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Writer:	
Reffi Erany	

Faculty supervisor:

Skule Strand and Tina Puntervold

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A Study of Scale and Scaling Potential during High Salinity and Low Salinity Waterflooding

Reffi Erany

University of Stavanger

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ABSTRACT

Formation damage has been observed to be one of the severe problems during field life operation. In the waterflood projects, proper design water injection at the beginning of field life is crucial to minimize effects of incompatibility between source water/formation water. If the incompatibility condition is created then the scale precipitation might occur. In many oil/gas field cases, detrimental loss production or even well abandonment are required. The supersaturation condition is one of the critical factors that cause formation. If the condition is reached, insoluble salts will precipitate through nucleation and crystal growth process [1].

In this thesis, literature studies are conducted to gain deeper understanding about the scales behaviors, types and how to inhibit and remove them. In addition, PHREEQC simulator is run to study incompatibility waters (FW/Injected water) with variation of temperature, pressure, mixing ratio and injected water salinity. Temperature is set from 25^OC to 150^OC. Pressure is run at 10atm, 50atm, and 100atm. The mixing ratios vary at 30%, 50%, and 70% of sea water. The injected water is sea water (SW), diluted 10 times SW and 50 times diluted SW. In addition, the effects of heterogeneity reservoir are studied to see the influences to scale formation. Subsequently, a study of scale prevention and removal are also performed to reduce impact on scale precipitation

The study shows that the scale potential is mainly dominated by Sulfate Scales ($CaSO_4$, $BaSO_4$, $SrSO_4$) and Carbonate Scales ($CaCO_3$, $MgCa(CO_3)_2$). The solubility of $BaSO_4$ scale increases with temperature and vice versa. It is observed that $CaSO_4$ (s) is extremely precipitated at high temperature followed by carbonate scales dissolution. Pressure drops from 100atm to 10atm creates insoluble salt precipitation, extremely found for carbonate scales with twice of solubility decreasing. The increase in mixing ratios leads to more scale precipitation, observed in an increase from 50%SW to 70%SW yields a triple reduction of $MgCa(CO_3)_2$ solubility. Injected water salinity reveals the significant impact on potential scale precipitation. Lower potential scales were observed in the mixing of FW/diluted SW than FW/SW. Most of the scales can be dissolved into solution, except $BaSO_4$ which is still precipitated out even in the mixing FW/diluted 50 times SW. Lastly, the heterogeneity of the reservoir influences the development of mixing incompatible waters in the reservoir where higher degree of heterogeneity will result in more scale precipitation.

By doing this study, it can be inferred that the less scale potential occurs by lowering salinity of injected water. It is related to the Low Salinity water injection that has been established recently, it offers not only the significant oil enhancement but also lower scaling potential than High Salinity water injection.

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1. INTRODUCTION

1.1 Introduction

The primary recovery is recognized typically only recover up to 10% of oil from reservoir [2]. This means that there is still a huge amount of hydrocarbon left from the well-known location that has not been recovered yet through the primary stage. It because the natural energy reservoir depleted during this stage so the oil can't be transported to the wellbore. Along these lines, it becomes crucial to maintain reservoir energy by injection water or gas to the reservoir.

The water injection or waterflood is the widely used to improve oil recovery among other secondary recoveries. Water flooding is performed as secondary recovery to enhance production by pressure support and/or displacing oil toward the producer wells. The water is a ready source and inexpensive technique, so it is practically used in the field operation. The increasing recovery for conventional waterflood is reported can reach 35%-50% of IOIP[2].

Sea water is commonly used as a source of injecting water, especially in the offshore field area. However, injecting natural sea water is recognized to have no significant effects on the oil recovery. The high content of the hardness ions, such as SO_4^{2-} and CO_3^{2}, are believed will induce more scale deposition when contacts with formation water. Costly treatment and environmental issue are being a constraint when applying conventional water injection.

Proper waterflood design at the beginning of field project is crucial. It must do incompatibility study between source water/formation water and source water/rock minerals to minimize potential scale deposition. Scales can be deposited from subsurface to surface equipment, creating the detrimental problem and resulting in decrease well productivity. Inorganic scales are the main problem in the North Sea wells and the most predominantly are insoluble $BaSO_4$ scale and $CaCO_3$ scale. It was reported that Scales problem can reduce almost 30% production of North Sea area[3]. In the extreme condition with high pressure, high temperature and with long line tie-back pipeline, an increase in scale deposition is very tremendous.

Recently, injecting brine composition with significant lower salinity than formation water is being established to cover more limitation of conventional water flooding including higher oil recovery, environment-friendly, lower capital and operation cost. Along these lines, it is important to conduct the study about scale potential during low salinity water flooding, so the understanding of scale behavior and the treatment to inhibit and remove them will be more organized.

1.2 Thesis Objectives

The main objectives of this thesis are:

1. To gain more understanding through literature studies about the scale formation, type and factor affecting their solubility

2. Evaluate Scale Potential during High Salinity and Low Salinity Waterflooding by:
   - Simulate incompatible water between FW/SW
   - Simulate incompatible water between FW/diluted SW
   - Do comparison of scale potential for both cases
   - Study scale potential under change in pressure, temperature, mixing ratios and heterogeneity reservoir

3. Study the Scale Inhibition and Prevention Methods

2. ROCK AND WATER PROPERTIES

2.1 Mineralogy of Reservoir

Sedimentary rocks are carried by water, ice or wind and accumulated in the fluvial, deltaic, beach, deep sea, and lake. Mostly the clastic deposition accumulation is in the aqueous environment so it is water wet by nature.

2.1.1 Sandstone Reservoir

Sandstone is dominated by quartz (SiO_2) and some limited minerals such as plagioclase, alkali feldspar, lithic fragments and muscovite. The matrix size of sandstone varies and through diagenesis process, they are bonded by cement. The most minerals cementing of sandstone are silica and calcium carbonate with a certain amount of clay, hematite, gypsum, anhydrite, barite and zeolite[4].

By having this characteristic, sandstone rock has the potential of scaling ion source by nature. When the dissolution of carbonate mineral cement takes place in the reservoir through diagenesis process or water injection, the produced carbonate ions and sulfate ion could form insoluble minerals when interacting with divalent like Ca^{2+}, Mg^{2+}, Ba^{2+}, and Sr^{2+}.

2.1.1.1 Porosity

Porosity is defined as the percentage of pore volume occupied by fluids. There are two types of porosity; effective porosity and total porosity. The effective porosity measures pore volume that is interconnected each other; this porosity contributes to fluid flow through the reservoir. While the total porosity measures the total of connected and unconnected pore volume exist in the reservoir. This means the effective porosity will be lower than total porosity. There are some factors affecting porosity such as cementation, grain size, grain distribution, compaction, leaching, weathering, and clay minerals[5].

According to geological time deposition, the porosity can be divided into two major categories. They are primary and secondary porosity. Primary porosity is the original porosity formed during sedimentation process while secondary porosity is pore volume formed after primary porosity through alteration, dissolution, fracturing and other chemical processes. The examples of secondary porosity such as fracture porosity, moldic porosity, vugy porosity, etc[4].

2.1.1.2 Permeability

Permeability is defined as the ability of reservoir rock to transmit the fluid from reservoir to the wellbore as a function of pressure drop, cross section area and fluid viscosity. It is expressed by Darcy or miliDarcy unit. The permeability is divided into 3 major categories; absolute permeability, effective permeability and relative permeability. Absolute permeability is the ability of reservoir to transmit single phase through the reservoir. However, when there are two or more phases flow

together in the reservoir then the term of effective permeability must be introduced. The ratio between effective permeability to absolute permeability is defined as relative permeability. If only single phase flows through the reservoir, then the relative permeability will be equal with 1.

Obviously, the effective porosity has good correlation with permeability than total porosity. The correlation between porosity/permeability is studied from 578 set data samples, seen in figure 2.1[5]. They divided into 3 regions. Region I (ϕ>28%, low k) has no good correlation between ϕ and k. This region is typical of carbonate rock. Region III (ϕ<5%, k<0.1mD) is not quite practically interested with respect to rate production. In general, the porosity and permeability are function of grain size, sorting and compaction.
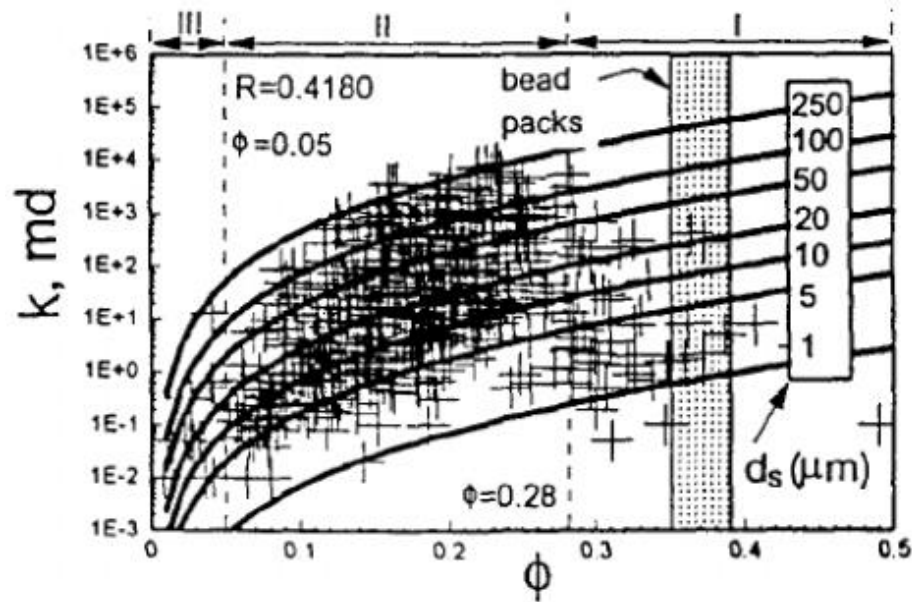
Figure 2.1 Porosity and Permeability Correlation from 578 Data Set Core Samples[5]

2.1.1.3 Minerals Dissolved in Sandstone Rock

Rock that is exposed to the surface will undergo to weathering process. The weathering process includes mechanical weathering and chemical weathering[4]. In the mechanical weathering process the rock is broken into smaller pieces without minerals alteration, for examples abrasion, frost wedging and root wedging process. For the chemical weathering process, the minerals contained in the sandstone are altered to the new minerals through some processes such as hydrolysis[4]. The hydrolysis is the reaction of silicate minerals with acidic water, as a result of CO_2 contact with water and form carbonic acid. The products of hydrolysis are clay minerals, soluble silica and metal cations. The metal cations, like Fe^{2+}, Mg^{2+}, Al^{2+}, Ca^{2+}, Na^{2+}, will act as binding of silicate minerals and some of them will dissolve into water and make the water rich dissolved minerals constituent.

2.1.2 Clay

Clays are typically formed as a result of chemical weathering of rock (feldspar) and hydrothermal activity. The clay minerals are mainly hydrous aluminum silicates and frequently appear ion iron, magnesium, alkaline earth, cation and alkali metal. Typically, clays are deposited in the low energy environment such as lake or marine basin. Generally, clay minerals are classified into four main groups, they are kaolinite, montmorillonite-smectite, illite, and chlorite[6].

Clay has an electrostatic charge so it has the ability to attract and hold the cations, such as Ca^{2+}, Na^+, K^+, Mg^{2+} and NH_4^+ , onto their negative surface charge. The Cation Exchange Capacity (CEC) is introduced to measure the amount of adsorbed cations per dry weight of rock at given pH condition and it is expressed by (meq/100g dry rock)[4, 6]

2.2 Mineralogy of Water

Chemical characteristic of water is related to the geological area where it flows. During transportation to the sea, the water will react with gas and rock minerals. Some minerals and ions will be released from the rock and will be dissolved by water until equilibrium condition. The water will carry contaminant ion (Mg^{2+}, Ca^{2+}, CO_3^{2-}, Fe^{2+}, Mn^{2+}, PO_4^3 etc), gas (Oxygen, H_2S, N_2, CO_2) and some amount of microorganism or suspended materials[7]. A number of dissolved minerals in the water is reported in part per million (ppm) or mg/L.

As water is transported to the sea, it will react and erode the rock fragment. The divalent like Mg^{2+}, Ca^{2+}, CO_3^{2-}, PO_4^{3-}, HCO_3^-, Na^+, K^+, Cl^-, contained in the rock minerals release and dissolve into water

2.2.1 Dissolved Minerals in Water

Many constituents are dissolved in the water as a result of leaching of marine sedimentary rock or minerals rock dissolution during water transportation process. These constituent are the main source of scale potential in the oil/gas field production. The water could dissolve inorganic materials, organic materials, gas and some microorganism[7].

- *Carbonate and Bicarbonate.* CO_2 dissolved in the water could react with dolomite or limestone, produce ion HCO_3^- and CO_3^{2-}. Carbonate ion is insoluble salt when forms complexes with Ca^{2+} or Fe^{2+}. At high pH and temperature, the bicarbonate will convert to carbonate ion and can be dissolved by adding acid or scale inhibitors.
- *Sulfate* dissolved in the water is originated by leaching of rock deposits containing $MgSO_4$, $FeSO_4$, or Na_2SO_4. If the SO_4^{2-} interact with Ca^{2+}, Mg^{2+}or Sr^{2+} the scale precipitation occurs.
- *Calcium, Barium* are divalent ions, they form an insoluble salt with sulfate, carbonate, fluoride, etc. Calcium has the ability to form complexes with maleic, organophosphonate or acrylic as an inhibitor for the scale of calcium based salt.

- *Iron and Ferrous* cause the serious problems in the operation. Fe^{2+} will be hydrolyzed to Fe^{3+} when contacting with air and form insoluble $Fe(OH)_3$. Adversely Inhibitor performance is reduced even at a small iron presence.
- *Chloride* is formed from leaching of marine sedimentary deposits or caused by water pollutant (brine, seawater or industrial waste). Chloride can create insoluble salt with cation
- *Sodium* is monovalent and forms relatively soluble salt when reacting with anions. So it is very seldom to find sodium deposition.
- *Other inorganics dissolved* in the water are Aluminum, Magnesium, Copper, Chromium, Strontium, Manganese, Silica, Selenium.
- *Oxygen*. When the oxygen exposed to the air, it will produce H_2S gas and induce corrosion problem. The oxygen also promotes bacteria growth which can block the reservoir pore throat.

2.2.2 Water Sources

Water is universal solvent since it has the ability to dissolve any substance naturally. There are 4 main categories of water source in the earth that are surface water, subsurface water, sea water and lake water. All these water bring many minerals constituent during their transportation to the sea as followed explanation [7].

Lake water is as main source of fresh water and most of dissolved constituent are affected by biological activity and stable under seasons or weather condition. As water is transported to the sea, it will contact and erode the rock fragment. The divalent ion like Mg^{2+}, Ca^{2+}, CO_3^{2-}, PO_4^{3-}, HCO_3^-, Na^+, K^+, Cl^-, contained in the rock minerals will release then dissolve into water. Water will rich cation minerals and this type of water is Surface water. It also carries organic material and solid particles to the ocean.

During transportation, there are the amount of water trapped in the pore space rock which is named as *Subsurface Water.* Its chemistry is much related to the geological area over which has passed. So therefore, it is common to find different water chemistry in the produced wells. The subsurface water contains dissolved Oxygen and the Oxygen will be consumed by the organism in the ground. It will produce CO_2, Fe^{2+} or Mn^{2+} as the source of corrosive agent.

Sea water or salt water contains hardness ions as the result of water circulation and chemical weathering of rocks. It mainly consists of ion Na+ and Cl- with some additional alkali ion, alkali metal earth such as Ca^{2+}, Mg^{2+}, Ba^{2+}, etc and microorganism or bacteria. Thus, it is more enriched and saline compare to fresh water.

2.3 Recovery Mechanism

Generally, hydrocarbon recovery is classified as primary recovery, secondary recovery and tertiary recovery. Recently, however, the tertiary recovery is conducted directly after primary recovery and

quite common to apply secondary or tertiary recovery at the early stage of field development to enhance more oil production.

2.3.1 Primary Recovery Mechanism

Primary recovery mechanism is the first stage producing hydrocarbon by natural energy, it means only internal energy reservoir used to flow the hydrocarbon toward production wells. The natural energy includes gas cap drive, solution gas drives, water drive, rock expansion and gravity drainage that are used to push the hydrocarbon toward production wells. The primary recovery stage also includes artificial lift operation using gas lift, SRP, ESP that improve oil lifting in the wellbore to the surface. The recovery factor of primary stage is commonly still low so the oil enchantment through secondary and tertiary recovery is under consideration. The primary recovery is recognized typically only recover up to 10% of oil from reservoir[2].

2.3.2 Secondary Recovery Mechanism

Secondary recovery mechanism is methods to produce hydrocarbon from reservoir beyond natural flow and artificial lift operation. Secondary mechanism is applied as the reservoir doesn't have the energy to maintain production and it needs external energy from the surface. The external energy from surface includes gas injection, water injection or thermal injection to maintain reservoir pressure and push oil toward producer wells. The most applied secondary recovery is water injection. The water is the easy source and inexpensive technique, so the water flooding is commonly used in the field operation. The increasing recovery for conventional waterflood is reported can reach 35%-50% of IOIP[2].

2.3.3 Tertiary Recovery Mechanism

Tertiary recovery is methods implemented after primary and secondary recovery. The main purpose of this stage is to extract remaining hydrocarbon which couldn't be recovered by primary and secondary recovery by improving displacement efficiency. The examples of tertiary recovery are surfactant flooding, ASP flooding, etc. Displacement efficiency as equation (2.1)[8], includes microscopic sweep efficiency and macroscopic sweep efficiency

$$Ed = \frac{1 - Sor - Swi}{1 - Swi}$$
Equation (2.1)

Where
Ed   : Microscopic Sweep Efficiency
Siw : Saturation Water Initial
Sor : Residual Oil Saturation

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Microscopic sweep efficiency measures the effectiveness of oil displacement when contact and displaces hydrocarbon in the pore scale. Its efficiency is a function of wettability and pore geometry. The technique to increase microscopic sweep efficiency is by lowering capillary pressure.

Macroscopic sweep efficiency is a function of the areal and vertical reservoir. The mobility ratio measures the effectiveness when displacing oil in the reservoir. It is reflected by the ratio between water as displacing fluid with oil as displaced fluid, as equation (2.2)[8]. A good displacement occurs when the mobility ratio is less than 1.

$$M = \frac{krw/\mu w}{kro/\mu o}$$
Equation (2.2)

Where
Krw : Water Relative Permeability
Kro : Oil Relative Permeability
μw : Water Viscosity
μo : Oil Viscosity

Then the total displacement efficiency is calculated by equation (2.3)[8], which product of microscopic sweep efficiency and macroscopic sweep efficiency

$$E_t = E_d * E_M$$
Equation (2.3)

Where
E_t : Total Displacement Efficiency
E_d : Microscopic sweep efficiency
E_M : Macroscopic sweep efficiency

2.3.3 EOR Methods

Enhanced oil recovery is implemented by various methods to extract remaining oil in the reservoir. The EOR methods are divided into 3 main categories[8]; chemical injection, thermal injection and gas injection. The gas injection is a process by injecting gas, such as CO_2, N_2, natural gas, into reservoir through miscible displacement process. The injection miscible gas can enhance oil production by maintaining reservoir pressure and reducing interfacial tension between oil and displacing gas, increase microscopic and displacement efficiency. Thermal Injection is commonly used in the reservoir which has high oil viscosity. It will reduce oil viscosity so mobility ratio and interfacial

tension can be decreased. For Chemical injection, the main purposes are reducing interfacial tension and mobility, the chemical is injected into reservoir includes the surfactant or alkaline flooding. By EOR methods, the remaining oil can be more extracted compared to primary and secondary recovery.

However, EOR methods discussed above are very costly and not often the environment issues come to be problems. Recently, Low salinity water injection has been studied as EOR methods. This water contains significant low salinity compared to formation water or conventional sea water. By lowering salinity of injected brine, it can disturb the chemical equilibrium within COBR and change to be more water wet[9]. The interfacial tension and capillary pressure between oil and water will be reduced then oil will flow easier. This technique is mainly performed in the sandstone reservoir even though the carbonate reservoir also shows the increasing oil trend. The successful of Low Salinity Water Injection (LSWI) has been confirmed by laboratory and field scale with significant recovery.

2.4 Water Flooding Design

The preliminary study should be conducted before waterflood is executed. From the economic point of view, the volume and the location of the remaining hydrocarbon reserves will determine the further step for water flood projects design. The design must consider the rock/fluid properties, the source of injected water, completion, water treatment and the environmental issues [10]. In some areas, the geopolitical and legislative factors must be included in the waterflood design, especially field operated with production sharing agreement, where the operators are not free to determine the depletion strategy and the choice of the water source.

2.4.1 Sources of Injected Water

The geographic location of remaining reserves is the key factor which determines the choices of injected water source. Practically for field operated in the near shore or offshore area, the sea water is commonly applied, while the field operated at onshore with significant distance to the sea could use subsurface aquifer, river or lake[10, 11]. Figure 2.2 shows availability of water source for injection.
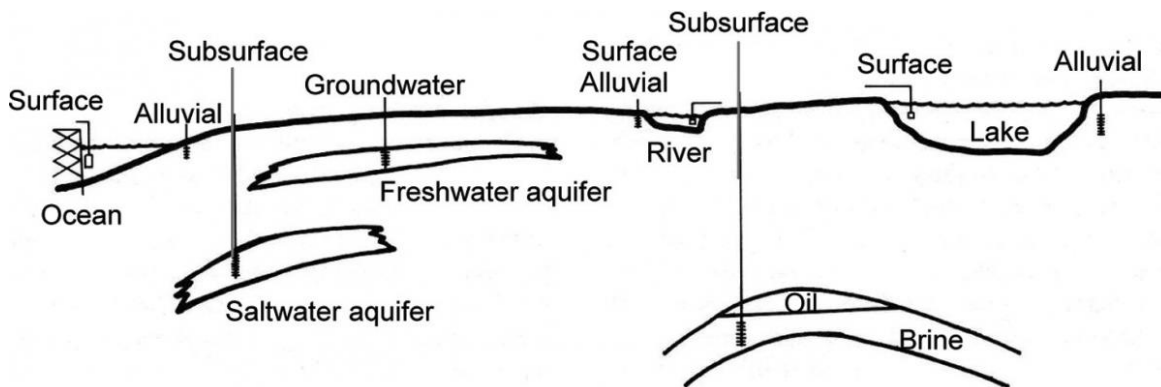
Figure 2.2 Source water for water injection[11]

The produced water is not commonly used as the source of injected water. However, there are some fields implement produced water as a source of injected water. For example, forties field and Prudhoe Bay operated by BP[10]. It can minimize the impact of incompatible waters; however, the worse effect could occur due to the high degree of impurities such as scaling and corrosion. The environmental issue is usually found as a constraint when applying produced water reinjection.

As the volume of injected water is not sufficiently enough, the additional water must be provided. Sea water is convenient used since it is the unlimited source and inexpensive. It also applicable for field operated in the onshore area.

2.4.2 Rock Properties Analysis

Study of rock minerals and type of rock before injecting water is crucial. Sandstone rock contains mineral clay which is initially in the equilibrium condition with the formation water. The clay is very sensitive with water properties, especially fresh water.   When the fresh water is injected through the reservoir, the possible clay swelling in the reservoir can't be avoided. The application of fresh water for sandstone rock is not a good choice since it will reduce reservoir permeability and lead to problem during drilling operation. When look upon on the carbonate reservoir, the interaction between injected water and rock mineral may soften the fragment or framework between the grains. It may cause the collapse and surface subsidence[12].

2.4.3 Water Properties Analysis

The proper chemical analysis of water either produced or injected water can't be overemphasized. In some field cases, the accurate data for water properties are sometimes difficult to perform and quite often it shows extremely lack of data. The collecting precise water and gas samples when analyzing water properties are a big concern. Any error in the water analysis will allow to the erroneous calculation for scale prediction and lead to disaster problems.

2.4.4 Well Completion Types and Well Pattern

The type of injection well completion influences the ability to deliver water into the reservoir. The free flow of water to the reservoir is critical. The good completion with sand controlling or sliding sleeves design will cause solid debris and insitu precipitation, reduce their function. Recently, the sand excluder completion is being established. It is found to be more effective due to the ability to filter and remove the suspended solid when going through the injection well[10].

The design of well injection placement, by five spot, seven spot or nine spot patterns, depends on the pore and permeability distribution in the reservoir. In the field located in the offshore area, it is not often to have a limitation on slot availability and platform construction. Thus, the good optimization includes well placement and trajectory is important to be studied before execution.

2.4.5 Water Treatments for Injection

Special treatments are necessary before the brine is injected into the reservoir. The treatments required for every water sources could be different depending on the water source type. If the water is not treated before injection, the solid and minerals will plug the downhole equipment and potentially block the pore throat. Below are the water treatment steps that are commonly applied for field waterflood projects with their detail explanation[13].

- *Solid removal*
  The grain size of suspended solid varies from coarsest to finest grain and depends on the type of water sources. The suspended solid in the sea water is commonly smaller than the lake water. Firstly, the greater solid particles (>50μm) with higher solid concentration (> 100mg/L) are removed using Desander and Coarse Strainers. Both the types of equipment are design to filter larger solid with high solid concentration. The process is continued by removing the remaining suspended solid in the solution using the sand filter, granular filter or cartridge filter.

- *Dissolved Gas Removal*
  The Oxygen, H_2S and CO_2 gas are dissolved in the water and the interaction between them will lead severe problems. For example, the interaction between oxygen and H_2S will sufficient to cause corrosion and promote bacterial growth that could plug the reservoir pore throat and surface/downhole equipments. For this reason, the impurities gas must be excluded from solution. There are some methods used for removing dissolved gas, they are the chemical scavenger, gas stripping and liquid extraction. The chemical scavenger are NH_4HSO_3, $Na_2S_2O_5$, SO_2 or Na_2SO_3

- *Biological Control*
  The bacteria dissolved in the water will possibly develop into colonies. The growth of bacterial can be suppressed by adding chemical biocides to injected water. The chemical biocide that is commonly used is chlorine because it is the inexpensive and reliable source.

- *Sulfate Removal*
  $BaSO_4$ and $SrSO_4$ scales are very less soluble and hard scale, make them extremely difficult to remove either chemically or mechanically. Hence, if these scales are precipitated, not often costly wellwork/workover projects are needed. This problem can be minimized by reducing the source of sulfate ion from sea water though Nanofiltration (NF) membranes. The detail discussion about sulfate removal will be discussed in chapter 5.

3. SCALING POTENTIAL DURING WATER INJECTION

3.1 Introduction

One of the difficult problems when designing water flood project is the preliminary study about the incompatibility water and the prediction of its effects on the future field development. This prediction should cover the type of scale deposition, the location where they form, how to inhibit and remove them [14]. The cost operational and environmental issues are also to be a big consideration when dealing with the scales.

Scales are potentially deposited in the matrix reservoir to the surface equipments as long as the supersaturated condition is reached [1]. Scale deposition could cause production losses and not often the high capital cost is required. In general, the type of scale occurs in the oil field are organic and inorganic scales, however, the inorganic scales are to be our main concerned further.

3.2 Mechanism of Scale Formation

In general, the scale start to form at supersaturated condition through nucleation, crystal growth and agglomeration process [15, 16]. Firstly the small minerals must grow from the solution. The unstable cluster of the atom at which the deposition of solid takes place is developed. This process is called as nucleation process, as seen in figure 3.1 and figure 3.2. The nuclei are ions cluster, ions pairs and crystal lattice particle. At the condition where the crystal nuclei flow together with solution in the system and not deposited onto the surface, the homogeneous nucleation is created [17]. If the nuclei come from the foreign particles, then the nucleation is categorized as heterogeneous nucleation, it is usually caused by the high degree of turbulence which leads more scale precipitation.
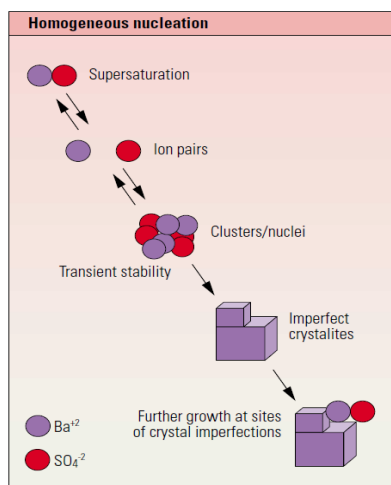
Figure 3.1. Homogeneous Nucleation[15]   Figure 3.2 Heterogeneous Nucleation[15]
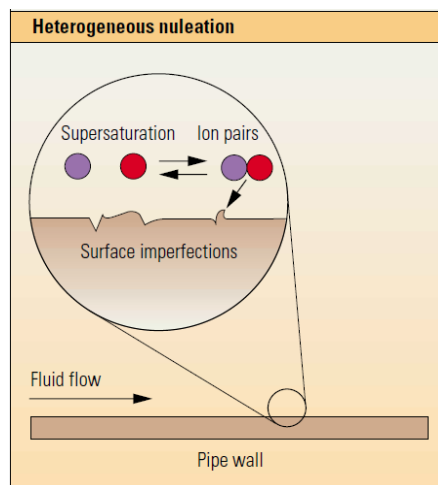
Secondly, the seeds crystal will grow and extent their size. The crystal will growth further and deposit onto nuclei. This condition will result in the higher degree of super saturation in the solution. The crystal changes to be more stable by continuous precipitation through agglomeration process and decrease solution concentration.

3.3 Solubility of Scale Formation

3.3.1 Solubility Concept

Solubility is defined as the maximum quantity of solute dissolved in the solvent under certain conditions. Solubility equilibrium is a dynamic equilibrium which occurs as the dissolution and precipitation have a constant rate and no net change in solution concentration. It is expressed by moles of solute per volume (mol/L), mass of solute per mass of solvent (g/g) or mass of solute per volume solvent (g/L) [18]

To express the solubility, the term SR or SI are commonly used [1]. The Saturation Ratio (SR) and Saturation Index (SI) explain the degree of super-saturation for salts in the solution. SR is defined as the ratio between the ion activity products to their solubility product while SI is logarithmic of SR. The SR and SI are shown in equation (3.1), (3.2) and (3.3).

$$SR = \frac{\left[X^{A+}\right]\left[Y^{B-}\right]}{Ksp}$$ Equation (3.1)

$$SI = Log\frac{\left[X^{A+}\right]\left[Y^{B-}\right]}{Ksp}$$ Equation (3.2)

$$SI = Log\left(\left[X^{A+}\right]\left[Y^{B-}\right]\right) + pKsp$$ Equation (3.3)

Where: $[X^{A+}]$ and $[Y^{B-}]$ represent the ion concentration (M) and pKsp = -Log Ksp.

Ksp, solubility product constant, is defined as the moles of ions per unit volume of solvent in the equilibrium condition. The potential of scales is shown by the SR or SI values. If the SR<1 or SI<0 then the solution is under-saturated and no scale precipitation observed. In this situation, the actual product of concentration ions is smaller than equilibrium condition, and the solutions will tend to dissolve more minerals. The condition at which the solution can't dissolve more solid and reach solubility limit is called as equilibrium condition shown by SR=1 or SI=0. The additional small amount of solid into solution could trigger the formation of crystal seeds and insoluble salt may precipitate. However, it depends on the kinetic precipitation rate since at some condition the precipitation does not occur spontaneously even at the supersaturated condition[1], shown by SR>1 or SI >0.

3.3.2 Factors Affecting Solubility

The solubility of specific mineral or substance in the solution could be different. It is influenced by the entropy change and the balance of intermolecular forces. The solubility is also related to the thermodynamic equilibrium between solid and solvent in the solution. The change in pressure, temperature, ionic strength, pH will disturb this equilibrium and the solubility will change[19].

The practical factors affecting solubility are pressure and temperature. Change in pressure and temperature does occasionally have a significant impact on solubility. Generally, the solubility of scale minerals increases as temperature decreases, i.e Barium Sulfate. However, it is found the opposite trend for other scale minerals. The temperature will affect the rate of nucleation and crystal growth in the solution and thereafter we observed there will be more scales precipitated out and loss from the solution at higher temperature [20].

The pressure drops from the reservoir to the surface also give significant impact on the solubility of mineral salt, for example, the carbonate system. Pressure drop causes dissolved CO_2 escape from solution and the pH will be increased due to releasing CO_2. It causes a growth of a dense layer of calcium carbonate crystals and leaving a solution saturated with calcium carbonate and precipitation will occur as limit solubility is reached [21].

The presence of dissolved other substances or excess of common ion in the solution will strongly affect reducing the solubility of the specific salt in the solution. For example, the solubility of $CaSO_4$ will be reduced as $BaSO_4$ is added into the solution. To a lesser extent, the solubility is influenced by ionic strength in the solution. The ionic strength measures concentration of ions presence in the solution and therefore solubility increases as ionic strength in solution increases [1, 19].

3.4 Scale Formation Process

The scale is precipitated during field production time especially when there is a change in physical condition such as pressure, temperature, salinity, etc. It is common to see scale precipitation during primary recovery stage at which formation water reached production well (water breakthrough) and in secondary or tertiary recovery stage at which mixing of injected water and formation water takes place. Generally, there are 3 common ways which trigger the scale formation; they are auto scaling, incompatible water and evaporation process[15].

3.4.1 Auto Scaling Process

The auto scaling process occurs due to change in environment condition such as pressure. The pressure drop when transporting formation water and hydrocarbon from reservoir to the wellbore could trigger the formation of crystal scales. For examples the formation of carbonate scales near wellbore caused by dissolved CO_2 gas escape from formation water [21], as equation (3.4). The auto scaling process is shown in figure 3.3.

$$Ca(HCO_3)_2 \Leftrightarrow CaCO_3 \downarrow +CO_2 \uparrow +H_2O \qquad \text{Equation (3.4)}$$
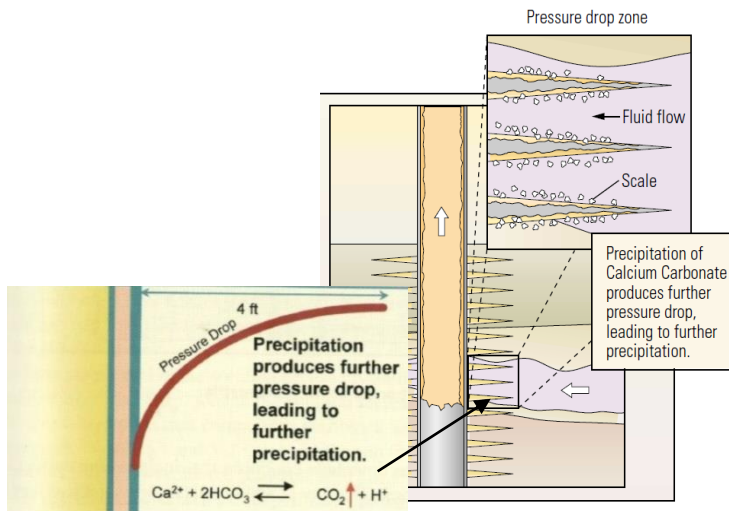
Figure 3.3 Auto Scaling Process near wellbore [15]
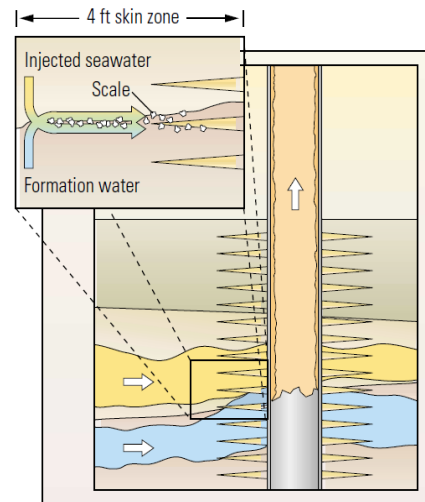
Figure 3.4 Incompatible Water Process[15]

3.4.2 Incompatible Water

When SW is injected into reservoir to push oil and insitu water toward production wells, the mixing of injected water and insitu water can't be avoided. In this situation, the scales, like $CaSO_4$, $BaSO_4$, $SrSO_4$ or $CaCO_3$ might be precipitated through incompatibility process, see equation (3.5) [14, 21]. Where ion A^{2+} represent Ca^{2+}, Ba^{2+}, Sr^{2+}, Mg^{2+}. The scales are possibly precipitated in the matrix pore reservoir and near wellbore or perforated interval, see figure 3.4.
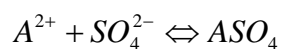
$$A^{2+} + SO_4^{2-} \Leftrightarrow ASO_4 \qquad \text{Equation (3.5)}$$

3.5 Type of Field Scales

As any change in physical condition such as pressure, temperature, salinity, pH the formation of scale in the reservoir and downhole to surface equipment will occur. There will be an interaction between ions or other dissolved minerals in the water that lead to supersaturated condition and crystal starts to develop. Generally, the type of scales can be divided into 2 main categories. They are inorganic scales and organic scales[21]. While the organic scales are deposition of high molecular weight of oil component onto surface metal or equipment, for examples wax, asphaltene, resin.

3.5.1 Inorganic Scales

Inorganic scales are insoluble salt that is precipitated due to the interaction between ions and forms insoluble complexes, such as $CaSO_4$, $BaSO_4$, $SrSO_4$, $CaCO_3$, FeS, ZnS, Hydrate, etc. Table 3.1 presents the types of inorganic scales commonly encountered in the oil field.

Table 3.1 Table of Inorganic Scales

Minerals	Formula	Minerals	Formula
Carbonate Scales		***Sulfate Scales**	
*Aragonite, Calcite, Vaterite	$CaCO_3$	Anhydrite	$CaSO_4$
Dolomite	$MgCa(CO_3)_2$	Gypsum	$CaSO_4.2H_2O$
Strontianite	$SrCO_3$	Hemihydrates	$CaSO_4.1/2H_2O$
Witherite	$BaCO_3$	Barite	$BaSO_4$
		Calestite	$SrSO_4$
*Iron Compound			
Ferrous Carbonate	$FeCO_3$	**Other Scales**	
Ferrous Hydroxide	$Fe(OH)_2$	Zinc Sulfide	ZnS
Ferrous Hydroxide	$Fe(OH)_3$	Hydrate, etc	
Ferrous Sulfide	FeS		

* taken from [1]

3.5.1.1 Carbonate Scale

As insitu water breakthrough in the producer wells, there is potential to generate carbonate scales near wellbore or perforated interval. A sharp pressure drop from reservoir to wellbore will release CO_2 from solution and leave the water oversaturated by ions carbonate or bicarbonate and ions i.e Ca^{2+}, Mg^{2+} then scale occurs as equation (3.4). More carbonate scales will be precipitated out when transporting fluid to the surface since more decreasing pressure along the system. $CaCO_3$ is classified into Calcite, Aragonite and Veterite. However, the Calcite has the greatest stability so it is commonly formed in oil field [22], according to equation (3.6)

$$Ca^{2+} + CO_3^{2-} \Leftrightarrow CaCO_3$$
<div align="right">Equation (3.6)</div>

3.5.1.2 Sulfate Scale

Sulfate scale is usually encountered when incompatible waters take place. For examples, formation water containing ions Ca^{2+}, Sr^{2+}, Ba^{2+} mixes with injected water containing high ion sulfate, SO_4^{2-}, as equation (3.7)[21]. Mixing of both water, in matrix reservoir, near or within wellbore and any production system, will cause sulfate scale precipitation and significant impact on well productivity.

$$M^{2+} + SO_4^{2-} \Leftrightarrow MSO_4$$
<div align="right">Equation (3.7)</div>

Where, M represents ions Ca^{2+}, Sr^{2+} and Ba^{2+}. The sulfate scale formation is affected by some factors such as temperature, pressure, ionic strength. The detail explanation will be discussed later.

The sulfate scales are considered as the hardest and insoluble acid scales, especially Barium sulfate and strontium sulfate. This means special treatments are required when dealing with this kind of scales. The detail discussions about scale inhibition and removal will be discussed in chapter 4.

3.5.1.3 Hydrate Scale

Hydrate, a water crystal, the formation is formed when water molecules and low molecular weight gas, usually smaller than n-penthane, react under certain pressure and temperature, typically at temperature less than 100^OF and pressure above 180 psi[23]. The water molecules will surround the gas molecule and form crystalline lattices. Figure 3.5 shows the pressure and temperature window at which hydrate scales are formed. According to figure 3.5, Hydrate can be minimized by increasing temperature and lowering pressure, hydrate scale deposition can be minimized.
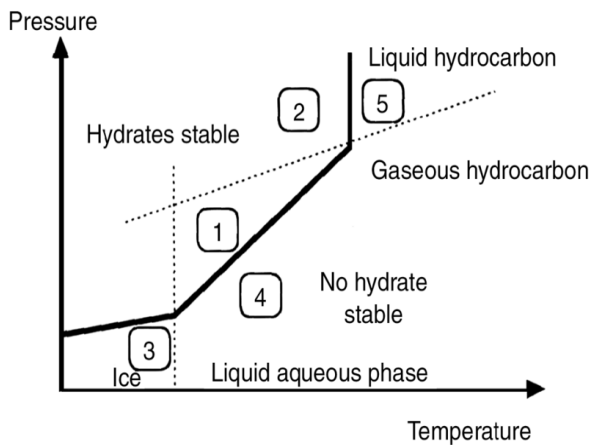
Remark:

1) Hydrate + gaseous hydrocarbon (+ excess liquid water)
2) Hydrate + liquid hydrocarbon (+ excess liquid water)
3) Ice + gaseous hydrocarbon
4) Liquid water + gaseous hydrocarbon
5) Liquid water + liquid hydrocarbon

Figure 3.5 Water/Hydrocarbon/Hydrate Phase Diagram[23]

E'tudes et Productions Schlumberger, Gas Hydrates Production (January 1998)][23]

3.5.1.4 Zinc Sulfide

Zinc Sulfide is an insoluble salt with chemical formula ZnS. The ZnS scale will be precipitated as the formation water containing Zinc ion reacts with H_2S gas as the chemical reaction in equation (3.8). The source of ion Zn^{2+} in the formation could be possible from drilling or wellwork/workover operation. The completion fluid or heavy brine (zinc bromide) contains Zinc ion and when it penetrates and invades into reservoir, it will react with H_2S and form insoluble salt ZnS [24].

$$Zn^{2+} + H_2S \Leftrightarrow ZnS + 2H^{2+}$$
<div align="right">Equation (3.8)</div>

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3.4.1.5 Iron Sulfide

Iron sulfide scale formation requires sources of hydrogen sulfide and iron. The iron is contained in the formation water especially sandstone reservoir while the hydrogen sulfide could be possible from injected water, thermal decomposition, reducing bacteria, or the well with gas lift operation. The mixing of hydrogen sulfate and iron will form iron sulfide scale [25], see equation (3.9). In nature, the iron sulfide consists of several crystalline forms as seen in Table 3.2

$$Fe^{2+} + H_2S \Leftrightarrow FeS + 2H^+$$
<div align="right">Equation (3.9)</div>

Table 3.2 Type of Iron Sulfide Crystalline [25]

Parameter	Mackinawite	Marcasite	Pryrite	Pyrrhotite	Troillite
Chemical Formula	Fe_9S_8	FeS_2	FeS_2	Fe_7S_8	FeS
Crystalline	Tetragonal	Orthorhombic	Cubic	Monoclinic	Hexagonal
Color	Bronzy	Tin-White	Pale Brassy	Bronze	Light
Hardness	Soft	6 – 6.5	6 – 6.5	3.5 – 4.5	3.5 – 4.5
Density (gr/cm³)	4.3	4.875	5.013	4.69	4.85
Solubility in Acids	Fast	Slow, Difficult	Slow, Difficult	Moderate	Rapid, Easy

3.5.2 Organic Scale

Transporting fluids from reservoir to the surface could potentially deposit organic scales. Organic scales are deposition of high molecular weight of crude oil near the wellbore, perforated interval and the surface metal equipment. The deposition of organic scales depends on some factors such as pressure, temperature, type of crude oil, and they are usually associated with inorganic scales [21].

3.5.2.1 Wax

Wax is formed from the crude oil containing long chain with length C_{18} to C_{75+}. The hydrocarbons contain n-paraffin, naphtha and iso-paraffin could deposit wax scale. As temperature decreases to the surface, the light component will evaporate and leave the higher molecular weight in crude oil. Through the process nucleation and particle growth, wax then is precipitated when the solution temperature is lower than wax appearance temperature (WAT) or the solubility limit is reached [26].

3.5.2.2 Resin - Asphaltenes

Resin and Asphaltenes are a large polar component composed of aromatic and naphthenic rings. The deposition is a function of the heavy component in crude oil by forming aggregates or micelles in solution and then mixed with the hydrocarbon to generate a colloidal system. Pressure, temperature and composition cause a solubility change of asphaltenes-resin association and lead

asphaltenes precipitation[21]. The content of SARA (Saturates, Aromatics, Resins, and Asphaltenes) in the crude oil also plays an important role in the asphaltenes deposition.

3.5.2.3 Naphthenate Deposit

The Naphthenate has chemical formula $C_NH_{2M+Z}O_2$ and consists of alkyl-substituted acyclic and cyclic structures. As oil and water are transported to the surface, the pressure drop along the system causes releasing CO_2 gas from the oil phases. It increases pH of the solution and naphthenic will dissociate. The anion RCOO- will react with Ca^{2+} or Na^+ from water to form the emulsion (CaN or NaN), see equation (3.10) to equation (3.11). The deposition of calcium Naphthenate will occur at pH > 6 [27].

$$RCOOH \leftrightarrow RCOO^- + H^+$$

Equation (3.10)

$$2RCOO^- + M^{2+} \leftrightarrow (RCOO)_2 - M$$

Equation (3.11)

3.6 Location of Scale Deposition

The scale is deposited along the water path wherever the injected brine commingles with formation water or under physical changes like pressure or temperature. The scales can be precipitated along the injection well, wellbore, reservoir, surface equipment as presented in figure 3.6.
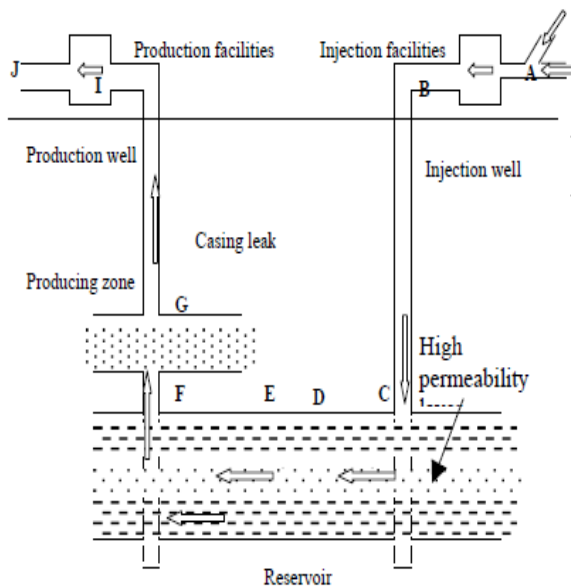
Figure 3.6 Location of Scale Deposition[22]

Potential Scale Deposition [22]

Location	Scale Formation
A to B	Mixing of Brine
B to C	Increasing Pressure&Temperature
C to D	Decreasing Pressure
C to F	Reaction with rock by cation exchange, dissolution, etc.
D to F	Mixing of Injecting water and formation water
E to J	Decreasing Pressure and temperature. Release CO_2 and water evaporation
F	Breakthrough of Mixing water
G	Mixing of produced brine from different zone
H	Mixing of produced brine with brine from casing leak

3.6.1 Reservoir Matrix

Scale deposition in the subsurface is the critical issue especially in the pore throat which impacts on porosity and permeability reduction, see figure 3.7. Carbonate scales and sulfate scales that are deposited near wellbore can block the perforation interval and reduce well productivity.

However, the scales precipitated deep in reservoir would not be a severe problem since they are not accumulated locally[28]. The more scales dropped out deep in reservoir, the lower scale potential would be at near or in the wellbore, depending on the mixing process and how deplete the scaling ion when reach the production well. For examples, if more $BaSO_4$ is precipitated out deep in the reservoir, it will reduce ion Ba^{2+} concentration and reduce scale potential as reach the wellbore.
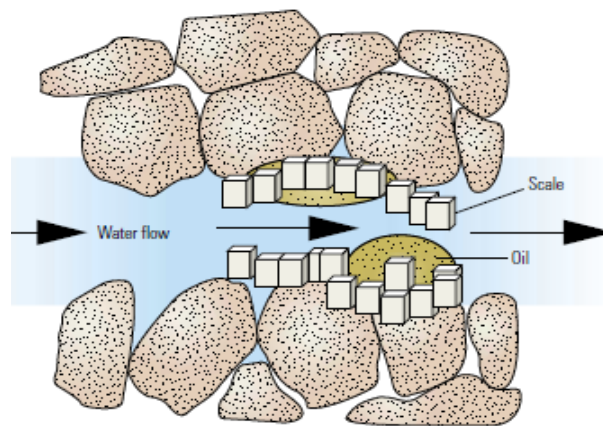
Figure 3.7 Scale deposition in the Matrix Reservoir[15]

3.6.2 Producer and Injector Wells

Deposition of scale in the tubing will increase the surface roughness of the pipe, see figure 3.8. It will reduce flow area and increase flow resistance inside the tubing. The carbonate and sulfate scale are possible deposited near and at the wellbore. They will block down-hole equipment including perforation interval, gas lift mandrel, nipple, etc, and the result of production losses is observed. The scales are also possible precipitated out in production equipment or surface pipelines. The severe problem occurs due to scales deposition was reported at the Miller field. The production declined dramatically from 30,000 bfpd to 0 bfpd within 24 hours. It was investigated that there was reduction up to 40% of flow area in the tubing due to buildup scales[23].

The injection wells have the potential for scale deposition through auto scaling process due to change in temperature and pressure along the wellbore. At the initial stage injection, scale possible occurs around wellbore due to contacting with formation water or completion water, as seen in figure 3.9.
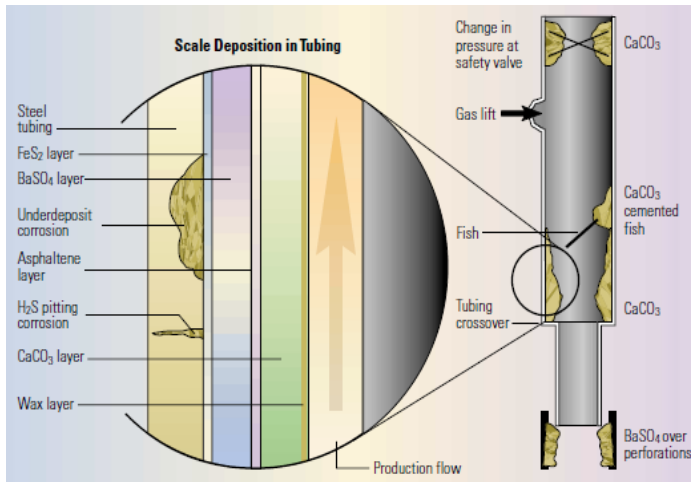
Figure 3.8 Scale deposition in the wellbore[23]
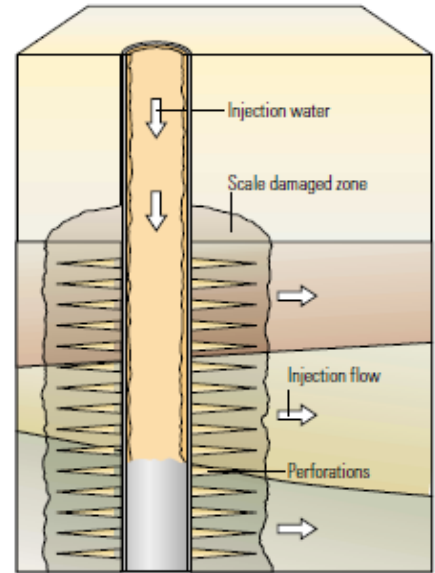
Figure 3.9 Scale Deposition in the Injection Well[23]

3.7 Scale Detection

Mitigate scale formation at earlier time is an important task to minimize severe problem resulting from scale deposition. There are several ways to detect scale formation during field life production

3.7.1 Visual Inspection

Visual inspection is the easiest, quick and cheap investigation since it can be the first step to identify the presence of scale. The sample can be taken from surface equipment for instance separator, pump, choke, etc. The sample can be analyzed in laboratory by microscopic investigation in terms of color, size hardness and odor

3.7.2 Core analysis

A lot of laboratory study had been conducted using core analysis to observe the scale deposition. The core sample was taken from reservoir and do laboratory experimental work. The core is dried and cut into the section. The Scanning Electron Microscopy (SEM) is used to study crystal habit, scale size, morphology and scale distribution in core[29].

3.7.3 Gamma Ray and Caliper log

Gamma Ray log and Caliper log are run down through tubing to detect scale deposition along the wellbore, as seen in figure 3.10 Caliper log is run to measure decreasing tubing inner diameter as the indication of scale deposition. In addition, Gamma Ray Log is run to detect radioactive radium Ra226.[15]. It is usually present together with scale especially barium sulfate, $BaSO_4$
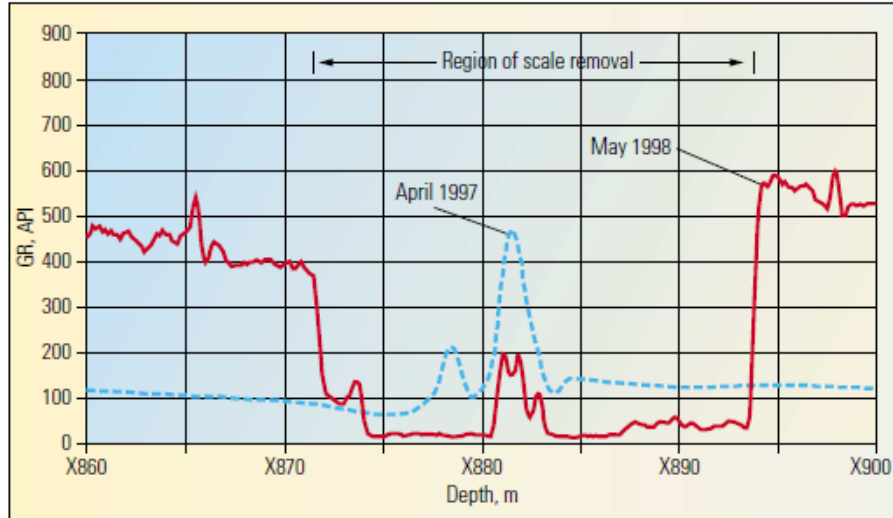
Figure 3.10 Gamma Ray Log to identify scale deposition in the wellbore[15]

Blue dash line represents Gamma Ray log run in April 1997 before scaling removal job. While red line represents Gamma Ray log run in 1998 after scaling removal job. The focused interval depth is X872m to X894m. As seen in figure 3.10, there was a peak API value (blue dash line) within the interesting depth, indicating scale deposition at the range of depth. After removal job at May 1998, the Gamma Ray log was run again into the wellbore. It was observed that significant reduction on API indicating the success of scale removal jobs.

3.7.4 Produced Water

Scale detection can be identified by study of produced water, especially if it coincides with decreasing production rate. Accurate sample water is taken from wells and conducts water chemical analysis. Potential of scale deposition is indicated by reducing scaling ion, such as Ca^{2+}, Mg^{2+} and Ba^{2+} in produced water, especially after injected water reaches producer wells[10].

4. SCALING PREVENTION AND REMOVAL

The problem of scale prevention has become important due to most of operated fields are mature fields and have already entered the secondary or tertiary recovery. Thus, the use of water injection or water based EOR to improve oil recovery becomes crucial. However, the problems will come when the incompatibility between injected water and formation takes place, not often the scale deposition in the field will cause high production loss and costly treatments.

4.1 Scaling Preventions

Through the concept of nucleation and crystal growth discussed earlier, the scale inhibitors are designed to stop the development of nucleation; scale growth and adherence to the surface thus potentially reduce the rate of scale formation [30]. Once the solid has been precipitated, the removal scales job operation should not-damage the reservoir, wellbore or other equipment.

In the physical prevention, there are some methods that are practically applied including the selection of injected fluid, water treatment before injection, pH control and some other physical methods[31] such as NMR, micro electrolysis, electrostatic, high pressure-high frequency and anti bond polymer methods. However these techniques are not widely used and their field practical is inefficient.

The formation of scales may also be mitigated by chemical treatments. Injecting diluted sea water which has low ion concentration could minimize the formation of scales since it reduces the active scaling ions in the solution. Moreover, scales can also be inhibited by adding scale inhibitors, ion exchange, chemical treatment, dilution to lower the solubility limit, etc. Especially for sulfate scales, the sequestering and chelating ions (Ca^{2+}, Sr^{2+} and Ba^{2+}) are possibly applied[32].

4.2 Scaling Inhibitor

Scale inhibitors are chemicals that are added into solution or injected water to stop the nucleation growth and prevent the crystals from adhering to the solid surface. The performance of scale inhibitor is a function of pH, temperature, divalent ions, and other chemicals presence[17].

4.2.1 Properties of Scale Inhibitor

The containing of ion composition, pH, salinity and temperature for every field region varies considerably [33]. For examples, the water properties in the central North Sea tends to have high barium contents with a pH range from 4.4 to 7.5. However, the typical water found in the Southern North Sea has high salinity with high sulfate content. Thus, the chemical scale inhibitor should have the characteristic which can withstand at insitu environment.

The chemical inhibitors have to be stable in brine containing rich divalent ions, stable in the presence of another chemical, stable at pressure and temperature, and has a good balance for adsorption-desorption, has low toxicity, high biodegradability, reasonably cost[34].

4.2.2 Techniques of Scale Inhibitor

The chemical scales inhibitors are placed into reservoir formation to mitigate scale depositions in the production zone. There are two techniques that are practically used in the field implementations, they are hydraulic fracturing and squeeze inhibitor.

Hydraulic Fracturing
It is often possible to place the chemical inhibitor along with the hydraulic fracturing treatment, see figure 4.1. The inhibitors together with proppant fracture fluid are injected down to the wellbore. Water soluble Polyphosphates is practically used and effective to minimize calcite and sulfate scales in the matrix reservoir[19]. However, this technique is expensive and needs proper fracturing design.
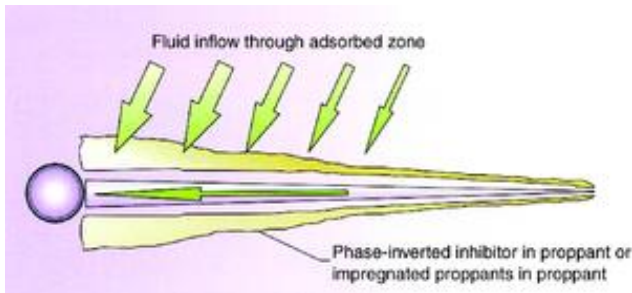
Figure 4.1 Hydraulic Fracturing Inhibition Treatment[15]
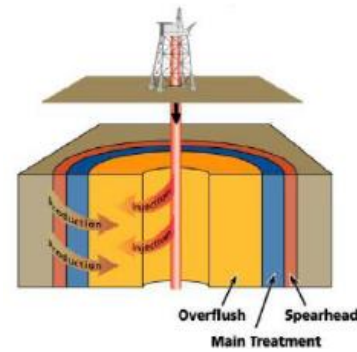
Figure 4.2 Squeeze Inhibition Treatment[35]

Squeeze Inhibition
Squeeze inhibition is a method to place the chemical inhibitor in the reservoir by pumping down through the wellbore. The chemical solution will penetrate to the near wellbore and further into reservoir, see figure 4.2. This method starts with pre-flush stage by injecting brine, it is then continued by squeezing stage where the chemical is injected and pushed further into the formation. The chemical will be adsorbed onto the surface rock and prevent the scale formation. Later, the over-flush stage and shut in the well for a period of time. The chemical will be produced afterward together with reservoir fluid [16, 19, 34]. This method will be repeated as the concentration of the chemical is no longer effective. Compared to the fracturing method, the squeeze inhibition method is inexpensive.

However, the adsorption of the chemical may change surface tension and rock wetability. For the reservoir having with water sensitive zone, a pumping large amount of water based chemical will reduce fluid production as a result of clay swelling and emulsion effect. For this, the oil soluble inhibitor, water in oil emulsion and mutual solvent preflush are used to minimize the impacts[14, 32].

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4.2.3 Type of Scale Inhibitor

Generally, scale inhibitor can be classified into Thermodynamic, Kinetic and Adherence inhibitors [36]. The thermodynamic inhibitor is chelating agent and complexes which are designed for specific scales like EDTA and Nitrilotriacetic Acid for $BaSO_4$ scale. The Kinetic Inhibitor is applied to inhibit the formation of Hydrate scale, however, it also possible to prevent the formation of scales. Lastly is Adherence Inhibitor, it works by preventing the crystal adherence onto the metal surface.

The scale inhibitors are also divided into organic and inorganic inhibitors, where Phosphorous compound is a basic constituent for inorganic scale inhibitors as seen in table 4.1

Table 4.1 The Organic and Inorganic Scale Inhibitors[16, 36]

Organic Inhibitors	Inorganic Inhibitors
Organic Phosphate Ester − Ethylenediamine Trimethylene Potassium Phosphate − Amino Trimethylene Zinc Phosphate Organic Phosphonates − Polyoxyethylene Phosphonate Ester − Amino Methylene Phosphonate Ester − Polyoxyethylene Pyrophophonate Ester Organic Aminophosphates Organic Polymers, sulfonated polymer Ester Polyacrylic acid (PAA) Phosphinocarboxylic acid	Inorganic Poly(phosphate)s - Sodium Tri Polyphosphate - Sodium Hexa Metaphosphate Condensed Phosphate - Poly(metaphosphate)s

Organic Phosphate are excellent for $CaCO_3$ scale since they have good chemical stability, not easy to hydrolyze, resistance to high water temperature and high alkalinity. While *Inorganic Polyphosphates* has a limitation on suffering hydrolysis, it is possible hydrolyzed to orthophosphate and could precipitate to $Ca_3(PO_4)_2$ scale if improperly used during application. For *Organic Phosphonate*, it works by preventing nucleation/crystal growth. This inhibitor is developed to cover limitation of Inorganic Polyphosphates. It has good thermal stability and not easy to hydrolyze [16, 17, 33, 36]. Figure 4.3 shows the Phosphonates inhibitors for carbonate and sulfate scales.
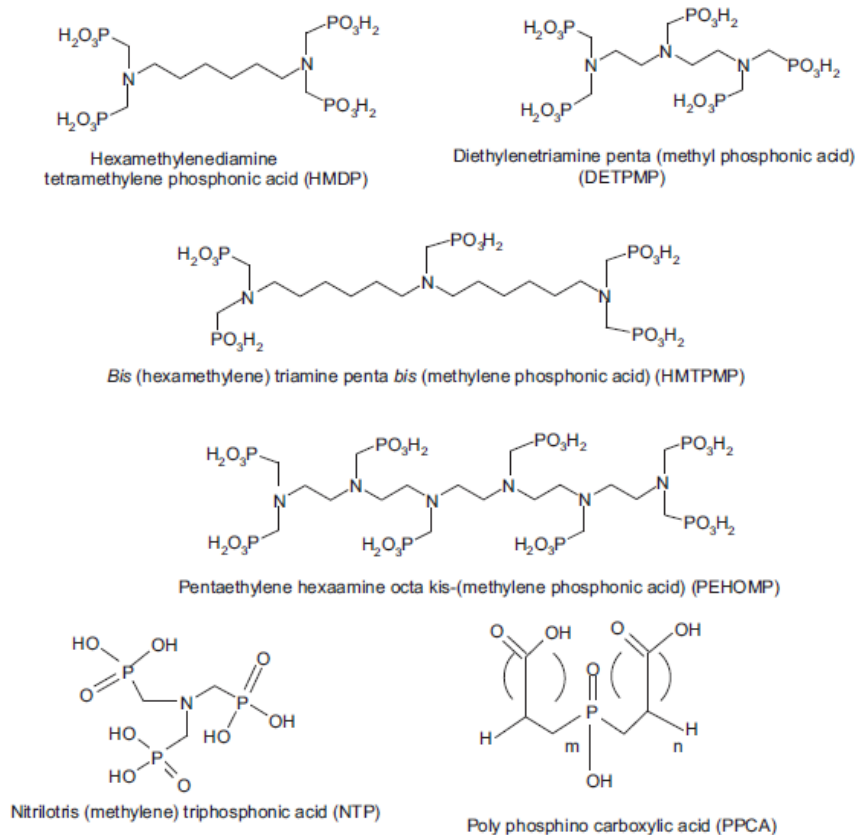
Figure 4.3 Chemical Formula for Phosphonates Scale Inhibitors[33]

4.2.4 Green Scale Inhibitor

The use of scale inhibitors must consider the problems arising during field operational, especially the environmental issue. Most of the phosphorous compounds mentioned in table 4.1 tend to have chemical pollution; therefore the environmental friendly inhibitors with good biodegradability are developed based on the non-phosphorous compound. They are PESA, PASP and CMI and detail explanation as followed[16, 33]

- *Polyaspartic Acid (PASP).*PASP is a Polymer Glycidyled of Amino, it has the ability to act as biodegradable polymer replacing the polluted chemical such as acrylic acid. The structural of PASP is shown in figure 4.4.The PASP has good characteristics, it is stable in high temperature, good Chelation to Ca^{2+}, Mg^{2+}, Fe^{2+}, Cu^{2+} and relatively use in small dosage

- *Carboxy Methyl Iinulin (CMI).* CMI has the ability to tolerate a condition with high calcium concentration. It is also biodegradable inhibitors with excellent ecotoxicity so CMI is suitable for sequestration of hard scale. The structural formula for CMI is shown in figure 4.5

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- *Polyepoxysuccinic Acid (PESA).* This inhibitor does not contain phosphorous and nitrogenous structure, see figure 4.6. The M represents the water soluble positive ions such as H^+, Na^+, K+, NH_4^+. Moreover, this inhibitor has resistance to alkalinity, good thermal stability and strong chelation to Fe^{2+}, Mg^{2+}, and Ca^{2+}.
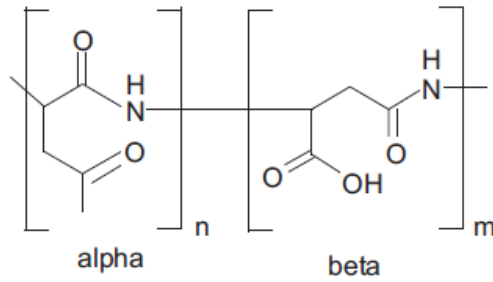
Figure 4.4 Structure of PASP[33]
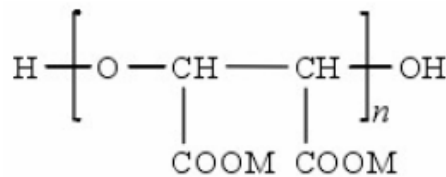
Figure 4.6 Structure of PESA[16]
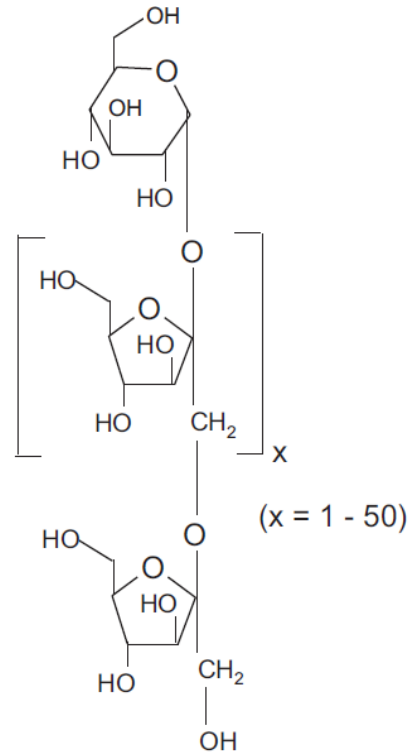
Figure 4.5 Structure of CMI[33]

4.2.5 Factor Affecting Performance of Scale Inhibitor

The performance of chemical inhibitor to suppress scale formation is related to the factor influencing the development of nucleation and crystal growth, thus any change in temperature, super-saturation, divalent ions, pH, and fluid compatibility will determine the effectiveness of inhibitor when works to scale minerals[30].

Temperature affects the scale inhibitor performance by increasing kinetic rate precipitation. At high temperature, the kinetic rate of nucleation and crystal growth is increased. It means there will be more salt precipitated out from solution with higher temperature. In this situation, the performance of scale to inhibit or suppress crystal growth is reduced. In general, every inhibitor has their own temperature window at which they can stable and work optimally. For example Homopolymers of vynils sulfonate and Copolymers of Acrylic that has the ability to withstand above 150^oC and it is different for other chemicals inhibitors [30].

Supersaturation. Effect of supersaturation on scale performance is basically correlated with temperature since the supersaturation condition is a function of temperature[20]. Therefore at the high degree of supersaturation, the performance of inhibitors will decrease.

Divalent ion presence. The performance of inhibitors to reduce scale formation will decrease in the brine solution containing divalent ion such as Ca^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+}. The divalent ion can react with chemical inhibitors and reduce its concentration in the solution and therefore the effectiveness to react with scales minerals is reduced. However, the choice of inhibitors is depending on the formation water and injected water used[34].

Compatibility Effect. Before chemical inhibitor is injected into reservoir or circulated within wellbore, the incompatibility test between chemical inhibitor and brine solution or hydrocarbon phases should be investigated since their interaction might lead further damage or emulsion, as explanation below[17, 30]

- Compatibility With formation and Injected Brine
  Formation water and injected water contain more dissolved scaling ions. The adding scale inhibitor to prevent a specific salt might induce the formation of other scales. For example, the inhibitor solution is injected to prevent the calcite salt deposition however at the same time the heavy scale $CaSO_4$ is deposited.

- Compatibility with Hydrocarbon
  The aqueous inhibitors have potential to form an emulsion when contact with oil. and form an emulsification

- Compatibility with other chemical presence
  It is common to add more chemical inhibitor in the solution such as chemical inhibitor and chemical corrosion. If there are more than one chemical presence in the brine system, there will be competition between them which can influence the performance of each.

4.2.6 Mechanism of Scale Inhibitor

In general, the mechanisms of scale inhibitors to reduce formation of scale are minimum suppression, lattice distortion, chelating mechanism and electric double layer, which are discussed as followed[3, 16, 17, 19, 25, 30, 34, 36]

- *Minimum Suppression Mechanism.* Precipitation is initially generated by little seeds that appear in the solution. Adding inhibitor as poisoning agent will suppress the growth of crystal seed in the solution and reduce scale precipitation

- *Lattice Distortion Mechanism.* After the crystal seeds are generated, they need the base or surface at which continuous growth of crystals occur. The inhibitors will inhibit the crystal seed for adhering to the solid surface.

- *Chelating Mechanism.* The chelating agent has coordination bonds that make it easy to form complexes compound with the scaling positive ions in the water, see equation (4.1)[19]. The example for the chelating agent is EDTA, Citric Acid and Gluconic Acid[36]. If the scaling ion in the water is decreased then potential scale formation is reduced. The limitation of EDTA is that one molecule of EDTA can only react with one specific scaling ion, called as "stoichiometric" reaction. Consequently, the large amount of EDTA is required if many scaling ions present.

$$EDTANa_2 + X^{2+} \leftrightarrow EDTAX + Na^{2+}$$ Equation (4.1)
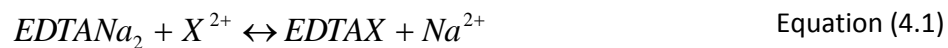
X2+ represents scaling ions such as Ca^{2+}, Mg^{2+}, Ba^{2+}, etc

- *Electric Double Layer.* The inhibitors will create an electric double layer in the boundary at which the crystal nucleation grow and preventing scaling ions from coagulating on the surface.

4.3 Scaling Removal

The scales can be removed either mechanically or dissolved chemically, and selecting of scale removal techniques are depending on the type, quantity, physical composition and the texture of scale. Generally, scales can be classified as soluble acid and insoluble acid scales. For thought scales with has low solubility in the acid solution the mechanical operations are commonly used.

4.3.1 Mechanical Removal

In the field operational, there are some methods that are often used for scale removal such as milling, jetting, bullheading, Brush/Scratcher, explosive and vibration. The mechanical methods are commonly used for the scale that has low solubility with acid solution, like barium sulfate. *Barium Sulfate* is the hardest and toughest scale among the others. It has low porosity so it is difficult for the chemical solution to have contact with surface scale and therefore the mechanical treatments are more suitable to remove $BaSO_4$ [3, 14, 29, 37].

4.3.2 Chemical Removal

One of the advantages using chemical methods is easy to be implemented compare to mechanical treatment. The contact area between surface scale and chemical agent is also an important parameter in the rate and effectiveness of scale removal process. The larger contact area, the faster the scale will be broken down. The soluble scales are divided into water soluble and acid soluble scales [19]. For water soluble scales, the use of fresh water is good enough for dissolving salt

precipitation such as NaCl, While for the scales such as $CaCO_3$, Iron Carbonate, Iron Sulfide, Iron Oxide (Fe_2O_3),the acid solution inhibitors will be more effective as scaling inhibitors. They can be removed with a sequestered acid using the solution containing HCl, Acetic Acid (CH_3COOH), Formic Acid (HCOOH), Citric Acid ($C_6H_8O_7$) and sulfamic acid (NH_2SO_3H). Recent research found that Na_2H_2EDTA has the ability to inhibit and remove the insoluble salt [15-17, 19].

4.4 Scaling Potential at High Pressure and High Temperature Well

Currently, the deep water field operation has been developed to overcome the energy needs in the future. Fields operated in the deep water have high pressure (15000-30000 psi), high temperature (150^oC-250^oC) and high TDS (>300.000 mg/L)[33]. Having this extreme condition in the field operation will make the risk managements are crucial, especially for scaling control and management.

Some scale potentials are pointed out when working under HPHT condition, such as:[33]

- Increase potential corrosion, brine tends to form acidic mixture under HPHT
- Water tends to dissolve sand (SiO_2) and forms orthosilicic acid (H_4SiO_4), as equation (4.2)
- Deposit stable silicate minerals (Ca_2SiO_4, Na_4SiO_4) as a result of dissociation of orthosilicic acid. The orthosilicic acid then react with divalent ion (Ca^{2+}, Na^+), as equation(4.3) to equation (4.6)

$$SiO_2 + 2H_2O \leftrightarrow H_4SiO_4$$ Equation (4.2)

$$H_4SiO_4 \leftrightarrow SiO_4^{4-} + 4H^+$$ Equation (4.3)

$$SiO_4^{4-} + 2Ca^{2+} \leftrightarrow Ca_2SiO_4$$ Equation (4.4)

$$SiO_4^{4-} + 4Na^+ \leftrightarrow Na_4SiO_4$$ Equation (4.5)

$$SiO_4^{4-} + 2Na^+ + Ca^{2+} \leftrightarrow Na_2CaSiO_4$$ Equation (4.6)

4.5 Inorganic and Organic Scale Prevention

- Sulfate and Carbonate scales preventions are discussed in chapter 5
- *Iron Sulfide Scale* occurs when the formation water containing Fe^{2+} contacts with H_2S. H_2S is produced from formation water or the injected/produced water containing sulfate ion. FeS can be mitigated by injecting nitrites, biocides or removing sulfide ion from injecting water[25].

- Hydrate Scale, can be prevented through chemical or operation treatments
  Chemical Treatment [38, 39]

  - Dispersant or antiagglomerant has long-chain quaternary ammonium salts to prevent agglomeration.
  - Polymer, carbon backbones or pendant groups are Kinetic Inhibitors. They will absorb into hydrate crystal surface and avoid crystal growth

- Emulsifier maintains the stabilization of small hydrate particle in the oil phase and avoid crystal growth
- Adding Inhibitor such as MeOH, MEG, Alcohol or Salt to lower the freezing point

Operational Treatment [38, 39]

- Increase temperature system. As figure 3.5 that higher temperature will bring to the "no hydrate" region. There are 3 methods such as insulating pipe (coating pipe), PIP (Pipe in Pipe) and gas insulating pipe (vacuum insulating pipe).
- Decrease Pressure system, to maintain the phases in the fluid phases
- Remove free and dissolved water using separators, glycol dehydrator, molecular sieves

- *Corrosion*[40]**,** potential corrosion occurs as equation (4.7) and equation (4.8)

$$CO_2(g) + H_2O(l) \leftrightarrow H_2CO_3(aq)$$ Equation (4.7)

$$Fe + H_2CO_3(aq) \leftrightarrow FeCO_3(s) + H_2$$ Equation (4.8)

To prevent corrosion problem can be treated by
- Increase pH in pipeline
- Injecting alkaline chemical (NaOH) to lean MEG in order to create CO_3^{2-}. It will generate thin protective film of $FeCO_3$ at the wall pipe to minimized corrosion

- *Wax/Paraffin Inhibition,* Wax and paraffin can be mitigated by [26]:
  - Raise temperature system, by installing Electric Heater
  - High Flow rate, will prevent the wax adhere to surface metal
  - Insulate pipeline
  - Inject Dispersant, by injecting dispersant the nuclei are kept from the agglomeration and make the pipe more water wet. It also avoids the wax to adhere onto surface pipe
  - Inject Crystal Modifier, such as Ethylene VynilAcetat, Maleic Acid Ester, etc. They will result in deformation of crystal wax and prevent aggregation.

- *Naphthane Inhibition.* Naphthenate can be mitigated by injection short chain organic acid or acetic acid to maintain the low pH [27] and the application of acid injection can reduce Naphthenate deposition as long as pH is less than 6 [41].

4.6 Inorganic and Organic Scale Removal

- Sulfate and Carbonate scales removal are discussed in chapter 5
- *Halite* can be removed using low salinity water and desulfation plant. Desulfation plant is a treatment at which the sulfate ion is removed from halite wash water, a case at Heron Field production system[37].

- *Hydrite Removal*[23, 39, 40]. The hydrite scale is possible formed whenever the light hydrocarbon (n-buthane or smaller) contacts with the water phase. Some methods are applied In field application when removing hydrite deposition, such as pigging pipe, Methanol or glycol injection, install heater, Hydrate depressurization of pipe from both side

- *Iron Sulfide Scale.* If we have iron sulfide scale in our system, it can be removed chemically and mechanically. FeS has good solubility in acid, hence acid minerals are used to remove iron sulfide scale as equation (4.9)[25]

$$FeS + 2H^+ \Leftrightarrow H_2S(g) + Fe^{2+}$$
<div align="right">Equation (4.9)</div>

The sulfuric acid and hydrochloric acid are used to enhance rate dissolution of iron sulfide. The rate dissolution of FeS reduces as the accumulation product of H_2S increases. Therefore, it is important to control forward reaction by using the chelating agent. In the field application, adding some additives in the inhibitor are required as followed [16, 17, 25]

  - Corrosion inhibitor, to avoid corrosion potential in the surface metal
  - Water wetting surfactant, to enlarge contact between scale surface and acid, by removing impurities and hydrocarbon from scale surface
  - H_2S scavenger, i.e aldehydes, ketones, oximes are used to enhance rate dissolution

- **Wax/Paraffin** can be removed through [26]
  - Cutting using coiled tubing can remove the wax/paraffin deposition in the wellbore
  - Pigging, to remove wax/paraffin deposition in the surface pipe
  - Chemical dissolution, such as oxylene, acidic ammonium chloride, sodium nitrite
  - Melting. Hot oil or hot water can be used to remove wax deposition, by pumping down to the wellbore to melt the wax and dissolve to the hot oil or hot water.

5. EVALUATING SCALE POTENTIAL DURING HIGH AND LOW SALINITY INJECTION

5.1 Water Injection

Among the secondary recovery, the conventional water flood is the most successful and widely used to improve oil recovery after primary recovery. Waterflood is injecting water into reservoir to support reservoir pressure and/or to push oil toward the producer well. Recently, It is recognized the primary recovery only recover a small amount of oil from reservoir[2]. The natural energy reservoir depleted during this stage so the oil can't be transported to the wellbore. When the remaining oil in the reservoir is still economic to be developed, the secondary recovery by water flooding is one of the choices.

5.1.1 High Salinity Water Injection

Water as a source of injected brine depends on the location where the field is being operated. For the conventional water injection, the injected brine may be taken from sea water or produced water. The field area where the number of offshore production well and facility are located, sea water is a major source that is practically applied. However before the water is injected into reservoir, it is necessary to treat the water from the impurities. The high content of dissolved minerals and gas in sea water are being a concern due to incompatibility problem may occur when having contact with formation water or rock minerals. The high capital cost for production facility and water treatment are usually found as a constrains in the water flood projects[10].

Recently, the new method in the waterflood injection is being established. The injection water with having significant lower salinity or ion presence than sea water or formation water obviously shows beneficial effects on the oil recovery, as seen in figure 5.1. According to experimental reported by Morrow and Bucley (2011)[42], the recovery can reach up to 80% of IOIP by low salinity water injection. The problem associated with dissolved undesirable minerals and gas in the water injection can be minimized. Additionally, it is applicable for onshore and offshore filed development.
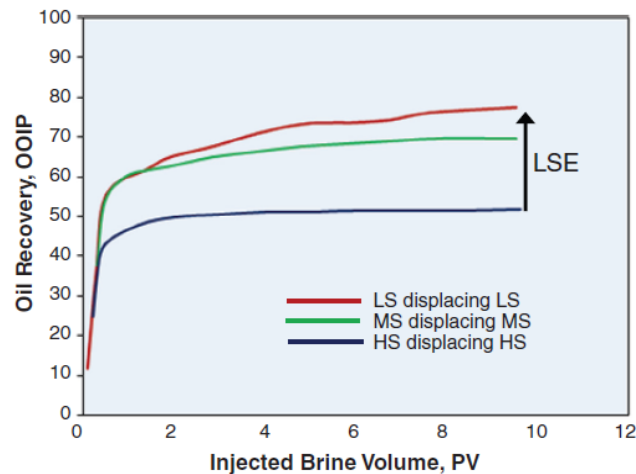

Figure 5.1 Oil Recovery for High Salinity and Low Salinity Injection[42]

5.1.2 Low Salinity Water Injection (LSWI)

Low salinity water injection is a technique to improve oil recovery by injecting water with significant lower salinity than formation water. It disturbs the chemical equilibrium within COBR and change to be more water wet[9]. This technique is mainly performed in the sandstone reservoir. In 1967, Bernard[43] found that oil recovery can be increased by lowering salinity brine composition to 0.1%. And since then, many laboratories experimental and studies had been conducted in the last decades by Tang and Morow[44], Lager[45] and Austad et al 2010[9]. Many Oil companies have also implemented LSWI method and additional oil recovery was reported.

The suggested low salinity mechanism was proposed by Austad et al 2010[9] , see figure 5.2. It was suggested that there is an effect of pH in the wettability alteration. Ion H^+ has the highest affinity to the clay surface. As the low salinity is injected into reservoir, ion H^+ from the water will react with clay. It will be adsorbed onto clay surface then the pH of water is increased. The organic material of oil will be released then it leads to be more water wetness. The recovery improvement was observed during the experiment. The optimum salinity to create desorption of organic compound from the clay surface is usually range between 1000 ppm to 2000 ppm, however, the effects can be observed until 5000ppm. The equation (5.1), (5.2) and (5.3) show the chemical reactions for COBR.
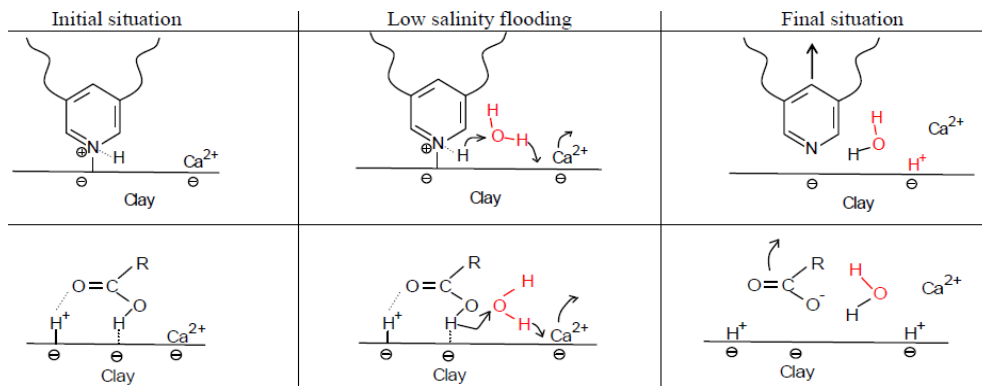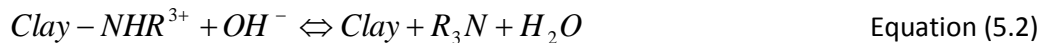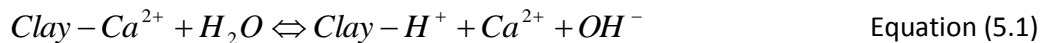

Figure 5.2 Proposed Low Salinity Water (LSWI) Mechanism

Desorption of organic material from clay surface (Austad. et al., 2010[9])

$$Clay - Ca^{2+} + H_2O \Leftrightarrow Clay - H^+ + Ca^{2+} + OH^- \qquad \text{Equation (5.1)}$$

$$Clay - NHR^{3+} + OH^- \Leftrightarrow Clay + R_3N + H_2O \qquad \text{Equation (5.2)}$$

$$Clay - RCOOH + OH^- \Leftrightarrow Clay + RCOO^- + H_2O \qquad \text{Equation (5.3)}$$

Initially, the native water in the reservoir is in the equilibrium with hydrocarbon, rock, or other minerals presence in the reservoir however when the injected water which has different mineral composition is injected, it will have interaction with insitu fluid and rock in the reservoir. It disturbs

the equilibrium condition and automatically readjusts a new equilibrium. This interaction is a function of temperature, pressure, the flow path and the degree of mixing ratio.

In this chapter, we will look at the potential of scale when the incompatibility water is involved. Some scenarios include sensitivity of:
- Injected water composition, to simulate high salinity and low salinity water case
- Mixing ratio of FW and SW, to simulate scale tendency of any proportion at various location
- Pressure, to simulate effect of pressure change during transportation to the surface

Later the prevention and removal of potential scale will be discussed

5.2 Evaluating Scale Potential during High Salinity and Low Salinity Water Flooding

5.2.1 Formation Water and Sea Water Characteristics

5.2.1.1 Water Composition

Table 5.1 present the water composition of formation water (FW) and sea water (SW) of the field located in the North Sea area. As seen from table 5.1 that the formation water is highly content of dissolved alkaline earth metals minerals. In general, the formation water is range from 10,000 ppm to 300,000 ppm depending on the concentration of ions presence in the brine, such as K^+, Ca^{2+}, Mg^{2+}, Ba^{2+} and Sr^{2+}, etc. The most common ions are Na^+ and Cl^- with the insignificant amount of SO_4^{2-} and HCO_3^-. In addition, formation water also contains more dissolved gas (CO_2,O_2,H_2S) as discussed in chapter 2. When comparing with formation water, the sea water is most dominated by anion SO_4^{2-}, Cl^- and HCO_3^-, with a small amount of alkali metal ions. The water composition as below is used to simulate of scale potential in varied conditions.

Table 5.1 Water Analysis of Formation Water and Sea Water (*Reservoir Chemistry Lecture)

Water Analysis of Sea Water (SW) and Formation Water (FW)		
Ion (mmol/L)	FW	SW
Cl^-	1446.8	525.1
SO_4^{2-}	0.0	24.0
HCO_3^-	0.10	2.0
Mg^{2+}	22.0	44.5
Ca^{2+}	100.0	13.0
Na^+	1156.0	450.1
K^+	7.00	10.1
Ba^{2+}	3.90	0.0
Sr^{2+}	18.0	0.0
TDS (g/L)	84.72	33.39

5.2.1.2 pH development of Formation Water and Sea Water

The PHREEQC simulation is run to identify the pH development with temperature for formation water and sea water. Pressure system is set 10 atm as a limit pressure to avoid boiling water. The pH trend of formation water (FW), sea water (SW), FW-equilibrium with CO_2 and de-ionized water (DI) is observed at temperature from 25°C to 150°C. Figure 5.3 shows the result of this simulation.
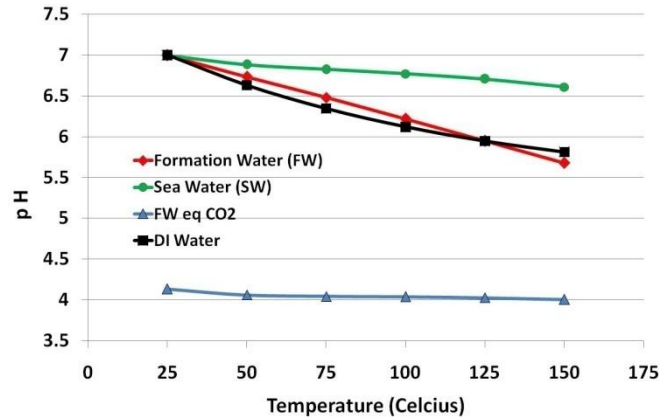

Figure 5.3 pH development with Temperature for FW, SW, FW-eq
CO_2 and DI water

The DI water or pure water contains hydrogen ion and hydroxide ion. The formation of both ions from the pure water is an endothermic process, where the heat is absorbed in the forward reaction as equation (5.4)[18]. The pH trend of de-ionized water (DI) in figure 5.3 declines with temperature. According to Le Chatelier's Principle[18], when the system in the equilibrium state is disturbed then it will shift to the site where the new equilibrium will be generated. For examples, if the temperature of pure water is increased then the equilibrium will move toward the lower temperature. This situation lines with the auto ionization water that shifts the equilibrium toward the right, producing more hydrogen and hydroxide ions.
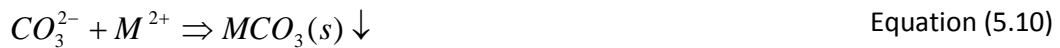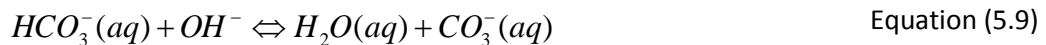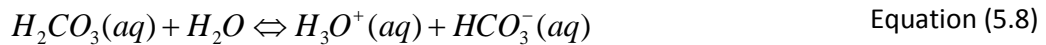
$$H_2O(l) \Leftrightarrow H^+(aq) + OH^-(aq)$$ Equation (5.4)

pH is defined as

pH = -Log [H_3O^+]   Equation (5.5)

The water constant solubility is expressed by *Kw*. It measures concentration product of hydrogen ions and hydroxide ion. The value of Kw will increase as temperature increase since the auto ionization water shifts toward the right, produces more H^+ and OH^-. The pH measures the concentration of [H^+], as seen in equation (5.5)[18]. Thus, we observe a reduction of pH as temperature.

Uniquely, DI water has characteristic as a neutral solution which has constant pH=pOH as temperature changes. Formation water and sea water have dissolved constituents, and the pH values are not same as the pure water/DI water. According to figure 5.3, they have higher pH values than the neutral water and this result the brine solutions are slightly alkaline than pure water. Thus decreasing pH is more driven by auto-ionization water and the dissolved constituent will influence the water alkalinity.

Figure 5.4 shows the concentration of calcite ($CaCO_3$) with temperature for SW and FW. SW has significant dissolved ions HCO_3^- thus, the concentration of calcite in SW is higher than FW. It increases for temperature up to 100-110°C and according to Le Chatelier's Principle[18], (CO_3^{2-}) as a product of calcite dissolution will shift the equilibrium toward HCO_3^- (see equation 5.9). It will consume [H_3O^+] and pH increase, equation (5.8). Thus, the reduction in pH is mainly due to auto ionization water and the effect of carbonate ions is to keep overall pH above neutral and formation water (FW), see figure 5.3.

$$CO_2(g) \Leftrightarrow CO_2(aq)$$ Equation (5.6)

$$CO_2(aq) + H_2O \Leftrightarrow H_2CO_3(aq)$$ Equation (5.7)

$$H_2CO_3(aq) + H_2O \Leftrightarrow H_3O^+(aq) + HCO_3^-(aq)$$ Equation (5.8)

$$HCO_3^-(aq) + OH^- \Leftrightarrow H_2O(aq) + CO_3^-(aq)$$ Equation (5.9)

$$CO_3^{2-} + M^{2+} \Rightarrow MCO_3(s) \downarrow$$ Equation (5.10)

We observed at temperature above 110°C, the concentration of calcite and carbonate ions in the solution decline. It seems likely due to ion carbonate forms complexes with other cation presence in the brine solution, such as Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+} through equation (5.10) and reduce its activity. If the supersaturation is reached, the potential of insoluble salt may occur like $CaCO_3$, $MgCa(CO_3)_2$, etc
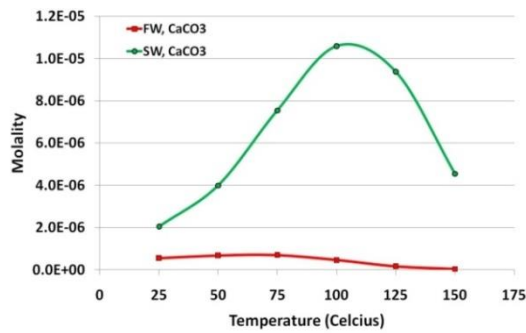

Figure 5.4 Plot of Calcite concentration with Temperature in FW and SW.

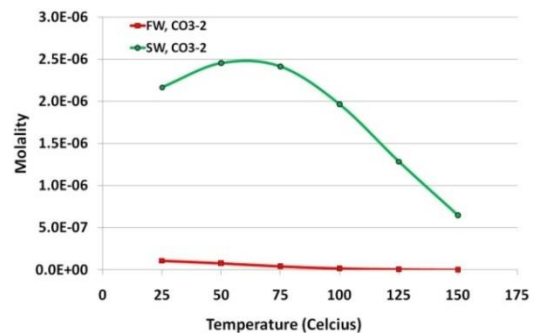Molality is expressed in (mol/kg)

Figure 5.5 Plot of carbonate ion (CO_3^{2-}) concentration vs Temperature in FW and SW.

Molality is expressed in (mol/kg)

According to figure 5.3, the FW equilibrium with CO_2 has the lowest pH. The brine is more acidic as CO_2 enters the system. CO_2 gas will react with water and form H_2CO_3. It will then more shift the equilibrium toward to the right, and produce more H^+, see equation (5.6), (5.7) and (5.8) and thereafter we observed the pH is low.

5.2.1.3 Potential Scale Precipitation in the Sea Water Brine

As brine, sea water contains dissolved minerals ion. The certain salt may precipitate when there is a change in the surrounding condition such as temperature, pressure or salinity. As discussed in the previous chapter the auto scaling may occur. The potential of scale precipitation in sea water brine is observed over range of temperature and shown in figure 5.6 and figure 5.7
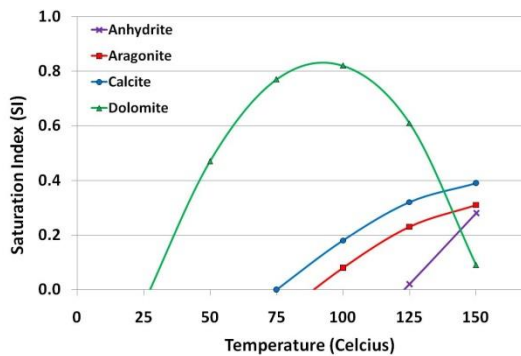

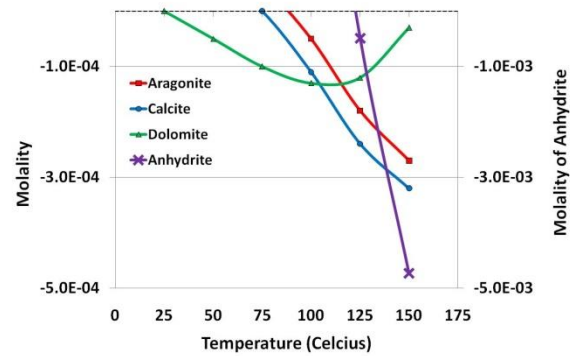Figure 5.6 SI vs Temperature in SW

Figure 5.7 Molality of precipitated minerals in SW

Negative values show potential scale. Anhydrite is plotted in secondary axis. Molality is in (mol/kg)

Figure 5.6 shows the potential of scale precipitation in the sea water brine. In the PHREEQC simulator, the potential of scale is illustrated by SI values greater than zero (SI>0). According to water composition in table 5.1, sea water brine contains high SO_4^{2-} and CO_3^{2-} as the source of scale minerals, so we observed that Anhydrite, Aragonite, Calcite and Dolomite scales in the sea water.

However, a limitation of PHREEQ is that the phases are not precipitated in the simulations, the solutions are simply treated as supersaturated when the SI > 0. Thus by plotting *molality difference* of each phase with temperature is likely more reasonable to see potential of precipitated minerals.

Figure 5.7 explains the *molality difference* of each phase, different molality between equilibrium condition and supersaturated condition. Precipitation is shown as negative values, as molality of the supersaturated brine is higher than the molality in equilibrium, then salts are precipitated out and lost from solution phase. The PHREEQC model for equilibrium condition is presented in Appendices (figure A.1 to figure A.10). When comparing figure 5.6 and figure 5.7, the trend for SI development matches the molal concentration of precipitate.

Hence according to figure 5.6, Dolomite is the first mineral to precipitate and already precipitates at temperature around 25-30°C. Aragonite and Calcite start to precipitate from solution at temperature above 75°C, while Anhydrite precipitates at temperature above 125°C. The SW brine composition is therefore only stable for temperature equal to or below 25°C.

5.2.2 Effect of Injected Water Composition

The effect of injected water composition to scale precipitation is studied. There is 3 type of injected water solution used, they are pure sea water, diluted 10 times sea water and diluted 50 times sea water. Each of this type will be mixed with formation water to simulate potential scale formation in the conventional sea water and low salinity water injection.

Table 5.2 shows the varied water composition, the pressure is set 10 atm and tested over range temperature 25°C to 150°C. The PHREEQC model simulation is presented in Appendices (figure A.11 and figure A.12)

Table 5.2 Water Composition of Formation Water,
Sea Water and Diluted Sea Water

Water Analysis of Sea Water (SW) and Formation Water (FW)			Diluted SW	
Ion (mmol/L)	FW	SW	10x	50x
Cl$^-$	1446.80	525.10	52.51	10.502
SO$_4^{2-}$	0.0	24.00	2.4	0.48
HCO$_3^-$	0.10	2.00	0.2	0.04
Mg^{2+}	22.00	44.50	4.45	0.89
Ca^{2+}	100.00	13.00	1.3	0.26
Na$^+$	1156.00	450.10	45.01	9.002
K$^+$	7.00	10.10	1.01	0.202
Ba^{2+}	3.90	0.00	0	0
Sr^{2+}	18.00	0.00	0	0
TDS (g/L)	84.72	33.39	3.339	0.6678

5.2.2.1 pH development of Mixing Brine

Figure 5.8 shows a plot of pH development vs temperature for mixing FW/SW, *DI water* (De-Ionized water), mixing of FW/d$_{10}$SW and mixing of SW/d$_{50}$SW. FW/d$_{10}$SW and FW/d$_{50}$SW are mixing of formation water with diluted 10 times SW and 50 times SW respectively.
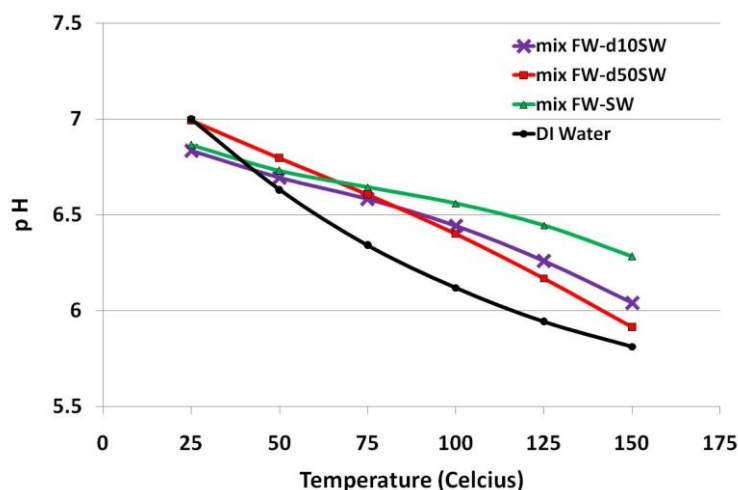
Figure 5.8 pH vs Temperature development for mixing brine

DI water. There are no other active ions than those formed by the water itself. The pH trend development is mostly driven by auto ionization water as discussed previously. As temperature increase then the reaction will shift toward the right and produced more [H$^+$], see equation (5.4). It means the pH will decrease as temperature is increased.

According to figure 5.8, the mixing brine water shows a similar trend with pH development that what seen for DI water. As the previous discussion, the decreasing pH as temperature is to a large extent connected with the shift in the auto ionization water, and the concentration of dissolved ions in the brines influencing the pH values, either higher or lower to neutral water/DI water.

In general in figure 5.8, the mixing of FW/SW brine has higher pH values than FW/diluted SW. Significant amounts of ions presence in the mixing of FW/SW will react with ion H$^+$ or OH$^-$ from water to form complexes such as HCl, NaOH, etc. It will reduce the active ion [H$^+$] that determines pH in the solution and thereafter higher pH for mixing of FW/SW is observed. Conversely, lower pH is found in FW/diluted SW due to dilution process will reduce concentration metal ions in the solution. It results in increasing activity of [H$^+$]in the solution and pH decreases.

5.2.2.2 Potential Scale Precipitation in the Mixing Brine

The SI values for different minerals that can precipitate during FW/SW and FW/diluted SW are plotted in figure 5.9 and figure 5.10 respectively. They are plotted in the same scale to compare both easier.
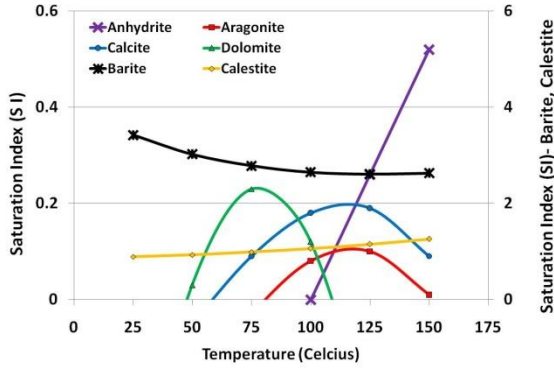
Figure 5.9 SI-values and development with temperature in mixing of FW/SW (HS case)

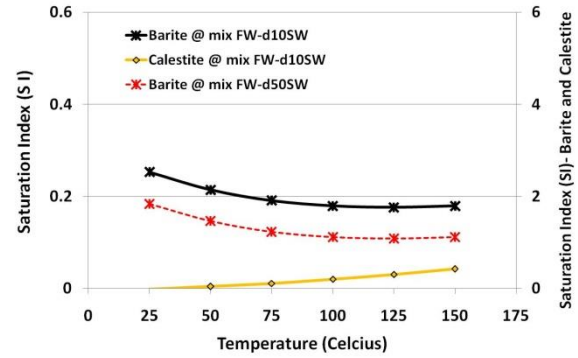Figure 5.10 SI-values and development with temperature in mixing of FW/diluted SW (LS case)

$BaSO_4$ $SrSO_4$ are plotted in the secondary axis

$BaSO_4$, $SrSO_4$ are plotted in the secondary axis

Mixing of FW/SW in the High Salinity case

When comparing figure 5.6 and figure 5.9, the mixing of FW/SW gives adversely impact on scale potential than individual sea water brine solution. FW rich alkali metal ions, like Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+} and SW rich anions, like SO_4^{2-} and CO_3^{2-}. When the sea water is mixed with formation water, the interaction between anion and cations in the mixture will form the insoluble salt, such as $CaSO_4$, $BaSO_4$, $SrSO_4$, $CaCO_3$ as equation (5.11), (5.12) and (5.13). Furthermore, the nucleation and the crystal growth process are influenced by the amount of dissolved impurities in term of the rate and form. In the mixing of FW/SW which has a significant amount of impurities than individual SW brine, the scales tend to be more precipitated[20].

$$Ca^{2+} + SO_4^{2-} \Leftrightarrow CaSO_4$$ Equation (5.11)

$$Ba^{2+} + SO_4^{2-} \Leftrightarrow BaSO_4$$ Equation (5.12)

$$Sr^{2+} + SO_4^{2-} \Leftrightarrow SrSO_4$$ Equation (5.13)

Anhydrite is plotted in figure 5.6 and figure 5.11 indicates potential precipitation for temperature above 125°C in the SW brine. $CaSO_4$ generally shows decreasing solubility with increasing temperature. Figure 5.6 points out how $CaSO_4$ is initially dissolved, but then precipitated for temperature above 125°C. However, when sea water is mixed with formation water, the mixture to be more saturated around 100°C-110°C and supersaturated for higher temperatures. The higher amount of precipitated $CaSO_4$ then is observed in the mixing FW/SW, see figure 5.11.
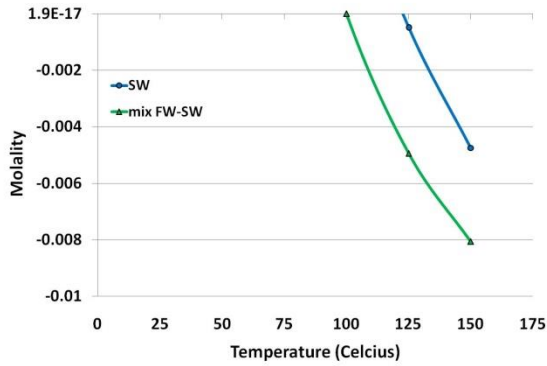
41

Figure 5.11 Molality of precipitated CaSO4 in pure SW and mixing of FW/SW brine

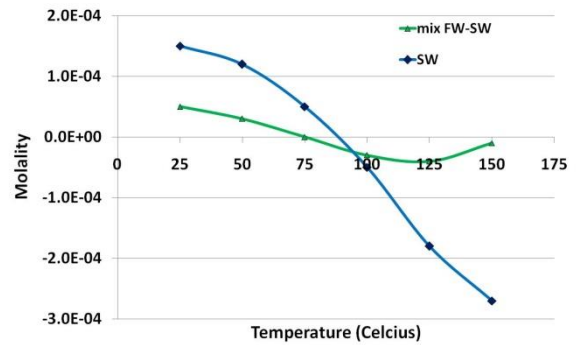Molality is expressed in (mol/kg)

Figure 5.12 Solubility of CaCO3 in pure SW and mixing of FW/SW brine

Molality is expressed in (mol/kg)

A similar trend for $CaCO_3$, generally the solubility of calcite decreases with temperature. However in the mixing of FW/SW, its solubility increases above 125^OC (see figure 5.12, green line) and it is followed by remarkable precipitation of Anhydrate (figure 5.9). The increased solubility of Calcite/Aragonite and decrease the solubility of Anhydrite seems likely due to strong binding of Ca^{2+} in complexes with SO_4^{2-} than CO_3^{2-} reducing the activity of Ca^{2+}. This agrees with figure 5.11 which indicates a significant amount of precipitated $CaSO_4$ at the higher temperature.

Dolomite SI development in figure 5.9 generally shows the same trend as seen in figure 5.6. In the SW brine solution, dolomite becomes less soluble up to temperature 75-100°C, above which it becomes more soluble again. The SI values are much lower in the mixing of FW/SW than in pure SW as Mg^{2+} concentration is diluted by the FW and SO_4^{2-} is present to form complexes with Mg^{2+} reducing its activity. Dolomite solubility increases for higher temperatures as $CaCO_3$ is precipitated and the active Ca^{2+} concentration is reduced

Calestite is another scale deposit when incompatibility water is mixed. When FW contains ion Sr^{2+} mixes with SO_4^{2-} in the SW, the $SrSO_4$ scale is formed. Celestite will be deposited with increasing temperature and therefore solubility will decrease with increasing temperature as seen.

Barite is common scale formed in the reservoir. It is formed due to the mixing of Ba^{2+} in FW and SO_4^{2-} in SW. Figure 5.9 shows Barite in the mixing of FW/SW and it will be more soluble at increasing temperature. However, as seen the decreasing solubility of $BaSO_4$ is insignificant and SI values are higher than zero over range temperature. The lowest solubility product of barite makes it as the insoluble scales by nature (see table 5.3). Among these lines, the Barite will always be precipitated over range given temperature.

Mixing of FW/Diluted SW in the Low Salinity case

As seen when comparing figure 5.9 and figure 5.10, the mixing of FW/diluted sea water shows a big impact on scale reduction. It decreases scale precipitation by reducing SI values. Almost all minerals are dissolved in FW/d_{50}SW, except $BaSO_4$ scales. Celestite is still precipitated in FW/d_{10}SW however it is totally dissolved in the mixing of FW/d_{50}SW.

Table 5.3 Table of Solubility Product Constant at 25°C[18]

Solubility Product Constant (Ksp) at 25°C			
Substance	Ksp	Substance	Ksp
Sulfate Scales		Carbonate Scales	
$BaSO_4$	1.08×10^{-10}	$CaCO_3$	3.36×10^{-9}
$CaSO_4$	4.93×10^{-5}	$MgCO_3$	6.82×10^{-6}
$SrSO_4$	3.44×10^{-7}		

The bicarbonate ion, HCO_3^-, dissolved in the FW/SW is higher than in the mixing of FW/diluted SW so we observed dissociation of $CaCO_3$ in the FW/SW is more significant as temperature increases up to 75°C. Above this temperature, the active concentration is decreased since the potential of scale precipitation increases. It consumes ion CO_3^{2-} and lost from solution (see figure 5.14). Carbonate ions in the solution may react with other cation to form complexes, like $BaCO_3$, $SrCO_3$, and $[Na^+(CO_3)^{2-}]^-$ through equation (5.10). However, $BaCO_3$ and $SrCO_3$ have not reached yet saturation limit so we couldn't find as positive SI values in figure 5.9 and figure 5.10. Actually, the chemical interactions in the solution are complex; they interact with each other and try to reach equilibrium. The trend decreasing ion concentration in the solution is presented in Appendices (figure A.18 to figure A.22)
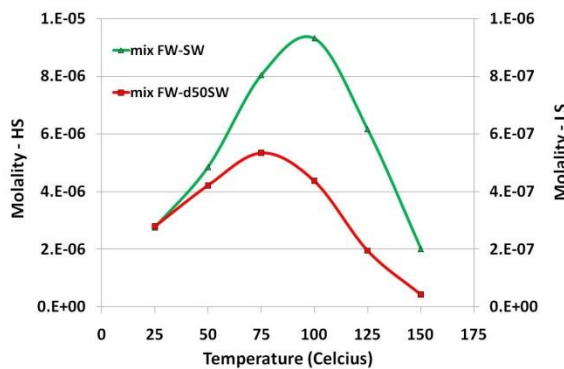

Figure 5.13 Calcite concentration development in the mixing of FW/SW and mixing of FW/d_{50}SW

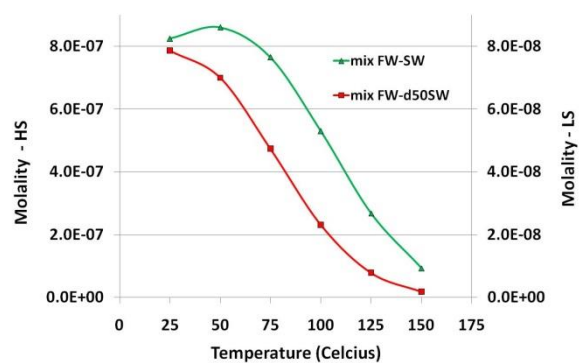Molality is expressed in (mol/kg). LS is plotted in the secondary axis.

Figure 5.14 CO_3^{2-} concentration development in the mixing of FW/SW and mixing of FW/d_{50}SW

Molality is expressed in (mol/kg). LS is plotted in the secondary axis.

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The lower concentration of impurities in the LS will reduce the supersaturation of solution, this yield lowering rate nucleation and crystal growth to form crystal salt[20]. Dolomite, Anhydrate, Celestite and Barite also indicate similar behavior. And thereafter we observed SI values decreases significantly in the mixing of FW/diluted SW as seen in figure 5.10 compared to figure 5.9.

5.2.3 Effect of Mixing Ratio

During water flood development, the injected water and formation water will mix at any proportion and location within the field. The degree of these mixing will determine the scale potential at any location under pressure and temperature change. In this part, however, we focus on the effect of mixing ratio at varied temperature by assuming constant pressure. Later, the scaling tendency under pressure change will be studied detail. PHREEQC simulator (see Appendices figure A.15 to figure A.17) is run with 3 cases with the proportion of SW is 30%, 50% and 70%, see table 5.4.

Table 5.4 The Mixing Ratio of Sea Water (SW) and Formation Water (FW)

Case	Ratio SW:FW
1	0.3 : 0.7
2	0.5 : 0.5
3	0.7 : 0.3

The results are presented in the figure 5.15 to figure 5.17. All graphs are plotted in the same scale to compare them easier. Recall figure 5.12 as the case of mixing brine with proportion 0.5SW:0.5FW. According to figure (5.15), (5.12), and (5.16) the increasing of SW proportion in the mixture will result in more scale tendency. It is generally caused by the presence of scaling ion SO_4^{2-} and ion CO_3^{2-} is increased in the mixture solution.
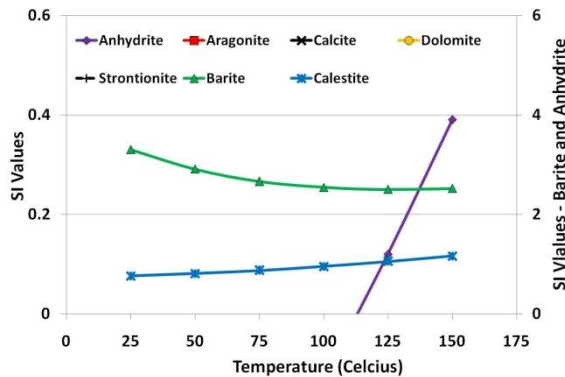
Figure 5.15 Saturation Index (SI) with temperature for mixing ratio 0.3SW:0.7FW

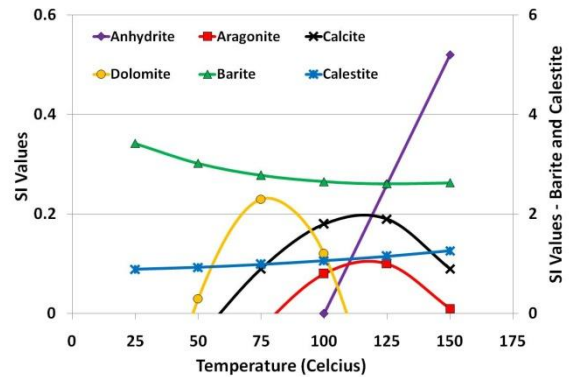Barite, Calestite are plotted in the secondary axis

Figure 5.12 Saturation index (SI) with temperature for mixing ratio 0.5SW:0.5FW

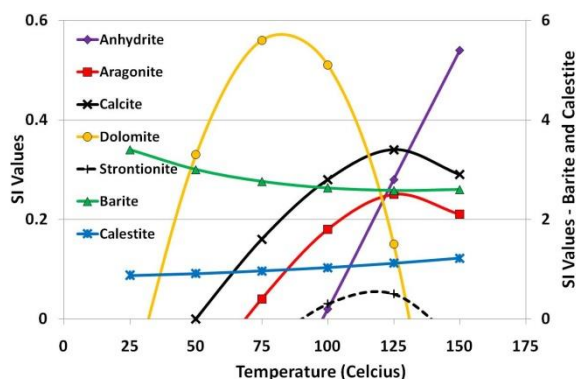Barite, Calestite are plotted in the secondary axis

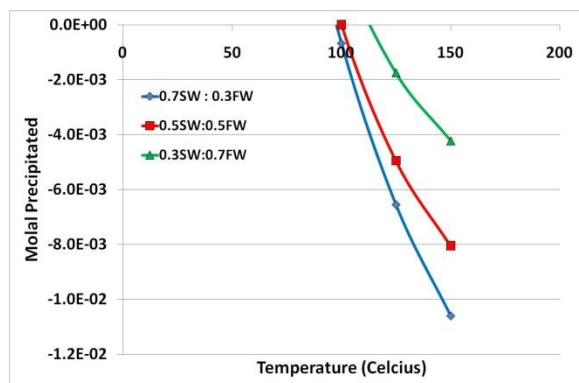Figure 5.16 Saturation Index (SI) with temperature for mixing ratio 0.7SW:0.3FW.

Barite, Calestite are plotted in the secondary axis

Figure 5.17 Molality of precipitated minerals for $CaSO_4$ in variation of mixing ratio

Molal precipitated minerals is increased as proportion of SW

The carbonate appears to be scales affected by salinity, especially dolomite. The solubility dramatically decreases which shown by triple increases of SI values when adding 50% SW to 70%SW. Strakhov (1967)[46] stated that in the sea water relatively contains rich alkali metals and somewhat saturated with dolomite constituent. The saturated dolomite will be easier to precipitate especially in the presence of ion $CaSO_4$, $MgSO_4$ and $MgCl_2$ in the solution. By increasing the salinity of 1%wt, the solubility of $CaCO_3$ will reduce to 5% while dolomite was at least 15% from initial values.

Sulfate scales are found as the first scales formed at the low proportion of SW, it is because most of the sulfate scales are formed due to mixing of incompatible water[47]. The severity of sulfate scaling resulted from SW brine is extremely found in the Barite. Barite has the lowest Ksp so make it as the insoluble salt. This is supported by figure (5.15), (5.12) and (5.16). They show how the Barite has the highest SI values over range temperature and small change solubility at any proportion. This result Barite will be precipitated out over range temperature. Barite is insoluble salt and tends to be detrimental precipitation at low SW brine[48]. $SrSO_4$ is commonly precipitated with $BaSO_4$

Another sulfate scale formed is Anhydrate. The amount, expressed by molality, of precipitated $CaSO_4$ is plotted in figure 5.17. It indicates the significant amount of $CaSO_4$(s) is at temperature above 100°C and in the mixture of 70%SW. At higher temperature, the rate of crystal growth increase and it results more solid precipitated out from the solution[22].

5.2.4 Effect of Pressure

PHREEQC is run to simulate the effect of different pressure for potential scale precipitation in the mixing of incompatible water. Pressure varies from 10atm, 50atm and 100atm to simulate various conditions within the field, see Appendices for PHREEQC model (figure A.13 and figure A.14).

Recall figure 5.12 as the case of pressure 10atm. As seen from the results shown in the figure (5.12), (5.18) and (5.19), as pressure decreases the scale potential is increased. Especially for carbonate scales which clearly show the decreasing solubility from 100 atm to 10 atm. Pressure drop will cause the partial pressure of CO_2 decreases yield decreasing solubility. CO_2 gas escapes from solution and leaving the solution more saturated in calcium carbonate resulting in increasing on the pH solution. The scale will be precipitated out exceeds the saturation limit in the solution[1, 14, 15, 19, 20, 22]. Figure 5.20 explains how the precipitated calcite scales at the different pressure.

Generally, the solubility of calcite decreases with temperature, however we observed at high temperature, it increases and followed by dramatically anhydrite precipitation, shown in figure (5.12), (5.18) and (5.19). As detail discussion previously, it is mainly due to the anhydrate start to precipitate out at high temperature and increase calcite solubility.
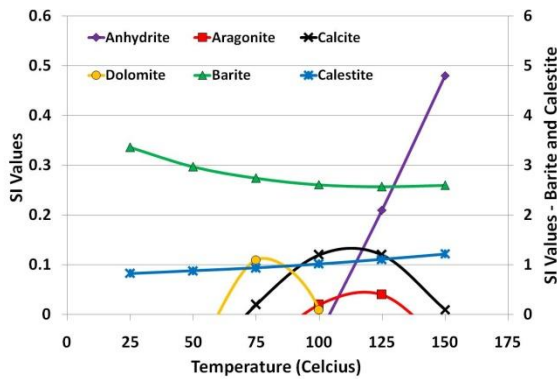
Figure 5.18 SI Values and development vs temperature at 100 atm

Barite, Calestite are plotted in the secondary axis
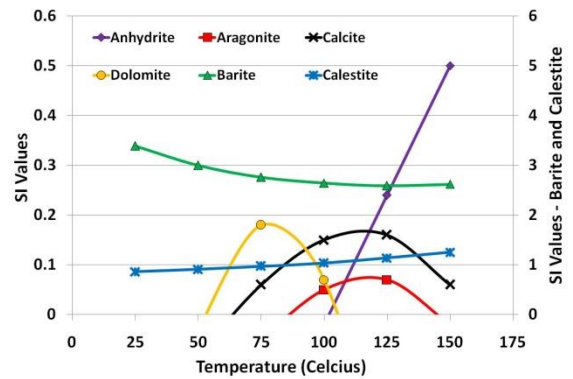
Figure 5.19 SI Values and development vs temperature at 50 atm

Barite, Calestite are plotted in the secondary axis
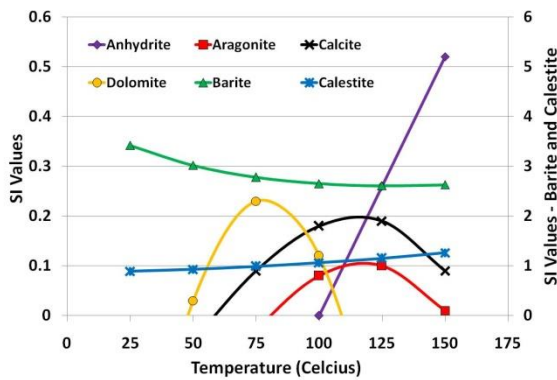
Figure 5.12 Values and development vs temperature at 10 atm
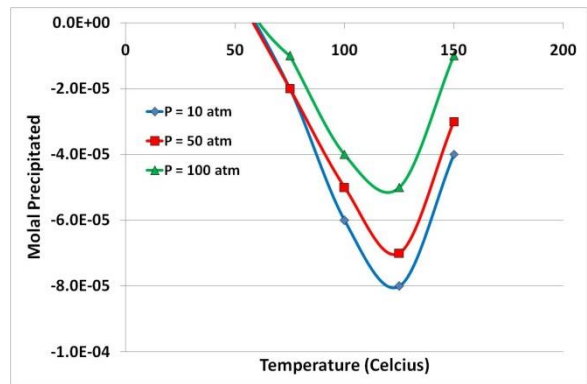Barite, Calestite are plotted in the secondary axis

Figure 5.20 Molal precipitated of calcite, $CaCO_3$, against temperature varied with pressure
Molal is expressed in (mol/kg)

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5.2.5 Effect of Reservoir Heterogeneity

The heterogeneity reservoir lead the scale deposition more complexes so this affect is necessary to be considered for potential scale formation. Study literature has been conducted to see this effect instead of PHREEQC simulation due to its limitation on reservoir modeling. Figure 5.21 shows the 1D reservoir cross section as injected water (IW) displaces connate water (CW) and oil toward producer wells. They show how the two phase zone will be developed instead of single full mixing zone between reservoir fluid and injected water. The mixing zone is located behind oil bank with injected water bank in the tail [28].

Figure 5.21 (a) has insignificant scale potential since a lower mixing zone or almost sharp front between CW and IW. On the other hand, the variation of local permeability tends to yield the spread or dispersed front between IW and CW. The mixing of CW/IW will be more developed and induce more scale precipitation due to incompatible water takes place.

a) Lower degree of Permeability   b) Higher degree of Permeability
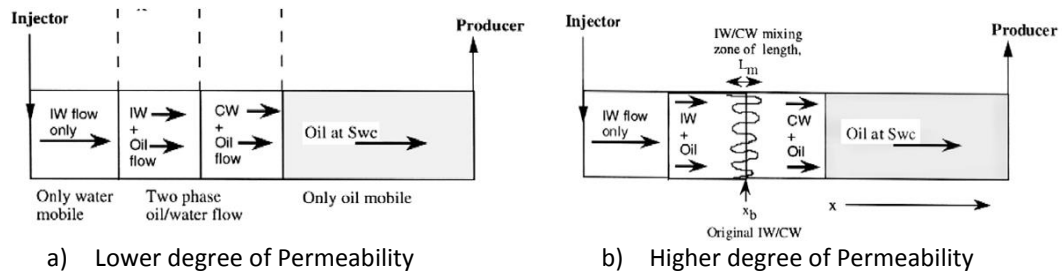
Figure 5.21 Effect of Permeability Anisotropy in the Reservoir[28]

The variation of the vertical section makes the analysis more complexes especially with the presence of aquifer having the different composition, see figure 5.22. Along with the time, the water from each layer will breakthrough and mixing in the wellbore can't be avoided. Variation in the areal section also affects the breakthrough time of injected water in the producer well, see figure 5.23. Thus, scale precipitation in the wellbore is a function of time.
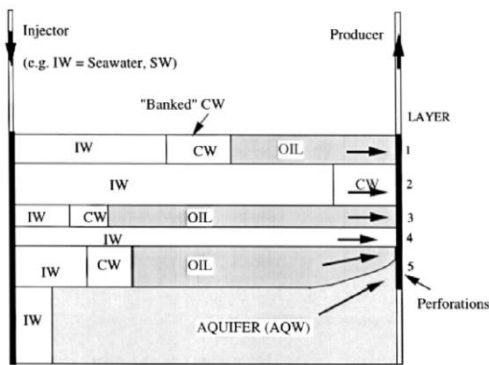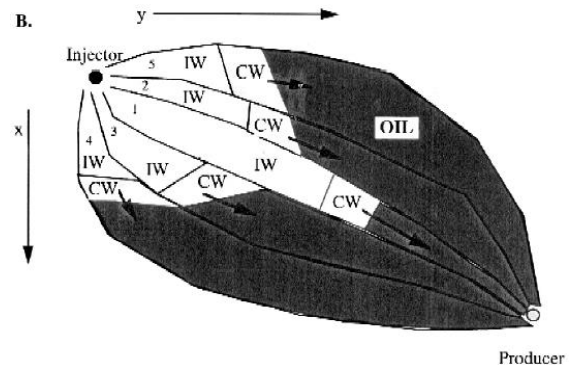

Figure 5.22 Vertical Section Heterogeneity[28]   Figure 5.23 Areal Section Heterogeneity[28]

Thus horizontal, vertical and areal heterogeneity reservoir affect the potential of scale formation and the various breakthrough time causes deposition of scale in the wellbore is a function of time.

5.3 Scale Prediction Simulation Summary

With the chemical analysis of formation water and injected water presented in table 5.2, we can determine the incompatibilities between water and forecast the effects on future field operations. The PHREEQC scale prediction model is used in this report to reflect subsurface and surface condition at which the potential of crystal salt is created. 3 cases were simulated over range temperature related to injected water composition (pure SW, 10x diluted SW, 50x diluted SW), pressure change (10 atm, 50 atm, 100 atm) and mixture ratios (30/70, 50/50, 70/30). Temperature is set from 25^OC to 150^OC.

The first scale prediction model considered the variation of temperature when formation water commingles with pure SW. In this case, High Salinity (HS) water injection was simulated and the scale prediction is presented in figure 5.9. The results of this simulation show a tendency of Sulfate scales ($CaSO_4$, $BaSO_4$, $SrSO_4$) and Carbonate scales ($CaCO_3$, $MgCa(CO_3)_2$) precipitation. It reveals how $BaSO_4$ scale is not sensitive to temperature variations. However, a limitation of PHREEQ is that the phases are not precipitated in the simulations, the solutions are simply treated as supersaturated when SI > 0. Thus by plotting *molality difference* of each phase, which is different molality between equilibrium and supersaturated condition, with temperature is likely more reasonable to see the potential of precipitated minerals, as explained in figure 5.7.

The second scales prediction model considered the variation of pressure. The summaries are presented in figure (5.18) to figure (5.20). This simulation shows how the pressure drop affects carbonate scales precipitation. As the pressure changes from 100atm to 10 atm, the solubility could decrease double. It is suggested mainly due to the partial pressure of CO_2 gas associated with carbonate scale formation is mostly a function of pressure. Also, $BaSO_4$, $SrSO_4$, and $CaSO_4$ precipitation occurred but not significant.

The third forecasting model takes a look at the variation of mixture ratios of SW/FW. The results are presented in the figure (5.15) to figure (5.17). This simulation reveals sulfate scales are the firstly created when incompatible waters are involved and that the worst condition to scale formation is when barium sulfate and strontium sulfate are precipitated out and loss from solution at low values of sea water/formation water ratio. Furthermore, the formation of carbonate scales is observed to be the tremendous effect when increasing SW proportion from 0.5 to 0.7 in the solution. The dolomite solubility decreases three times and a new scale, $SrCO_3$, is created. It observed as SW proportion is increased the dangerous scale potential will be.

A great improvement can be achieved with the scale prediction model as lowering the salinity by dilution of injection sea water. The formation water commingles with diluted SW, 10 times and 50 times, then potential of scale precipitation is observed. In this case, Low Salinity (LS) water injection

was simulated and the scale prediction is presented in figure 5.10. The graph shows the hardest scale, barium sulfate, is still precipitated even in the mixture FW/diluted-50times SW. However, in general, a great result is presented and seen how the horrible insoluble crystal salts that are formed in HS injection did not appear and totally dissolved in the solution FW/dilutedSW.

By doing this study, it is observed that reduction of scale potential is more influenced by lowering salinity of injected water. It shows how the mixing of FW/diluted SW could reduce mostly of insoluble salts and it related to the low salinity water injection has been established recently. By lowering salinity injected water, not only offer the significant oil enhancement but also scaling potential reduction than conventional sea water injection

5.4 Scaling Removal Treatment

According to the result from PHREEQC simulation, the sulfate scales and carbonate scales are the main scale depositions. Below some methods applied for removing sulfate and carbonate scale

- **Carbonate Scales**
  Carbonate scales can be dissolved by strong acid Hydrochloric Acid (HCl) with 5% to 15% concentration[47], as equation (5.14)

$$CaCO_3 + 2HCl \rightarrow H_2O + CO_2 + CaCl_2 \qquad \text{Equation (5.14)}$$
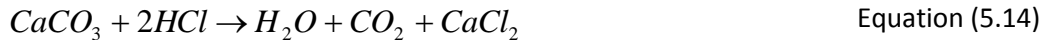
Adding corrosion inhibitor and surfactant are also required to avoid corrosion and make the surface more water wet. Recently, chemical like EDTA and DTPA can be used to dissolve $CaCO_3$ as equation (5.15), (5.16) and (5.17)[49]
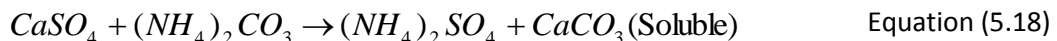
$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O \qquad \text{Equation (5.15)}$$
$$Ca^{2+} + EDTA^{4-} \leftrightarrow CaEDTA^{2-} \qquad \text{Equation (5.16)}$$

Equal with:

$$CaCO_3 + 2H^+ + EDTA^{4-} \leftrightarrow CaEDTA^{2-} + CO_2 + H_2O \qquad \text{Equation (5.17)}$$
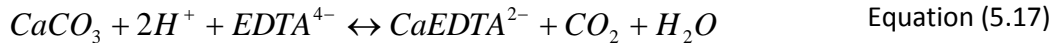
- **Sulfate Scales**
  Sulfate scales, especially calcium Sulfate has low solubility in the acid thus, the dissolution is by converting to acid soluble compound, i.e. $CaCO_3$ or $Ca(OH)_2$ through reaction with $(NH_4)_2CO_3$, Na_2CO_3, NaOH or KOH. The product of acid soluble is then be dissolved with hydrochloric acid (HCl) as equation (5.18) and equation (5.19)[19, 47]

$$CaSO_4 + (NH_4)_2CO_3 \rightarrow (NH_4)_2SO_4 + CaCO_3 \text{(Soluble)} \qquad \text{Equation (5.18)}$$
$$CaCO_3 + 2HCl \rightarrow H_2O + CO_2 + CaCl_2 \qquad \text{Equation (5.19)}$$
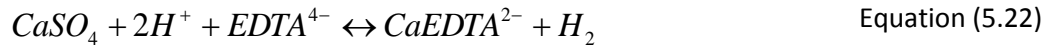
Recently, chemical like EDTA and DTPA can be used to dissolve $CaCO_3$ or $CaSO_4$ without conversion. EDTA has low toxicity, good dissolving capacity, and lower corrosion effect. One ion Ca^{2+} reacts with one molecule of ionized EDTA. Through dissolution and chelation process, the scale removal process is shown in equation (5.20), (5.21) and (5.22)[19, 47, 49].

For $CaSO_4$ Removal:

$$CaSO_4 + 2H^+ \rightarrow Ca^+ + H_2$$ Equation (5.20)

$$Ca^{2+} + EDTA^{4-} \leftrightarrow CaEDTA^{2-}$$ Equation (5.21)

Equal with:

$$CaSO_4 + 2H^+ + EDTA^{4-} \leftrightarrow CaEDTA^{2-} + H_2$$ Equation (5.22)

- **Barium Sulfate ($BaSO_4$)**

  Barite is one of the hardest and toughest scale to be dissolved, either mechanically and chemically. It has low porosity and insusceptible to chemical inhibitor so mechanical removal is often used for barium scale removal. Recently, Schlumberger had developed EDTA U104 that is applicable and success to remove barite and calcium sulfate scales[15].

5.5 Scaling Inhibition

5.5.1 Sulfate Removal Technology

Nanofiltration (NF) technology is now being applied to remove SO_4^{2-} from sea water before it is injected into reservoir. It has the ability to remove ion particles with size up to 1 nanometer (10 ^{O}A). The success of nanofiltration method has been reported by Marathon oil UK operated in the UK sector of North Sea, where SO_4^{2-} can be reduced up to 96%-98%[50] and reduced dramatically potential sale problems during field operation.

Figure 5.24 and figure 5.25 show how the effect of sulfate removal technique. Figure 5.24 illustrate the condition where the sea water or high salinity water is injected into reservoir without sulfate removal treatment. The ion concentration is observed in the production well. It was observed at the breakthrough time of injected water in early 1990, the SO_4^{2-} concentration increases drastically followed by reduction of barium concentration, than barite scale deposition is observed near and within the wellbore. Compare to figure 5.24, figure 5.25 shows very insignificant scale potential since the limited concentration of SO_4^{2-}.
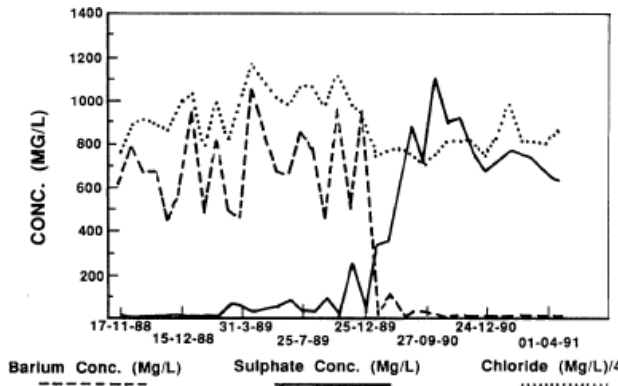
Figure 5.24 Injection of High Sulfate[50]
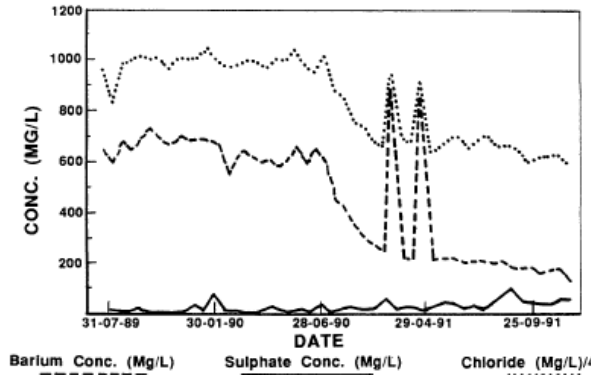Concentration observed in the production wells

Figure 5.25 Injection of Low Sulfate[50]
Concentration observed in the production wells

5.5.2 Chemical Inhibitor

Sulfate scales are the common scales occurred during field operation, they can be inhibited by adding chemical Ester, Phosphonates, Polyepoxysuccinic Acid (PESA) and Polyaspartic Acid (PASP), EDTA, chelating agents. Ester has good thermal stability up to 200^OF-250^OF and it is also stable at the acid environment. While at the condition at which high temperature condition exist, the application of Phosphonate is more suitable. The inhibitors for Barite are Polyelectrolyte, PASP, EDTA, Ester, Nitrilotriacetic acid, Phosphonates are commonly applied.[17, 30, 36]

Carbonate Scale can be inhibited by Phosphonates, Ester, Polyphosphates, Organic Phosphorus Acid, Poly carboxylic acid and PESA. Phosphonates are highly recommended for calcite and even at fairly modest temperature. This chemical is inexpensive and soluble in water. However, it can be possible to form orthophosphates at low temperature, which reduce inhibitor activity. Esters tolerate the acid environment and withstand up to 200^OF-250^OF. At the strong acid environment (pH<5.5), the phosphate Esters is used as scaling control for $CaSO_4$, $SrSO_4$,$BaSO_4$ [16, 17, 30, 36].

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6. CONCLUSION

A study of scales is conducted through the literature study and demonstrated by using PHREEQC simulation to predict incompatibility waters effects under the change in pressure, mixing ratio, water composition and also tested over range temperature 25^OC to 150^OC. The following are the research findings:

1. The main scale formation has been investigated. Scale potential is mainly dominated by Sulfate Scale ($CaSO_4$, $BaSO_4$, $SrSO_4$) and Carbonate Scales ($CaCO_3$, $MgCa(CO_3)_2$).
2. Both sulfate and carbonate are influenced by pressure. However, carbonate solubility shows the double decrease compared to sulfate scales as pressure drops from 100 atm to 10 atm.
3. Sulfate scales are the firstly created at low values of sea water/formation water ratio. Barium sulfate and strontium sulfate is the worst condition to scale formation
4. About triple reduction of dolomite solubility is observed when adding 20% SW, from 50% to 70%, into mixture solution which is in the lines with the Strakov et al.[46] , sea water is already saturated by dolomite so increasing small amount of salinity yields great reduction on solubility.
5. A significant reduction of potential scale formation as lowering salinity through dilution of injection sea water is shown in figure 5.10. The horrible insoluble crystal salts that are formed in HS injection did not appear and totally dissolved in the solution FW/diluted SW, except $BaSO_4$
6. The insoluble and hardest scales can be mitigated by sulfate removal technology or chemical inhibitors before the injected of sea water. However, the capital cost, operational limitation and environmental issues become a big constraint. Thus by implementing of low salinity water injection, not only cover the limitation of conventional sea water for scaling control and management but also offer significant oil enhancement

7. FUTURE WORK AND RECOMMENDATION

Based on literature studies and simulation summarized in this thesis, below are some recommendations for future work that can be a consideration to analyze scale potential during high and low salinity water flooding

- To use sophisticated models that can simulate the precipitation and adherence process and be able to take into account of rock minerals interaction. Thus, the precise prediction of scaling potential can be defined.
- Laboratory test might be one of the consideration to confirm what the simulation result prove, however the good screening criteria should be conducted prior the execution

SYMBOLS AND ABREVIATIONS

φ	Porosity
k	Absolute Permeability,mD
μw	Water Viscosity, cP
μo	Oil Viscosity, cP
$[X^{A+}]$	Ion Concentration, M
ASP	Alkaline Surfactant Polymer
^{O}C	Celcius
CEC	Cation Exchange Capacity
CMI	Carboxy Methyl Iinulin
COBR	Crude, Oil, Brine, Rock
DI	De-Ionized water
DTPA	Diethylene Triamine Penta Acetic Acid
d_{10}SW	Diluted 10 times Sea Water brine
d_{50}SW	Diluted 50 times Sea Water brine
Ed	Microscopic Sweep Efficiency
EDTA	Ethylenediaminetetraacetic Acid
Em	Macroscopic Sweep Efficiency
Et	Total Displacement Efficiency
EOR	Enhanced Oil Recovery
ESP	Electric Submersible Pump
^{O}F	Fahrenheit
FW	Formation Water
Krw	Water Relative Permeability, mD
Kro	Oil Relative Permeability, mD
Ksp	solubility product constant
L	Litre
LWSI	Low Salinity Water Injection
mD	miliDarcy
meq	miliequivalent
mix	mixture
mg	mass of solute (milligram)
PASP	Polyaspartic Acid
PESA	Polyepoxysuccinic Acid
ppm	part per millions
psi	pound per square inch
SARA	Saturates, Aromatics, Resins, and Asphaltenes
SEM	Scanning Electron Microscopy
SI	Saturation Index
Sor	Residual oil saturation, %
SR	Saturation Ratio
SRP	Suck Rod Pump
SW	Sea Water
Swi	Residual water saturation, %
TDS	Total Dissolved Gas, g/L
WAT	wax appearance temperature

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APPENDICES

A1   PHREEQC Simulation Model

A1.1. Equilibrium Model of Each Mineral Phases

Below are parameters used in the PHREEQC model to set up equilibrium condition of each phases. Temperature is set from 25°C to 150°C. Water chemical composition is based on table 5.1.
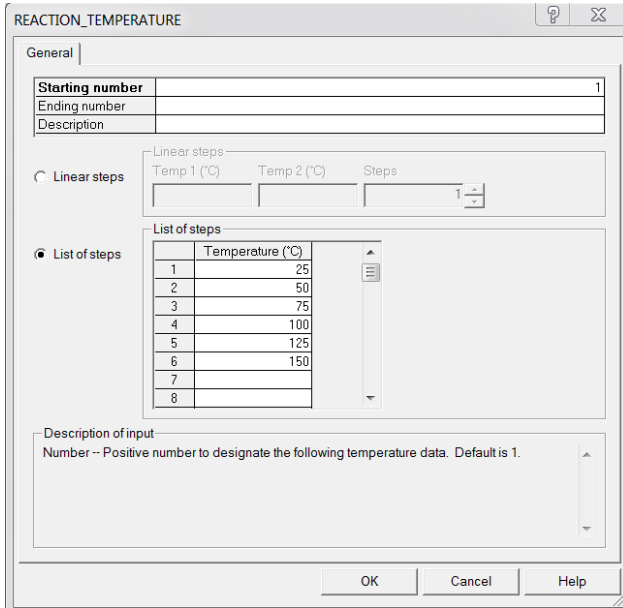
Figure A. 1 Range of Temperature

Figure A. 2 Sea Water Composition

Figure A. 3 Formation Water Composition
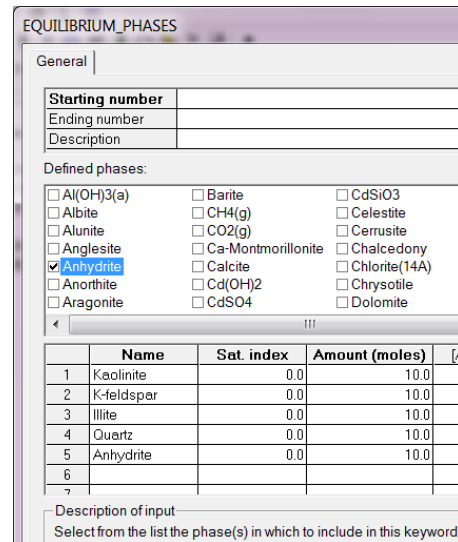
Figure A. 4 Equilibrium phase for **Anhydrite**

Kaolinite, K-Feldspare, illite and quartz are added to simulate sandstone reservoir

Figure A. 5 Equilibrium phase for **Aragonite.**
Kaolinite, K-Feldspare, illite and quartz are added to
simulate sandstone reservoir

Figure A. 6 Equilibrium phase for **Barite**.
Kaolinite, K-Feldspare, illite and quartz are
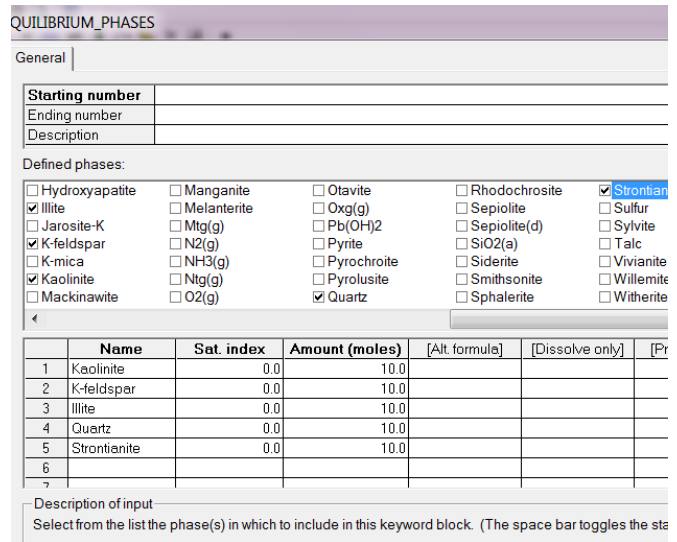added to simulate sandstone reservoir

Figure A. 7 Equilibrium phase for **Calcite.**
Kaolinite, K-Feldspare, illite and quartz are added to
simulate sandstone reservoir

Figure A. 8 Equilibrium phase for **Calestite.**
Kaolinite, K-Feldspare, illite and quartz are
added to simulate sandstone reservoir
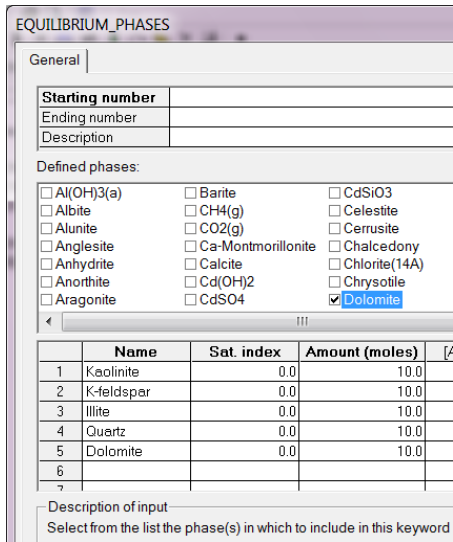
Figure A. 9 Equilibrium phase for **Dolomite** Kaolinite, K-Feldspare, illite, quartz are added to simulate sandstone reservoir

Figure A. 10 Equilibrium phase for **Strontionite.** Kaolinite, K-Feldspare, illite and quartz are added to simulate sandstone reservoir

A1.2. Effect of Water Composition

The parameters used are similar what have done in A1. However the water composition is varied 10 times dilution and 50 times dilution of SW. Each mineral is run in equilibrium condition (as shown in A1), then the molality is compared with actual molality from solution. As molality of the actual is higher than the molality in equilibrium, salts are precipitated out from solution phase.
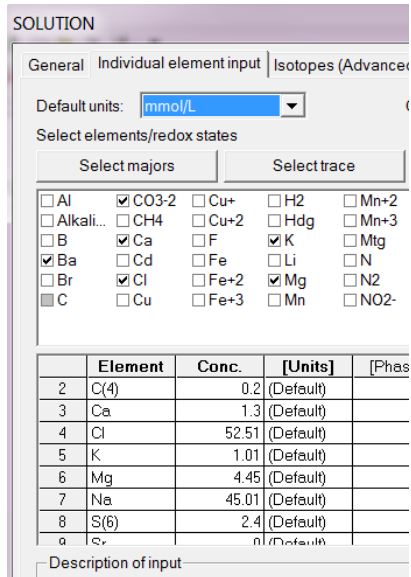
Figure A. 11 Diluted **10 times** Sea Water
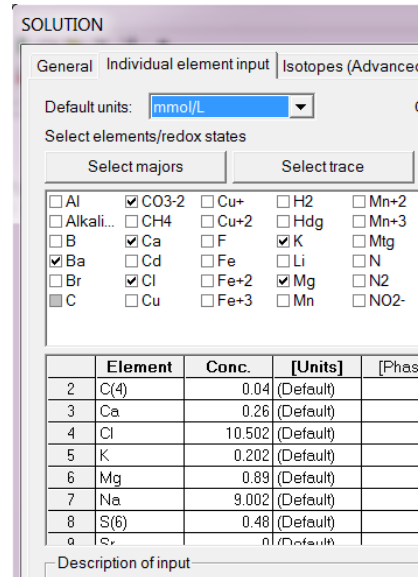
Figure A. 12 Diluted **50 Times** Sea Water

A1.3. Effect of Pressure Change

The parameters used are similar what have done in A1, however pressure is set 50 atm and 100 atm
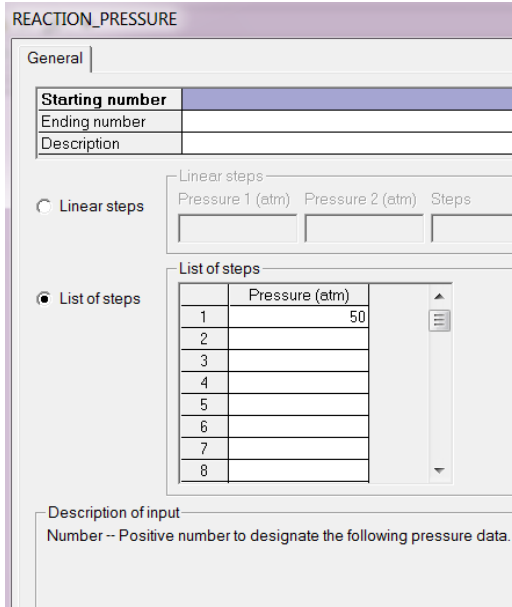
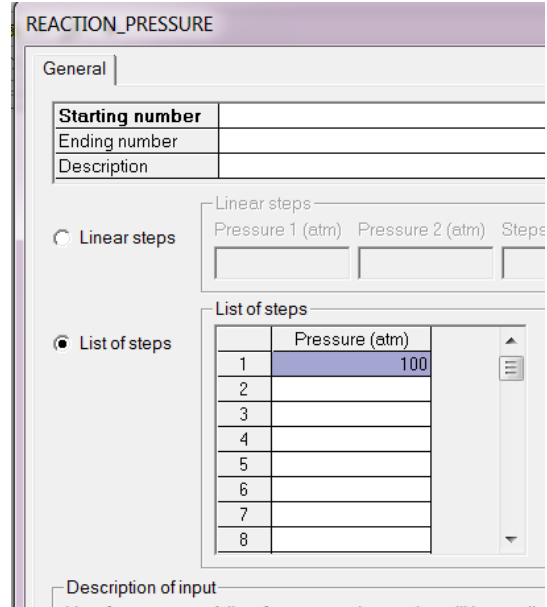

Figure A. 13 Pressure is **50 atm**

Figure A. 14 Pressure is **100 atm**

A1.4. Effect of Mixing Ratio

The parameters used are similar what have done in A1, however the mixing ratios are varied as 0.3SW:0.7FW ; 0.5SW:0.7FW ; 0.7SW:0.3SW as model below
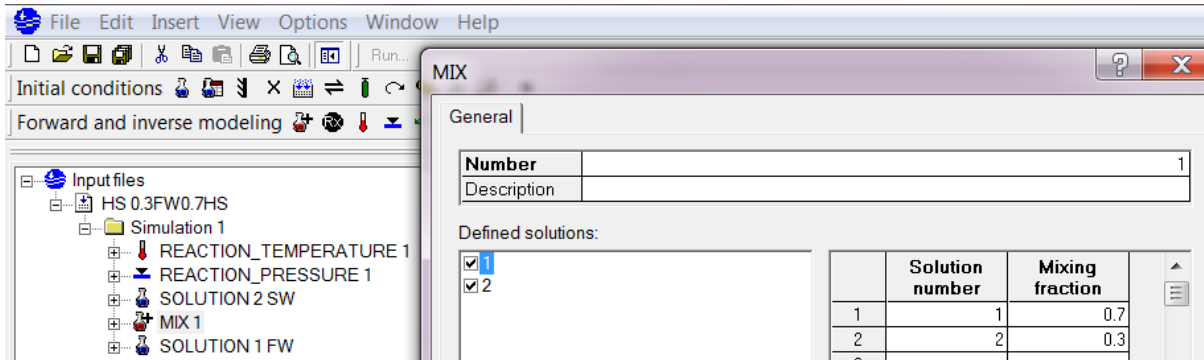

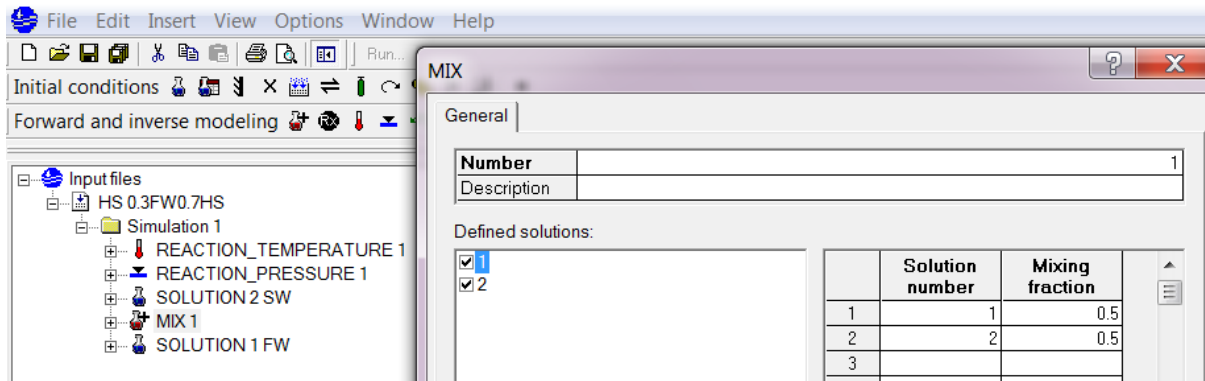Figure A. 15 Mixing Ratios is **0.3SW:0.7FW**
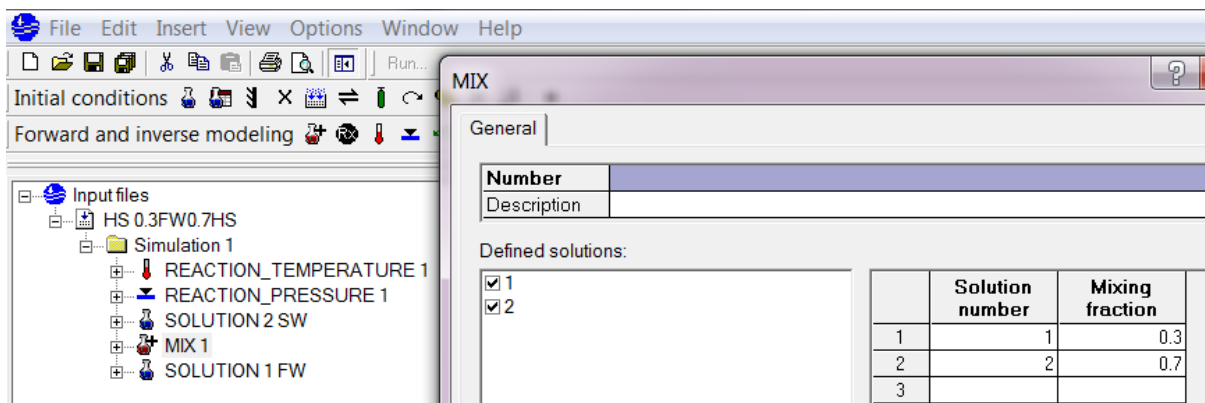
Figure A. 16 Mixing Ratios is **0.5SW:0.5FW**

Figure A. 17 Mixing Ratios is **0.7SW:0.3FW**

A2. Concentration Ion Development for FW/SW and FW/d₅₀SW

Below is the result of PHREEQC Model simulation for sensitivity of Injected Water Composition
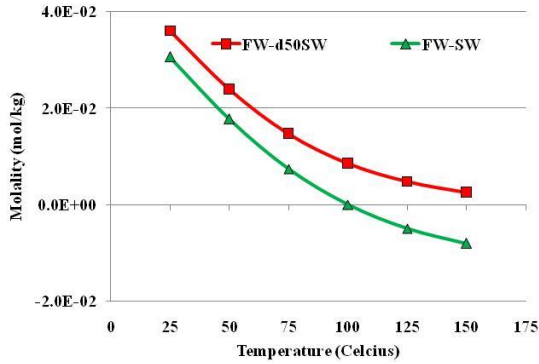

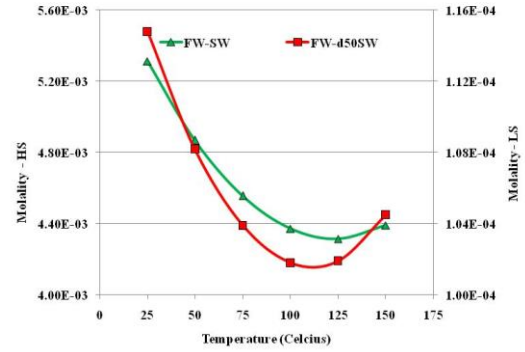Figure A. 18 Solubility of CaSO$_4$
Solubility is expressed in (mol/kg)

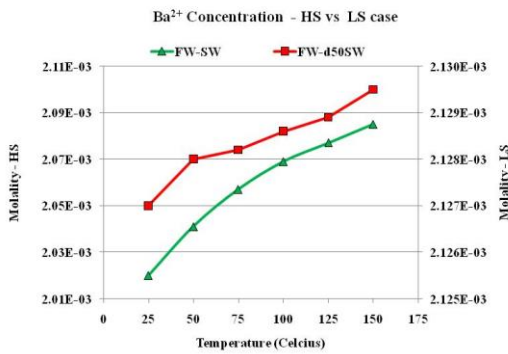Figure A. 19 Concentration development of ion SO$^{2-}_4$
Molality is expressed in (mol/kg)

Figure A. 20 Concentration development of ion Ba^{2+}
Molality is expressed in (mol/kg)
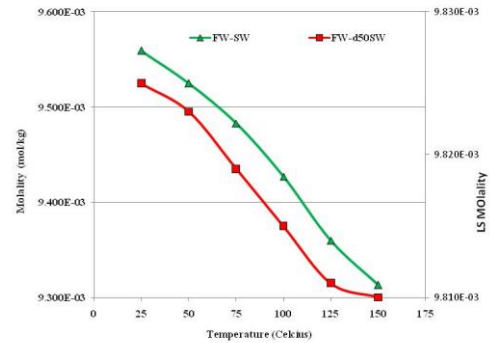

Figure A. 21 Concentration development of ion Sr^{2+}
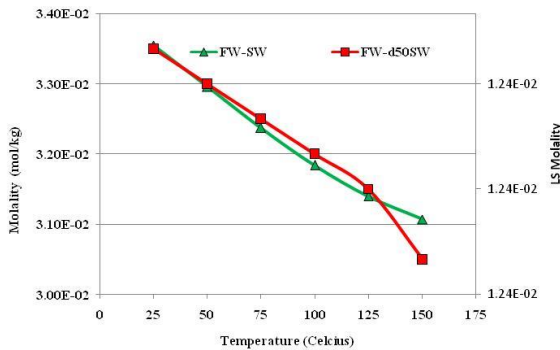Molality is expressed in (mol/kg)

Figure A. 22 Concentration development of ion Mg^{2+}
Molality is expressed in (mol/kg)

A3. Presentation Slide Related to the Thesis Content

A Study of Scale and Scaling Potential during High Salinity and Low Salinity Waterflooding

- **Background**
  - Formation damage is one of the severe problems causing detrimental loss production or even well abandonment
  - Conventional injected water contains high hardness ions, SO_4^{2-} and CO_3^2, will induce more scale deposition
  - Costly treatment and environmental issue

- **Objectives**
  - To gain more understanding through literature studies about the scale formation, deposition and factor affecting their solubility
  - Evaluate Scale Potential during High Salinity and Low Salinity Waterflooding
  - Study the Scale Inhibition and Prevention Methods

Rock and Water Characteristics

Mineralogy of Rock

Sandstone Rock

- **Composed:** quartz (SiO_2) and limited Plagioclase, alkali feldspar, lithic fragments and muscovite

- **Cementing minerals** : silica, $CaCO_3$ with certain amount of clay, hematite, $CaSO_4$, $BaSO_4$ and zeolite
  → potential source of scaling ion through dissolution and diagenesis process

- **Weathering Process** : Mechanical and Chemical
  - *Mechanical Weathering :* without minerals alteration (abrasion, frost wedging and root wedging)
  - *Chemical Weathering :* New minerals are generated through hydrolysis

Mineralogy of Rock

Minerals dissolved in Sandstone

- ***Product of chemical weathering***

  - Clay minerals

  - Soluble silica

  - Metal Cations: Fe^{2+}, Mg^{2+}, Al^{2+}, Ca^{2+}, Na^{2+}

  $\rightarrow$ Act as the bond between silicate minerals and will be dissolved into water as water transportation

- ***Clay Minerals***

  - Deposit : low energy environment i.e marine basin and lake

  - Composed mainly hydrous, Al, Si with certain ion Fe, Mg, K, alkali

  - Has electrostatic charge to hold cation Ca^{2+}, Na^+, Mg^{2+}, NH_4^+

  - Cation Exchange Capacity (CEC) : measure amount of adsorbed cations per dry weight of rock (meq/100g dry rock)

Mineralogy of Water

- **During transportation to the sea**
  - Water reacts with gas and rock minerals
  - Some minerals and ions will be released from the rock fragment and dissolved by water

- **Mineral dissolved in the water**

  - Inorganic materials : Mg^{2+}, Ca^{2+}, CO_3^{2-}, Fe^{2+}, Mn^{2+}, PO_4^3 etc
  - Organic materials : humid acid, fulvic acid, tannins
  - Gas : Oxygen, H_2S, N_2, CO_2
  - Microorganism : bacteria, algae, fungi
  - Suspended Matter : clay, silt, oil, fat, grease

Water sources

- **Source of Water**
  - Subsurface Water : water trapped in the pore space rock and the mineralogy is much related on geological area over which has passed
  - Sea Water : water containing hardness ions as result of water circulation and chemical weathering of rocks
  - Lake Water : dissolved constituent are affected by biological activity
  - Surface Water

Recovery Mechanism

- **Primary Recovery**
  - Natural energy reservoir; gas cap drive, solution gas drive, water drive, gravity, rock expansion
  - Low recovery

- **Secondary Recovery Mechanism**
  - Methods used to produce hydrocarbon from reservoir beyond natural flow and artificial lift operation, example : water flooding
  - Macroscopic Efficiency

- **Tertiary Recovery Mechanism - EOR**
  - Methods used to extract remaining hydrocarbon which couldn't be recovered by primary and secondary recovery
  - Expensive operation
  - Environment issues constraint – because of chemical additives
  - Improve Microscopic and Macroscopic Efficiency

  → Low Salinity Water Injection

Water Flooding Design

- **Source of Water Injection**
  - Produced water, sea water, aquifer, river or lake
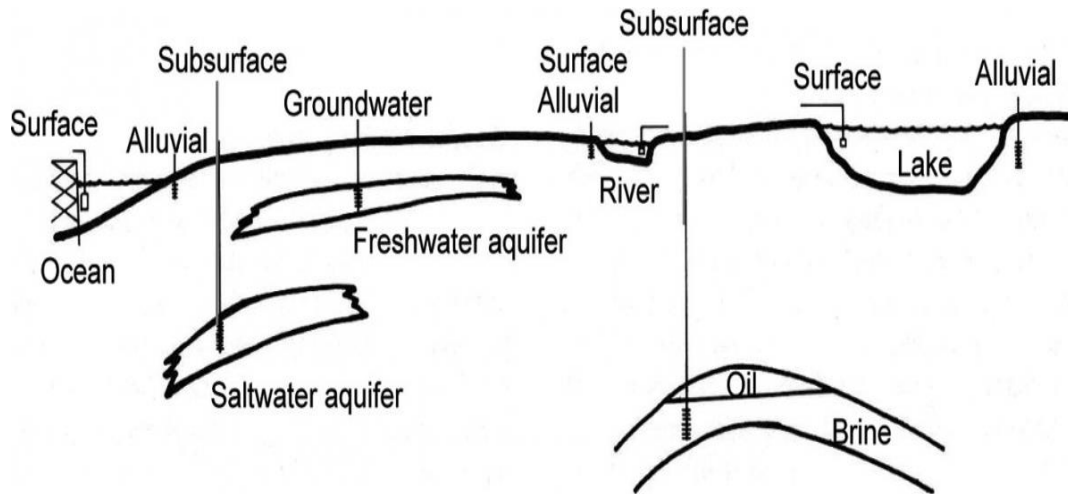
- **Rock Properties Analysis**
  - Swelling, soften rock fragment, subsidence, collapse
- **Water Properties Analysis**
  - Incompatibility issue
- **Well Completion Types and Well Pattern**

Water Treatment

- Sea water commonly contains solid minerals, dissolved gas, dissolved organism, highly dissolved sulfate ion
- Water treatments are necessary before injection to avoid :
  - plugging at pore throat, perforation , downhole and surface equipment, etc
  - Dissolved solid : abrasive to metal surface
  - Scale depostion due to incompatible water
  - Reduce well productivity
- Water treatment includes:
  - Solid Removal: Desander , Coarse Strainers, sand filter, cartridge filter.
  - *Dissolved Gas Removal :* chemical scavenger, gas stripping and liquid extraction
  - *Biological Control :* chemical biocide i.e chlorine
  - *Sulfate Removal :* Nano Filtration (NF), SRF

Scaling Potential During Water Injection

Mechanism Of Scale Formation

- ## Mechanism of Scale Formation

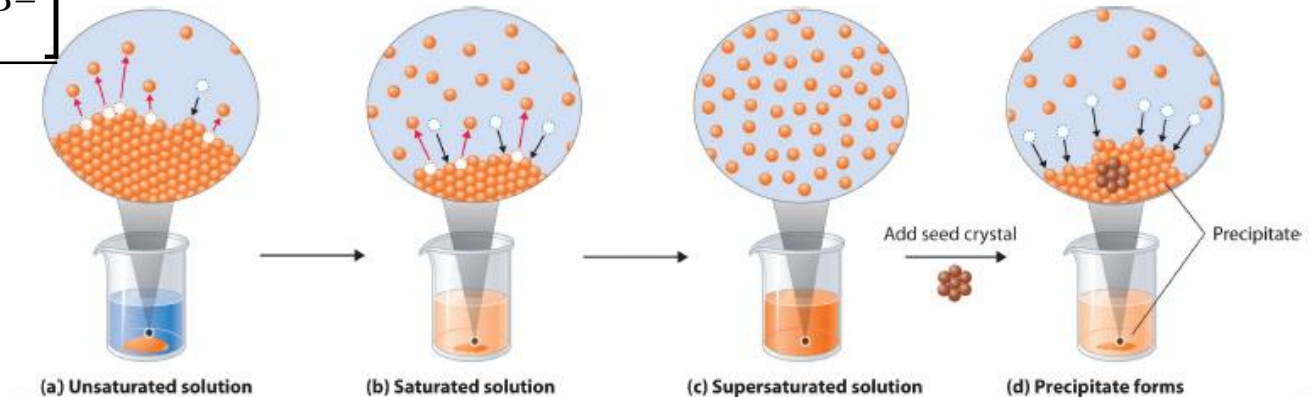 Nucleation → Crystal Growth → Agglomeration

Saturation Index (SI)

Explain the degree of super-saturation for salts in the solution

$$SR = \frac{[X^{A+}][Y^{B-}]}{Ksp}$$

$$SI = Log\frac{[X^{A+}][Y^{B-}]}{Ksp}$$

Where
- SR<1 or SI<0 : undersaturated , no precipitation
- SR=1 or SI=0 : equilibrium condition
- SR>1 or SI >0 : supersaturated, potential precipitation

(a) Unsaturated solution   (b) Saturated solution   (c) Supersaturated solution   Add seed crystal   (d) Precipitate forms   Precipitate

Solubility of Scale

- **Solubility of Scale**
  - Maximum solute concentration dissolved in the solvent under certain conditions
  - Expressed by molarity, molality, mole fraction, mole ratio

- **Factors Affecting Solubility**
  - Pressure
  - Temperature
  - Presence other substance
  - Ionic Strength
  - Ion concentration

Scale Formation Process

- **Scale Formation through**

  - Auto Scaling Process : Self Scaling due to change in physical condition (P,T)

  - Incompatible Water : mixing incompatible water (SW and FW)

    - Sea Water (SW) rich of ion SO_4^{2-}, HCO_3^-

    - Formation Water (FW) rich of ion Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}

    $\Rightarrow$ $CaSO_4$, $BaSO_4$, $SrSO_4$ or $CaCO_3$, etc

  - Evaporation : releasing gas from water phase as P,T decreases (Gas Well)
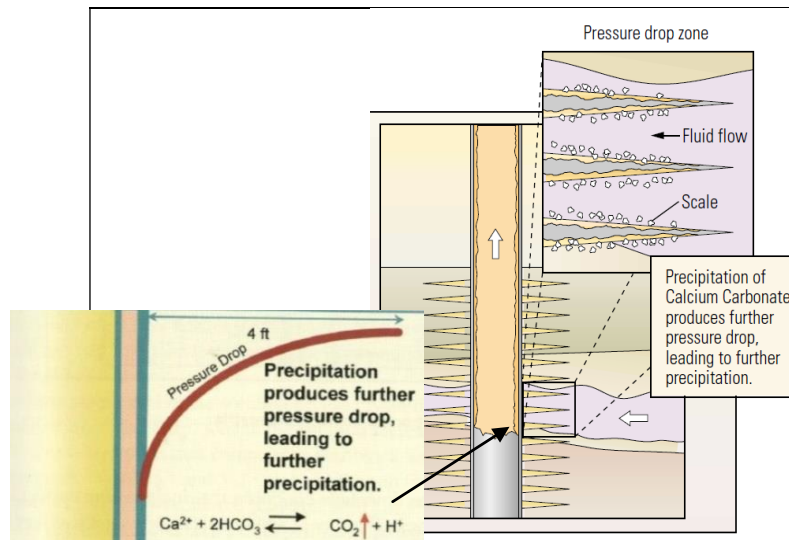

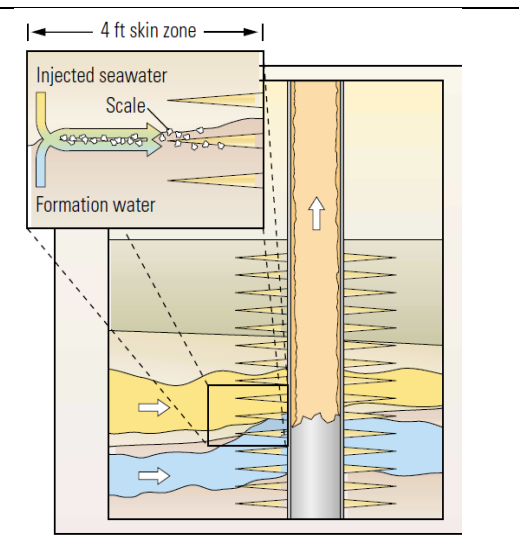**Figure 3.1** Auto Scaling Process near wellbore[23,24]

Figure 3.2 Incompatible Water Process[23]

Type of Oil Field Scales

- **Inorganic Scales**
  - Inorganic scales are insoluble salt that is precipitated due to interaction between ions to form insoluble complexes, such as $CaSO_4$, $BaSO_4$, $SrSO_4$, $CaCO_3$, FeS, ZnS, Hydrate, etc

Minerals	Formula	Minerals	Formula
Carbonate Scales		**Sulfate Scales**	
Aragonite, Calcite, Vaterite	$CaCO_3$	Anhydrite	$CaSO_4$
Dolomite	$MgCa(CO_3)_2$	Gypsum	$CaSO_4.2H_2O$
Strontianite	$SrCO_3$	Hemihydrates	$CaSO_4.1/2H_2O$
Witherite	$BaCO_3$	Barite	$BaSO_4$
		Calestite	$SrSO_4$
Iron Compound			
Ferrous Carbonate	$FeCO_3$	**Other Scales**	
Ferrous Hydroxide	$Fe(OH)_2$	Zinc Sulfide	ZnS
Ferrous Hydroxide	$Fe(OH)_3$	Hydrate, etc	
Ferrous Sulfide	FeS		

- **Organic Scales**
  - Organic scales are deposition of high molecular weight of crude oil near wellbore, perforated interval and the surface metal equipment
  - Scales : Wax, Resin – Asphaltenes, Naphthenate, Paraffin

Location of Scale Deposition

- **Location of Scale deposition**

  – Any point along the water path under change in physical condition i.e pressure, temperature, salinity

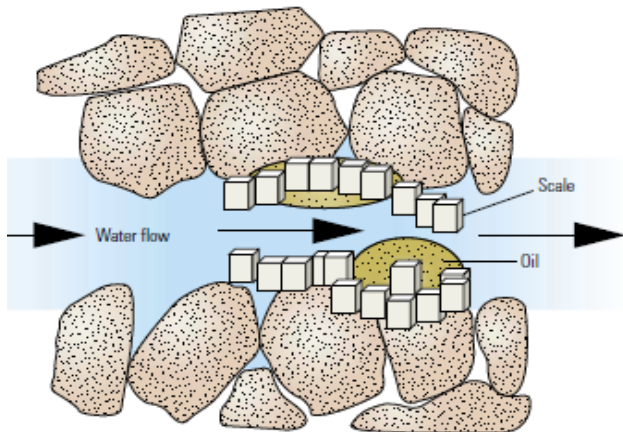 – Reservoir, injection well, production well, down hole and surface equipment

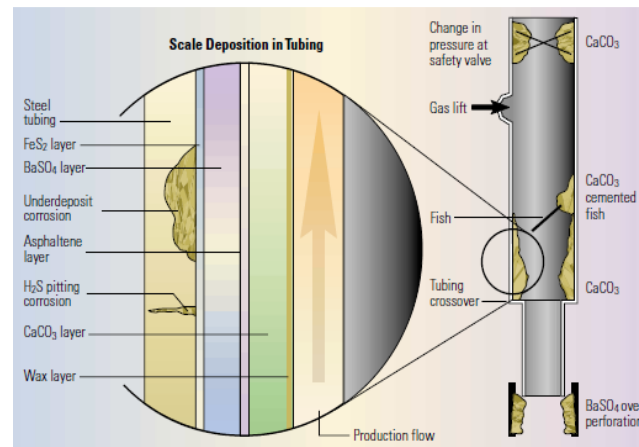**Figure 3.1** Scale deposition in the Matrix Reservoir[23]

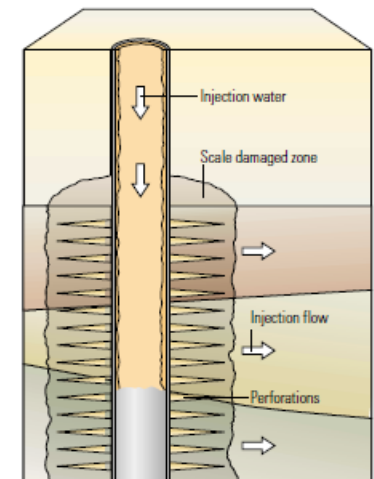**Figure 3. 1** Scale deposition in the wellbore[23]

Figure 3. 2 Scale Deposition in the Injection Well[23]

Scale Detection

- **Scale can be detected by**
  - Visual Inspection
    - easiest, quick and cheap investigation (separator, pump, choke, etc)
  - Core analysis
    - Representative core are required
    - Using Scanning Electron Microscopy (SEM) to analyze crystal habit, size, morphology and distribution
  - Produced Water
    - Representative samples water are required
    - Analyze the water chemistry and properties.
    - If any reducing scaling ion Ca^{2+}, Mg^{2+}, Ba^{2+}, etc at produced water $\rightarrow$ scale is precipitated
  - Gamma Ray and Caliper log

Scale Detection

- **Scaling detection using Wireline Log**

  - Gamma Ray and Caliper log

    - GR and Caliper log are run down to wellbore

    - Caliper : measures the decreasing tubing inner diameter as indication of scale deposition

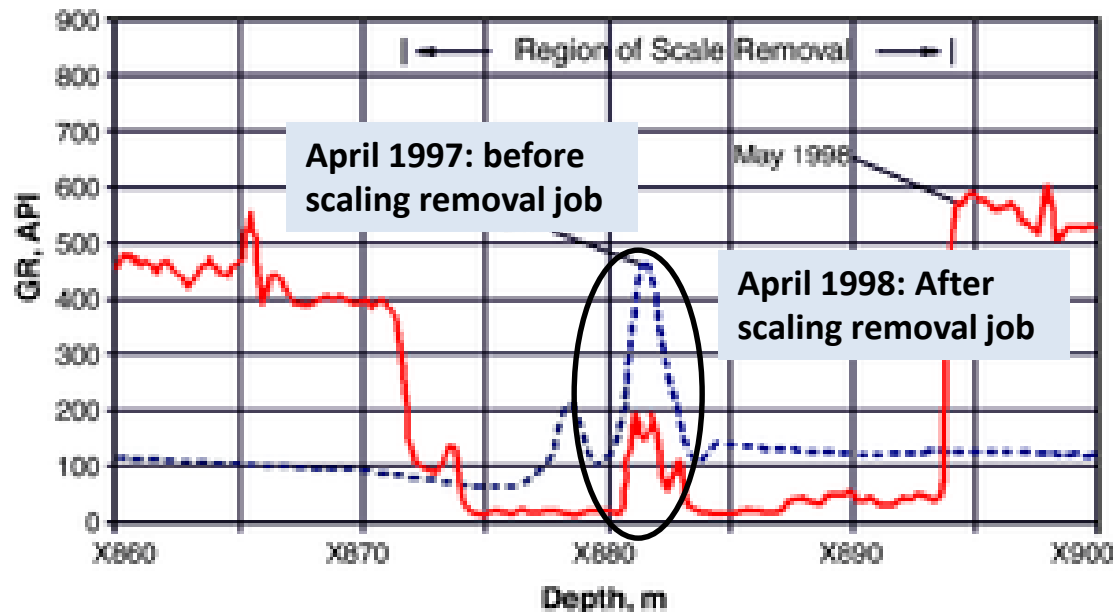   - Gamma Ray Log : detect radioactive radium Ra226. (present with scale, especially $BaSO_4$)

Figure 3. 1 Gamma Ray Log to identify scale deposition in the wellbore[3]

Scaling Prevention and Removal

Scale Prevention

- **Scale Prevention**
  - Function of scale type, amount, composition, and location
  - Suppress development of nucleation and crystal growth
  - Stop adherence to surface metal
  - Reduce rate of scale precipitation

- **Methods**
  - Water treatment : remove dissolved solid, gas, biogenic and ion sulfate
  - pH control
  - Chemical Treatment : scale inhibitor, ion exhange, chelating agent, or injecting diluted sea water
  - Physical Treatment : NMR, micro electrolysis, anti bond polymer, electrostatic ,etc

Scaling Inhibitor

- **Scaling Inhibitor**
  - Chemicals added into solution or injected water to stop the nucleation and prevent the crystals from adhering to the solid surface
  - Chemical scale inhibitor should have characteristic which can withstand at insitu environment.
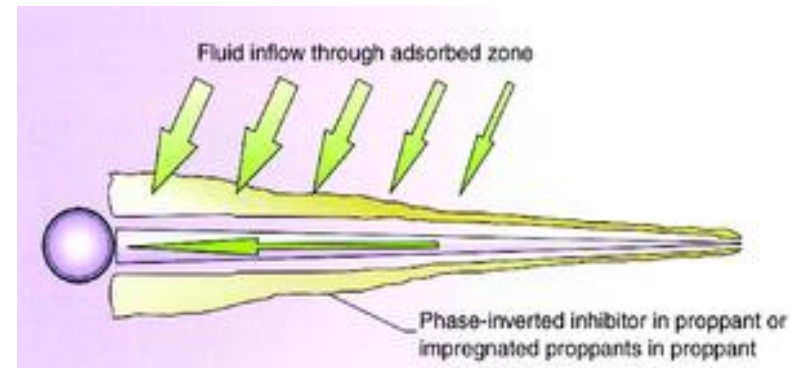
- **Chemical Characteristics**
  - Stable in brine containing rich divalent ions
  - stable in presence other chemical : corrosion inhibitor, surface active agent
  - Withstand at insitu pressure and temperature
  - Good balance for adsorption-desorption
  - Low toxicity and High biodegradability
 - Reasonably cost

Techniques of Scale Inhibitor

- **Hydraulic Fracturing**
  - Placement of chemical inhibitor along with hydraulic fracturing treatment
  - The inhibitors and proppantor fracture fluid are injected down to the wellbore

Fluid inflow through adsorbed zone

Phase-inverted inhibitor in proppant or impregnated proppants in proppant

- **Squeeze Inhibition**
  - Placement of chemical inhibitor by pumping down through wellbore
  - The chemicals will penetrate and adsorb onto rock at near wellbore and further into reservoir
  - The chemical will be produced afterward with reservoir fluid

Overflush   Spearhead

Main Treatment
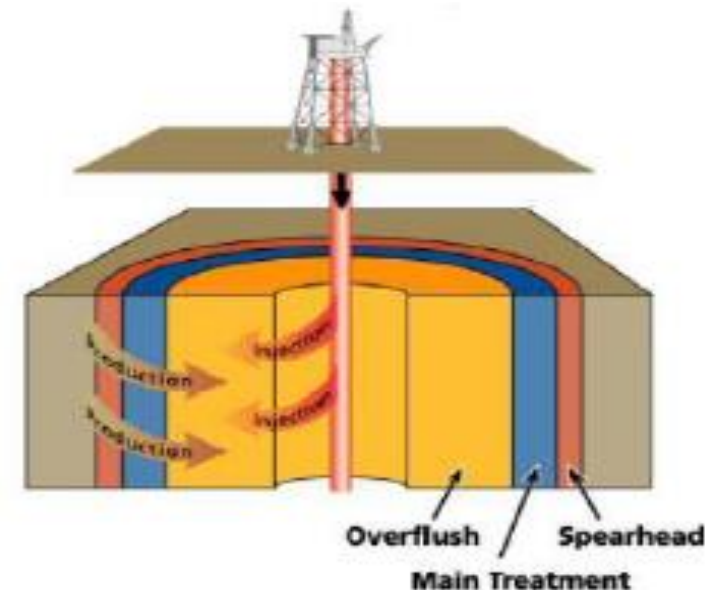
Type Of Scale Inhibitors

- **Scale Inhibitor can be divided as**
  - Thermodynamic
  - Kinetic
  - Adherence
- **Inhibitors can be classified as Organic and Inorganic Inhibitors**

  - **Organic Inhibitors**
    - Organic Phosphate Ester
    - Phosphate
    - Organic Phosphonates
    - Organic Aminophosphates
    - Organic Polymers, sulfonated polymer
    - Ester

  - **Inorganic Inhibitors**
    - Condensed Phosphate
      - ✓ Poly(metaphosphate)s
    - Inorganic Poly(phosphate)s
      - ✓ Sodium Tri Polyphosphate
      - ✓ Sodium Hexa Metaphosphate

Green Inhibitors

- **Characteristics**
  - Good biodegradability
  - Non-phosphorous compound
  - Environmental friendly

- **Type of Green Inhibitors**
  - Polyaspartic Acid (PASP)
    - Act as biodegradable polymer replacing the polluted chemical such as acrylic acid
    - Characteristics : good thermal stability, stable at high Ca^{2+} concentration, good chelation
  - Polyepoxysuccinic Acid (PESA)
    - Not contain phosphorous and nitrogenous structure
    - Characteristic: Rsistance to alkalinity, good thermal stability and strong chelation
  - Carboxy Methyl Iinulin (CMI)
    - Suitable for sequestration of hard scales
    - Characteristics : tolerate high Ca^{2+} conc, biodegradable inhibitors , excellent ecotoxicity

Factor Affecting Performance of Inhibitors

- **Temperature**
  - Higher temperature : reduce performance of scale inhibitors
- **Supersaturation**
  - Higher degree of supersaturation: reduce performance of scale inhibitors
- **Presence of divalent ions**
  - Reduce chemical inhibitor concentration→ reduce performance of scale inhibitors
- **Compatibility**
  - Inhibitor/Brine
  - Inhibitor/Hydrocarbon
  - Inhibitor/Inhibitor

# Mechanism of Scale Inhibitors

- **Minimum Suppression**
  - Suppress the growth of crystal seed in the solution

- **Latice Distorsion**
  - Inhibit the crystal seed for adhering to the solid surface

- **Chelating Mechanism**
  - Form complexes compound with the scaling positive ions
  - Chelating agents: EDTA, Citric Acid and Gluconic Acid
  - Stoichiometric reaction: one molecule EDTA react with one specific scaling ion

$$EDTANa_2 + X^{2+} \leftrightarrow EDTAX + Na^{2+}$$ **X^{2+}** is scaling ions (Ca^{2+}, Mg^{2+}, Ba^{2+})
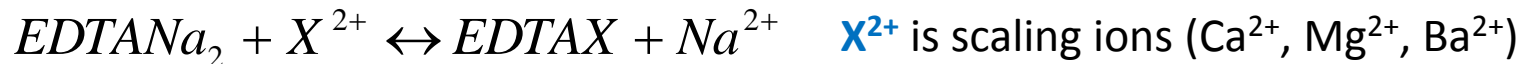
- **Electric Double Layer**
  - Create electric double layer in the boundary at which the crystal nucleation grow and preventing from coagulating on the surface.

Scaling Inhibitors – Inorganic scale

Inorganic Scales

- **Iron Sulfide Scale**
  - Mitigated by injecting nitrites and biocides
- **Hydrate Scale**
  - Chemical Prevention : Dispersant, Polymer, Emulsifier, MeOH, MEG, Alcohol or Salt
  - Operational Prevention : Increase temperature, lowering pressure, remove dissolved water by separators, glycol dehydrator, molecular sieves
- **Corrosive Prevention**
  - Increase pH
  - Inject alkaline chemical (NaOH) to create thin protective film in wall pipe

Scaling Inhibitors – organic scale

Organic Scales

- **Wax/Paraffin Inhibition**

  – Raise temperature system

  – Insulate pipeline

  – High Flow rate

  – Inject Dispersant and Crystal Modifier

- **Naphthane**

  – Lowering pH by injection short chain organic acid or acetic acid

Scale Removal

- Scale removal techniques are function of scale type, quantity, physical composition and texture of scale

- 2 common methods for scale removal:

  - **Mechanical Removal**

    - Commonly applied for insoluble acid and thought scales

    - Examples : milling, jetting, bullheading, Brush/Scratcher, explosive, vibration

  - **Chemical Removal**

    - Fresh Water, applied for water soluble scales such as NaCl

    - Sequestered acid : HCl, Acetic Acid (CH_3COOH), Formic Acid ($HCOOH$), Citric Acid ($C_6H_8O_7$), sulfamic acid (NH_2SO_3H) and Na_2H_2EDTA

      → Applied for acid soluble scales : $CaCO_3$, $FeCO_3$, FeS, (Fe_2O_3), etc.

Inorganic Scale Removal

- **Calcium Sulfate**
  - Low solubility in acid
  - Removal:
    - **Conversion Method** : reaction with $(NH_4)_2CO_3$, Na_2CO_3, NaOH or KOH
      $\rightarrow$ to convert to acid soluble compound , i.e. $CaCO_3$ or $Ca(OH)_2$
      $$CaSO_4 + (NH_4)_2CO_3 \rightarrow (NH_4)_2SO_4 + CaCO_3 \text{(Soluble)}$$

    - **No Conversion Method**: reaction with EDTA and DTPA

      $$CaSO_4 + 2H^+ \rightarrow Ca^+ + H_2$$
      $$Ca^{2+} + EDTA^{4-} \leftrightarrow CaEDTA^{2-}$$

      Equal with:
      $$CaSO_4 + 2H^+ + EDTA^{4-} \leftrightarrow CaEDTA^{2-} + H_2$$

Inorganic Scale Removal

- **Calcium Carbonate**
  - Soluble Acid Scales
  - Removal : strong acid Hydrochloric Acid (HCl) with 5% to 15% concentration
  - Reaction :

$$CaCO_3 + 2HCl \rightarrow H_2O + CO_2 + CaCl_2$$

- **Barium Sulfate (BaSO$_4$)**
  - Barite is one of the hardness and toughest scale
  - low porosity and insusceptible to chemical inhibitor
  - Removal:
    - Mechanical : Commonly applied for Barite, like
    - Chemical : EDTA U104 (Schlumberger)

- **Halite,** can be remove by low salinity water

Inorganic Scale Removal

- **Iron Sulfide**
  - Good solubility in acid
  - Removal : Acid solution, sulfuric acid, hydrochloric acid
  - Reaction :

$$FeS + 2H^+ \Leftrightarrow H_2S(g) + Fe^{2+}$$
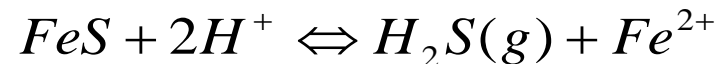
- **Hydrite**
  - The light hydrocarbon (n-buthane or smaller) contacts with water phase
  - Removal : Hydrite Depressurization, Inject chemical methanol or glycol, install heater

Organic Scale Removal

- **Wax/Paraffin**
  - Cutting, Pigging
  - Chemical : oxylene, acidic ammonium chloride, sodium nitrite
  - Melting : pumping down hot oil or water through wellbore

$$FeS + 2H^+ \Leftrightarrow H_2S(g) + Fe^{2+}$$
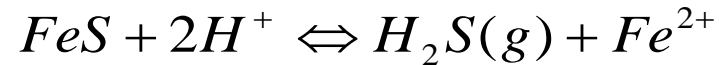
Evaluating Scale Potential During High and Low Salinity Water Injection

Evaluating Scale in HS and LS brine

Objectives

1) Evaluate of Scaling Potential using PHREEQC simulation by sensitivity of:

- Injected water composition
    - simulate high salinity and low salinity water Injection
- Mixing ratio of FW and SW
    - simulate scale tendency of any proportion at various location
- Pressure
    - simulate effect of pressure drop during transportation to surface
- Heterogeneity Reservoir
    - simulate effect of horizontal, vertical and areal heterogeneity

2) Study of scale Inhibitors and Removal

Parameters

- Brine : Formation Water, Sea Water, Diluted Sea Water
- Temperature range $25^O C - 150^O C$
- Water Composition is shown in Table 5.2

Water Composition

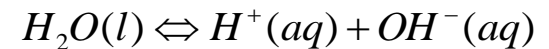Table 5.2 Water Composition of Formation Water,
Sea Water and Diluted Sea Water

Water Analysis of Sea Water (SW) and Formation Water (FW)			Diluted SW	
Ion (mmol/L)	FW	SW	10x	50x
Cl^-	1446.80	525.10	52.51	10.502
SO_4^{2-}	0.0	24.00	2.4	0.48
HCO_3^-	0.10	2.00	0.2	0.04
Mg^{2+}	22.00	44.50	4.45	0.89
Ca^{2+}	100.00	13.00	1.3	0.26
Na^+	1156.00	450.10	45.01	9.002
K^+	7.00	10.10	1.01	0.202
Ba^{2+}	3.90	0.00	0	0
Sr^{2+}	18.00	0.00	0	0
TDS (g/L)	84.72	33.39	3.339	0.6678

Brine Characteristic

pH Development
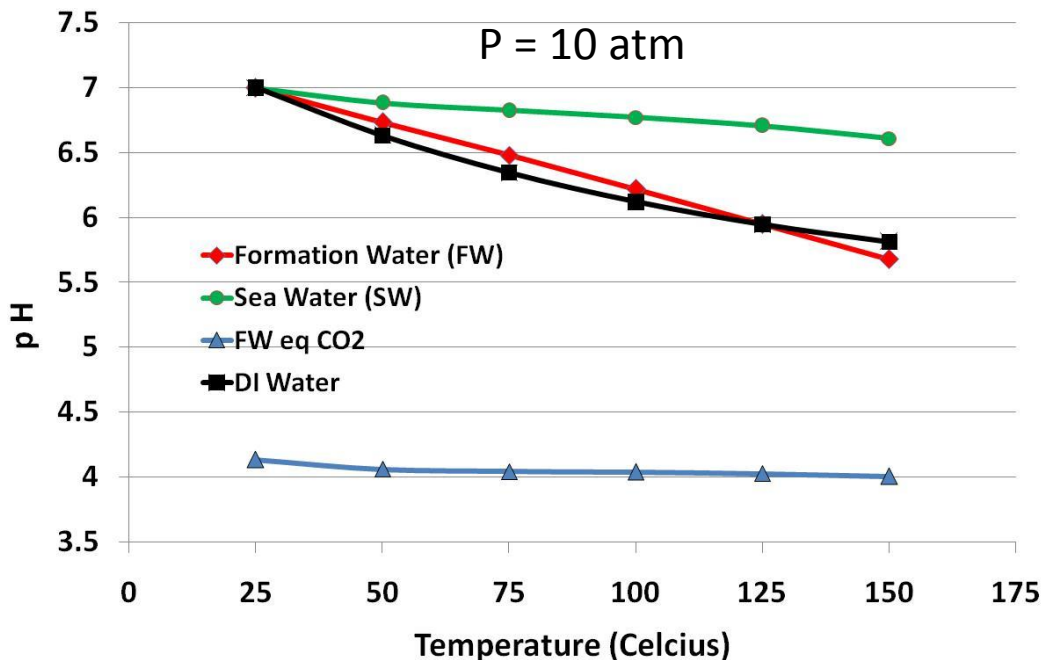
P = 10 atm

(Chart: pH vs Temperature (Celcius) showing curves for Formation Water (FW), Sea Water (SW), FW eq CO2, and DI Water)

• Decreasing pH is driven by auto ionization water
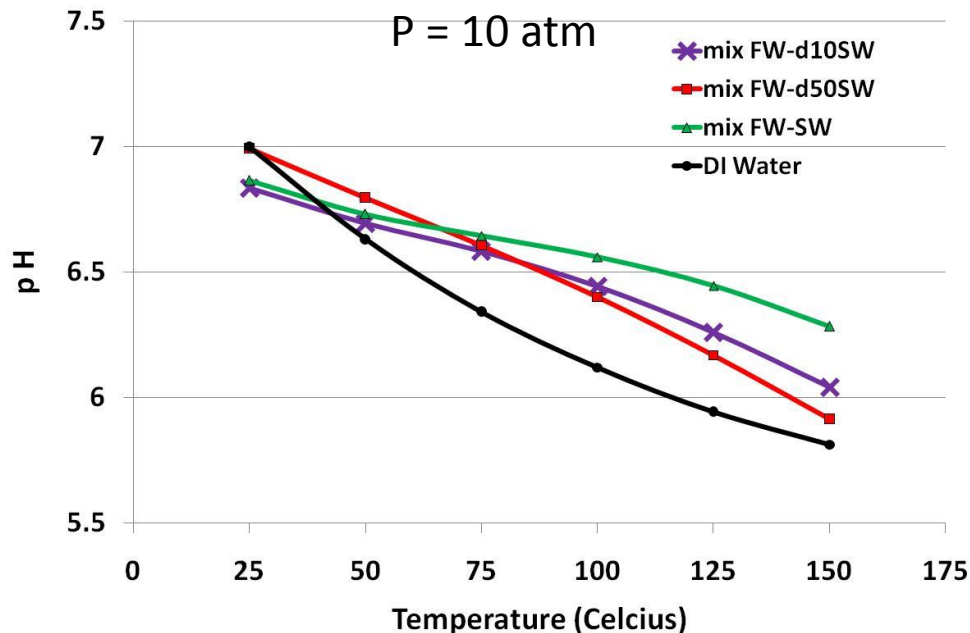
$$H_2O(l) \Leftrightarrow H^+(aq) + OH^-(aq)$$

$$pH = -Log[H^+]$$

• As temperature increases, the reaction more shift toward right and produce more [H^+]

- DI water is pure water which has pH=pOH over range temperature
- Dissolved Constituent in the brine affect the brine alkalinity wrt DI water
  - Formation water and Sea Water are more alkaline wrt DI water since they have dissolved alkali metal constituent, such as Ca^{2+}, Mg^{2+}, Ba^{2+}
  - FW-eq CO2 is more acidic due to CO_2 gas react with water and form H_2CO_3

Case 1 : Injected Water Composition

pH Development

P = 10 atm

Legend:
- mix FW-d10SW (purple, ×)
- mix FW-d50SW (red, ■)
- mix FW-SW (green, ▲)
- DI Water (black, ●)

Chart: pH vs Temperature (Celcius)

- • Decreasing pH is driven by auto ionization water

$$H_2O(l) \Leftrightarrow H^+(aq) + OH^-(aq)$$
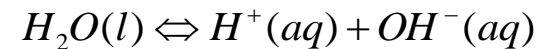
$$pH = -Log[H^+]$$

- • As temperature increases, the reaction more shift toward right and produce more [H^+]

- • Mixture Brine is more alkaline than DI water due to effect of dissolved alkali ions
- • pH of mixture FW/SW is higher than FW/diluted SW, due to
  - – Mixture FW/SW has significant dissolved ions than FW/diluted SW
  - – Dissolved ions have interaction with H^+ or OH^-, forming HCl, NaOH, etc
  - – Reduce active ion H^+ that determines pH in the solution

Case 1 : Injected Water Composition

Potential of Scale Precipitation
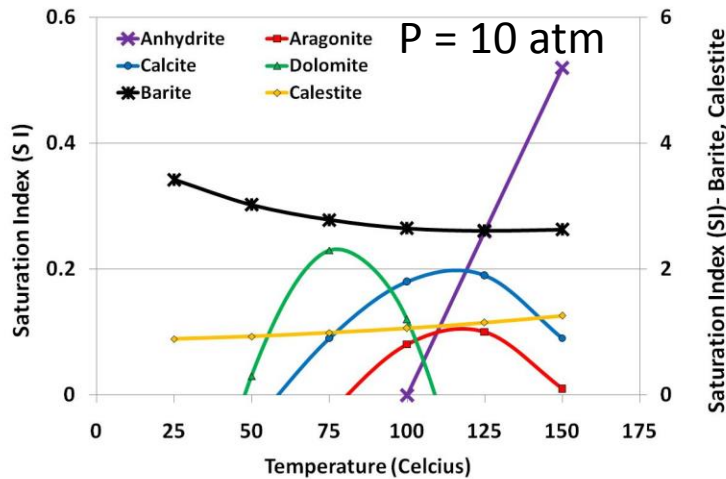
Figure 5.9 SI-values and development with temperature in mixing of FW/SW **(HS case)**

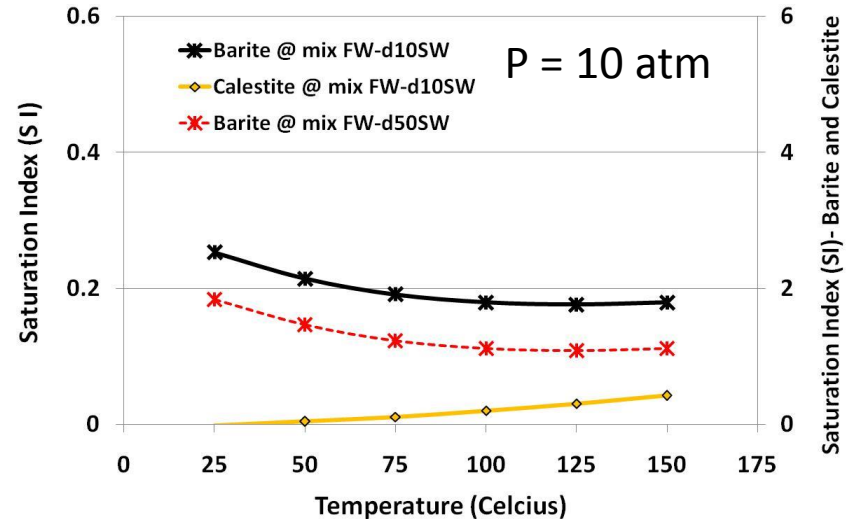$BaSO_4$ $SrSO_4$ are plotted in the secondary axis

Figure 5.10 SI-values and development with temperature in mixing of FW/diluted SW **(LS case)**

$BaSO_4$, $SrSO_4$ are plotted in the secondary axis

- FW/SW has more dissolved impurities than FW/diluted SW
  - Increases rate of nucleation and the crystal growth process
  - Increase degree of supersaturation in the solution
  - scales tend to be more precipitated

Case 1 : Injected Water Composition

Potential of Scale Precipitation

- HS brine solution

  - Potential Scale formed are $CaCO_3$, $CaSO_4$, $MgCa(CO_3)_2$, $BaSO_4$, $SrSO_4$

  - Barite solubility decreases as temperature however opposite trend for the others

  - Calestite is identified to be precipitated following $BaSO_4$

  - Anhydrite scales has tremendous scale precipitation at high temperature (>100 ^{O}C)

  - Calcite shows increasing solubility at high temperature followed by tremendous Anhydrite precipitation

- LS brine solution

  - SI values decease dramatically

  - Almost all minerals are dissolved in the mixture FW/diluted SW, except $BaSO_4$

  - Barite has low solublity in the solution shown by lowest Ksp, so it forms a hardness and though scales

Case 2 : Mixing Ratio

Potential of Scale Precipitation

- Simulate scale tendency at any mixning proportion in the field

- Sensitivity of Mixing Ratio between SW and FW

- Result:

| Case	Ratio SW:FW
1	0.3 : 0.7
2	0.5 : 0.5
3	0.7 : 0.3
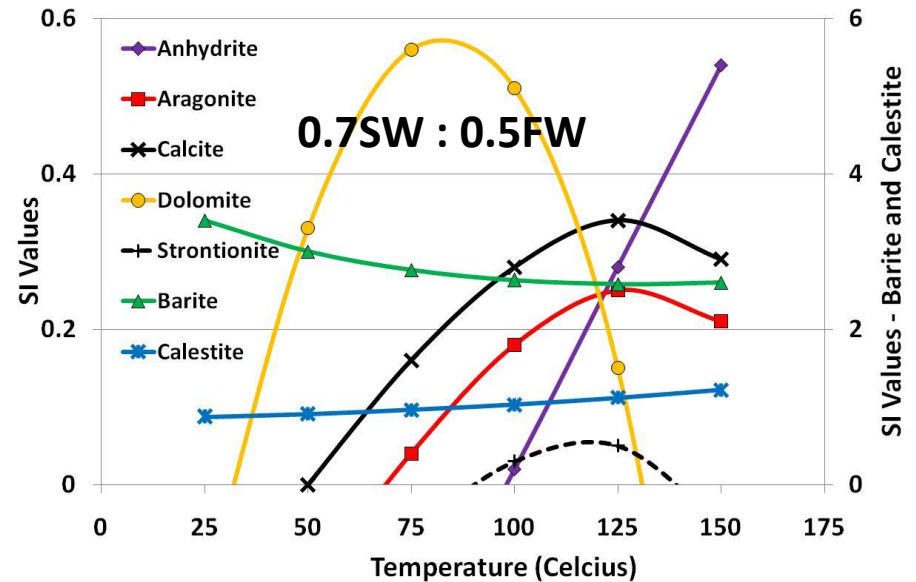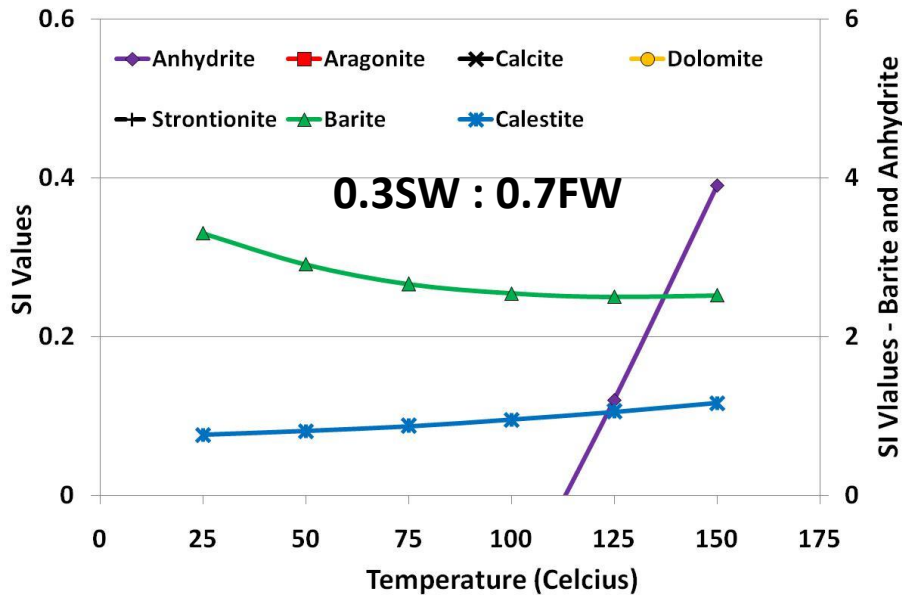
Case 2 : Mixing Ratio

Discussion

- Increase SW proportion will increase scale tendency

    - Increases presence scaling ion SO_4^{2-} and ion CO_3^{2-} in the mixture solution

- The carbonate scale appears to be more affected by salinity, especially dolomite

    - SI values increase triple when adding 50% SW to 70%SW

    - SW brine has already saturated by dolomite,

    - → According to Trask, et.al 1937 : salinity is increased of 1%wt, the solubility of $CaCO_3$ reduced to 5% while dolomite was at least 15% from initial values.

- Sulfate scales are precipitated at low proportion of SW and their solubility decreases as SW brine proportion increases

    - Barite has the highest SI values and will be precipitated out over range temperature

    - Anhydrite is founded as detrimental precipitation at high temperature and high SW proportion

Case 3 : Effect of Pressure Change

Potential of Scale Precipitation

- Simulate scale tendency as pressure drops along the system

- Pressure was varied from 10atm, 50atm and 100atm

- Result:
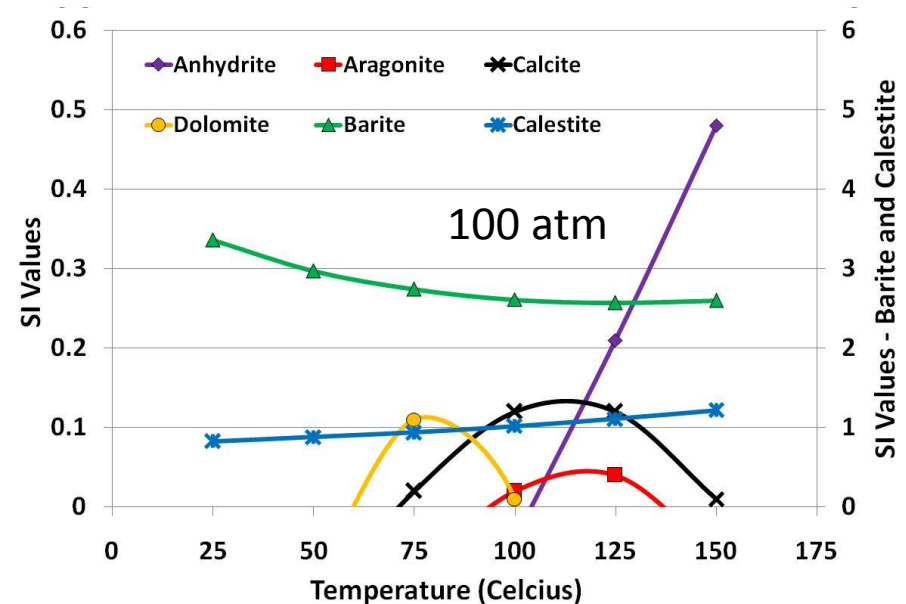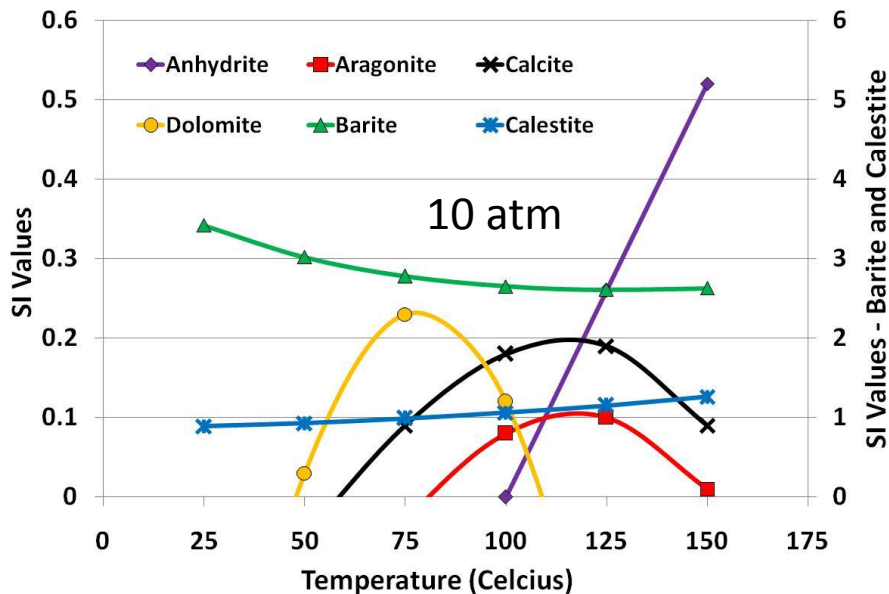
Case 3 : Effect of Pressure Change

Discussion

- Decrease pressure will increase scale tendency

  - Carbonate scales : Calcite, Aragonite and Dolomite

    - Pressure drop will cause CO_2 gas escapes from solution

    - leaving the solution more saturated in calcium carbonate and will be precipitated as exceed saturation limit in the solution

  - Sulfate Scales: Anhydrite, Barite and Calestite

    - Anhydrite show small decreasing solubility as pressure decreases

    - Barite and Calestite are not significantly affected by pressure drop

Case 4 : Effect of Reservoir Heterogeneity

Horizontal Anisotropy

- Heterogeneity reservoir lead the scale deposition more complexes

- The mixing zone is located behind oil bank with injected water bank in the tail

Result:

- **Case (a) :** has insignificant scale potential due to lower mixing zone created, almost sharp front between CW and IW

- **Case (b) :** has significant scale potential due to development of mixing CW/IW and induce more scale precipitation
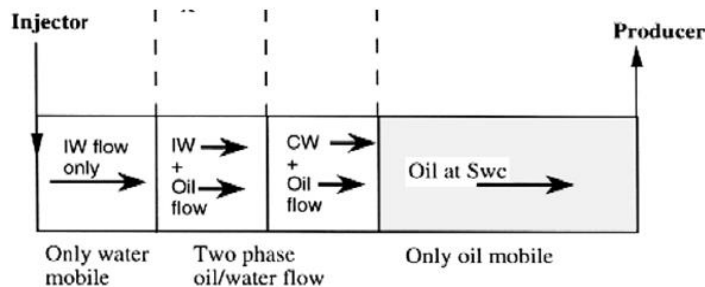
Case (a)
Lower Degree of Permeability Anisotropy
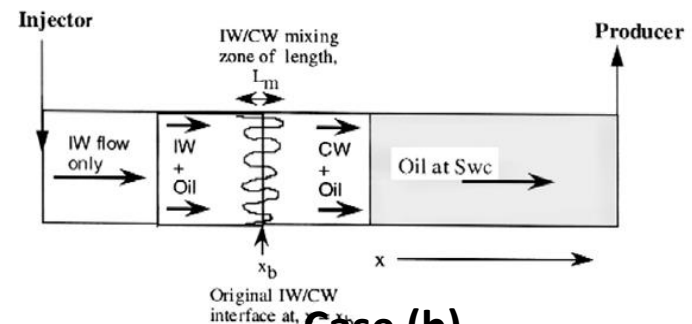
Case (b)
Higher Degree of Permeability Anisotropy

Case 4 : Effect of Reservoir Heterogeneity

Vertical and Areal Heterogeneity

- Vertical variation has different composition of each layer → makes the scale analysis more complexes

- Vertical and Areal variation affect the water breakthrough time in the wellbore

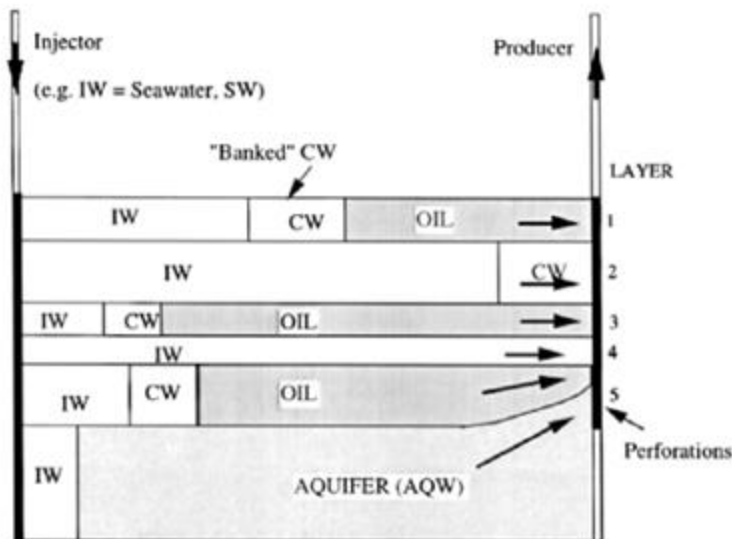- Scale precipitation in the wellbore is a function of times
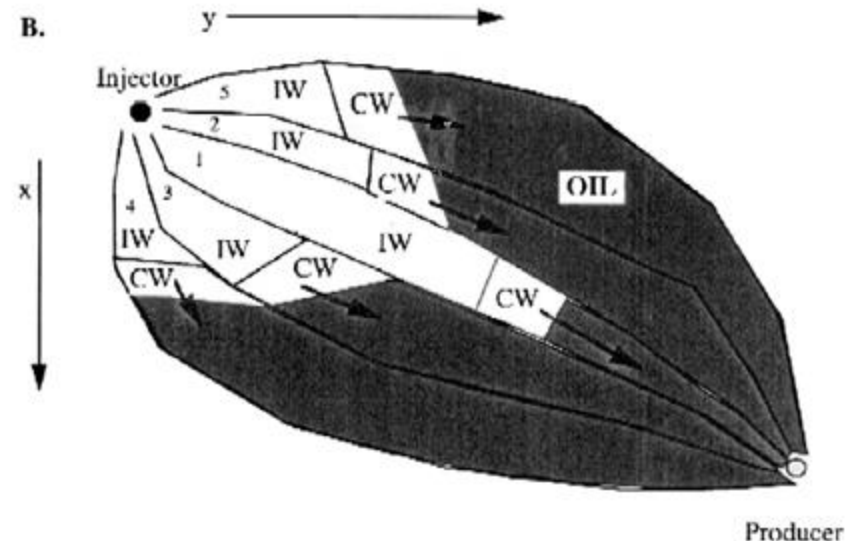

Figure 5.22 Vertical Section Heterogeneity

Figure 5.23 Areal Section Heterogeneity

Scale Potential in the HPHT Well

HPHT condition

- Pressure : 15000 psi - 30000 psi

- Temperature : 150^OC - 250^OC

- TDS >300.000 mg/L

Challenges

- The risk managements are crucial

- Need precise calculation on scale predicting, scale controlling and prevention

- Lower Performance Inhibitors

Potential Scale Problems

- Increase potential corrosion, brine tend to form acidic mixture under HPHT

- Water tends to dissolve sand (SiO_2) and forms orthosilicic acid (H_4SiO_4)

$$SiO_2 + 2H_2O \leftrightarrow H_4SiO_4$$
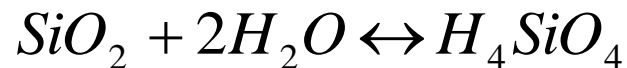
- Deposit stable silicate minerals (Ca_2SiO_4, Na_4SiO_4)

$$SiO_4^{4-} + 4Na^+ \leftrightarrow Na_4SiO_4$$
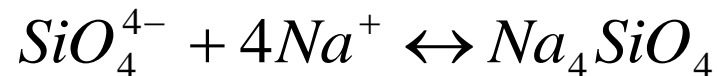
- Flow assurance dramatically decreased caused by some problems above

Scaling Prevention and Removal - Scaling Inhibitors

Inorganic Scales

- **Carbonate Scales**

  – Chemical Inhibitors: Ester, Phosphonates, Polyphosphates, Organic Phosphorus Acid, Poly carboxylic acid and PESA
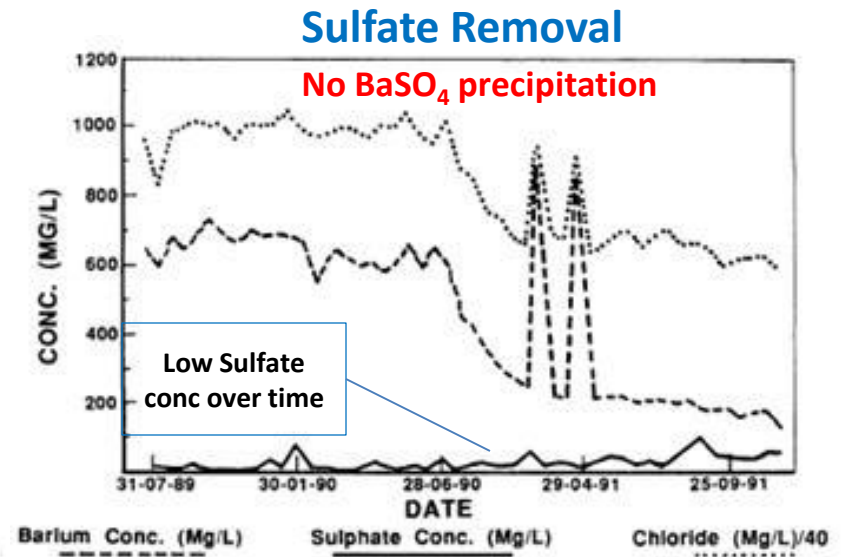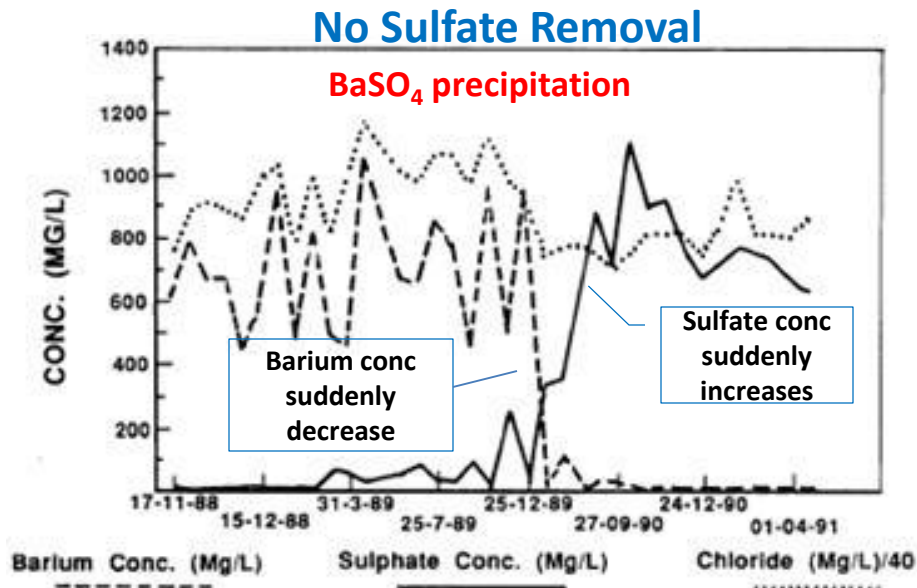
- **Sulfate Scales**

  – Chemical Inhibitors: Ester, Phosphonates, PESA, PASP, EDTA, chelating agent

  – $BaSO_4$ scales : Polyelectrolyte, PASP, EDTA, Ester, Nitrilotriacetic acid, Phosphonates

  – Sulfate Removal Technology or Nanofiltration (NF)

Scaling Prevention and Removal - Sulfate Scale Inhibitors

Sulfate Scales

– Sulfate Removal Technology or Nanofiltration (NF)

  • Uses membrane separation with size up to 1 nanometer (10 ^{O}A)

  • Reject sulfate ion up to 96%-98% (case of Marathon oil UK in the Northsea)

– Sulfate ion and Barium ion are observed as injected water breakthrough in the producer wells

Conclusions

- Scale potential is mainly dominated by Sulfate Scale ($CaSO_4$, $BaSO_4$, $SrSO_4$) and Carbonate Scales ($CaCO_3$, $MgCa(CO_3)_2$).

- Carbonate solubility decrease double compared to sulfate scales as pressure drops from 100 atm to 10 atm.

- Sulfate scales are the firstly created at low values of sea water/formation water ratio. Barium sulfate and strontium sulfate is the worst condition to scale formation

- Triple reduction of dolomite solubility is observed when adding 20% SW, from 50% to 70%

Conclusions

- A significant reduction of potential scale formation as lowering salinity by dilution of injection sea water is shown in figure 5.10. The horrible insoluble crystal salts that are formed in HS injection did not appear and totally dissolved in the solution FW/diluted SW, except $BaSO_4$

- The insoluble and hardest scales can be mitigated by sulfate removal technology or chemical inhibitors before sea water injection. However, the capital cost, operational limitation and environmental issues become a big constraint. Thus by implementation of low salinity water injection, not only cover the limitation of conventional sea water for scaling control and management but also offer significant oil enhancement

Thank You