems and challenges caused by water that may be faced by petroleum and natural gas engineers and geologists in upstream oil and gas operations. Corrosion and scaling are among those problems that strike fear into the hearts of engineers.

By focusing on scaling, as its recognized as one of the major problems associated with oil and gas production, as it poses a lot of serious threats in field production, this research is an analysis of the present knowledge of the formation, removal, and prevention of scale, as it will aim to show us the causes for those problems, knowing the conditions that lead to them, when and where they occur, and how can we predict them.

Furthermore, this research guides us through the range of potential treatments and solutions. The survey comprises information that is gathered from Libyan oil fields and different publications.

Keywords: Water; oil and gas fields; scaling potential; scaling index; solutions.

ÖZET

Bu çalışma, petrol ve doğal gaz alanlarında su kontrolünün önemini göstermekte olup, akaryakıt ve gaz operasyonlarında mühendislerin karşılaştığı suyun neden olduğu sorunları ve zorlukları tartışmaktadır. Korozyon ve Taşlaşma, mühendislerin kalbine korku saldıran sorunlar arasındadır.

Taşlaşma konusu, petrol ve gaz üretimi ile ilgili en büyük sorunlardan biri olarak kabul edildiği gibi, saha üretiminde birçok ciddi tehdit oluşturduğu için, ölçeklendirmeye odaklanarak, bu sorunların nedenlerini bize bildirmeyi amaçlayacaktır. Onlara, ne zaman ve nerede gerçekleştiklerini, onları nasıl tahmin edebileceğimizi gösterebilir ve ayrıca, bu araştırma bizi potansiyel tedaviler ve çözümler yelpazesi boyunca yönlendirir. Anket, Libya petrol sahalarından ve farklı yayınlardan toplanan bilgileri içermektedir.

Anahtar Kelimeler: Su; petrol ve gaz alanları; potansiyel taşlaşma; taşlaşma indeksi; çözeltiler.

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LIST OF ABBREVIATIONS

EDTA:	Ethylenediamenetetraacetic acid (EthyleneDiameneTetraAceticAcid)
GPG:	Grams Per Gallon
HTHP:	High-Temperature, High-Pressure
LSI:	Langelier Saturation Index
PPM:	Parts Per Million
PSI:	Puckorious Scaling Index
RSI:	Ryznar Stability Index
TDS:	Total Dissolved Solids
TPHL:	Three-Phase Fluid Holdup Log
WFL:	Water Flow Logs
WOR	Water/Oil Ratio

CHAPTER 1
INTRODUCTION

1.1 Purpose

This thesis mainly aims to investigate scaling formation tendency in terms of Ryznar Stability Index (RI) against pH, Calcium Ion Concentration, Bicarbonate Ion Concentration, Total Dissolved Solid Concentration and Temperature of the reservoir waters.

Pure water is a polar inorganic compound that is transparent chemical substance that has no color, taste, nor odor; and considered as the main constituent of earth's streams, lakes, and oceans, and an essential part of all living organisms. It has a chemical formula of H_2O, meaning that it has two hydrogen atoms bonded with one oxygen atom. The type of bonds between the molecules is covalent bonds.

Earth’s surface is covered by around 71% of water, leaving only about 29% of the planet’s crust as land; water is commonly referred to the substance liquid state, but it can be found in the three states of matter, solid as in ice, and gaseous as in steam or water vapor. Different phases of water in nature are shown in Figure 1.1 (Potter and Ehlers, 2018).

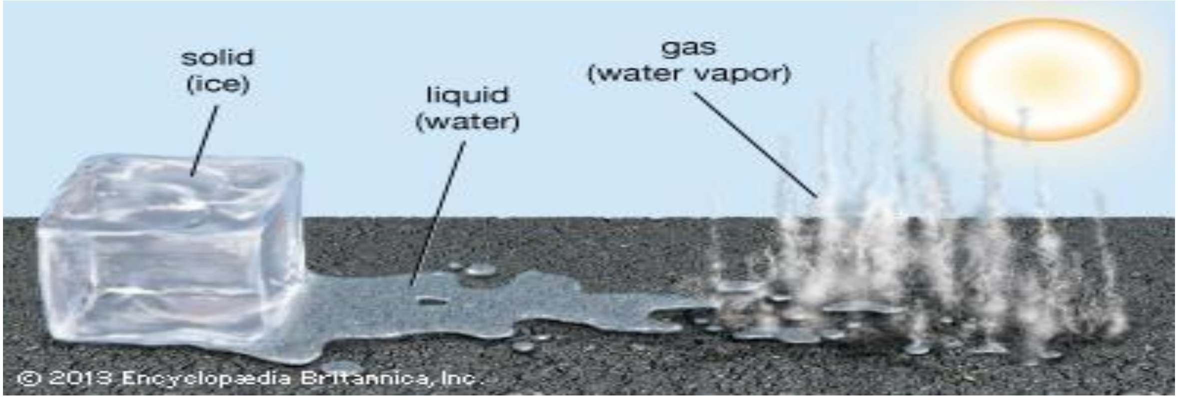


Figure 1.1: Different phases of water in nature (Potter and Ehlers, 2018)

Water on earth keeps moving continuously through the water cycle which involves the exchange of energy leading to change in temperatures. Water is also known as the universal solvent, because it has the ability to dissolve variety of different substances.

1.2 Physical Properties of Water:

Water is primarily a liquid under standard conditions, unlike when hydrogen bonds with other gases of the oxygen family in the periodic table, like nitrogen, phosphorus, sulfur, fluorine, and chlorine forming gases under standard conditions; this phenomena happens because of the high electronegativity of oxygen (3.44) compared to the surrounding elements, except fluorine (3.98) (Pauling, 1988).

Due to repulsive forces, an angle of 104.5^o is formed between the two hydrogen atoms as shown in Figure 1.2, causing nonlinearity to the water molecule, or bent (Schwartz et al., 1997). Due to the electronegative difference between oxygen and hydrogen (2.2), a negative partial charge generates near the oxygen and a positive partial charge generates near the hydrogen; making it easier for a water molecule to be attracted to other molecules of water and form hydrogen bonds; water can also be attracted to other polar molecules and ions. In contrast, non-polar molecules, such as oil and fats, don’t interact well with water.

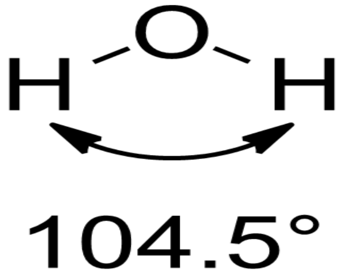


Figure 1.2: Angle between hydrogen atoms in water molecule

At high temperatures the hydrogen bonds between the water molecules break completely causing the molecules to escape into the air as gas (water vapor or steam); on the other hand, at low temperatures the molecules of water forms a crystalline structure maintained by the hydrogen bonds between them.

1.3 Chemical Properties of Water:

Hydrogen bonding between the water molecules is the reason of water's high specific heat (4.184 Joules), compared to other substances such as Zinc (0.387 Joules), Lead (0.128 Joules), or Aluminum (0.900 Joules) (Specific Heat Capacity Table 2006); as a result, the water takes a longer time to heat and a longer time to cool compared to here mentioned substances (Shapley, 2011). Due to this resistance to sudden changes in temperatures, the water is considered as an excellent habitat.

The liquid form of water has an unusual high boiling point temperature, a value of 100^{o}C. Compared to Ethanol 78.37^{o}C, Methanol 64.7^{o}C. Because of the hydrogen bonding network between the water molecules, huge energy amount is needed to evaporate one gram of liquid water into water vapor, this amount of required energy is called heat of vaporization. Heat of vaporization of water is 40.65 kJ/mol. Ethanol 38.60 kJ/mol, Methanol 35.20 kJ/mol.

Water's high surface tension (water cohesion) is another property caused by the hydrogen bonds between the water molecules; this property gives the ability for denser substances than water to float on the water's surface. Adhesion can also be observed when we place capillary tubes in a glass of water, as the water climbs up the tube, regardless of the gravity effect. This type of adhesion is called capillary action. In the liquid state small percentage of the water molecules turns into equal amounts of hydrogen (H^+) and hydroxide (OH^-) ions; maintain the liquid neutral at stable pH equal to 7.

Unlike most other substances, water molecules are pushed farther apart when the temperature decreases below 4^{o}C, causing lower density of water solid form than its liquid form, because of its less dense, ice floats on the surface of liquid water. Highest water density is found at 4^{o}C as shown in Table 1.1 (Shapley, 2011).

Table 1.1: Density of liquid water at different temperatures (Shapley, 2011)

Temp (°C)	**Density (kg/m^3)**
+100	958.4
+80	971.8
+60	983.2
+40	992.2
+30	995.6502
+25	997.0479
+22	997.7735
+20	998.2071
+15	999.1026
+10	999.7026
+4	999.9720
0	999.8395
-10	998.117
-20	993.547
-30	983.854

The values below 0 °C refer to supercooled water

CHAPTER 2

BASIC CONCEPTS AND LITERATURE SURVEY

Water is used widely by humans in everyday duties and different purposes, including agriculture, transportation, cooking, and industrial purposes.

2.1 Water in the Industry

In oil and gas industry, water is also used in different purposes, and it affects all stages of oilfield life, starting from exploration stage, passing through the development stage and the production stage; such as pressure maintenance, drilling fluids, hydraulic fracturing, and cooling for power generation, etc. Figure 2.1 shows the continuous movement and flow of water through a reservoir, into production tubing and surface-processing facilities, where it end up being extracted for disposal or injected again into the reservoir for maintaining the reservoir pressure, in a process called the ‘water cycle’. Oil companies aim to improve their production efficiency, and controlling the water is proven to be a fast and a low cost route compared to other ways used to reduce operating costs and improve hydrocarbon production simultaneously.

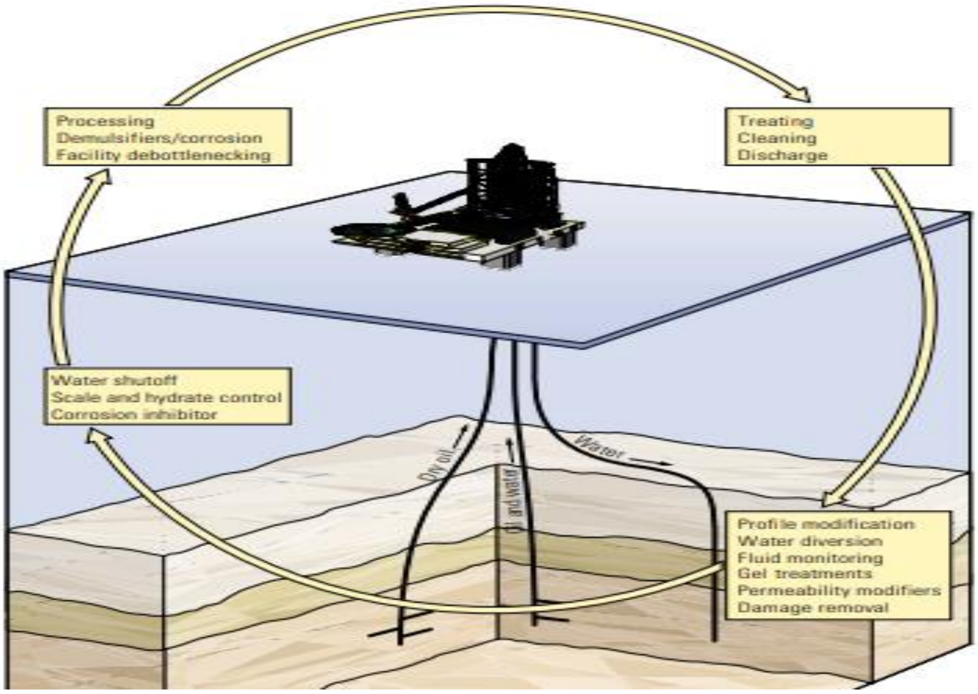


Figure 2.1: Water cycle in oil industry (Bailey et al., 2000)

2.2 Water in the Reservoir

Water is also found naturally in petroleum reservoirs (Formation Water), as those reservoirs mostly contain hydrocarbons, such as crude oil or natural gas, and water. Possible formation layers of petroleum reservoirs are shown in Figure 2.2 (Fathallah, 2016). Understanding the formation water chemistry leads to an improved perception of the reservoir and how it can be approached. During production this water might come to the surface as a byproduct alongside the oil and gas, this water is called produced water. Produced water also includes water injected into the formation and any additives included during drilling, production, or stimulation. Significant volumes of water produced usually accompany the conventional production of oil, and gas.

Nowadays, oil companies averagly produce three barrels of water for each barrel of oil from their depleting reservoirs.

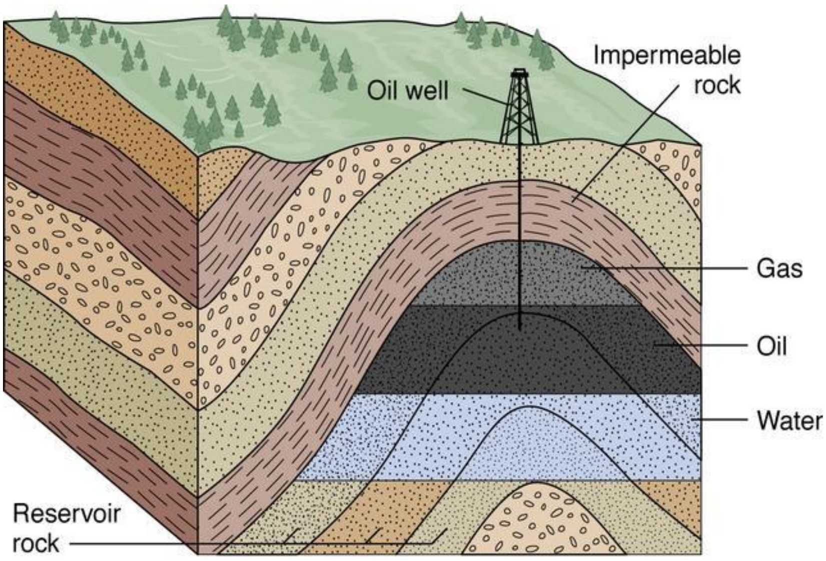


Figure 2.2: Petroleum reservoir possible formation layers (Fathallah, 2016)

2.3 Water Sources and Water/Oil Ratio (WOR)

Water is found in all oil fields and is the most abundant fluid on the field. When it comes to oil production, the difference between sweeping, good (acceptable) and bad (excess) water is a key issue.

Water/Oil Ratio (WOR) is the ratio of water produced along with the production of the hydrocarbons. As most wells mature, the WOR increases with production due to the increase of water quantities. In the long run, the expense of dealing with the water approaches the value of oil being produced and the WOR 'economic limit'. Water control cause the reduction in the amounts of water produced enabling continued economic oil production and resulting in increased economic recovery in the well. The water control effect on Water/Oil Ratio and its economic limit is shown in Figure 2.3 (Bailey et al., 2000).

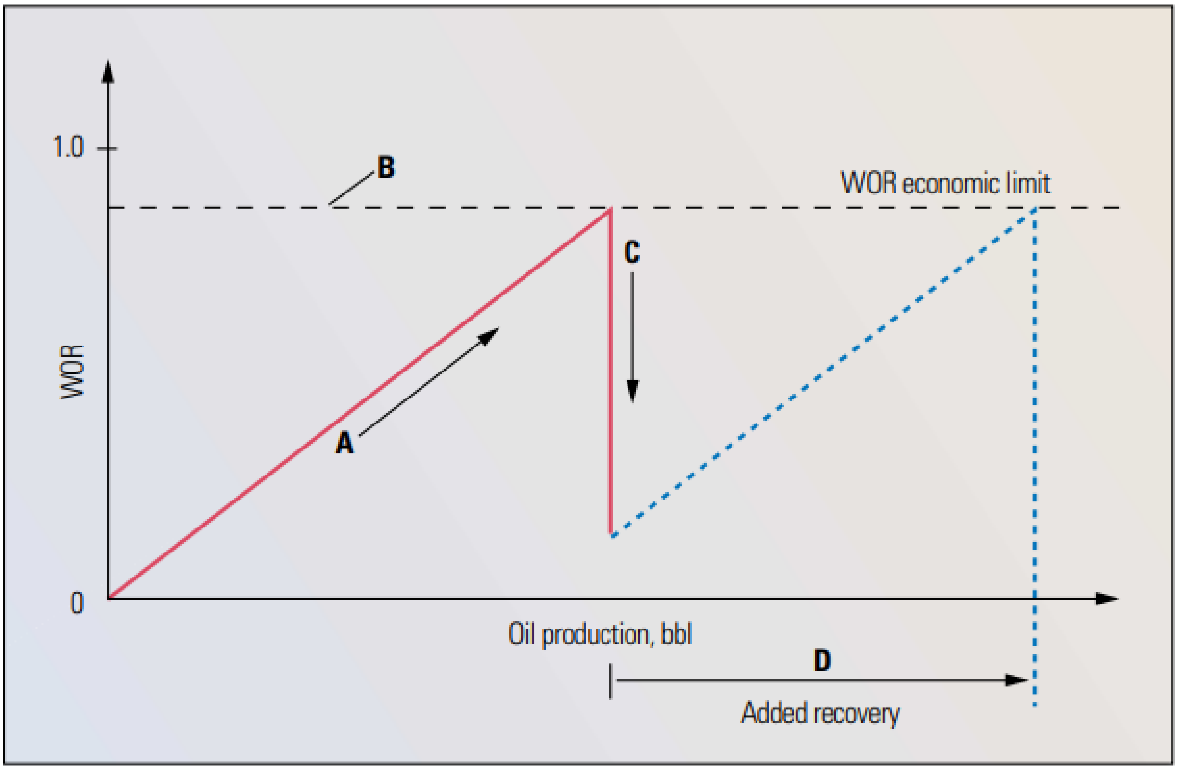


Figure 2.3: Water control effect on Water/Oil Ratio (WOR) and it's economic limit (Bailey et al., 2000)

In Figure 2.3, "A", Shows the WOR is increasing as the oil production is increasing. "B", Shows the WOR economic limit where the oil produced by the well is no longer economically sufficient to pay for the handling of the produced water. "C", shows that by water controlling the water produced is decreased causing the reduction in the WOR and getting it under the economic limit. "D", Shows the incremental oil produced and the added economic recovery in the well caused by the control of water.

Sweeping water comes either from an injection well or from an active aquifer that helps to sweep oil out of the reservoir. Managing this water is a vital part of reservoir management and can be a deciding factor in well production efficiency.

Good water is the water produced into the wellbore accompanied with oil and flowing at a rate below the water/oil ratio (WOR) economic limit. Bad water is the water produced in the wellbore and does not produce oil or produces insufficient oil to cover the cost of water handling, where it flows at a rate above the WOR economic limit.

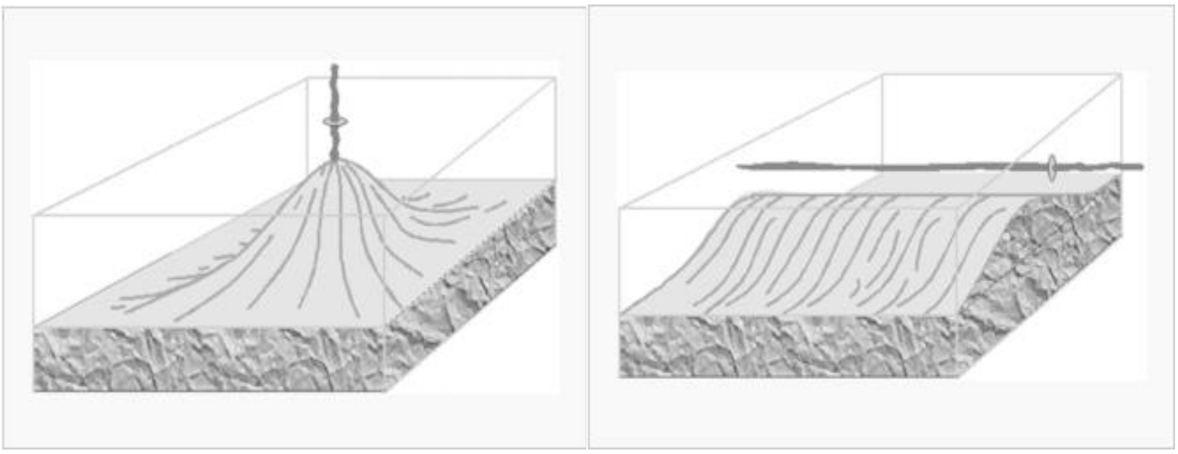
CHAPTER 3

DESCRIPTION OF PROBLEM AND METHODS OF SOLUTION

Water is often considered as essential evil in mature fields, as primary production and secondary recovery is driven and assisted by water, the excess water produced, cause problems such as water-in-oil emulsion, scale, and corrosion, representing a significant liability and cost to the oil and gas producer.

3.1 Coning

Water coning is a production problem (mainly due to higher daily production rate than the daily optimum production rate) in which the bottom water infiltrates or breakthrough the perforation zone in the near-wellbore area replacing all or part of the hydrocarbon production, causing reduction in oil production. Once breakthrough has occurred the problem tends to worsen as the well suffers increasing water cut. The term coning is used because of the inverted cone shape that appears in the vertical wells as shown in Figure 3.1. The cone becomes more of a crest in a horizontal well, but the phenomenon is still commonly called coning.



(a) **(b)**

Figure 3.1: (a) Coning in a vertical well, (b) Coning in a horizontal well

The maximum oil production rate without producing water through a cone, called the critical coning rate, is often too low to be economic. Most coning prediction methods predict a ‘critical rate’ at which a stable cone from the fluid contact to the nearest perforations can exist.

The theory is that, the cone will not reach perforations and the well will produce the desired single phase, at rates below the critical rate. But when the rates are equal to or greater than the critical rate, the second fluid will eventually be produced and increases in amount over time. However, these critical rates based theories do not predict when breakthrough will take place nor do they predict the WOR after the break through. Other theories predict these time behaviors, but due to the simplifying assumptions, the accuracy is limited.

Coning can be affected by different variables such as, the density differences between the water and oil, the distances from contacts to perforations, the fluid viscosities and relative permeability, the vertical and horizontal permeability. The tendency to cone is quite dependent on some of these variables and insensitive to other variables. Coning can be dealt with by shutting off the flooded perforations and re-perforating higher in the reservoir or, in extreme cases, by drilling a new well (Kuchuk and Sengul, 1999).

3.2 Casing, Tubing and Packer Leaks

When leaking occurs in casing, tubing or packer, hydrocarbon fluids may be released into zones where they cannot be retrieved or water enters the production string from the non-oil-productive zones, causing a negative impact on the well production, and could damage the productive zone depending on the severity of the leakage. Most of the leaks reported were an outcome of poor cementing and/or long exposure to corrosive gases. Leaking detection and applying solutions are highly dependent on the well configuration.

These problems may be sufficiently diagnosed by using the basic production logs such as temperature, spinner, and fluid density. In more complex wells, Water Flow Logs (WFL), or multiphase fluid logging such as the three-phase fluid holdup log (TPHL) can be valuable. Solutions for such problems usually consist of squeezing shut-off fluids and mechanical shut-off using plugs, cement and packers.

3.3 Corrosion

Corrosion by water in the oil industry such as in pipelines, refineries, and petrochemical plants is a common naturally occurring event due to the impurity of the water (containing hardness salts, chlorides, and dissolved gases) causing a lot of economic loss; produced water or injected water for secondary recovery can cause severe corrosion for completion strings.

Since it is almost impossible to completely prevent corrosion, decreasing and controlling the rate of corrosion is becoming the most economical solution. By recognizing the occurrence of corrosion, and by understanding its mechanisms, corrosion engineers may begin to get rid of corrosion by different and various ways; material selection, the use of corrosion inhibitors, painting, and cathodic protection are the most commonly used methods.

3.3 Hard Water and Scaling

Hard water term is used to illustrate high mineral content water which is usually created when water percolates through limestone and chalk deposits which are mainly composed of calcium and magnesium carbonates.

Water hardness is determined by the concentration of multivalent cations in the water; which are metal complexes with a positive charge greater than +1. Common cations found in hard water include Ca^{+2} and Mg^{+2}, usually entering the water supply by leaching from minerals within an aquifer. Figure 3.2 shows the increase of the water hardness as the concentration of the multivalent cations is increased.

Figure 3.2: Concentration of multivalent cations in water

3.4 Scaling in Oil and Gas Field

Scale is the coating or the deposit formed on the surface of a metal, rock, or other material. In oil and gas field, scale formation is a familiar problem for the oilfield engineer; as water containing dissolved ions will always be present in natural gas reservoirs, most scales formed in oil fields are developed by either direct precipitation from naturally occurring water found in the rocks of the reservoir, or due to produced water becoming oversaturated with scaling components; causing clogging of the wellbore and prevention of the fluid flow which leads to the loss of millions of dollars every year in lost production. Figure 3.3 shows the difference between a tube with and without scale deposits (Carbtree et al., 1999).

Figure 3.3: Tube with and without scale deposition (Carbtree et al., 1999)

Scale can also be developed in the formation pores, causing reduction in the formation porosity and permeability as shown in Figure 3.4 (Carbtree et al., 1999), this phenomena occures when incompatible waters (in terms of their ionic molecule contents) get in touch in the reservoir which happens in different cases (water displacement as a secondary recovery application, any water influx through natural fractures, well stimulation operations such as acidizing or hydraulic fracturing, Etc.), solid precipitation and scale formation occur.

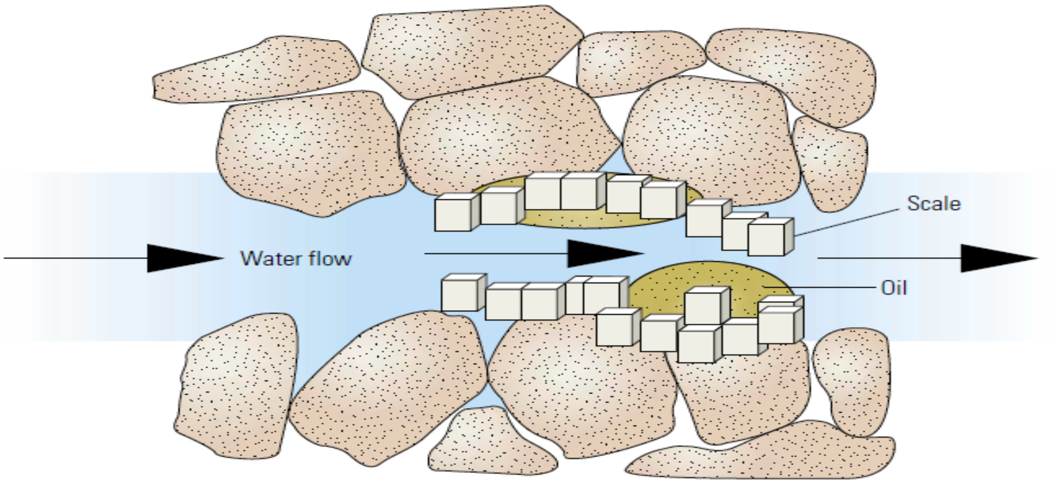


Figure 3.4: Scale deposition in the formation results in a loss of permeability (Carbtree et al., 1999)

Scaling can cause several production problems; which include the increase of the surface roughness in the production system, and reduction in the flowing area for hydrocarbons. Therefore, the driving pressure rises and production decreases. Also causes limited access to the lower wellbore, and in extreme cases, tubing can bridge-off if the scale is able to fill it as shown in Figure 3.5 (Kuchuk and Sengul 1999).

Kuchuk and Sengul (1999), show that the most common oilfield scales are:

- Calcium carbonate ($CaCO_3$) – calcite or aragonite.
- Cacium sulfate ($CaSO_4$) – anhydrite, gypsum, hemihydrate.
- Strontium sulfate ($SrSO_4$) – celesite.
- Barium sulfate ($BaSO_4$) – barite.

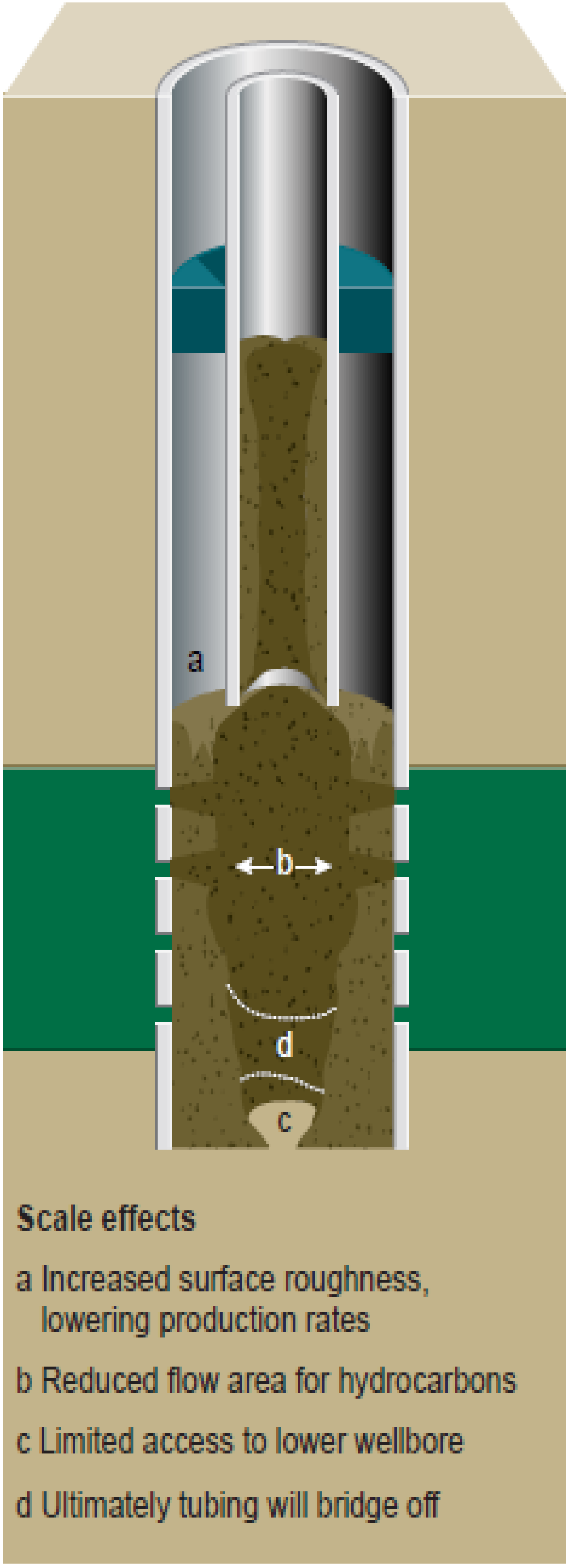


Figure 3.5: Scale effects in tube, which may lead to bridge-off in extreme cases (Kuchuk and Sengul, 1999)

3.5 Sources of Scale

Water has the main and the primary contribution if the oilfield scale, as the sole potential of creation of scale is water production. For many materials, water is considered as a good solvent and can contain large quantities of scaling minerals. Obtained in the natural environment by the interaction with mineral phases, dissolved components are consisted in all natural waters.

Deep water linked with gas or oil is enhanced with ions by sedimentary mineral alteration. When any natural fluid's state is disturbed to a point where the solubility limit is exceeded for one or more components, scale begins to form and build-up.

3.6 Forming Scale

Scales typically form when:

- High bottom-hole pressure drops.
- Water with high concentrations of minerals breaks through.
- Fluid rising in the tubing as pressure fall.
- Minerals come out of solution in the tubing.

But those are only driving force for scale formation. For the purpose of generating a scale it shall be grown from a solution. In a process referred to as homogeneous nucleation shown in Figure 3.6, the establishment of unbalanced clusters of atoms is the first progress in a saturated fluid. Small seed crystals that are formed by the atom clusters (called eutectic point), consequently raise by ions adsorbing onto deficiencies on the crystal surfaces enlarging the size of crystal. The energy of the crystal growth of seed is determined by the decrease in the surface area free energy of the crystal, which quickly decreases with an increase in radius beyond the critical radius, hence implying that large crystals favor further development of crystals and that small seed crystals can also be re-dissolved. Which means increase in the growth of scale deposits will be encouraged by a given large enough degree of supersaturation (Carbtree et al., 1999).

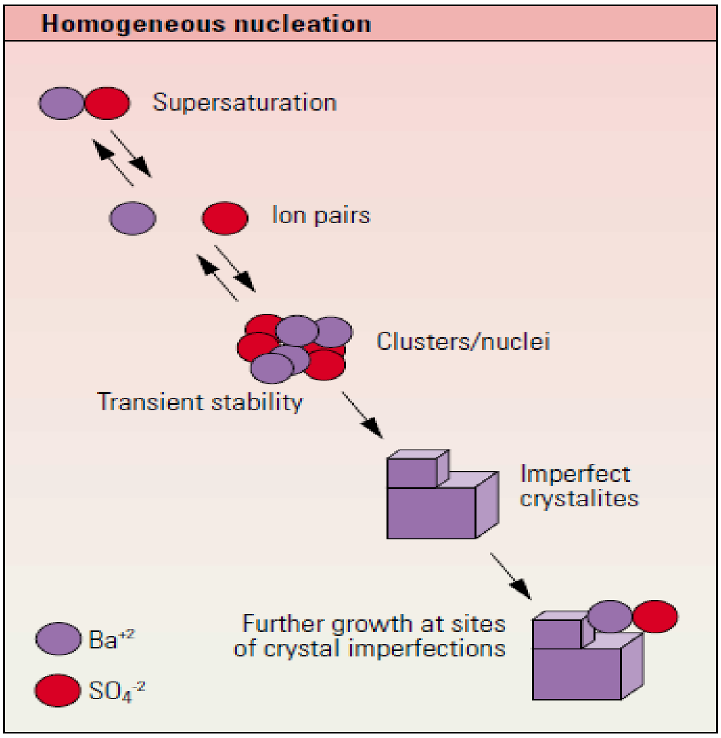


Figure 3.6: Homogeneous nucleation
(Carbtree et al., 1999)

Figure 3.7 displays the heterogeneous nucleation process, crystal could be grown on a pre-existing fluid-boundary surface that the mentioned process. The positions of heterogeneous nucleation consist surface deficiencies for instance, perforations in production liners or pipe surface roughness, or even joints and seams in tubing and pipelines.

Heterogeneous nucleation sites include surface deficiencies such as pipe surface roughness or perforations in production liners, seams and joints may occur in tubing and pipelines. Crabtree et al. (1999), by the means of the comprehension of the nucleation phenomena, scale inhibitors that utilized chemicals specifically designed to envenom the nucleation and scale creation growth stages and decrease the scale creation rate approximately near zero.

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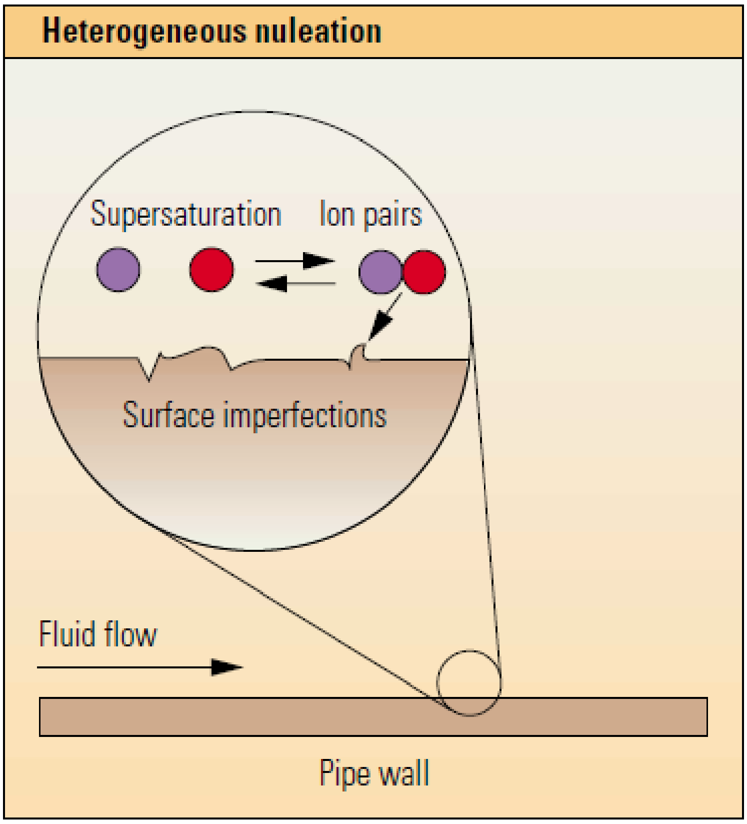


Figure 3.7: Heterogeneous nucleation
(Carbtree et al., 1999)

3.7 Common Scaling Scenarios

According to Carbtree et al. (1999), there are four ordinary cases that are classically come across hydrocarbon production that increase scale formation, listed as following:

a) *Incompatible mixing:* The scale formation could take place by the mixing of the incompatible injection and formation waters. Throughout minor and superior-recovery operations, seawater, which characteristically contains in SO_4^{-2} anions, is repeatedly inserted into reservoirs, resulting to mixing of fluid in the near-wellbore area with the creation waters containing Ca^{+2} and Ba^{+2}divalent cations, that usually manufactures new fluids with combined ion concentrations that are greater the solubility limits for sulfate minerals. Sandstone formations are formed Strontium Sulfate [$SrSO_4$] and Barium Sulfate [$BaSO_4$] scales form, for limestone formations are formed by Calcium Sulfate [$CaSO_4$] and Magnesium Sulfate [$MgSO_4$] scale.

However, it is difficult to eliminate chemically and unbearable to eliminate mechanically these scales buildup in the formation. Through tubing Incompatible water mixing could be occurred, creating scales that are reachable to both mechanical and chemical removal.

b) *Auto-scaling:* Due to the changes in temperature and pressure the reservoir fluid faces during production, its composition can be taken beyond the solubility limit, causing minerals to hurry as scale, this phenomenon is referred to self-scaling or auto-scaling. Carbonate scales could also hurry from produced fluid comprising acid gases where the pressure drop throughout production outgasses the fluid resulting an increase in pH above 7 out of 14. These carbonate depositions could be extended from the near-wellbore area, along tubing and into the equipment surface.

c) Evaporation-induced scale: The simultaneous production of hydrocarbon gas and formation of brine could also associate scale deposition. The volume of the hydrocarbon gas expands and the still hot brine phase evaporates as a result of the decrease in the hydrostatic pressure in the production tubular, resulting in dissolved ions being concentrated in excess of mineral solubility in the remaining water, which is an extremely common reason of halite scaling in high-temperature, high-pressure (HTHP) wells, however it is possible for other scales to form this way.

d) Gas flood: Operators use CO_2 gas to flood the formation for secondary recovery which could lead to formation of scale, where water comprising CO_2 develops acidic and decreases scaling potential at the beginning, but additionally it is going to dissolve calcite in the formation, subsequent droplets in pressure of the formation surrounding a producing well be able to make CO_2 to running away of solution which will lead to carbonate scale to precipitate in the perforations and in the formation pores near the wellbore. This formed scale is going to result in a further reduction in pressure and even more precipitation in the near-wellbore environment.

3.8 Scaling at Injection Facilities

The most common formed scale in seawater injection facilities is calcium carbonate, as the water passes through heat exchangers or down the injection well. During the water injection, even marginal temperature changes and turbulence in passing through the injection pumps can initiate scaling; so control measures are required at all times (Kuchuk and Sengul, 1999).

3.9 Scaling in the Near-Wellbore area

Reservoir temperature and pressure on the injection water, and mixing of injection and formation waters, are the main consideration in the effect on the near-wellbore area; both can lead to the blocking of the pore and reduction in permeability by causing scale formation, which are typically carbonate or sulfate (Kuchuk and Sengul, 1999).

3.10 Scaling of Oil Production Well and Facilities

Produced waters in most fields are mixture of the true formation water and the injection water that has broken through. The relative proportion of these waters is a crucial factor in determining the likelihood of scaling.

During production, the pure formation water or the formation/injection water mixture will be subjected to large temperature and pressure changes, turbulence and gas breakout. These dramatic physical changes are the trigger for scale deposition in production systems (Kuchuk and Sengul, 1999).

Scale development can be predicted by various predictive models, which large numbers of them are computerized. This predictive work requires accurate water samples, which means collecting individual downhole, flowlines, and wellhead samples. It’s extremely difficult to obtain representative sample of water in any sequence due to the continuous change of the composition of water with depth, and changes laterally within a single aquifer layer.

Various parameters of water composition such as pH, carbon dioxide and bicarbonate content are crucial for accurate prediction of scale.

3.11 Identifying Scale

The first step in designing a cost-effective remediation program is identifying the location and composition of the scale deposit. The increase in the amounts of produced water is often indicative of potential problems of scale, particularly if the oil production is simultaneously reduced. Normally, the produced water chemistry, specially its dissolved ion content is observed and tracked by operators. Significant changes in the concentrations of scaling ions that synchronize with the increase in water cut and reduction in oil production can indicate that injection water has broken through and scale is beginning to form.

Since scale can form and build-up in wells within 24 hours or less, early identification, warning and prediction of scale forming potential would be valuable to operators. Nowadays, operators use chemical methods that are available to predict the nature and extent of scaling from detailed fluid conditions. All rely on basic input data such as pressure, temperature, and elemental-concentration analysis. Many scale-prediction programs which cover the range from spreadsheet models to highly developed geo-chemical models designed to simulate fluid and chemical transport in porous formations, are now available as public domain software.

3.12 Scale Detection Methods

Garba and Sulaiman (2015), reported few methods of scale detection including X-rays, where the radium Ra^{226} radioactive element precipitated with barium sulfate scale; water chemistry, where water is continuously tracked and sampled; and chemical modeling, where scaling potential is detected by using the history of thermodynamics principle and geo-chemical data of a field, depending on parameters such as ions concentration, pressure, and temperature.

Scale can also be indicated and predicted by using one of the most commonly used indicators which include the Langelier Saturation Index (LSI), the Ryznar Stability Index (RSI), and the Puckorious Scaling Index (PSI). These predictive tools were designed to indicate calcium carbonate scale only, as they are not suitable for indicating calcium sulfate, calcium phosphate, or magnesium silicate scale (Cavano, 2005).

3.13 Ryznar Stability Index

The Ryznar index is a tool that is used to predict the likelihood of calcium carbonate scale to form in a given sample of water. It was created by John Ryznar in the 1940s in an attempt to provide the scientific community with a more accurate predictor of calcium carbonate scaling. The Ryznar Stability Index formula is:

$$\mathrm{RI} = 2(\mathrm{pH_s}) - \mathrm{pH} \tag{3.1}$$

Where, $\mathrm{pH_s}$ is the saturation pH (pH of water when it is saturated in calcium carbonate). For determining the RSI value, firstly we must determine the measures of pH and $\mathrm{pH_s}$; those values are obtained by the equation:

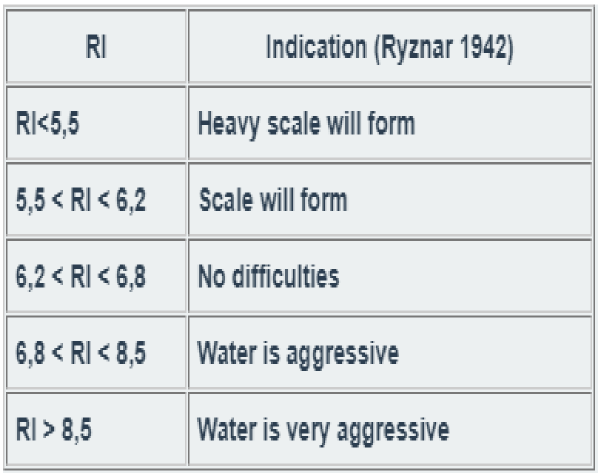
$$\mathrm{pH_s} = [(9.3 + A + B) - (C + D)] \tag{3.2}$$

Where, "A" is the total dissolved solids in mg/l, "B" is temperature in °C,
"C" and "D" are calcium carbonate Hardness and alkalinity in mg/l $CaCO_3$ respectively.

- $A = (\text{Log}_{10}[\text{TDS}] - 1)/10$
- $B = [-13.12 \times \text{Log}_{10}(°\text{C} + 273)] + 34.55$
- $C = \text{Log}_{10}[\text{Ca}^{+2} \text{ as } \text{CaCO}_3] - 0.4$
- $D = \text{Log}_{10}[\text{alkalinity as } \text{CaCO}_3]$

After obtaining pH and pH_s values from equation (3.2), we can obtain the value of RSI by substituting in equation (3.1).

The Ryznar index is logarithmic; where the neutral zone of the Ryznar index is around the numerical value 6. Where, any value less than 6 indicates that the water is likely to form a calcium carbonate scale; and a value more than the number 6 indicates that the water will be acidic and will dissolve calcium carbonate formations.



RI	Indication (Ryznar 1942)
RI<5,5	Heavy scale will form
5,5 < RI < 6,2	Scale will form
6,2 < RI < 6,8	No difficulties
6,8 < RI < 8,5	Water is aggressive
RI > 8,5	Water is very aggressive

Figure 3.8: Ryznar Stability Index, 1942 (lenntech calculators).

Ryznar Stability Index is affected by 5 main factors which are:
1) pH value.
2) Total dissolved solids.
3) Calcium ions (Ca^{+2}).
4) Bicarbonate ions (HCO_3^-).
5) Temperature.

By using the Ryznar Stability Index calculation, it’s found that the pH value, calcium and bicarbonate ion, and the temperature, have an inverse proportion with the Ryznar Index value, as per any increase in any of those parameter, Ryznar Index will decrease indicating more scale formation potential; and the total dissolved solids is directly proportional with the Ryznar Index, as the value of Ryznar Index increase by the increase in the TDS, indicating more corrosion potential and less scaling.

Once the water has been sampled, examined and the scale predictions made, the reservoir engineer must choose the most effective way for treatment. The first step to design a cost-effective remediation program is to make accurate diagnosis of water and identify the composition and location of the scale deposit. Scale-removal techniques should be fast, safe, non-damaging, and effective in avoiding re-precipitation, in the well-bore, tubing or formation environment.

3.14 Fluid Modifications

As discussed earlier; seawater, which is enriched with SO_4^{-2} anions, is often injected into reservoirs for improved oil recovery. The presence of these ions signifies scale potential. Thus, to remove these sulfate ions, some modifications must be made thereby minimizing and mitigating the sulfate scale formation.

3.15 Scale Removal

Best technique for scale removing depends on the type, quantity, and the physical composition or texture of scale; bad decision of elimination procedure could improve quick scale recurrence. In tubulars, texture and the strength of the scale play important roles in selecting of the elimination procedure. Textures and strengths differ from delicate, crystals with great micro-porosity or brittle whiskers, to rock-like, low-permeability, low-porosity layers.

Removal techniques include:

a) *Chemical Techniques:* Chemical scale elimination systems are frequently the least expensive, and the first approach, particularly where conventional mechanical elimination approaches are unproductive or expensive to organize (Carbtree et al., 1999). For instance, carbonate minerals are extremely soluble in hydrochloric acid and consequently be able to easily dissolve. Chemical techniques depend basically on scale surface area that the chemical has access to, where the important factor in the elimination process speed and effectiveness is surface-area-to-mass ratio. In tubing, scales have minor external area for a huge entire deposited mass, making chemical treatment not a practical removal method. Although hydrochloric acid is an excellent choice and frequently the first approach for handling the calcium carbonate scale, it has a downside, where the spent acid solutions of scale by-products are good initiators for the formation of scale. As an improvement in the scale chemical removal techniques, Ethylenediamenetetraacetic (EDTA) was an early candidate to be a chemical that dissolve and chelate calcium carbonate, breaking the re-precipitation cycle, and is still utilized today in various forms. Treatment with EDTA is slower and more expensive than hydrochloric acid, but they play well on deposits requiring chemical approach. Schlumberger lately established the U105, an upgraded EDTA-based scale dissolver, as a cost operative dissolver specifically designed for calcium carbonate, nevertheless is also effective in contrast to iron carbonate and iron oxide scales (Carbtree et al., 1999).

b) *Conventional Mechanical Methods:* Mechanical technique offers wide range of tools which most of them have a limited range of applicability depending on the area of scale deposits and the well position. Mechanical approaches are amongst the most successful techniques for tubular scale elimination (Jonson et al, 1998). Table 3.1 shows some of the mechanical scale-removal techniques.

Table 3.1: Mechanical scale-removal techniques (Carbtree et al., 1999)

Tool	**Description**	**Clean hard bridges**	**Other advantages**	**Other disadvantages**
Positive displacement motor and mill	Fluid-powered ‘Moineau’ motor and mill. Mill removes deposits by grinding.	Yes. Clean rate may be very slow.	Positive surface indication of cleaning. Small cuttings make hole cleaning easier.	Motor stator and mill are expensive expendables. ~300°F [150°C] limit. Not compatible with scale dissolvers. Mill can damage tubulars.
Impact hammer	Fluid powered percussion hammer. High shock forces shatter brittle deposits.	Yes. Clean rate may be very slow.	Positive surface indication of cleaning. Simple, robust tool.	Large cutting size makes hole cleaning more difficult. Not compatible with scale dissolvers.

c) *Explosive Techniques:* Explosives were one of the earliest approaches for scale removing. Scale is removed using the high-energy impact provided by the explosives, but regularly, this technique damage tubes and cement.

3.16 Scale Prevention

The cost to eliminate scale from one well could be reached to $2.5M (Carbtree et al., 1999). While in medical practice, prevention is better than cure, keeping the well healthy and preventing scale in the first place is more efficient and less costly than treating the scale. In most cases, the preferred method for preventing scale and maintaining well productivity is through the chemical inhibition. Most scale inhibitors are phosphate compounds; these phosphate chemicals such as inorganic polyphosphates, organic phosphate esters and organic amino-phosphates diminish and reduce scale deposition by uniting crystal dispersion and stabilization of scale. Dispersion stops minor seed crystals of scale from abiding to tube walls and other crystal particles, where stabilization chemically modifies the deposited scale structure, block extra crystal attachment as shown in Figure 3.9 (Carbtree et al., 1999).

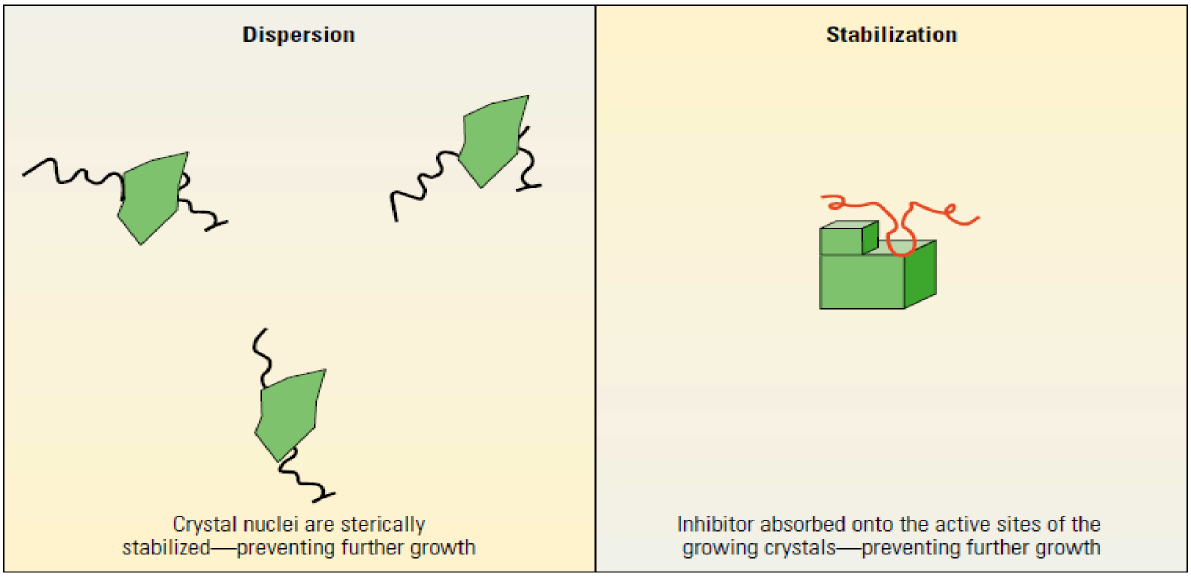


Figure 3.9: Dispersion and Stabilization (Carbtree et al., 1999)

CHAPTER 4
SCALE CASE STUDY

By using qualitative research method, different case studies have been collected to show how several oil fields indicate and solve their scaling problem.

4.1 Abu Dhabi’s Bu Hasa Field

The scaling problem in Abu Dhabi’s Bu Hasa Field was discussed by (Kuchuk and Sengul, 1999) as it was first identified in 1989. The severity of the problem ranged from complete plugging of the tubing string or surface facilities, to build up in the tubing or subsurface safety equipment. In most wells, analysis showed that the scale was mainly calcium carbonate, which could be dissolved by acid treatment. The response the problem included:

- Trials to clear the obstruction using wireline tools.
- Acid used 15% hydrochloric acid plus additives.

The wireline trials had little success in clearing the problem. The acid wash, though more successful in short term, could not prevent recurrence of scaling in some treated strings over a relatively short period. More than 40 wells in the field were found to have some form of scaling problem.

Scaling problems in Bu Hasa Field caused by the deteriorating quality of injected water and permeability reductions. Deteriorating water quality led to scaling, sludge deposition, erosion and loss of water-injection potential.

Water samples were collected from different locations from the oil filed, and their analysis are shown in table 4.1.

Table 4.1: Water analysis from Bu Hasa Field (Kuchuk and Sengul, 1999)

	Aquifers	**Wells**	**Surface facility**	**Injection well**	**Reservoir**	**Production well**	**Surface facility**	**Disposal Well**
Flow media	Porous	Pipe	Pipe	Pipe	Porous	Porous		Pipe
Flow type	Single	Single	Single	Single	Multiphase	Multiphase	Multiphase	Multiphase
Brine	Single	UER + SIMS	Mixed	Mixed	Mixed	Mixed	Mixed	Mixed
No. of mix brines	1		2	2	3	3	>4	>4
Temperature, °C	64	65						
Pressure, psig	1900			1820			3	
pH	5.7	5.55		6.4	6.3	6.4	6.4	6.5
Specific gravity	1.13	1.142		1.1318	1.13	1.1304	1.0732	1.0631
GWR, scf/bbl	1.35	1.182						
Bubble point, psig	99							
Ionic species, mg/l								
Carbon dioxide, CO_2	649	636		535		268	348	273
Hydrogen sulfide, H_2S	229	160		238	45	142	31	19
Sodium, Na	57,613	60,793		58,701	52,294	55,498	34,442	22,429
Calcium, Ca	14,0.33	16,066		13,707	15,529	15,168	7375	6493
Magnesium, Mg	3024	3031		3306	1256	2281	1750	3161
Barium, Ba	1	1				0		
Strontium, Sr	546	599			738	369		
Iron, Fe	1	4		0.7	1160		15.5	13.2
Chloride, Cl	122,028	130,605		124,110	112,597	118,354	70,920	54,963
Bicarbonate, HCO_3	244	207		232	265	249	134	161
Sulphate, SO_4	420	399		372	659	516	441	385
TDS	159,825	211,103		200,428	184,543	192,486	115,062	87,592
Analysis zone	A	B	C	D	E	F	G	H

The field study at Bu Hasa used a computer model to predict calcium carbonate and minor calcium sulfate scaling tendencies throughout the fluid flow system. These predications were verified by field scale analysis reports. The severity of the scaling problem would have to be assessed using reliable scale prediction software, a rock/water chemical simulator and an up-to-date field database.

4.2 Diffra Oil Field of Muglad Basin in Sudan

Diffra oil field case was discussed by Eltaib and Rabah (2012), stating that the study was based on well and pipeline historical data of the years 2007, 2008, and 2009. The data included production data such as net oil and water cut, pipeline pressures, water qualities and scale composition. The study revealed that the main cause of scale formation is the presence of Ca^{+2} and Mg^{+2} in the produced water. Investigations on removal methods revealed that the chemical removal method being used is effective. However, the washing of the pipeline with chemicals required well shut down for at least 24 hours depending on the magnitude of the scale; leading to a loss in production. Eltaib and Rabah later suggested the use of both mechanical and chemical methods at different parts of the pipeline resulting in the possibility of avoiding huge economical loss caused by well shut down for cleaning.

4.3 El-Sharara Oil Field

The El Sharara oil field is an oil field found in the southwest part of Libya, It was discovered in 1980, it’s owned and operated by Repsol. It’s estimated that El Sharara Oil Field produce 300,000 barrel per day. This study is based on a water sample gained from a production well; In order to calculate the scaling tendency using Ryznar Index inserting the given data:

pH = 7.09, $[Ca^{+2}]$ = 900 mg/L, $[HCO_3]$ = 600 mg/L, TDS = 9169 mg/l,

Temperature = 25 °C.

Equation (3.1): $\mathrm{RI} = 2.\mathrm{pH_s} - \mathrm{pH}$

Equation (3.2): $\mathrm{pH_s} = [(9.3 + \mathrm{A} + \mathrm{B}) - (\mathrm{C} + \mathrm{D})]$

Where:

- $A = (\mathrm{Log_{10}}[\mathrm{TDS}] - 1)/10 = 0.30$
- $B = [-13.12 \times \mathrm{Log_{10}}(°\mathrm{C} + 273)] + 34.55 = 2.09$
- $C = \mathrm{Log_{10}}[\mathrm{Ca^{+2}} \text{ as } \mathrm{CaCO_3}] - 0.4 = 2.55$
- $D = \mathrm{Log_{10}}[\text{alkalinity as } \mathrm{CaCO_3}] = 2.78$

➢ $\mathrm{pH_s} = [(9.3 + 0.29 + 2.09) - (2.55 + 2.77)] = 6.35$

➢ $\mathrm{RI} = (2 \times 6.36) - 7.09 = 5.61$

Considering previous calculations, and referring to Figure 3.8, scale formation is indicated under these conditions and treatment should be applied. Sodium and calcium cations are the main reason for scale formation tendency. Repsol use aminophosphates and inorganic polyphosphates as chemicals for scale prevention.

By inserting Al-Sharara, Diffra, and Bu-Hasa's water analysis data in table 4.2

Table 4.2: Comparing between case studies water analysis data

RI Calculation

Scaling Parameters	**Water Analysis**		
	Al Sharara Oilfield, Libya	**Diffra Oilfield, Sudan**	**Bu-Hasa Oilfield, Abu Dhabi**
pH Value	7.09	8.2	5.7
Ca ion Concentration, mg/lt	900	150	14033
Bicarbonate Concentration, mg/lt	600	1820	244
Total Dissolved Solid, mg/lt	9169	2282	159285
Temperature, °C	25	25	64
A=(Log10[TDS] – 1)/10	0.30	0.24	0.42
B = [-13.12 x Log10(°C + 273)] + 34.55	2.09	2.09	1.39
C = Log10[Ca+2 as CaCO3] – 0.4	2.55	1.78	3.75
D = Log10[alkalinity as Bicarbonate]	2.78	3.26	2.39
pHs=[(9.3+A+B)-(C+D)]	6.35	6.59	4.97
RI=2.pHs-pH	5.61	4.98	4.25

4.4 Analyzing data of Al Sahara, Diffra and Bu-Hasa Oilfield Waters in Terms of Ryznar Stability Index

As mentioned in Subtitle 3.13, Ryznar Stability Index is function of 5 main factors which are pH value, Total dissolved solids, Calcium ions (Ca^{+2}), Bicarbonate ions (HCO_3^-), and Temperature. By using these parameters in Table 4.2 Ryznar Stability Indexes (RI) are calculated for each of three different oil field water samples data at the bottom line of the table. Thus, following graphs are obtained by correlating obtained RI values versus, above mentioned parameters individually; Where Figure 4.1, shows the relation between RI and the pH values, Figure 4.2, shows the relation between RI and the calcium ion concentrations in mg/lt, Figure 4.3, shows the relation between RI and bicarbonate ion concentrations in mg/lt, Figure 4.4, shows the relation between RI and the total dissolved solid concentrations in mg/lt, and Figure 4.5, shows the relation between RI and the temperature in °C.

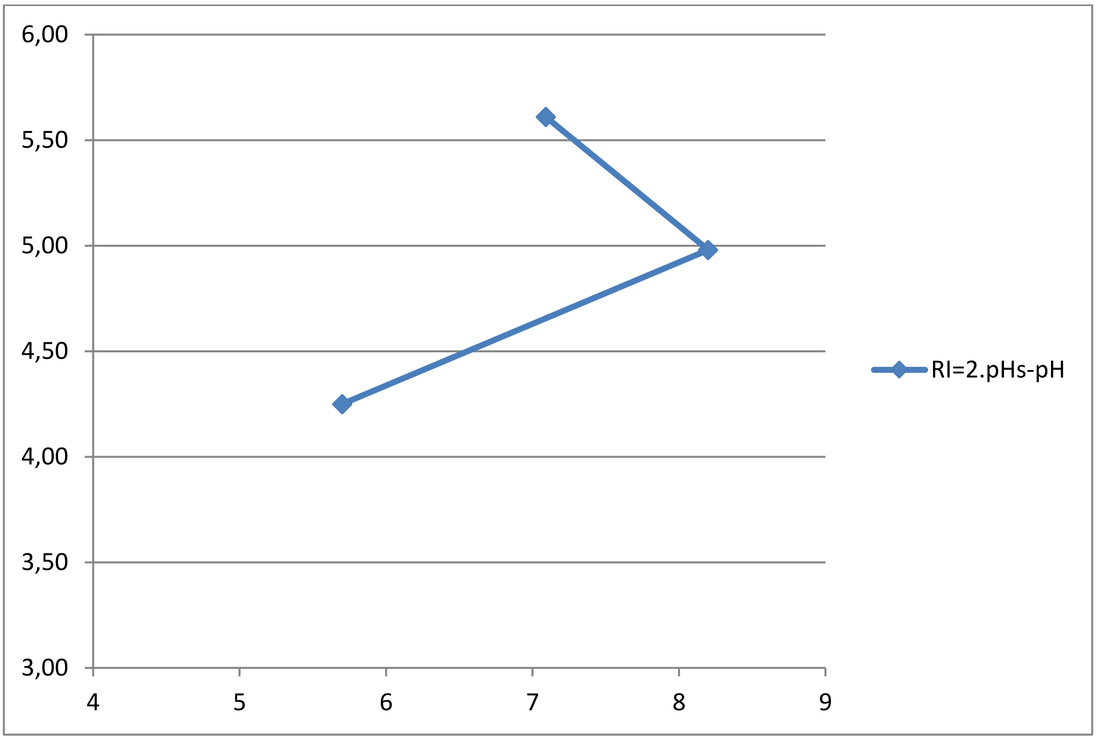


Figure 4.1: RI versus pH value

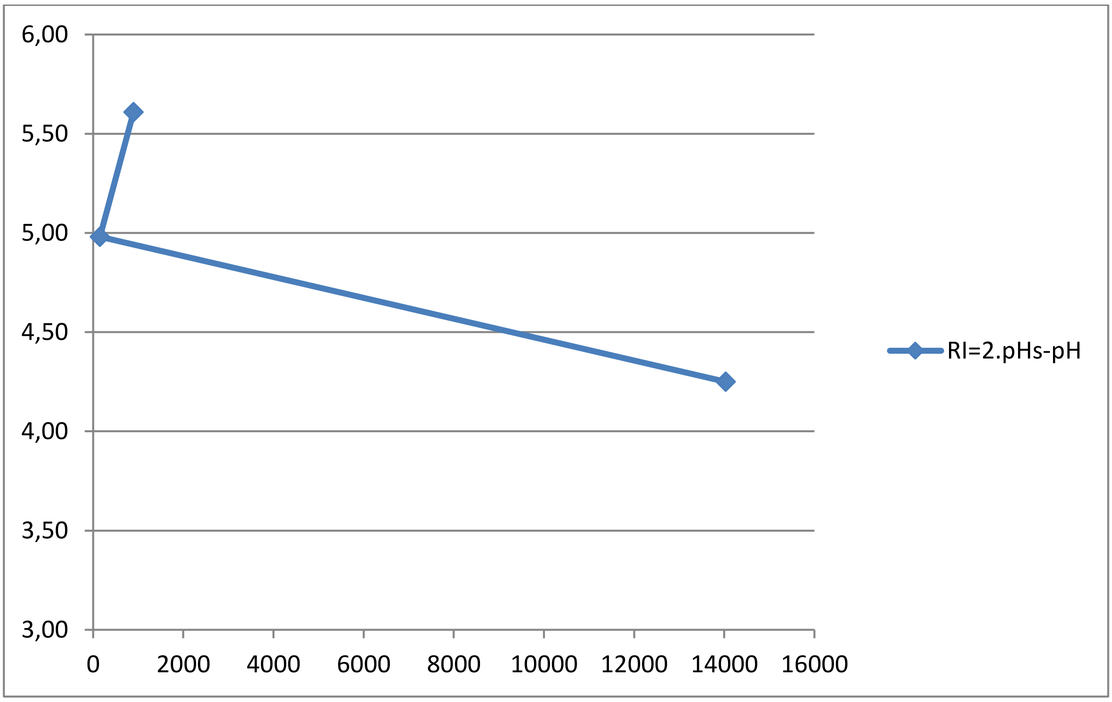


Figure 4.2: RI versus Calcium Ion Concentration, mg/lt

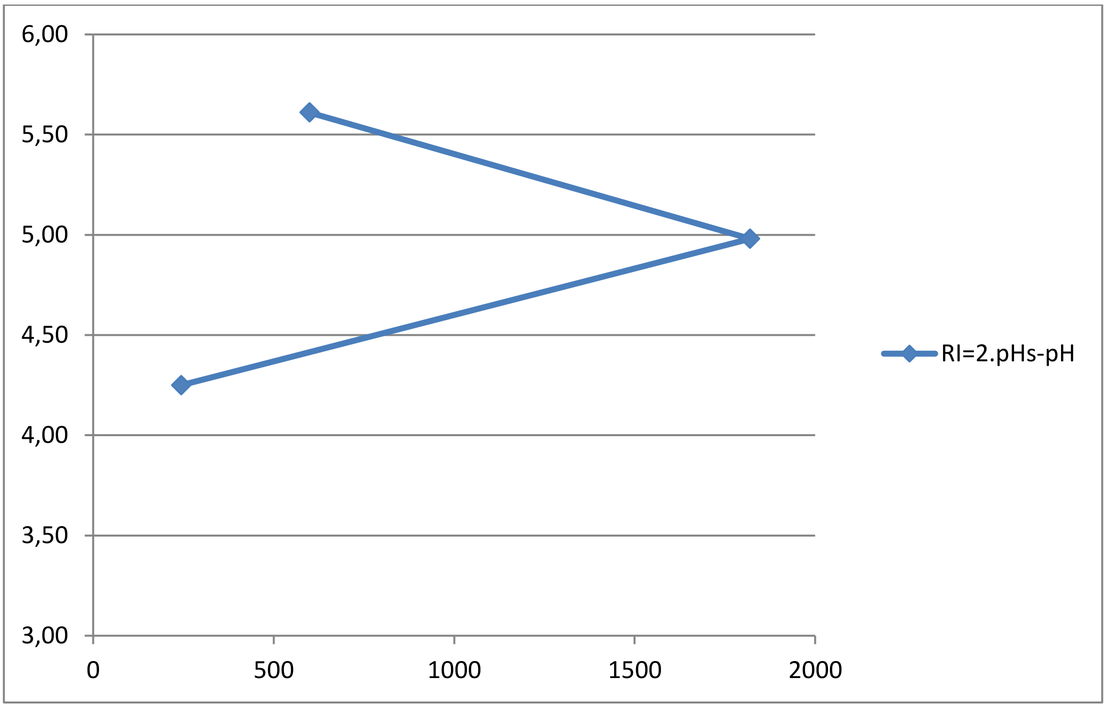


Figure 4.3: RI versus Bicarbonate Ion Concentration, mg/lt

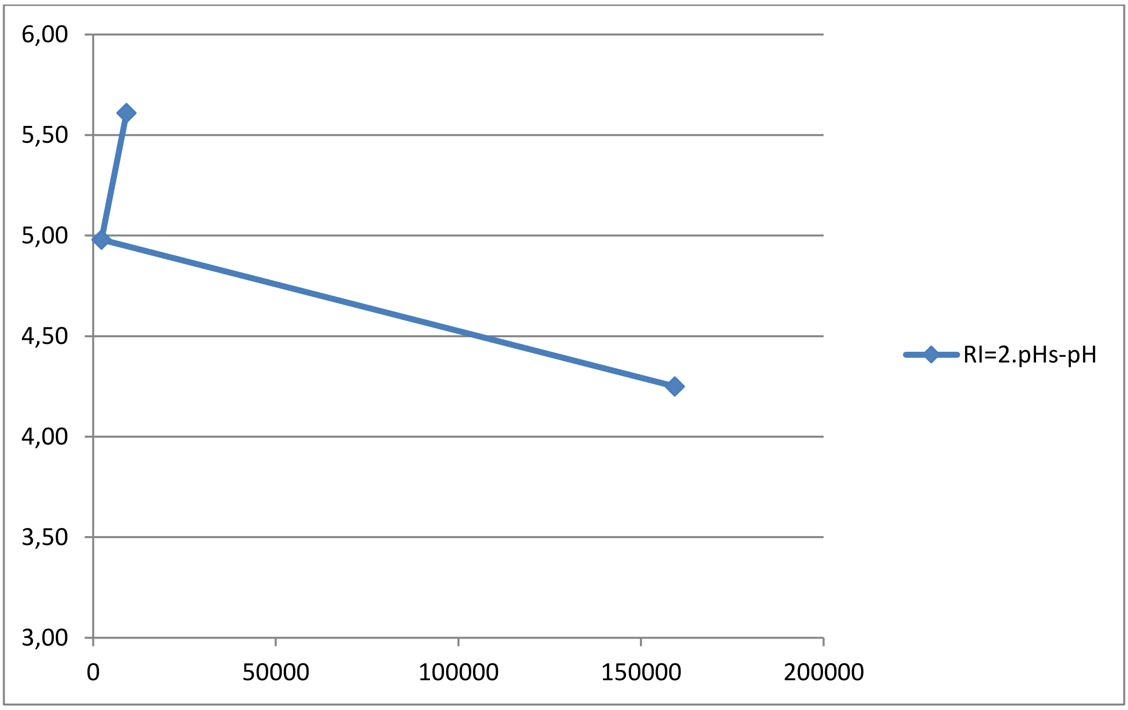


Figure 4.4: RI versus Total Dissolved Solid Concentration, mg/lt

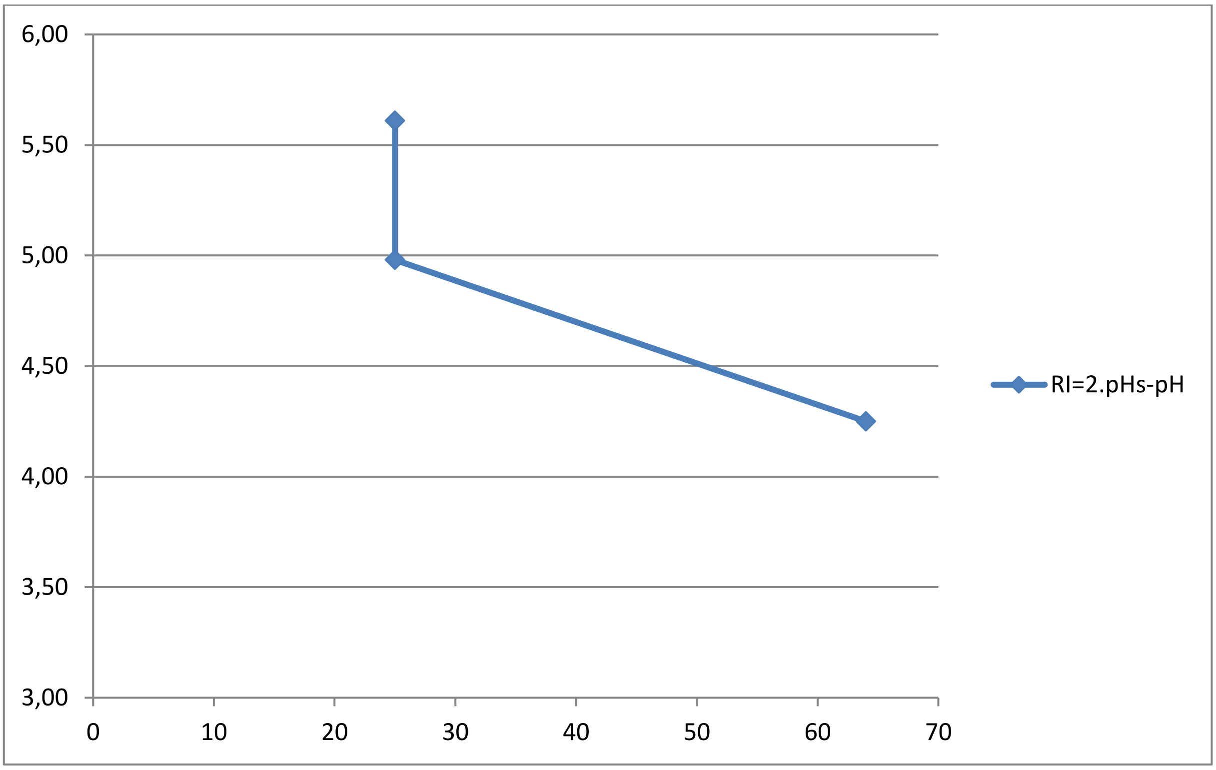


Figure 4.5: RI versus Temperature, °C

CHAPTER 5

CONCLUSIONS & RECOMMENDATIONS

5.1 Conclusions

The present syudy was aimed to investigate scaling formation tendency in terms of pH, Calcium Ion Concentration, Bicarbonate Ion Concentration, Total Dissolved Solid Concentration and Temperature of hydrocarbon reservoir waters by using Ryznar Stability Index. For this purpose, water data from three different oilfields have been analysed as case study.

The major difficulty in this investigation was obtaining water analysis data of hydrocarbon reservoir waters from owner companies and institutions. Fortunately, water data from three different oil reservoirs have been obtained, and this study carried out.

Within the boundaries of limited available data, it has been conclusively found out that:

- The tendencies of individually change in pH value, carbonate ion concentration, bicarbonate ion concentration, and total dissolved solid do not display any functional behaviour against changes in Ryznar Stability Index since there are two values of dependent variable against any single value of independent variables.

- The tendency of change in water temperature versus Ryznar Stability Index displayed a functional relation so that increasing water temperature reduces Ryznar Stability Index, resulting increase in scaling tendency. It can be concluded that, due to a temperature gradient from surface to the bottom of the well, scaling gradually will be highest at the bottom of the well while lowest at the well head.

- Scaling problems are more severe in geothermal reservoirs due to higher geothermal gradient.

- Reducing temperature cannot be in the scope, especially in geothermal wells since higher temperature vapours are in favour.

- Calcium Carbonate scale can be easily removed by acid treatment with convenient corrosion inhibitors but this will not stop the recurrence of scaling over a relatively short period.

- Selection of producing tubing material with low adhesive property against scaling.

- In some cases it’s better to combine more than one treatment method in order to have the optimum production rate and best revenue.

5.2 Recommendations

To discover the physical and chemical reasons behind scaling for any individual case is the basis to design preventing and mitigating actions.

It is recommended that by using more reservoir water data for new investigations on scaling issue are to be done to get statistically higher confidence.

Vigilance is the key to maintaining consistently high production rates and relatively trouble-free operations. Regular checks or a comprehensive monitoring program, though expensive, will allow the early diagnosis and treatment that will prove more cost-effective in the long-run.

The improved scale indicators are helpful in determining initial operating limits and treatments required, but they can’t fully replace a complete water analysis and the careful performance monitoring.

Each new technology introduced in the aim of scale control improves one aspect in this process; by combining those technologies, one can apply great surveillance methods in order to identify scale formation tendency and develop the optimum strategy to reduce production losses and repair costs associated with scaling.

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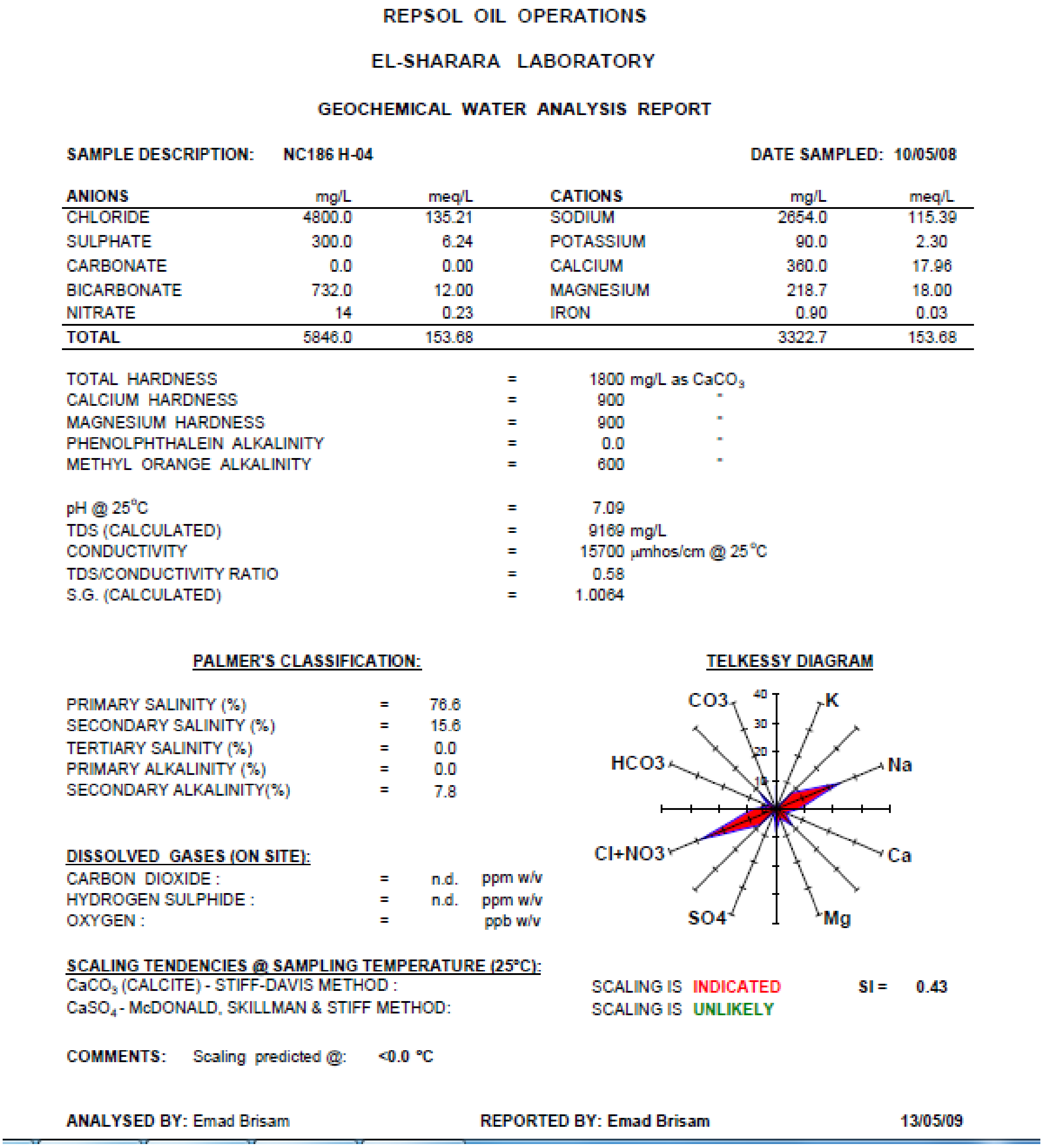
APPENDICIES

APPENDIX 1

WATER ANALYSIS DATA

Water Analysis Report from one of El Sharara Oil Field Production Wells



REPSOL OIL OPERATIONS

EL-SHARARA LABORATORY

GEOCHEMICAL WATER ANALYSIS REPORT

SAMPLE DESCRIPTION: **NC186 H-04** **DATE SAMPLED:** **10/05/08**

ANIONS	mg/L	meq/L	**CATIONS**	mg/L	meq/L
CHLORIDE	4800.0	135.21	SODIUM	2654.0	115.39
SULPHATE	300.0	6.24	POTASSIUM	90.0	2.30
CARBONATE	0.0	0.00	CALCIUM	360.0	17.96
BICARBONATE	732.0	12.00	MAGNESIUM	218.7	18.00
NITRATE	14	0.23	IRON	0.90	0.03
TOTAL	5846.0	153.68		3322.7	153.68

TOTAL HARDNESS = 1800 mg/L as $CaCO_3$
CALCIUM HARDNESS = 900 "
MAGNESIUM HARDNESS = 900 "
PHENOLPHTHALEIN ALKALINITY = 0.0 "
METHYL ORANGE ALKALINITY = 600 "

pH @ 25°C = 7.09
TDS (CALCULATED) = 9169 mg/L
CONDUCTIVITY = 15700 μmhos/cm @ 25°C
TDS/CONDUCTIVITY RATIO = 0.58
S.G. (CALCULATED) = 1.0064

PALMER'S CLASSIFICATION:

PRIMARY SALINITY (%) = 76.6
SECONDARY SALINITY (%) = 15.6
TERTIARY SALINITY (%) = 0.0
PRIMARY ALKALINITY (%) = 0.0
SECONDARY ALKALINITY(%) = 7.8

TELKESSY DIAGRAM

DISSOLVED GASES (ON SITE):

CARBON DIOXIDE : = n.d. ppm w/v
HYDROGEN SULPHIDE : = n.d. ppm w/v
OXYGEN : = ppb w/v

SCALING TENDENCIES @ SAMPLING TEMPERATURE (25°C):

$CaCO_3$ (CALCITE) - STIFF-DAVIS METHOD : SCALING IS INDICATED **SI =** **0.43**
$CaSO_4$ - McDONALD, SKILLMAN & STIFF METHOD: SCALING IS UNLIKELY

COMMENTS: Scaling predicted @: **<0.0 °C**

ANALYSED BY: Emad Brisam **REPORTED BY:** Emad Brisam **13/05/09**

APPENDIX 2

GLOSSARY

Adhesion: The attraction between the unlike molecules.

Bridge-Off: The build-up or accumulation of material, such as sand or scale, within the wellbore making it completely plugged, which leads to severe obstruction of the flow of fluids, or passage of tools or downhole equipment.

Brine: Water containing more dissolved inorganic salts than typical seawater.

Clogging: To cause something to become blocked or filled so that movement or activity is difficult.

Cohesion: The attraction between the like molecules.

Completion: Process of making a well ready for production or injection by preparing the bottom hole to the required specifications.

Corrosion: Natural occurring process that gradually destruct materials (usually metals) by chemical or electrochemical reactions with their environment.

Emulsion: It’s a mixture of two normally immiscible liquids, in oil and gas field, it is most commonly refers to water droplets in oil phase.

Formation Water: Water that occurs naturally within the pores of the rock, it might not have been present during the formation of the rock.

Hard Water: Water that contains high mineral content.

Injected Water: Water that is injected to the well, usually to stabilize pressure and minimize pressure drop, and to stimulate production.

Mature Fields: Term used to describe oil and gas fields that have reached to their peak production point and their production rate is declining.

Multivalent Ions: Ions that have a charge +2 or more.

Outgassing: The release of a gas that was dissolved, trapped, or absorbed in some material.

Packer: A device that can be run into a wellbore with a smaller initial outside diameter that then expands externally to the seal the wellbore.

Permeability: The measure of the ease with which a fluid can move through a porous rock.

Petroleum Reservoirs: It's a subsurface area filled with mostly hydrocarbons and water in the pores or the fractured rock formations.

Polar: Polarity of a substance indicates that there is a difference in the electronegativity more than 0.5 and the bonds between the atoms must be geometrically asymmetric in at least one direction.

Porosity: The measure of how much a rock is open space.

Produced Water: Term used to describe the byproduct water that is co-produced from a petroleum field alongside with the main products of oil and gas.

Scale: Metal deposit or coating formed in the surface of another metal.

Specific Heat: The amount of heat required to raise the temperature of 1 gram of a substance by 1 degree Celsius.

Standard Conditions: Standard Conditions are 25^oC of temperature and 1 atm of pressure.

Surface Tension: It's the elastic tendency and the ability of a liquid caused by the attraction of its particles in the surface layer to withstand being ruptured and minimizes the surface area.

Water Cycle in oil and gas fields: It describes the continuous movement of flowing water through reservoir, into production tubing and surface-processing facilities, and eventually extracting it for disposal or reinjection for reservoir pressure maintenance.

Water Cycle: It describes the continuous change in the state of water, by the physical process of evaporation and condensation.