MODELING AND PREDICTION OF SCALE FORMATION IN PETROLEUM RESERVOIRS DURING WATER INJECTION PROCESS

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CERTIFICATION

This is to certify that this research project report entitled '**MODELING AND PREDICTION OF SCALE FORMATION IN PETROLEUM RESERVOIRS DURING WATER INJECTION PROCESS'**, submitted to the Department of Chemical Engineering, University of Lagos, Akoka, Yaba, Lagos, Nigeria, for the award of the **DEGREE OF BACHELOR OF SCIENCE (B.Sc. Hons) IN PETROLEUM AND GAS ENGINEERING** is a record of the original work carried out by **AREGBE, AZEEZ GBENGA.**

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The Head,
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Dear Sir,

LETTER OF TRANSMITTAL

In accordance with the regulation of the University of Lagos, Akoka, the Faculty of Engineering and the Department of Chemical Engineering, I hereby submit this research project report entitled **'MODELING AND PREDICTION OF SCALE FORMATION IN PETROLEUM RESERVOIRS DURING WATER INJECTION PROCESS'**. This is in partial fulfilment of the requirements for the award of BACHELOR OF SCIENCE (B.Sc. Hons) DEGREE in Petroleum and Gas Engineering, at the University of Lagos, Akoka.

Yours faithfully,

_____

AREGBE, AZEEZ GBENGA

DEDICATION

This research project is dedicated to Almighty God for his mercy, unquantifiable favour and sparing my life till this day.

I cannot but also dedicate it to the memory of my late Mum and Dad. May their souls rest in peace.

ACKNOWLEDGEMENT

My greatest gratitude goes to God Almighty, for His grace, faithfulness and enduring mercy, especially throughout the duration of this research project and to my Late Mum and Dad (May their souls rest in peace, Amen), for their undying Legacy.

A thousand thank to you my Uncle, brothers and sisters as well as my friends, Mr Adeyanju, O. A., and my supervisor, Prof. Oyekunle, L. O., as well as to all that contributed in kind to the success of this project, for their relentless efforts.

ABSTRACT

The formation of mineral scale in petroleum reservoir is one of the most severe oil field problems that inflict water injection process primarily when two incompatible waters are involved. Typical examples are sea water, with high concentration of sulphate ions and formation water, with high concentrations of calcium, barium, and strontium ions. Mixing of these waters, therefore, could cause precipitation of calcium sulphate, barium sulphate and/or strontium sulphate. Different mathematical models currently exist in the literatures that predict the tendency of scale formation during water injection technique but not the amount of scale mineral that would be precipitated. This research work was conducted to develop a mathematical model that will be able to predict the amount of scale minerals that would be formed at different locations few inches from the injection well toward the petroleum reservoir. The relationship that exists among the saturation index, solubility product and concentration of scale precipitated was used as the basic principle in deriving the mathematical model. The results of the research work show that in Siri – C oil field, at saturation index of -3.00, the mass of Gypsum precipitated was 3986.455mg but when the saturation index increased to 0.4, the mass reduced to 3985.001mg. In Siri – D oil field, at saturation index of -1.20, the mass of Gypsum precipitated was 4792.014mg, but when the saturation index increased to 0.1, the mass reduced to 4792.001mg. In Siri – E oil field, at saturation index of -3.50, the mass of Gypsum precipitated was 9184.572mg, but when the saturation index increased to -0.4, the mass also reduced to 9184.000mg. This trend was similar for Barite and Celestite. It was inferred from the analysis that the amount of scale precipitated is dependent on the saturation index of the scale and the ionic composition of the system.

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LIST OF SYMBOLS

$a_{H_2O}^{S}$	Activity coefficient of water due to the salt effect
$a_{H_2O}^{N}$	Activity coefficient of water due to the cosolvent effect
$a_{H^+}^{*}$	Hydrogen ion activity in the mixed solvent
a_m, a_n	The activity of a cation or anion
a, b, c, d, e, f, g	Constant
C_B	Solution concentration of the scaling salt ($mole/Kg$)
C_i	Concentration at the solution-salt crystal interface ($mole/Kg$)
C_S	Solubility of the scaling salt
ΔC	Supersaturation driving force
E	Crystallization reaction activation energy
I	Ionic strength ($mole/KgH_2O$-atm)
K_C	Conditional Solubility
K_D	Mass Transfer Coefficient
K_H	Henry's Constant
K_R	Surface Reaction Kinetic Coefficient
K_{sp}^{MA}	The Solubility Product of a mineral salt
K_1, K_2	The 1st and 2nd dissociation constants of carbonic acid
P	Pressure in psia
P_c	Power Coefficient
P_{CO_2}	Partial Pressure of gaseous carbon dioxide (psig)
PH_{MR}	Observed PH in mixed solvent when the PH electrode has been calibrated using normal aqueous buffers

ΔPH_j	Correction term to represent the changes in electrode response due to the present of salt
r	Ionic Radius
R	Universal gas constant
R_i	Depositional flux (Kg/sm^2)
S	Supersaturation Level
SI	Saturation indices of mineral salt
SR	Saturation ratio
t	Time
T	Absolute Temperature
V	Velocity
X	Layer thickness
γ^N	Activity coefficient due to impurity effect
γ_M^N, γ_A^N	Activity coefficient of cation or anion due to the cosolvent effect
$\gamma^{N\pm}$	Mean activity coefficient due to cosolvent effect
γ^S	Activity coefficient due to the salt effect
γ_M^S, γ_A^S	Activity coefficient of cation or anion due to the salt effect
Y	Inverse of the saturation ratio
σ	Scale crystal surface energy
δ	Correction term used to represent the changes in electrode respond due to the presence of cosolvent
θ	The contact angle of crystal on the surface
τ	The extent of induction period
ρ_s	Scale bulk density

CHAPTER ONE

1.0 INTRODUCTION

Water injection is a process that enhances the production of crude oil from the reservoir by increasing the reservoir pressure. It is an effective means of sustaining the reservoir bottom-hole pressure and typically increases the recovery factor of the oil – bearing reservoir. Moreover, it can create a great danger through the formation of mineral scale in the reservoir. Scale is deposition of inorganic crystalline minerals formed as a result of precipitation of solids from brines present in the reservoir and production flow systems. The precipitation of these solids occurs as a result of changes in the ionic composition, pH, pressure and temperature of the brines. When two incompatible waters are mixed, dense and adherent precipitates (scales) are formed. Incompatible waters are waters that react chemically and formed mineral precipitates. Typical examples are seawater rich in high concentration of SO_4^{2-} and formation water with high concentration of Ca^{2+}, Ba^{2+} and Sr^{2+}. when the above sea water is injected into a reservoir with these kinds of ions; they could form precipitates like $CaSO_4$, $BaSO_4$ and $SrSO_4$ (Amer Badr et al, 2007) . Scale typically forms when a change in the physical conditions or compositions of the compounds occurs. Common disturbances include a change in temperature, pressure, or composition of the formation water. When the injected sea water travels down the injection well-string, it cools the surrounding formations and its temperature and pressure increases. If the water is saturated at the surface condition with salts whose solubility decreases with increasing temperatures, scales may be formed. The change in the equilibrium condition causes the inorganic salt to establish a new equilibrium as it is being

produced. In many instances, this new equilibrium is achieved by the loss of dissolved solids.

There are three basic mechanisms by which scales formed in the petroleum reservoir:

1. Decrease in pressure and/ or increase in temperature, goes to a reduction in the solubility of the salt (most commonly the precipitation of carbonate scales like $CaCO_3$).

$$Ca(HCO_3)_2 \Leftrightarrow CaCO_3 + CO_2 + H_2O$$

2. Reaction between two incompatible waters. Typical example is seawater with high concentration of SO_4^{2-} and formation water with high concentration of Ca^{2+}, Ba^{2+} and Sr^{2+}. when the above sea water is injected into a reservoir with these kinds of ions; they could form precipitates like $CaSO_4$,

$$Ca^{2+} + SO_4^{2-} \Leftrightarrow CaSO_4$$

   Other fluid incompatibilities include sulfide scales where hydrogen sulfide gas mixes with iron, zinc or lead rich formation water.

3. Brine evaporation, resulting in salt concentration increasing above the solubility limit and goes to salt precipitation (as may occur in high pressure/ high temperature gas wells where a dry gas stream may mix with a low rate brine stream resulting in dehydration and most commonly precipitation of NaCl.

There are other causes of scale formations. The amount and location of scale formed are also influenced by several factors. Supersaturation is the major cause of mineral precipitation. A supersaturated condition is when a solution contains dissolved materials which are at higher concentrations than their equilibrium concentrations. The degree of supersaturation, also known as the scaling index, is the driving force for

the precipitation reaction and a high super saturation condition, therefore, implies higher possibilities for scale formation.

1.1 OBJECTIVE OF THE WORK

The objective of this research work was to develop a mathematical model that can accurately predict scale formation and the amount that will precipitate out of a given solution. This was achieved by using the saturation index approach to predict the tendency of scale formation and a mathematical model was developed to accurately predict the amount of scale that will precipitate out of a given solution.

1.2 SCOPE OF THE WORK

The scopes of this work were divided into two sections and they are:

1) The Saturation index method was used to predict the tendency of scale formation at locations few inches from the petroleum reservoir.
2) A mathematical model that relates saturation index to the amount of mineral scale precipitated out of any reservoir was developed.

1.3 TECHNICAL CHALLENGES

The problem encountered in this research work was the difficulty in obtaining the appropriate data to validate the developed mathematical model to test its precision and accuracy.

1.4 JUSTIFICATION OF THE RESEARCH WORK

Scale deposition in petroleum reservoir during water injection technique is one of the most serious problems affecting the oil and gas industry because of its immense effect on productivity. If left untreated, it can reduce the productivity of the well by blocking the flow paths of the oil and gas into the well bore from the reservoir. Downhole and surface hardware can be damaged by the accumulation of scale, further reducing the

ability to produce and transport hydrocarbons. Scale formation has been recognized as a major causes of formation damaged either in injection well or production well.

In addition to reduction in productivity, Scale also contributes to equipment wear and corrosion. Scales do the most damage in the wellbore when there are major fall in pressure but hardly any temperature changes (khelil et al., 1979).

Furthermore, different analysis are needed to evaluate scale formation probability, to quantify risk reduction, and to establish practical operational criteria for safe and optimum production, which includes scale monitoring techniques, which allows real – time quantitative scale tracking, capacity to predict scale formation onset, scale quantities, scale formation rate and equipment damage risk.

Different mathematical models currently exist in the literatures that predict the tendency of scale formation during water injection technique. The short – coming of all these models was their ability to predict the tendency but not the amount of scale precipitated. This research work is carried out to correct the anomalies by developing a mathematical model that will be able to predict accurately the amount of scale minerals that would be formed at different locations few inches from the injection well toward the petroleum reservoir.

CHAPTER TWO

2.0 LITERATURE REVIEW

Scale deposition during water injection operations usually occurs as a result of incompatibility of the injected and formation waters. It has been a problem in connection with oil production for the at least 100 years. During this period, several models, and in the later years also computer programs have been presented in the literature to deal with scale predictions. The first models were design to predict scaling of sulphates,$CaSO_4$, $BaSO_4$, and/ or $SrSO_4$. Such models are fairly simple, because it is not necessary to calculate the pH and the phase distribution of CO_2 or other gases. It is however, necessary to have an accurate model to describe the non – ideal behaviour of brines as well as the estimation of the amount of scale that will precipitate out of a given solution. Several models have been published since Debye and Hückel presented their limiting law. These models are outlined below.

Wright et al (1994) researched on scale prediction, measurement, and control in a subsea satellite field. Predictions and workover findings revealed that sulphate and carbonate scale problems have a significant impact on the Glamis field production. Scale predictions closely agreed with the findings. An estimation of the findings governing the kinetics of calcium carbonate was analyzed. Specific treatment facilities, permitting Downhole injection and inhibitor squeezing were incorporated into the designs of the recompleted satellite wells to combat the scaling mechanisms.

Jordan et al (1996) presented an approach for screening commercial sulphate and carbonate scale inhibitors for field application. The screening results, which include data from statistic/ dynamic inhibitor efficiency, static adsorption, compatibility and thermal stability, were used to rank the performance of commercial scale inhibitors

They analyzed an overview of life cycle flow assurance management for a platform/subsea development by focusing on the scale control. To illustrate this approach, examples of scale control methods for deep water subsea fields were cited covering aspects such as;

1. Treatment of the reservoir prior to production to prevent scale formation within the near wellbore (solids and fluids systems for inhibitor development).
2. Downhole scale control using continuous injection (gas lift, capillary), and
3. Squeeze treatment as the production wells move through their life cycle and water cut rises.

Mackay et al (2000) presented results from a near wellbore simulator, which was used to model scale inhibitor treatments in the horizontal wells. A technique for modeling such treatment was developed, which gave an improved understanding of where the chemical would be placed under different injection strategies, and how the placement would impact the squeeze life. Various treatment designs were tested to assess the impact of varying such parameters as indicator slug volume and concentration, over flush volume and injection rate. The performance of various chemicals under reservoir flow conditions were modeled, with a clear best choice emerging from the study.

Norris et al (2001) described the formation of porous scale inhibitor impregnated proppants and highlighted the initial returns from field trials performed on land wells on the North Slope of Alaska. They developed the impregnated proppants technology and two treatments were both designed to stimulate production and to protect the fracture against future scaling scenarios. They also describes the design criteria used to select this method of protecting the future performance of the fracture and the execution of the treatment while highlighting the fracture performance and scale

inhibitor return profiles generated by recent treatment performed in the British and Norwegian sectors of the North Sea.

Amy et al (2002) studied the effect of hydrate inhibitors on oil field sale formation and presented a self – consistent activity model to predict the effect of methanol on carbonate equilibrium, calcite, barite, gypsum, and Celestine and halite solubility in a gas/methanol/water/salt solution. Excellent agreements between the model prediction versus both experimental and literature results were observed. The efficiency of common phosphate inhibitors in methanol and ethylene glycol containing brines were also discussed.

The model generated didn't take into consideration the scaling tendency or potential of brine presence in the reservoir as well as its mineral conpositon and flow parameters. It also doesn't consider the rate at which scale will be precipitated.

Moghadasi et al (2003) presented the mechanism of scale formation by water in the oil fields and suggested an accurate model capable of predicting scale phenomena in Iranian field operations due to mixing of incompatible waters or change in thermodynamics, kinetics and hydrodynamic conditions of the system. A new and reliable scale prediction model which could predict scaling tendencies of common oil field water disposal wells, water flooding systems and in surface equipment and facilities was developed.

To further their previous work, **Mackay et al (2003)** outlined the risk assessment process required prior to undertaking produced water re – injection. The factors that were considered are locations of scale deposition around fractured and unfractured injection wells, formation damage potential and impact, and retardation effect on injected scale inhibitors. They also drew upon computer modeling techniques, laboratory generated core flood data, and field result that will demonstrate the impact

of the following factors on the long term water injectivity; via scaling tendency, suspended solid content, suspended oil content, injection temperature, reservoir type and completion type.

Kaasa et al (2005) presented a thermodynamic model that could accurately predicts pH, scale potential, gas solubility and salt solubility in systems with MEG(Mono ethylene glycol) concentrations form 0 – 95wt%. The model was based on a large amount of experimental data in MEG containing systems, both from the literature and the present work. With the model they were able to accurately predict pH and scale potential as a function of pressure, temperature, composition of water and hydrocarbon phases and MEG concentration. They considered the influence of gas phase, a liquid hydrocarbon phase (oil or condensate) and an aqueous phase in the model.

Tomson et al (2006) proposed a semi – empirical approach to correlate the effect of hydrate inhibitors on scale formation from empirical solubility measurement of halite, barite, gypsum, calcite, and carbonate equilibrium chemistry. Details about how to predict hydrate-inhibitor-induced scale formation and case studies that demonstrate severity of methanol and scaling tendency were discussed. Finally, barite nucleation and kinetics are studied in the presence and absence of methanol. A semi-empirical equation to predict the nucleation time was proposed.

Bedrikovetsky et al (2006) derived analytical model based method for determination of kinetics coefficient from laboratory coreflood on quasi steady state commingled flow of injected and formation waters and further extended the method and as well derived formulae for calculation of formation damage coefficient from pressure drop measurement during coreflood. They derived an analytical model for simultaneous flow of incompatible waters in porous media with sulfate salt precipitate; determine

typical values of kinetic reaction coefficient from coreflood and what the impact will be on productivity impairment during sulfate scaling.

Moghadasi et al (2008) presented the mechanism of scale formation from oil field formation water. An accurate model for predicting the scaling phenomena due to mixing of incompatible waters, changes in thermodynamics, kinetic and/or hydrodynamic conditions in oil field operations was developed. The model developed was able to predict scaling tendency of common oilfield waters in disposal wells, water – flooding systems and in surface equipment and facilities.

The model was developed based on experimental data and empirical correlations which match the oilfield conditions accurately. The simultaneous deposition of different oilfield scales and the competition of different ions to form scale were incorporated into the model. The model was used to investigate the potential for scale precipitation in various Iranian on – shore and off – shore oilfields, where water injection is being performed for the water disposal of desalting units.

Merdhah et al (2009) conducted a study to investigate the permeability reduction caused by deposition of strontium sulphate in sandstone cores from mixing of injected sea water and formation water that contained high concentration of strontium ion at various temperatures and differential pressures. The solubility of strontium sulphate scale formed and how its solubility was affected by changes in salinity and temperatures were also studied.

The deposition of $SrSO_4$ scale during flow of injected waters into the porous media was shown by Scanning Electron Microscopy (SEM) micrographs. The results were used to build a general reaction rate equation to predict $SrSO_4$ deposition in sandstone cores for a given temperature, brine super – saturation and differential pressures.

Amiri et al (2010) presented the prediction of the amount of Barium Sulfate Scale formation in Siri Oilfield using OLI ScaleChem Software. OLI ScaleChem software predicts mineral scaling potentials of 54 solids for vitually any oil and gas well and has the following advantages over other commercially available scaling software:

1. By including all brines in the calculations, the well and processing facility are modeled more accurately,
2. Scaling potential and scale build up are reported at each calculation point,
3. Automatic correction of pH and charge balance, therefore the chance of unexpected problems from bad water analysis decrease,
4. Automatic removal of organic acids concentrations from the measured alkalinity, therefore producing a true brine alkalinity and
5. Accurately predicting the behavior of any mixture of chemicals in water and mixed solvent.

Bahadori et al (2012) analyzed the composition of different formation waters from a few disposal wells of southwest Iranian crude oil desalting plants. A new correlation for estimating the critical concentration of Iron ions, Fe^{2+}(ferrous ion), which will stay in solution at various pH values and a wide range of H_2S concentration in crude oil desalting plants' disposal wastewaters was developed. This correlation eliminates the need for compatibility assessment, which is usually assessed either by solubility calculations or by experimental testing, for water mixtures that contains Iron ions and dissolvedH_2S. Finally, a real case field problem was analyzed and based on the correlation's results, three different potential solutions were recommended for further field trial implementation.

In the literatures review above, it was observed that all the models developed could only predict the tendency but not the amount of scale precipitated. Hence, in this research work, a mathematical model was developed to predict accurately the amount of scale minerals that would be formed at different locations few inches from the injection well toward the petroleum reservoir.

2.1 THEORETICAL PRINCIPLES

2.1.1 Water Injection Technique

This refers to the process whereby water is injected into the reservoir to increase pressure and thereby stimulate oil production. Water injection wells can be found both on- shore and off – shore, to increase oil recovery from an existing reservoir.

Normally only about 35% of oil in a reservoir can be extracted but water injection increases that percentage (known as recovery factor) and maintains the production rate of a reservoir over a longer period. The water injected performs the following functions:

- It supports the pressure of the reservoir,
- It also displaces oil from the reservoir and push it into the well

Different sources of bulk water are being used as injection water. The following sources of water are typically use for oil recovery;

- Produced water; this is often used as an injection fluid. It reduces the potential of causing formation damage due to incompatible fluids as well as the risk of scaling or corrosion in injection flowlines or tubing. This provides readily available source of water for the recovery operation.
- Aquifer water; this is the water from water – bearing formation other than the oil reservoir but in the same structure. It is the purest form of water available

for the recovery technique but not readily available and relatively costly to obtain.

- River water; this always requires filtration and biociding before injection.
- Sea water; this is obviously the most convenient source for off – shore production facilities and may be pumped on – shore for use on land fields. Where possible, water intake is placed at sufficient depth to reduce the concentration of algae; however, filtration, deoxygenation and biociding are required.

2.1.2 Causes of Scale Formation

Scale typically formed when there is a change in the physical conditions or composition of brine. Depending on the nature of the scale and fluid composition, deposition can take place within the reservoir which causes formation damage or in production equipment where blockage can cause severe operational problems.

The table below shows the major ionic compositions of four different types of sea water in (mg/L).

TABLE 2.1: IONIC COMPOSITIONS OF DIFFERENT TYPES OF SEAWATER

Major Ions (mg/L)	**Typical Seawater**	**Eastern Mediterranean**	**Arabian Gulf at Kuwait**	**Red Sea at Jeddah**
Chloride (CL^-)	18.980	21.200	23.000	22.219
Sodium (Na^+)	10.556	11.800	15.850	14.255
Sulphate (SO_4^{2-})	2.649	2.950	3.200	3.078
Magnesium (Mg^{2+})	1.262	1.403	1.765	742
Calcium (Ca^{2+})	400	423	500	225
Potassium (K^+)	380	463	460	210

Bicarbonate (HCO_3^-)	140	-	142	146

The two main types of inorganic scale which are commonly found in oil fields are carbonate scales and sulphate scales. While the formation of carbonate scale is associated with changes in pressure and pH of the reservoir or production fluid, that of sulphate scale is mainly due to the mixing of incompatible waters i.e. formation water and injection water.

2.1.3 Factors affecting Scale Formation

There are different factors affecting the formation of scales. The most prominent factors are described below:

- Supersaturation
- Reaction Kinetics
- Changes in Temperature and Pressure
- Mixing of Incompatible waters
- Presence of other compounds

Supersaturation

A supersaturated solution contains more ions than it can dissolve at a particular temperature and pressure, meaning that sooner or later, precipitation will occur. This is the most important property with respect to the mineral that will be precipitated. Scale can occur at any point within the reservoir at which supersaturation occur. Supersaturation can be generated in formation water by changing its pressure and temperature conditions or by mixing incompatible waters. The degree of supersaturation is the driving force for the precipitation reaction and a high

supersaturation therefore implies a high possibility of scale formation but not the amount of salt that will be precipitated.

Reaction Kinetics

The kinetics of a reaction will determine how fast a reaction proceeds in order to attain thermodynamic equilibrium. There are many factors governing the kinetics of a chemical reaction in which temperature is most important.

Changes in Temperature and Pressure

In the reservoir, brine is in chemical equilibrium with its surroundings at a given temperature and pressure. As the brine is produced, equilibrium is disturbed since the brine is moved to a lower temperature and pressure. Pressure drop will decrease the solubility (the limiting amount of a solute, which can be dissolved in a solvent under a given set of physical condition) of inorganic minerals, and thereby increase the rate of scale formation. Unlike pressure drop, temperature drop will have the opposite effect. The net effect of temperature and pressure drops may be an increase or a decrease in the rate of scale formation depending on the temperature change relative to pressure change.

Mixing of Incompatible waters

Waters are said to be incompatible if they react chemically and precipitate minerals when mixed. Hence the presence of two incompatible waters increases the tendency of scale formation. Sea water is often injected into the reservoir to maintain the reservoir pressure and increase oil recovery.

Effects of other compounds and impurities

The presence of other compounds will influence the saturation index of the precipitating salt in various ways. Presence of organic acids will directly influence the pH and thereby the potential for scale formation.

2.1.4 Types of Inorganic Scales

The presence of common oilfield scales, along with the primary variables which affect their solubility are shown in table 2.1, (Moghadasi et al, 2003).

TABLE 2.2: MOST COMMON OILFIELD SCALES, (Moghadasi et al, 2003)

Names	Chemical Formula	Primary Variable
Calcium Carbonate:	$CaCO_3$	Partial pressure of CO_2, temperature, total dissolved salt, and pH
Calcium sulphate: Gypsum Hemihydrate Anhydrate	 $CaSO_4.2H_2O$ $CaSO_4.{}^1/_2\,H_2O$ $CaSO_4$	Temperature, total dissolved salt, and pressure
Barium Sulphate	$BaSO_4$	Temperature and pressure
Strontium Sulphate	$SrSO_4$	Temperature, pressure, and total dissolved gas
Iron Compounds: Ferrous Carbonate Ferrous Sulphide Ferrous Hydroxide Ferrous Hydroxide	 $FeCO_3$ FeS $Fe(OH)_2$ $Fe(OH)_3$	Corrosion, dissolved gases, and pH

2.1.5 Nature of common Oil Field Scales

- Calcium sulphate scales

They are composed mainly of sulphate and calcium ions, but when deposited from complex polymetallic solutions can contain traces of other ions. Calcium sulphate is complicated by the fact that it can crystallize from aqueous solution in three forms:

- Gypsum $CaSO_4.2H_2O$
- Hemihydrate $CaSO_4.{}^1/_2\,H_2O$
- Anhydrate $CaSO_4$

The chemical compounds may be stable depending on temperature and ionic strength. They have decreasing solubility (limiting amount of a solute, which can be dissolved in a solvent under a given set of physical conditions) with increasing temperature above 40℃.

Solubility of Calcium Sulphate Scales

Solubility is defined as the limiting amount of a solute, which can be dissolved in a solvent under a given set of physical conditions. Once this solubility is exceeded, the compounds precipitated from solution as solid.

Therefore, precipitation of solid materials to form scale will occur if:

- The water contains ions which are capable of forming compounds of limited solubility.
- There is a change in the physical conditions or water compositions which result into decrease in solubility.

The solubility of calcium sulphate increases with increasing temperature up to 40℃ and then decreases with increasing temperature above 40℃ in water but increases with pressure. This increase is due to the fact that when the scale is dissolved in water, there is decrease in the total volume of the system. The dissociation of calcium sulphate in water is shown below:

$$CaSO_4 + H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + H_2O \qquad (2.01)$$

Also agitation and vaporization increases scale formation. The evaporation of water evolves gas in or around the well and may cause supersaturation condition producing Calcium sulphate.

- Calcium Carbonate Scales

Calcium carbonate scales are large crystals which might be found together with impurities. Deposition of calcium carbonate scale results from precipitation of calcium carbonate according to the chemical reaction below:

$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3 \quad (2.02)$$

Calcium carbonate scale can also be formed by the combination of calcium and bicarbonate ion, and this reaction is the major cause of calcium carbonate deposition in oilfield operations.

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \quad (2.03a)$$

$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3 \quad (2.03b)$$

Factors that influence the formation of Calcium carbonate scales

- Effect of carbon dioxide (CO_2) on partial pressure: most oilfield reservoirs contain carbonate mineral cements and carbon dioxide, therefore, the formation water is normally saturated with calcium carbonate under reservoir conditions where the temperature can be as high as 200℃ and the pressure up to 30MPa. When carbon dioxide comes in contact with water, it dissolves and forms carbonic acid according to the equation below;

  $$CO_2 + H_2O \leftrightarrow H_2CO_3 \quad (2.04)$$

  The ionization of the carbonic acid is illustrated below;

  $$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \quad (2.05a)$$

  $$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \quad (2.05b)$$

It is believed that calcium carbonate does not exist in solution as calcium ion and carbonate ion but as calcium ion and bicarbonate ion. Thus, the precipitation of calcium carbonate can be expressed by the following equations;

$$Ca^{2+} + 2HCO_3^{2-} \leftrightarrow Ca(HCO_3)_2 \leftrightarrow H_2O + CO_2 + CaCO_3 \downarrow \quad (2.06)$$

By the principle of Le Chatelier, which states that 'when one of the factors affecting the equilibrium position is distorted, the equilibrium position will shift in order to annul or neutralize the change in the factor', it is obvious that increase in concentration of CO_2,will result in production of more $Ca(HCO_3)_2$. Hence, it can be seen that the solubility of $CaCO_3$ is greatly influence by the CO_2content of the water.

At any point in the system where a pressure drop occur, the partial pressure of CO_2in the gas phase decreases, CO_2comes out of the solution, and the pH of the water rises. This shifts the reaction equation above to the right and may cause $CaCO_3$ precipitation.

- ✓ Effect of total pressure: the solubility of $CaCO_3$in a 2 – phase system (oil – gas or oil – water system) increases with increase pressure for two reasons:
  - Increased pressure increases the partial pressure of $CO_2$and increases the solubility of $CaCO_3$ in water.
  - Increased pressure also increases the solubility due to thermodynamic consideration.
- ✓ Effect of temperature: contrary to the behaviour of most minerals, $CaCO_3$becomes less soluble as temperature increases. The hotter the water becomes, the more likely the $CaCO_3$ $precipitation$.

- ✓ Effect of pH: the lower the pH of the water, the less likely is $CaCO_3$ precipitation. Conversely, the higher the pH, the more likely the precipitation will occur.
- ✓ Effect of Dissolved salts: $CaCO_3$ solubility increases as the dissolved salt content of the water increases. The higher the total dissolved solids (not containing calcium or carbonate ions), the greater the solubility of $CaCO_3$ in the water, the lower the scaling tendency up to a maximum of about 200g/L.

2.1.6 Mechanisms of Scale Formation

Mineral scale precipitation is a crystallization process which involve four different stages outlined below;

2.1.6.1 Attainment of supersaturation/ induction Period

The most important single factor which determines the intensity of scaling is the supersaturation level of the scale forming species. Supersaturation conditions are achieved when a solution is concentrated beyond the solubility limits of one or more of its constituents by evaporation. Supersaturation conditions can be achieved by a change in temperature. Most of the frequently encountered scaling salts exhibit inverse solubility characteristics, i.e. solubility salt in contact with a hot surface can attain supersaturation by the inverted solubility effect and deposit scale on the hot surface. A supersaturated solution is at an unstable equilibrium and relieves its supersaturation by precipitating a solid phase. Attainment of supersaturation alone is not sufficient for a system to begin precipitation. At relatively moderate supersaturation limits, the solution can remain for a certain period, named *delay time* or *induction period,* without precipitation. Only at a sufficiently high supersaturation

level, the induction period is virtually absent and precipitation is instantaneous.

2.1.6.2 Nucleation

The physical mechanisms governing the induction period are the nucleation processes; a formation of unstable clusters of atoms. The atom clusters form small seed crystals triggered by local fluctuations in the equilibrium ion concentration in supersaturation solutions. The energy for the crystal growth is driven by a reduction in the surface free energy of the crystals, which decrease rapidly with increasing radius after a critical radius is exceeded. This implies that small seed crystal will encourage an increase in growth of scale deposits.

Nuclei are of visually unobservable microscopic dimensions. Their formation is facilitated by the presence of a deposition surface so that in all practical systems nucleation can be assumed to be of heterogeneous nature. Induction time data may be correlated with the supersaturation level S by assuming that τ (the extent of the induction period) is inversely proportional to the heterogeneous nucleation rate:

$$\ln \tau = C_1 \frac{\sigma^3 . f(\theta)}{T^3 . (\ln S)^2} + C_2 \qquad (2.07)$$

Where T is the absolute temperature prevailing on the deposition surface, σ is the scale crystal surface energy, θ is the contact angle make by the crystal on the surface andC_1, C_2 are constants of the system. Induction times are seen to be highly dependent on the supersaturation level.

2.1.6.3 Scale Layer Growth

Once an initial scale layer is formed, subsequent deposition is facilitated. Growth of a crystal layer on a flow surface involves several consecutive processes;

I. Diffusion transport of the crystal forming ions towards the crystallizing layer,
II. Incorporation of the ions on growth sites of the crystal lattice, and
III. Adhesion and removal processes.

The interfacial process of crystallization (step 2) is viewed as surface reaction process. In the absence of removal effects, the deposition flux 'r' (corresponding to a scale growth velocity of $^{dx}/_{dt}$, m/s) is obtained by equating the transport rate of the scale constituents to the crystallization surface with the rate of the crystallization reaction:

$$r = \rho_s . \frac{dx}{dt} = K_D(C_B - C_i) = K_R(C_i - C_s)^p \quad (2.08)$$

Where x is the layer thickness, ρ_s is the scale bulk density, K_D is the mass transfer coefficient, K_R is the surface reaction kinetic coefficient, $C_B$is the solution concentration of the scaling salt, C_i is its concentration at the solution – scale crystal interface and C_s is the solubility of the scaling salt.

The mechanism of scale formation can also be described by the trend shown below;

Water and Soluble Minerals

↓

Dissolution and Stabilization

↓

Supersaturation

↓

Nucleation and Precipitation

↓

Crystal Growth

↓

Mineral Scale

2.1.7 Effect of Impurities on Scale Formation

A tenacious well – bonded scale deposit can form only when the water precipitates a pure crystalline deposit. Fortunately, most practical systems contain impurities to some extent or other. Impurities tend to adsorb on active sites of a crystallizing deposit and interfere with the formation of a well – ordered solid structure. Such processes can induce a significant decrease in both the nucleation rate and the crystal growth rate, often accompanied by a change in precipitate morphology. Deposits formed mixed salts and in the presence of impurities have a weakened adherence and the net scaling rate will be lowered due to partial removal of the deposit by shear force acting on the flow surface.

The effects of the major impurities are outlined below;

Effect of metallic impurities

A literature review focusing on the effect of Zn^{2+} ions on $CaCO_3$ precipitation provides credible evidence that Zn^{2+} and other ions can generate a useful scale suppression effect. Experimental findings indicate that various metal ions can exert retarding effect on the nucleation and crystal growth and can also affect the crystal lattice. It is evident that both Zn^{2+} and Cu^{2+} ions can exert an inhibitory action on the scale formation and that their full potential for scale suppression has been very scantily exposed.

2.1.8 Scale Control Techniques

The severity of a potential scaling difficulty in a desalination process depends on the nature and concentration of the scaling species present in the raw feed water. The three main approaches used in controlling scale formation are:

Removal or reduction of scale forming species

- Water Treatment is an effective way of eliminating a scaling problem, which is a measure designed to eliminate the scaling constituents present in the feed water. For instance, acidifying the raw water and degassing CO_2 released from carbonates can prevent alkaline scale formation. Ion exchange columns can readily remove scale – forming ions.
- Water hardness can also be reduced by nanofiltration (NF) membranes. Because of their negative charge, NF membranes preferentially retain divalent ions and thus reduce the concentration of the ions involved in the precipitation of carbonate and sulphate scales. Nanofiltration softening is constrained by economic considerations but could have a potential in integrated membrane systems.
- Chemical Treatment is often the first and the lowest cost approach, especially when scale is not easily accessible or exists where conventional mechanical removal methods are ineffective or expensive to be used. This is carried out by making use of chemical acids and/or chelating agents; compounds that break up acid – resistant scale by isolating and locking up the scale metallic ions within their closed ring – like structure, which dissolve the scale minerals by increasing their solubility. Most chemical treatments are controlled by how well the reagents gain access to the scale surface. Consequently, the surface area to volume ratio is an important parameter in the speed and efficiency of the removal process. Large reactants surface areas, such as porous materials, react quickly, since the acid or the reactant volume surrounding the surface is large. Smaller surface area to volume ratio in thick, non – porous sheets of scale are slow to react with any but the strongest chemical reactants.

CHAPTER THREE

3.0 METHODOLOGY

3.1 BASIC ASSUMPTIONS

The following assumptions were made in developing the mathematical model.

- The formation water and injection water are incompatible and there is perfect mixing
- The formation water contains mineral ions like Ca^{2+}, Ba^{2+} and Sr^{2+}
- The injection water is sea water containing mostly SO_4^{2-}, and other impurities
- Modeling is at location few inches from the petroleum reservoir around wellbore.

The basic method employed in this research work was based on the analytical method using saturation index as the basis. Saturation index is a measure of the tendency of scale to precipitate out of a given solution, i.e. to form precipitate (Moghadasi et al, 2003).

Mathematically,

$$SI = log \frac{[Cation] \times [Anion]}{K_C} \quad (3.01)$$

Where 'SI' represents the Saturation Index, K_C is the solubility product and the brackets represent concentrations in molar units. From the equation (3.01) above, the term saturation ratio (SR) which is the ratio of the ionic activity product to the solubility product can be defined mathematically as;

$$SR = \frac{[Cation] \times [Anion]}{K_c} \quad (3.02)$$

Simplifying equation (3.01), using the rules of logarithm;

$$SI = \log\{[Cation] \times [Anion]\} - \log K_c \quad (3.03)$$

Simplifying this further by replacing $-\log K_c \ with \ pK_c(T, P, I)$, because K_c is a function of temperature, pressure and ionic strength of any given solution,

$$SI = \log\{[Cation] \times [Anion]\} + pK_c(T, P, I) \quad (3.04)$$

But,

$$pK_c = a + bT + cT^2 + dP + eI^{0.5} + fI + gI^{0.5}T \quad (3.05)$$

Therefore, substituting for pK_c as in (3.05) into (3.04), it becomes;

$$SI = \log\{[Cation] \times [Anion]\} + a + bT + cT^2 + dP + eI^{0.5} + fI + gI^{0.5}T \quad (3.06)$$

Where the brackets represent concentration in molar units,

$-\log K_c = pK_c(T, P, I)$ and a, b, c, d, e, f, g are constants that depend on brine (salt solution) and the well condition.

The solubility K_c is the solubility under the conditions of temperature, pressure and ionic strength of a given solution (Moghadasi et al, 2003). It is then possible to calculate the scaling tendency of the formation water at any point in the reservoir.

If Saturation index (SI) = 0.0, the solution is at equilibrium with respect to the ions present and no scale will be precipitated. The equilibrium condition is based upon undisturbed water at constant temperature, which is allowed to remain undisturbed for an infinite period of time (Moghadasi et al, 2003). A negative value of SI indicates an undersaturated solution and will dissolve the scale if any is formed i.e. non scaling condition of the solution with respect to the ions. If SI has a positive value, the solution is supersaturated and will lead to the precipitation of mineral salts known as scale. Although a solution with a positive value of SI, in principle will result into precipitation of mineral salt, in practice it is observed that scale does not form in a

non-turbulent clean water system until the SI exceed a value of about 0.55 for carbonate scales and relatively much less for sulphate scales.

3.2 SCALE FORMATION IN PETROLEUM RESERVOIR DUE TO MIXING OF INCOMPATIBLE WATERS

When sea water mixes with formation water, precipitation occurs. The compositions of the two waters largely affect the thermodynamic of the system. Due to production from the reservoir, oilfield brine are often close to saturation as they enter the well, and even a small amount of sea water rich in sulphate ions is sufficient to induce precipitation of mineral salts. The scaling tendency of sparingly soluble minerals in sea water/ formation water system is observed to be order of magnitude larger than in the brine alone.

Using the saturation index approach (Moghadasi, et al 2003), the tendency of formation of scale minerals (calcite, Barite, Gypsum, Celestine, and Halite) can be analysed using the set of equations below:

$$SI^{\text{Barite}} = \log\left\{\frac{[Ba^{2+}][SO_4^{2-}].\, y^S_{Ba^{2+}}.\, y^S_{SO_4^{2-}}.\left(y^{N\pm}_{BaSO_4}\right)^2}{K_{sp}^{\text{Barite}}}\right\} \tag{3.07}$$

$$SI^{\text{calcite}} = \log\left\{\frac{[Ca^{2+}][HCO_3^-]^2.\, y^S_{Ca^{2+}}.\, y^N_{Ca^{2+}}.\left(y^S_{HCO_3^-}\right)^2.\left(y^N_{HCO_3^-}\right)^2.K_2}{P_{CO_2}.\gamma_{CO_{2,g}}.K_H.K_1.K_{sp}^{\text{calcite}}}\right\} \tag{3.08}$$

$$SI^{\text{Celestite}} = \log\left\{\frac{[Sr^{2+}][SO_4^{2-}].\, y^S_{Sr^{2+}}.\, y^S_{SO_4^{2-}}.\left(y^{N\pm}_{SrSO_4}\right)^2}{K_{sp}^{\text{Celestite}}}\right\} \tag{3.09}$$

$$SI^{Gypsum} = \log\left\{\frac{[Ca^{2+}][SO_4^{2-}].\, y^S_{Ca^{2+}}.\, y^S_{SO_4^{2-}}.\left(y^N_{CaSO_4}\right)^2.\left(a^S_{H_2o}\right)^2.\left(a^N_{H_2o}\right)^2}{K_{sp}^{Gypsum}}\right\} \tag{3.10}$$

$$SI^{\text{Halite}} = \log\left\{\frac{[Na^{+}][Cl^{-}].\, y^S_{Na^{+}}.\, y^S_{Cl^{-}}.\left(y^{N\pm}_{NaCl}\right)^2}{K_{sp}^{\text{Halite}}}\right\} \tag{3.11}$$

3.3 PROCEDURES USED IN THE SCALE PREDICTION MODEL

The following procedures were used to estimate the effect of sea water on mineral solubility at a specific temperature, ionic strength, and co solvent concentration:

1. The thermodynamic equilibrium constants of Scales at specific temperature were determined.
2. Concentration unit was converted to moles/Kg of water. Solution phase measurement of concentration is generally made by taking a specific volume of sample.
3. The ionic interaction activity coefficient was determined with one of the activity coefficient equations.
4. The pH of the mixed incompatible waters was also determined.
5. The effects of the activity coefficients of the major components of sea water was determined using the thermodynamic equilibrium constant
6. If the solubility composition , the saturation index value can be calculated via 1 – 5
7. Lastly, the amount of inorganic mineral that will precipitate out of petroleum reservoir of known composition was then calculated.

3.3.1 Determination of thermodynamic equilibrium constants of different scale minerals in seawater/brine system

The temperature dependence of thermodynamic constant is well established in the literature (Moghadasi et al, 2003) as:

$$pK_c = a + bT + cT^2 + dP + eI^{0.5} + fI + gI^{0.5}T \quad (3.12)$$

Where pK_c = the negative log of the conditional solubility constant and a, b, c, d, e, f, and g are constants that depend on brine composition and the well condition. The cross product term ($I^{0.5}T$) was introduced at low conditional solubility constants to

vary as function of ionic strength in conjunction with temperature and is found to be significant for all salts except calcium carbonate. The cross product between temperature, pressure and second order ionic strength (IT^2) is also significant (Moghadasi et al, 2003).

3.3.2 Conversion of Concentration unit to moles/Kg H_2O

This conversion is necessary because concentration in unit of moles/KgH_2O, also known as Molality, is temperature independent, whereas molar concentration (mg/L) changes with temperature as solution density changes. Solution phase measurements of concentration are generally made by taking a specific volume of sample mg/L which can easily be converted to molarity unit (mol/L). If density and ionic strength are known, the mg/L can easily be converted to moles/KgH_2O basis.

A relationship between ionic strength (I) and density (ρ) has been established by curve fitting the density of brine vs. ionic strength (Kaasa et al, 2005).

$$\rho(g/mL) = 0.9991 + 0.6358(I * 10^{-6}) - I * 10^{-6} \quad (3.13)$$

$$\therefore Concentration\left({}^{moles}/_{KgH_2O}\right) = \frac{Concentration\ \left[{}^{moles}/_{L\ (H_2O)}\right]}{\rho_{brine}(Kg/L)} \quad (3.14)$$

3.3.3 Determination of the free ion activity coefficient

The free ion activity coefficient describes the relation between the activity and the concentration of a free ion species. There are several theoretically – based expressions that can be used to estimate the single ion activity coefficient. However, each is only good for a limiting range of ionic strength.

3.3.3.1 Debye – Hückel Equation

Limiting Law

For $I < 10^{-2}$ $\quad \log\gamma_i = -Az_i{}^2 I^{0.5}$ (3.15)

Extended Debye – Hückel Equation

$$\text{For I} < 10^{-1} \quad \log\gamma_i = \frac{-Az_i{}^2 I^{0.5}}{(1 + a_i.B.I^{0.5})} \tag{3.16}$$

3.3.3.2 Davies Equation

$$\text{For } I < 0.5 \qquad \log\gamma_i = -Az_i{}^2\left(\frac{I^{0.5}}{1+I^{0.5}} - 0.21\right) \tag{3.17}$$

Where;

$$I = \frac{1}{2}\sum C_i z_i{}^2 \tag{3.18}$$

$$A = 1.82 * 10^6(\varepsilon T)^{-1.5} \tag{3.19}$$

$$B = 50.3(\varepsilon T)^{-0.5} \tag{3.20}$$

Where

z =charge on the ion,

a = adjustable parameter (angstroms) corresponding to the size of the ion,

ε = dielectric constant

3.3.4 Determination of the pH of mixed Incompatible Waters System

Alkalinity is the most important parameter controlling pH in aqueous solutions. Even though, there are several misunderstandings of what the alkalinity actually means. The easiest way to start with is the electro neutrality equation. An aqueous solution cannot have a positive or negative charge so the sum of all negative charged species must equal the sum of positive charged species, (Kaasa et al, 2005). For an aqueous solution containing$NaCl$, $NaHCO_3$ and acetic acid, the electro neutrality equation is;

$$m_{Na^+} + m_{H^+} = m_{OH^-} + m_{Cl^-} + m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{Ac^-} \tag{3.21}$$

If the equation is rearranged to get all pH dependent species on one side and pH independent on the other side we obtain;

$$m_{Na^+} - m_{Cl^-} = m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{Ac^-} + m_{OH^-} - m_{H^+} \tag{3.22}$$

The definition of total alkalinity is therefore;

$$A_T = m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{Ac^-} + m_{OH^-} - m_{H^+} \quad (3.23)$$

Using the equation (3.22) above, it is easy to identify which components affect alkalinity. Addition of $NaCl$ will obviously not change the alkalinity as both $Na^+$and Cl^- enters the same side of the equation with opposite signs. Less obvious is that addition of CO_2 by changing the CO_2 pressure either will change the alkalinity. From equation (3.22), it is easy to see that the left hand side is constant as well as the right hand side is also constant. Addition of CO_2 will change the pH and all the concentrations on the right hand side will change, but the sum is constant.

Similarly, the pH of the mixed incompatible waters system can be determined using the relation given by (Moghadasi et al, 2005);

$$pH = \log\left\{\frac{[HCO_3^-]}{Py_g^{CO_2} f_g^{CO_2}}\right\} - \log\{K_1 K_{aq}^{CO_2}\}(T, P, I) \quad (3.24)$$

To use the equation above, three issues are to be addressed and they are as follow;

- The T, P, and I dependence of the equilibrium constants.
- The thermodynamic non - ideality of the gas phase CO_2 at high pressure.
- The variation of the mole fraction of CO_2 in the gas phase with pressure and with gas/oil/water volumetric ratios.

3.3.5 Determination of the effects of Sea water components' Activities Coefficients

From the first principle, the total concentration of an element (m_t) can relatively be determined. This is usually what can be most easily measured analytically. The concentration of the ion or specie is of upmost important (Davies equation), hence, the need to convert total concentration (m_t), to the concentration of the ion or species

(m_i). In order to calculate (m_i) from (m_t) we need to do an equilibrium calculation of the percent free which is express as (f_i). Thus;

$$m_i = m_t \times f_i \tag{3.25}$$

For the case where the element is (Ca_t) but Ca^{2+} is required, hence the need to calculate the ratio:

$$f_{Ca^{2+}} = \frac{[Ca^{2+}]}{Ca_t} = \frac{[Ca^{2+}]}{\{[Ca^{2+}] + [CaSO_4] + [CaCO_3]\}} \tag{3.26}$$

From the concentration of the free ion (m_i)**,** it is converted to the activity of the free ion (a_i). The free ion activity coefficient (γ_i) which corrects for electrostatic shielding by other ions is used for the conversion. This correction is written a

$$a_i = \gamma_i \times m_i \tag{3.27}$$

Where;

γ_i = free ion activity coefficient for that specie

m_i = molal concentration of a free ion

The total expression for a_i using both correction factors will be;

$$a_i = \gamma_i \times f_i \times m_t \tag{3.28}$$

Where also;

f_i = the percent of the total concentration (m_t) that is free

m_t = the total ion concentration

Sometimes, it is preferable to combine γ_i and f_i together and called the total activity coefficient (γ_t). Then,

$$a_i = \gamma_t \times m_t \tag{3.29}$$

Where; $\gamma_t = \gamma_i . f_i$

Example: a solution containing Ca^{2+}, SO_4^{2-} and CO_3^{2-} forms the complexes $CaSO_4$ and $CaCO_3$, then, $\gamma_{t,Ca}$ will be;

$$\gamma_{t,Ca} = f_{Ca^{2+}} \times \gamma_{Ca^{2+}}$$

$$= \frac{[Ca^{2+}]}{Ca_t} \times \gamma_{Ca^{2+}}$$

$$= \frac{[Ca^{2+}]}{\{[Ca^{2+}] + [CaSO_4] + [CaCO_3]\}} \times \gamma_{Ca^{2+}}$$

3.3.6 Determination of the Amount of Scales precipitated in Petroleum Reservoir (Siri Oil Fields)

The amount of inorganic scale mineral that will precipitate (Ppt_{salt} in the unit of mol/kgH_2O) from a solution of known composition in formation water/ injected sea water solution can be estimated thus, with reference from the research work conducted by 'Moghadasi et al, 2005' in estimating the K_{sp} of common scale minerals formed in petroleum reservoir.

Considering the chemical equation shown below;

$$aA + bB = cC + dD \tag{3.30}$$

The law of mass action for the chemical equation above states;

$$K_{sp} = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \tag{3.31}$$

Where '[ ]' signifies the concentration in Molarity ($moles/Kg$), and thus;

$$K_{sp} = f(Molarity) \tag{3.31'}$$

Also, the Molarity from chemistry is defined as;

$$Molarity = \frac{Moles\ of\ solute\ (scale\ mineral)}{Mass\ of\ solvent\ (incompatible\ waters)} \tag{3.32}$$

For a particular mass of solvent, the Molarity can be expressed as a function of moles of solvent as;

$$Molarity = f(moles\ of\ solute)\ at\ constant\ mass\ of\ solvent \tag{3.32'}$$

The number of moles of solute is defined mathematically as;

$$Moles\ of\ solute = \frac{Mass\ of\ solute\ precipitated(Kg)}{Molar\ mass\ of\ solute\ \ (Kg/moles)} \tag{3.33}$$

The molar mass of any compound is constant and as a result equation (3.33) becomes

$$Moles\ of\ solute = \ f\ (\ Mass\ of\ solute\ precipitated) \tag{3.33'}$$

Therefore from equations (3.31'), (3.32'), and (3.33'), it can be inferred that;

$$K_{sp}\ = f(Molarity) = f(Moles\ of\ solute) = f\ (Mass\ of\ solute) \tag{3.34}$$

Using the general quadratic formulae; $aX^2\ + bX\ + C\ = 0$

Where 'X' is the unknown, therefore replacing the variable 'X' with our unknown variable 'Ppt_{salt}' which is the amount of scale that will be precipitated, we have;

$$a(Ppt_{salt})^2\ + b(Ppt_{salt})\ + c\ = 0 \tag{3.35}$$

For a particular inorganic salt, let say$BaSO_4$, the dissociation reaction is as shown below;

$$BaSO_4 \rightleftharpoons\ Ba^{2+} +\ SO_4^{2-} \tag{3.36}$$

From the above,

$$a\ = 1 \qquad b\ =\ [Ba^{2+}] +\ [SO_4^{2-}] \qquad c =\ [Ba^{2+}]\,[SO_4^{2-}] -\ SR^{-1}$$

Where SR = Saturation Ratio, for $BaSO_4$

$$SR = \frac{[Ba^{2+}][SO_4^{2-}].\,y_{Ba^{2+}}^{S}.\,y_{SO_4^{2-}}^{S}.\left(y_{BaSO_4}^{N\pm}\right)^2}{K_{sp}^{Barite}} \tag{3.37}$$

If $Y = SR^{-1}\ therefore,$

$$Y_{Barite}\ = \frac{K_{sp}^{Barite}}{[Ba^{2+}][SO_4^{2-}].\,y_{Ba^{2+}}^{S}.\,y_{SO_4^{2-}}^{S}.\left(y_{BaSO_4}^{N\pm}\right)^2} \tag{3.37'}$$

Using the quadratic formulae to solve for the unknown 'Ppt_{salt}' in (3.35)

$$\frac{-b\ \pm\ \sqrt{b^2\ -4ac}}{2a} \tag{3.38}$$

$$= \frac{-\{[Ba^{2+}] + [SO_4^{2-}]\} \pm \sqrt{\{[Ba^{2+}] + [SO_4^{2-}]\}^2 - 4\{\{[Ba^{2+}][SO_4^{2-}]\} - Y\}}}{2}$$

$$Ppt_{Barite} = \frac{-\{[Ba^{2+}] + [SO_4^{2-}]\} \pm \mathcal{X}}{2} \tag{3.39}$$

Where;

$$\mathcal{X} = \sqrt{\{[Ba^{2+}] + [SO_4^{2-}]\}^2 - 4\{\{[Ba^{2+}][SO_4^{2-}]\} - Y\}} \tag{3.40}$$

The mineral scales are calcite, Barite, Gypsum, Celestine, and Halite.

$$Y_{Barite} = \frac{K_{sp}^{Barite}}{[Ba^{2+}][SO_4^{2-}].y_{Ba^{2+}}^{S}.y_{SO_4^{2-}}^{S}.\left(y_{BaSO_4}^{N\pm}\right)^2} \tag{3.41a}$$

$$Y_{Calcite} = \frac{P_{CO_2}.\gamma_{CO_{2,g}}.K_H.K_1.K_{sp}^{\text{calcite}}}{[Ca^{2+}][HCO_3^-].y_{Ca^{2+}}^{S}.y_{Ca^{2+}}^{N}.\left(y_{HCO_3^-}^{S}\right)^2.\left(y_{HCO_3^-}^{N}\right)^2.K_2} \tag{3.41b}$$

$$Y_{Celestite} = \frac{K_{sp}^{\text{Celestite}}}{[Sr^{2+}][SO_4^{2-}].y_{Sr^{2+}}^{S}.y_{SO_4^{2-}}^{S}.\left(y_{SrSO_4}^{N\pm}\right)^2} \tag{3.41c}$$

$$Y_{Gypsum} = \frac{K_{sp}^{Gypsum}}{[Ca^{2+}][SO_4^{2-}].y_{Ca^{2+}}^{S}.y_{SO_4^{2-}}^{S}.\left(y_{CaSO_4}^{N\pm}\right)^2.\left(a_{H_2o}^{S}\right)^2.\left(a_{H_2o}^{N}\right)^2} \tag{3.41d}$$

$$Y_{Halite} = \frac{K_{sp}^{Halite}}{[Na^{+}][Cl^{-}].y_{Na^{+}}^{S}.y_{Cl^{-}}^{S}.\left(y_{NaCl}^{N\pm}\right)^2} \tag{3.41e}$$

Note: if Ppt_{salt} is negative, this correspond to dissolution and hence, no scale will be precipitated.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

In order to examine the impact of mineral scale on petroleum reservoir under realistic field conditions, typical brine and well conditions (Moghadasi et al, 2003) were selected for the research work. This was used to evaluate the amount of mineral scale that would be precipitated using the model developed in this research work. Microsoft excel was used to simulate the model and the results obtained are analysed below;

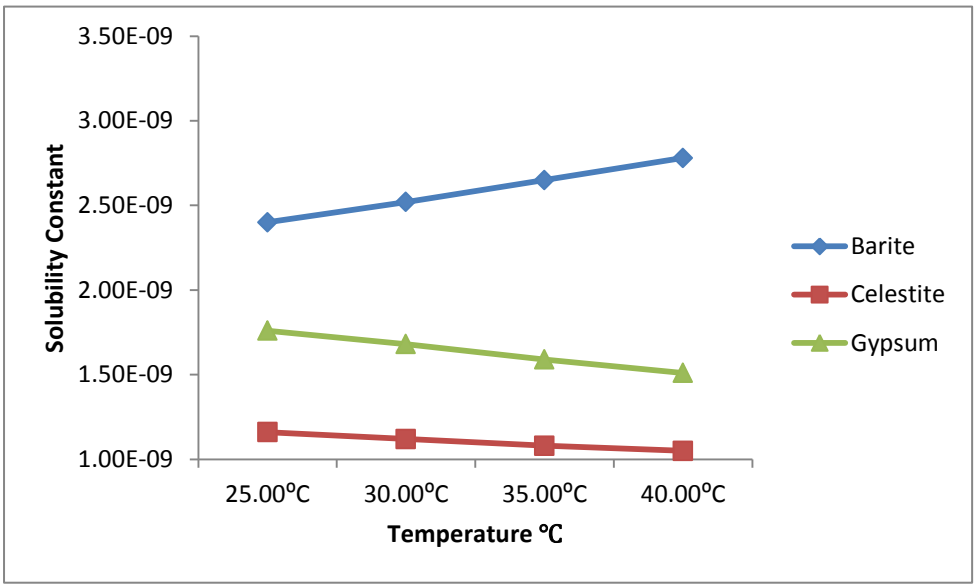

FIG. 4.1: VARIATION OF SOLUBILITY CONSTANTS OF SCALES WITH TEMPERATURE AT CONSTANT PRESSURE

Figure 4.1 shows how the solubility constants of common mineral scales vary with temperature. The solubility constant of Barite increases approximately linearly with temperature and has its highest value when temperature is 40^0C. For Gypsum, its solubility constant has an inverse relationship with temperature and has its lowest value at temperature of 40^0C. The solubility constant of Celestite is approximately constant with respect to change in temperature. Among the three mineral scales, Barite has the highest solubility constant while Celestite has the lowest solubility constant at any given temperature.

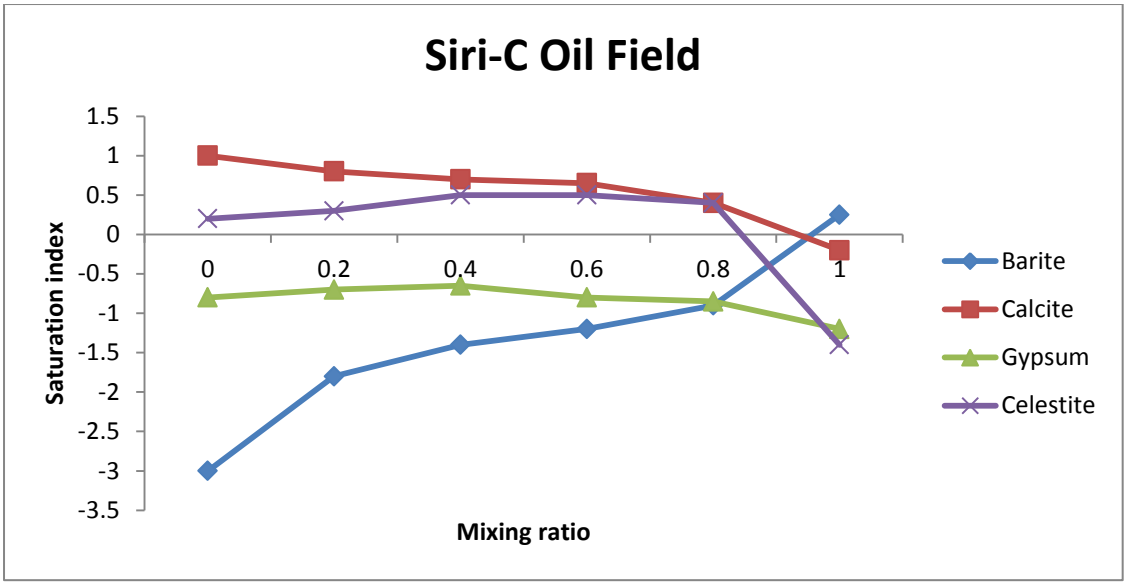

FIG. 4.2: VARIATION OF SATURATION INDICES OF SCALES WITH MIXING RATIO OF PERSIAN GULF WATER AT CONSTANT TEMPERATURE AND PRESSURE

Figure 4.2 shows the variation of saturation index of common scales with mixing ratio of Persian Gulf water at constant temperature and pressure in Siri-C oil field. It was observed that as the mixing ratio increases the saturation indices of the mineral scales also change. The saturation index of Calcite has an inverse relationship with the mixing ratio of the Persian Gulf water. It has the highest value when the mixing ratio is 0 and the lowest value when it is 1.0. For Barite, the saturation index has a direct relationship with the mixing ratio, having its lowest value when the mixing ratio is 0 and its highest value when the mixing ratio is 1.0. The saturation index of Gypsum is approximately independent on the mixing ratio. It has little variation with change in the mixing ratio of the Persian Gulf water. The saturation index of Celestite also increases with increasing mixing ratio up to its maximum value when the mixing ratio is 0.6 and then starts declining as the mixing ratio increases.

Figure 4.3 shows the variation of saturation index of common scales with mixing ratio of Persian Gulf water at constant temperature and pressure in Siri-D oil field. It was observed that as the mixing ratio increases the saturation indices of the mineral scales also change.

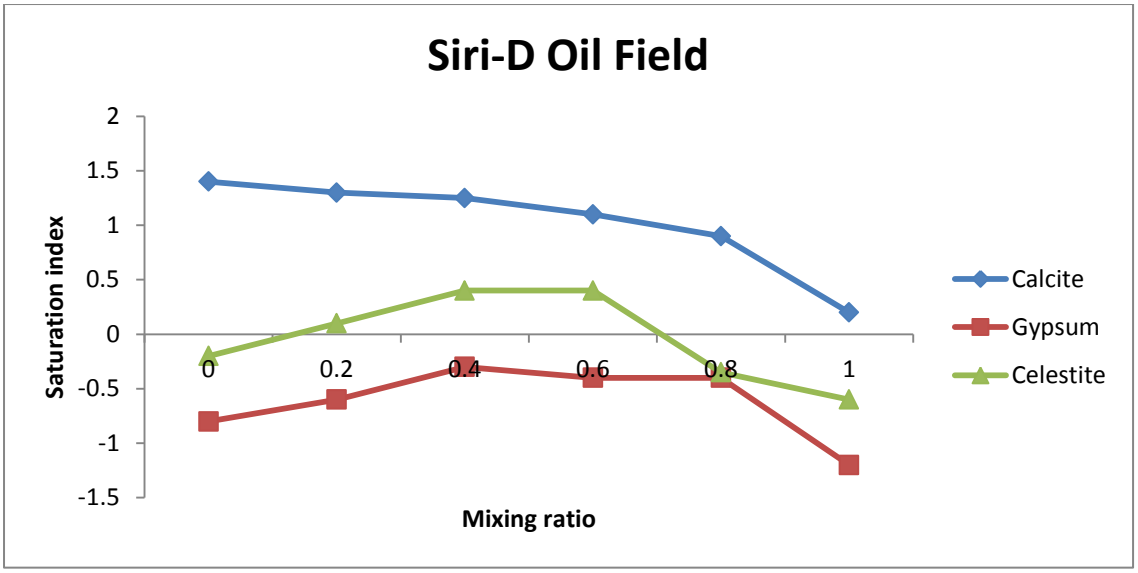

FIG. 4.3: VARIATION OF SATURATION INDICES OF SCALES WITH MIXING RATIO OF PERSIAN GULF WATER AT CONSTANT TEMPERATURE AND PRESSURE

The saturation index of Calcite has an inverse relationship with the mixing ratio of the Persian Gulf water. The saturation index has its maximum value when the mixing ratio is 0 and its lowest value occurs when the mixing ratio is 1.0. The saturation index of Celestite also increases with the mixing ratio up to its maximum value when the mixing ratio is 0.4, which remain constant till 0.6 and starts to decline. For Gypsum, the saturation index increases with mixing ratio till the point where the mixing ratio is 0.4, it remains constant till 0.8 and then starts to decline gradually. Figure 4.4 shows the variation of saturation index of common scales with mixing ratio of Persian Gulf water at constant temperature and pressure in Siri-E oil field. It was observed that as the mixing ratio increases the saturation indices of the mineral scales also change. The saturation index of Calcite has an inverse relationship with the mixing ratio. Its maximum value occurs when the mixing ratio is 0 and its lowest value occurs when the mixing ratio is 1.0. For Gypsum, its saturation index increases with the mixing ratio up to 0.4, it declines a little bit, then increases again till 0.8 and finally decreases gradually. For Celestite, the saturation index is directly proportional to the mixing ratio.

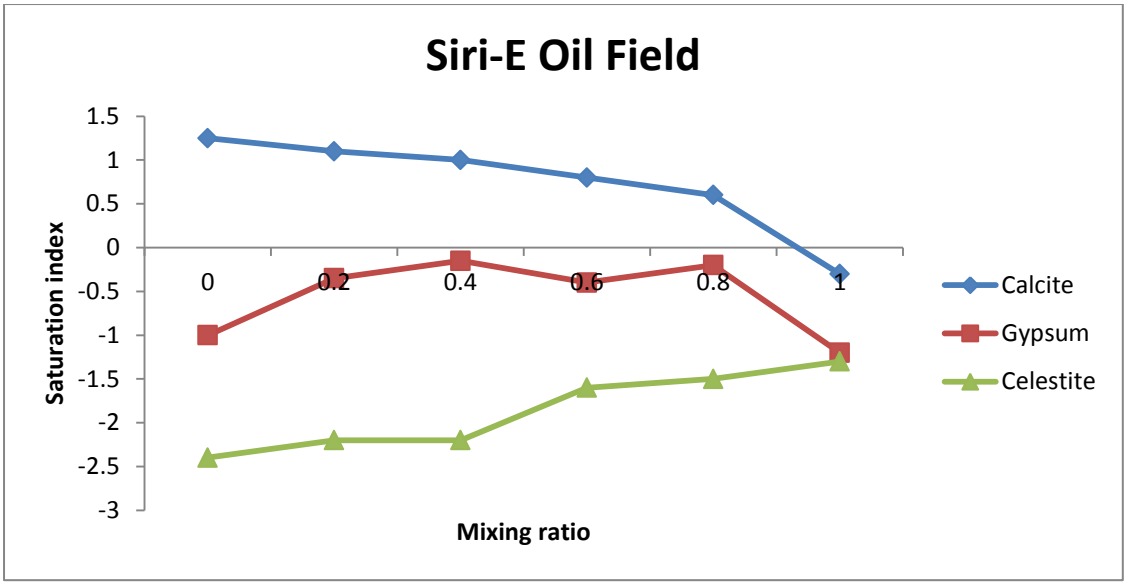

FIG. 4.4: VARIATION OF SATURATION INDICES OF SCALES WITH MIXING RATIO OF PERSIAN GULF WATER AT CONSTANT TEMPERATURE AND PRESSURE

Figure 4.5 shows the amount of barite that would be precipitated in Siri –C field at the different values of the saturation index. It was observed that as the saturation index increases from -3 to -1.8, the amount of precipitate increases and beyond -1.8, the amount of precipitate formed remains fairly constant.

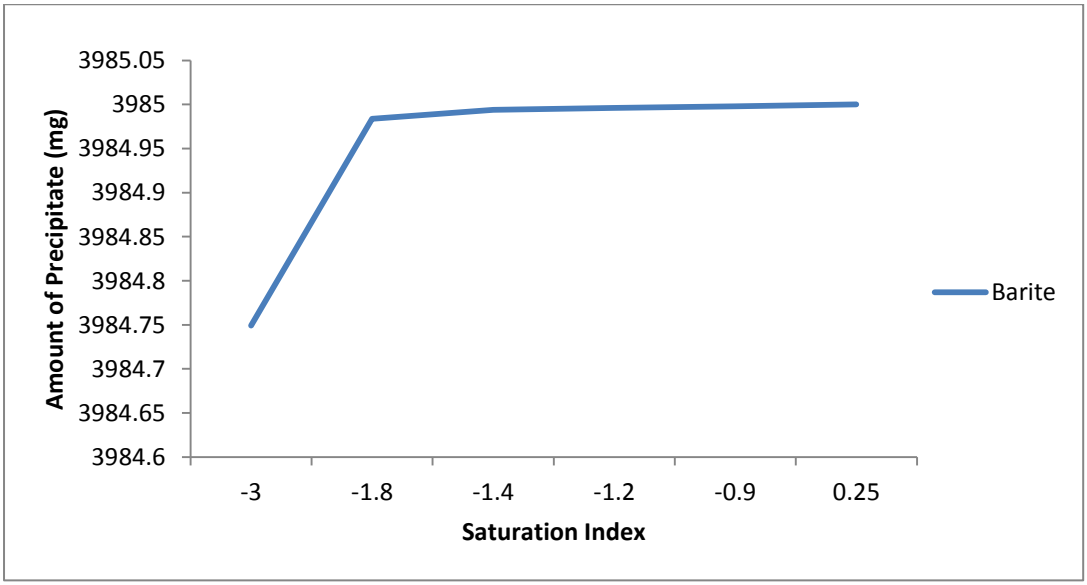

FIG. 4.5: AMOUNT OF BARITE PRECIPITATED IN SIRI-C OIL FIELD

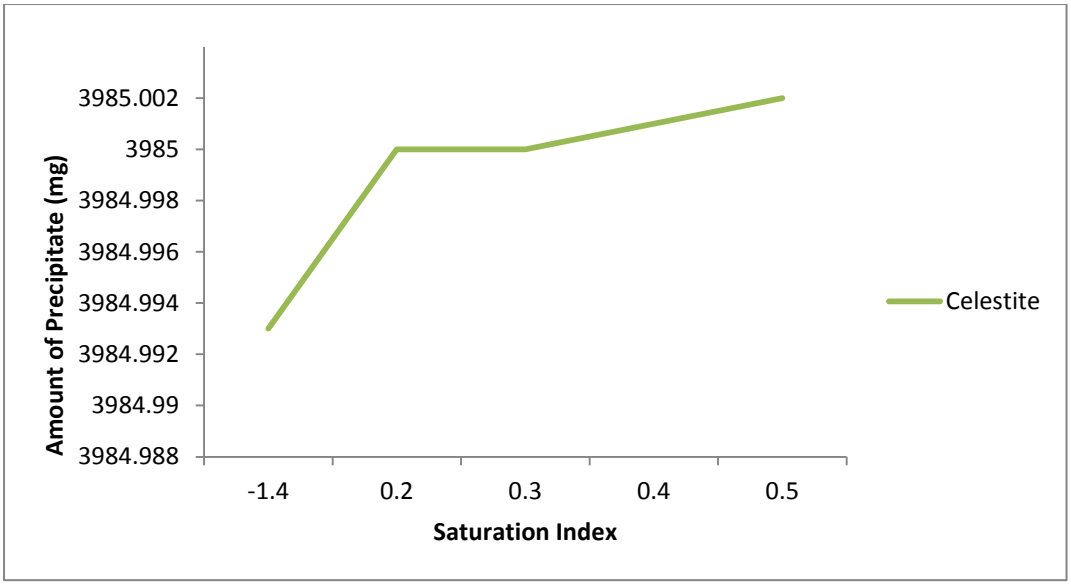

FIG. 4.6: AMOUNT OF CELESTITE PRECIPITATED IN SIRI-C OIL FIELD

Figure 4.6 shows the amount of Celestite that would be precipitated in Siri –C field at the different values of the saturation index. It was observed that as the saturation index increases from -1.4 to 0.2, the amount of precipitate increases linearly and beyond 0.2, it remains fairly constant till the saturation index reaches 0.3 and starts to increase again.

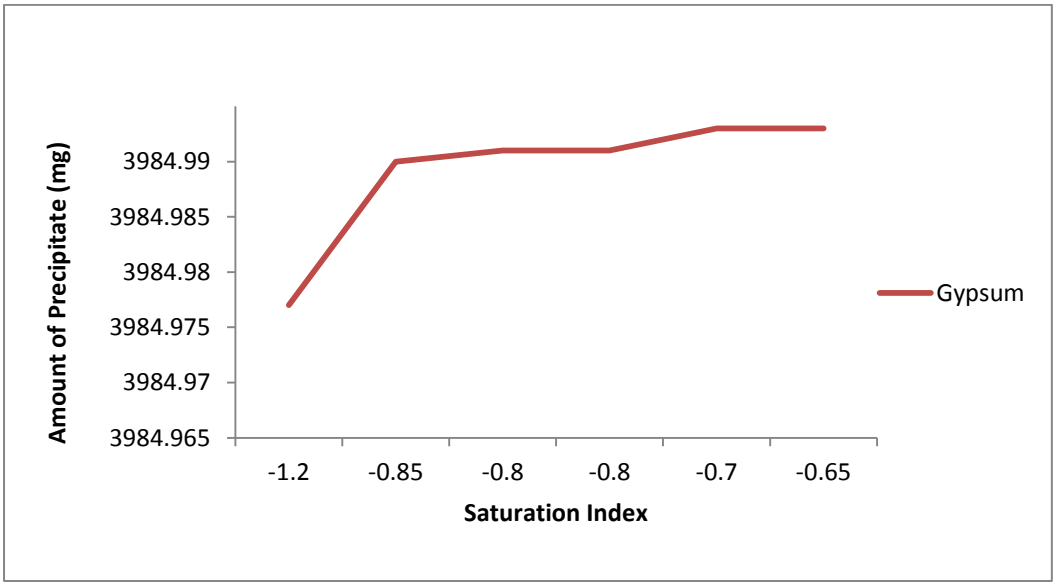

FIG. 4.7: AMOUNT OF GYPSUM PRECIPITATED IN SIRI-C OIL FIELD

Figure 4.7 shows the amount of Gypsum that would be precipitated in Siri –C field at the different values of the saturation index. It was observed that as the saturation

index increases from -1.2 to -0.85, the amount of precipitate increases linearly and beyond -0.85, it increases slightly with the saturation index.

In figure 4.8, the different scales that will be precipitated in Siri-C oil field are plotted on the same graph. It was observed that at saturation index of -3, Gypsum has the lowest amount of precipitate that will be formed while those of Barite and Celestite are approximately the same. But when the saturation index is -1.4, the three scales have the same amount of precipitate formed and they remain approximately constants beyond this point.

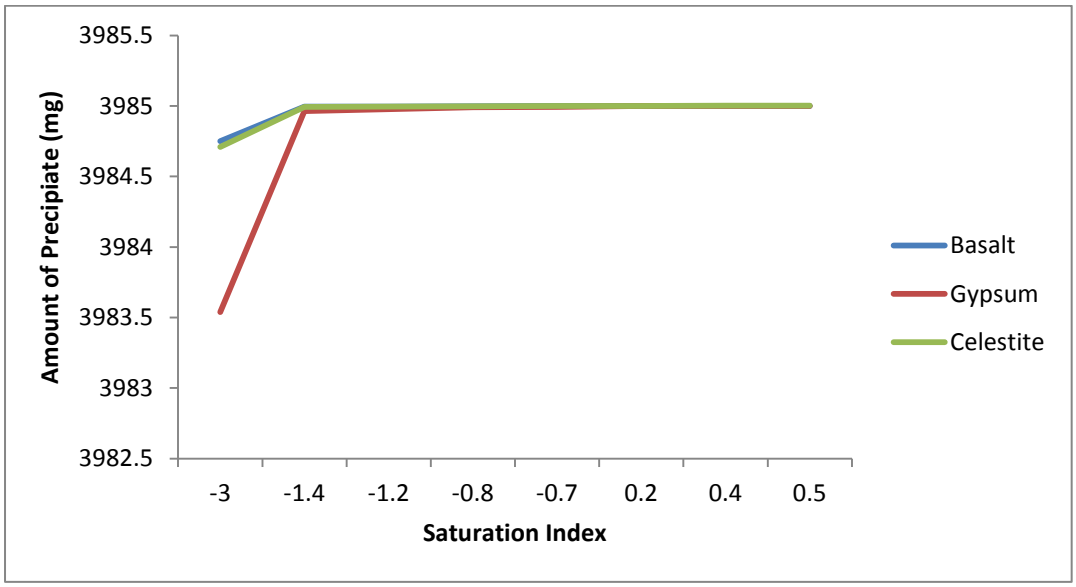

FIG. 4.8: AMOUNT OF SCALES PRECIPITATED IN SIRI-C OIL FIELD

Figure 4.9 shows the amount of Gypsum that would be precipitated in Siri –D field at the different values of the saturation index. It was observed that as the saturation index increases from -1.2 to -0.80, the amount of precipitate increases slightly, at -0.8, it decreases with the saturation index till 0.6 where it picks up again and increases up till the saturation index of -0.4. Beyond this region, the amount of Gypsum remains approximately constant with increase in saturation index.

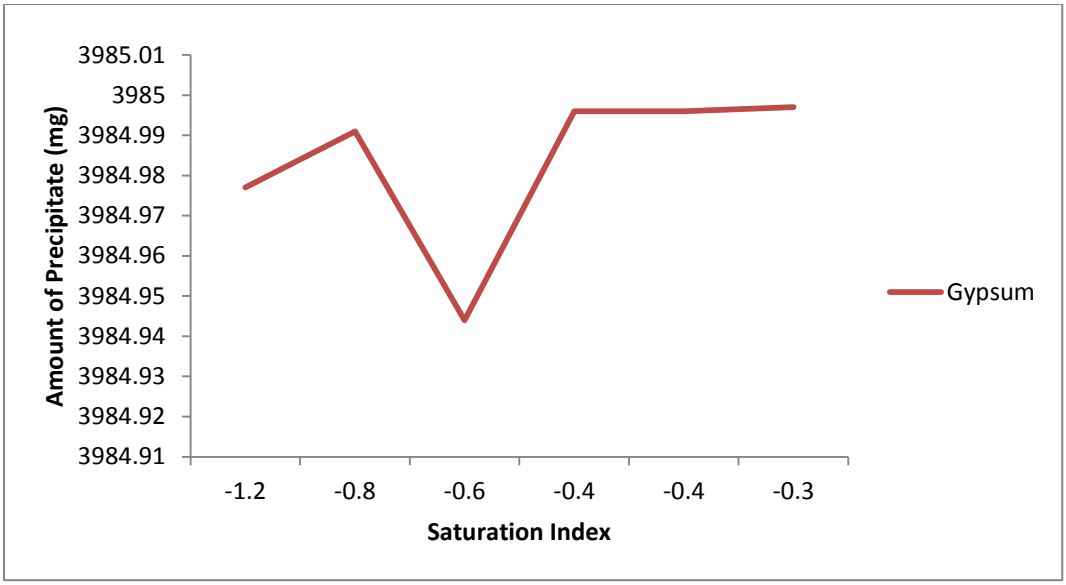

FIG. 4.9: AMOUNT OF GYPSUM PRECIPITATED IN SIRI-D OIL FIELD

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Figure 4.10 shows the amount of Celestite that would be precipitated in Siri –D field at the different values of the saturation index. It decreases with increase in saturation index from -0.6 to -0.2 and beyond this point, it increase linearly up till 0.4.

FIG. 4.10: AMOUNT OF CELESTITE PRECIPITATED IN SIRI-D OIL FIELD

In figure 4.11, the different scales that will be precipitated in Siri-D oil field are plotted on the same graph

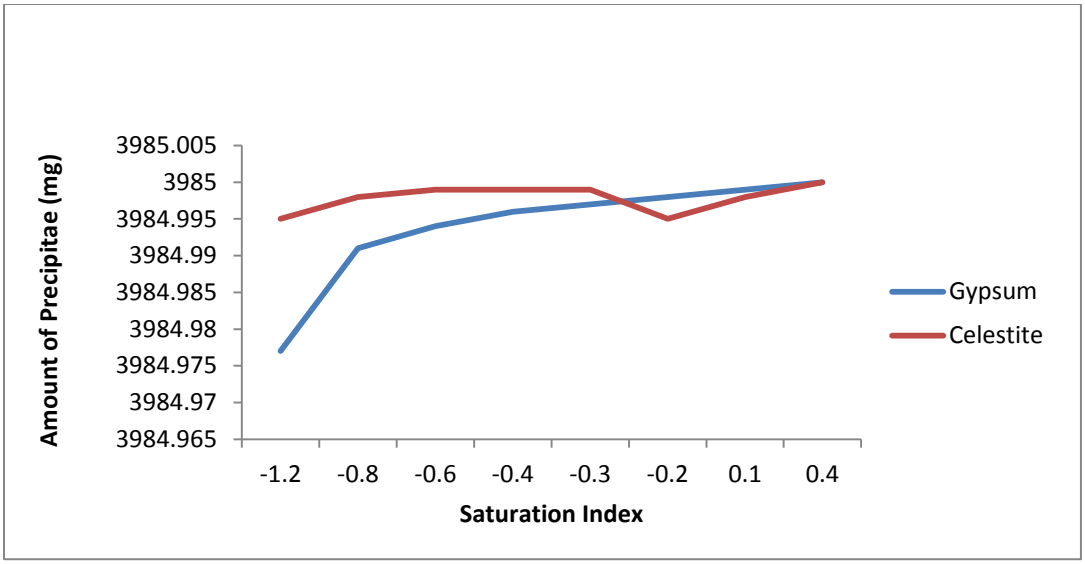

FIG. 4.11: AMOUNT OF SCALES PRECIPITATED IN SIRI-D OIL FIELD

It was observed that at saturation index of -1.2, Gypsum has the lowest amount of precipitate that will be formed. As the saturation index increases, the amount of Gypsum that will be precipitated increases considerably while that of Celestite increases slightly for a little and remains fairly constant. At -0.3, the amount of Celestite decreases for a while and picks up again. For Gypsum, the amount precipitated increases slightly and then equals that of Celestite.

FIG. 4.12: AMOUNT OF GYPSUM PRECIPITATED IN SIRI-E OIL FIELD

Figure 4.12 shows the amount of Gypsum that would be precipitated in Siri –E field at the different values of the saturation index. The amount of gypsum precipitated increases slightly from -0.4 to -0.15, it decreases abruptly beyond -0.15 up till -1.2 and increases gradually with increase in saturation index.

Figure 4.13 shows the amount of Celestite that would be precipitated in Siri –D field at the different values of the saturation index. It increases with increase in saturation index from -0.35 to -0.3, decreases a little and increases slightly up till -1.6. It remains constant till -1.5 and then decreases abruptly with further increase in saturation index.

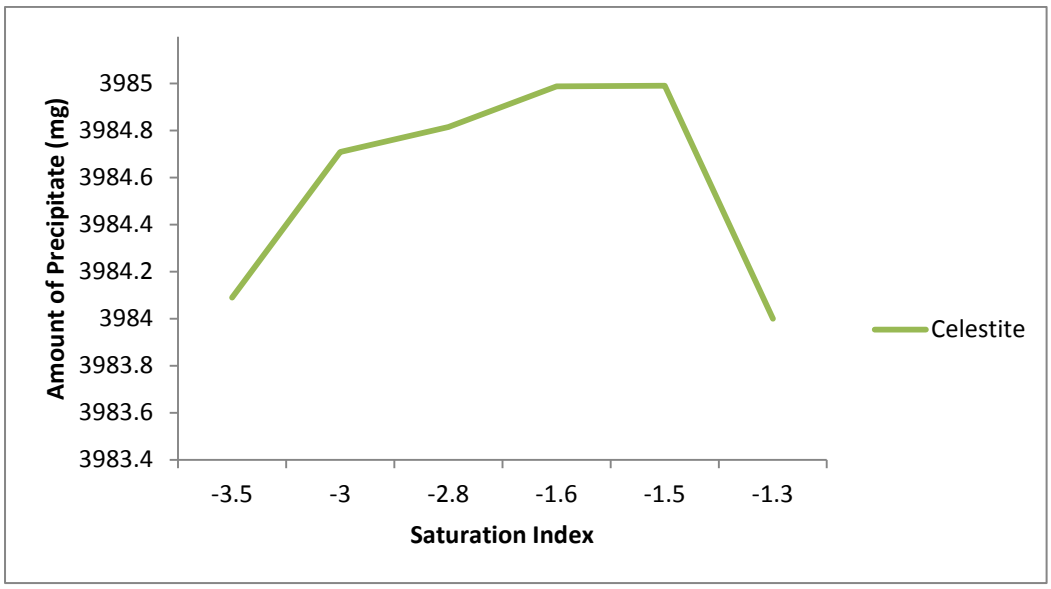

FIG. 4.13: AMOUNT OF CELESTITE PRECIPITATED IN SIRI-E OIL FIELD

In figure 4.14, the different scales that will be precipitated in Siri-E oil field are plotted on the same graph. It was observed that at saturation index of -3.5, Gypsum has the lowest amount of precipitate that will be formed while that of Celestite is fairly high. As the saturation index increases, the amount of Gypsum that will be precipitated increases considerably while that of Celestite increases slightly and then, remains fairly constant. At -1.5, the amounts of Celestite and Gypsum precipitated coincide and remain fairly constant with further increase in saturation index.

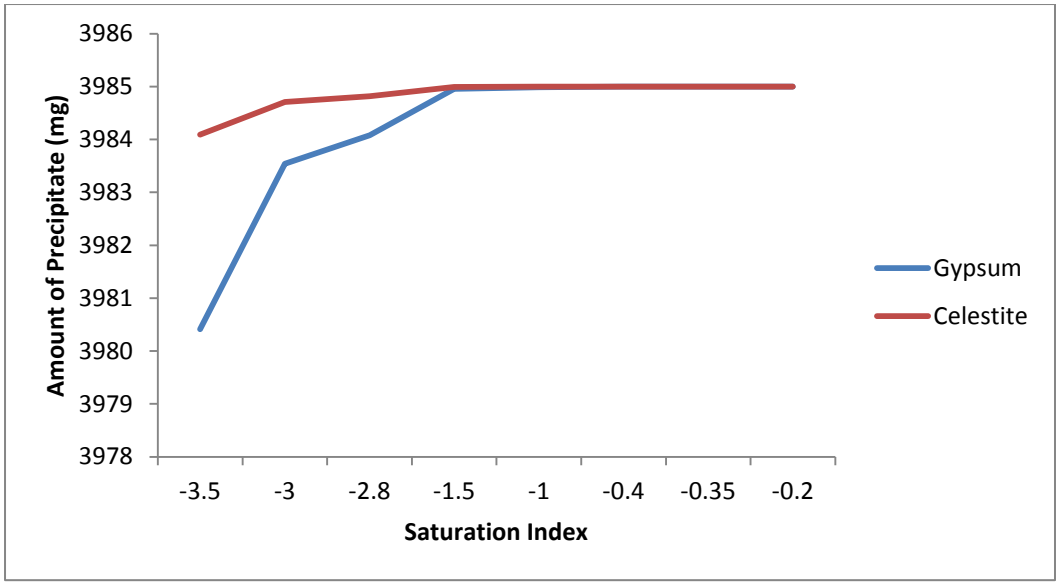

FIG. 4.14: AMOUNT OF SCALES PRECIPITATED IN SIRI-E OIL FIELD

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Scale formation has been cited as a severe problem not only in the reservoir but also in the production lines. The various processes that lead to scale formation were investigated and the predictions of the amounts of scale that will be precipitated in selected fields were carried out.

It was concluded at the end of this research wok that in the absence of impurities that aid scale formation, knowing the amount of scale that will be precipitated will enhance a proper scale control technique and as such enhance crude oil production. Also the saturation indices of the scales have impact on the amount of scales precipitated. At saturation index of -3.50, Celestite has the lowest amount of scale precipitated, while at -2.80, Gypsum has the lowest amount of scale precipitated. But when the saturation index increases to 0.5, Celestite has the greatest amount of scale precipitated, followed by Gypsum. Thus, the higher the saturation index of any scale, the higher the amount of the scale that will be precipitated and vice versa.

5.2 RECOMMENDATION

In order to effectively control scale formation as well as enhance crude oil production, the amount of scales that will be precipitated should be properly determined. And if the saturation indices of the scales are as low as possible, it will minimize the amount of scales precipitated.

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APPENDIX

TABLE A.1: THE VALUES OF THE CONSTANTS 'a, b, c, d, e, f, and g' FOR DIFFERENT MINERAL SCALES

SCALE	a	b	c	d	e	f	g
$BaSO_4$	10.03	-4.80×10^{-3}	11.40×10^{-5}	-4.80×10^{-5}	-2.62	0.89	-2.00×10^{-3}
$CaSO_4$	2.52	9.98×10^{-3}	-0.97×10^{-6}	-3.07×10^{-5}	-1.09	0.50	-3.30×10^{-5}
$CaSO_4.\frac{1}{2}H_2O$	4.04	-1.90×10^{-3}	11.90×10^{-6}	-6.9×10^{-5}	-1.66	0.49	-0.66×10^{-3}
$CaSO_4.2H_2O$	3.47	1.80×10^{-3}	2.50×10^{-6}	-5.90×10^{-5}	-1.13	0.37	-2.00×10^{-3}
$SrSO_4$	6.11	2.00×10^{-3}	6.40×10^{-6}	-4.60×10^{-5}	-1.89	0.60	-1.90×10^{-3}

TABLE A.2: IONIC COMPOSITIONS OF PERSIAN SEA WATER AND FORMATION WATER IN SIRI OIL FIELDS

Major Ions (mg/L)	Siri – C Field	Siri – D Field	Siri – E Field	Persian Sea Water
Na^+	42215	35391	42800	11750
Ba^{2+}	-	-	-	0.09
Ca^{2+}	3032	4525	8917	267
Sr^{2+}	547	760	-	3.4
Cl^-	73942	70740	83324	23000
SO_4^{2-}	635	310	142	3350

TABLE A.3: THE VALUES OF 'SI' AND '$(SR)^{-1}$' FOR SCALES IN SIRI-C OIL FIELD

$BaSO_4$		$CaSO_4$		$SrSO_4$	
SI	$(SR)^{-1}$	SI	$(SR)^{-1}$	SI	$(SR)^{-1}$
-3.00	0.0010	-0.80	0.1585	0.20	1.5849
-1.80	0.0159	0.70	0.1995	0.30	1.9953
-1.20	0.0631	-0.80	0.1585	0.50	3.1623

-0.9	0.1259	-0.85	0.1413	0.40	2.5119
0.25	1.7783	-1.20	0.0631	-1.40	0.0398

TABLE A.4: THE VALUES OF 'SI' AND '$(\mathbf{SR})^{-1}$' FOR SCALES IN SIRI-D OIL FIELD

$CaSO_4$		$SrSO_4$	
SI	$(\mathbf{SR})^{-1}$	**SI**	$(\mathbf{SR})^{-1}$
-1.20	15.8489	-0.60	3.9811
-0.80	6.3095	-0.35	2.2387
-0.60	3.9811	-0.20	1.5849
-0.40	2.5119	0.10	0.7943
-0.30	1.9953	0.40	0.3981

TABLE A.5: THE VALUES OF 'SI' AND '$(\mathbf{SR})^{-1}$' FOR SCALES IN SIRI-E OIL FIELD

$CaSO_4$		$SrSO_4$	
SI	$(\mathbf{SR})^{-1}$	**SI**	$(\mathbf{SR})^{-1}$
-1.00	10.0000	-3.50	3125
-0.40	2.5119	-3.00	1000
-0.35	2.2387	-2.80	632.911
-0.20	1.5849	-1.6	39.8105
-0.15	1.4125	-1.5	31.6226

Where; $SI = Saturation\ Index\ and\ SR = Saturation\ Ratio$