



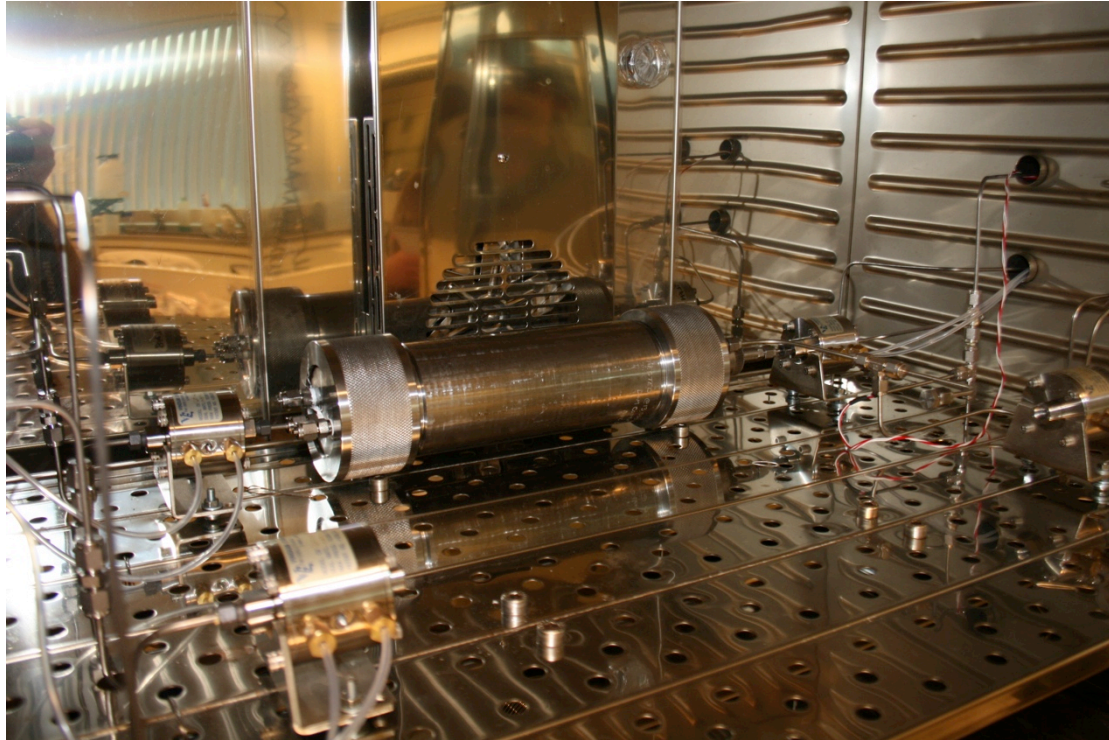
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Improving Squeeze Scale Inhibitor Adsorption and Flow Back Characteristics with Surfactants



Master Thesis
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Abstract

The most common method for preventing downhole scale deposition is by the use of a scale inhibitor in a scale squeeze treatment. The process consists of injecting a scale inhibitor down a producer well into the near wellbore formation. It is believed that a change in the rock wettability will enhance the scale inhibitor adsorption to the rock, hence increasing the treatment lifetime. This master thesis discusses the effect of a surfactant preflush on scale inhibitor lifetime and also flow back characteristics.

Particular attention is given to laboratory corefloods tests, where the field conditions of an oil field reservoir are simulated, in an attempt to give the most accurate and relevant results. Six coreflood tests were completed using Berea sandstone core plugs, five of them with more oil wet characteristics and one core plug with water wet conditions to use as base line.

The study clearly shows an improvement in the potential squeeze lifetime when a surfactant/ solvent is used as a preflush. The results also show that the change in the wettability is not the only factor influencing the treatment lifetime. This is validated by data showing the product with the biggest change in wettability is not the showing the largest improvement in the treatment lifetime.

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Nomenclature

DHSV =	Downhole safety valve
TDS =	Total dissolved solids
FW =	Formation water
SW =	Seawater
PW =	Production water
HPHT =	High pressure high temperature
NORM =	Naturally occurring radioactive material
SRBs =	Sulfate reducing bacteria
K =	Permeability
Ko =	Oil Permeability
Kw =	Brine Permeability
Sw =	Water Saturation
Swi =	Irreducible Water Saturation
ϕ =	Porosity
Po =	Overburden Pressure
Pp =	Pore Pressure
Pc =	Capillary Pressure
T =	Temperature
RPM =	Revolutions per Minute
FW =	Formation Water
PV =	Pore Volume of the Core
S.E.M.=	Dry Scanning Electron Microscopy
SI =	Scale Inhibitor
Swi =	Irreducible Water Saturation
Swr =	Residual Water Saturation
Sor =	Residual Oil Saturation
FW =	Formation Water
LiCl =	Lithium Chloride
PV =	Pore Volume of the Core
DV =	Dead Volume of the Coreflood System
BHPMP =	Bis(hexamethylenetriamine) penta (Methylenephosphonic Acid)

1 Introduction

Inorganic scale deposition is present in every oil field around the world. It is considered together with corrosion and hydrates one of the biggest water related operational challenge in the oil industry. Especially in offshore fields, where injection of incompatible seawater is a common operational method activity for pressure support.

The production of crude oil is based on effective management of flow assurance in economic ways. There are two general approaches when dealing with scale deposition, one is to prevent the formation of the scale layer deposition by the use of a scale inhibitor, and the second is by removing the already formed layer of scale. This can be done by either mechanical or chemical methods. This thesis focuses especially on the preventive method of scale inhibition and particularly in the improvement of the scale squeeze inhibition treatment.

Scale squeeze is one of the most effective and used method to prevent the deposition of inorganic scales in the wellbore and near wellbore formation. It consists of five stages: (i) a preflush to condition the formation rock; (ii) the main treatment with concentrated SI; (iii) an overflush designed to push the scale inhibitor into the formation; (iv) a shut in period to allow the scale inhibitor to adsorb on the rock (12 to 24 hours); (v) the well is brought back onto production. A successful scale squeeze treatment depends on the time the produced fluids are above the minimum inhibition concentration (MIC).

Adsorption is complicated phenomenon that involves the interaction of many different factors such as solution chemistry, temperature, formation mineralogy, operational parameters and crude oil properties. Of particular interest is the effect of mineralogy combined with crude oil properties. Given the geochemical composition of crude oil, oil producing reservoirs are rarely extremely water wet and thus sites on mineral surfaces are unavailable for inhibitor adsorption.

This master thesis will be centered on testing the assumption that changing the rock wettability to a more water wet condition will enhance SI adsorption and this change will increase the scale squeeze treatment lifetime and therefore make the process more cost efficient.

2 Literature review

2.1 What is Scale?

“Scale formation is the deposition of sparingly soluble inorganic salts from aqueous solutions” [2] (figure 2.1), it is caused by a change in the saturation equilibrium when there is a variation in temperature, pressure, or change in the solution chemistry [3].

Scale is present in some extent in every oil field, and is considered together with corrosion and hydrates one of the biggest and most expensive water related operational costs in the oil industry, especially in regions like the North Sea and Canada [3]. Scale can deposit on almost any surface; wherever it precipitates, a layer of the inorganic salts begin to form and the layer will continue to grow unless it is treated [2].



Figure 2.1 Scale deposit in a pipe [4]

“Most scale found in oil fields forms either by direct precipitation from the water that occurs naturally in reservoir rocks, or as a result of produced water becoming oversaturated when two incompatible waters meet downhole” [3].

The two most common scales are carbonates and sulfates; carbonate scales are caused mainly by CaCO_3 precipitation due to reservoir pressure depletion;

sulfate scales are formed by the incompatible mixing of injection water (seawater) which contains high concentration of sulfate ions and formation water a brine with high concentration of group II metal ions [2, 5]. Injection of seawater for pressure support is a frequently used technique in the North Sea oil and gas fields, however the incompatibility between formation water and seawater may cause sulfate scale to form in the production system [6].

There are two main mechanisms of scale formation proposed by Crabtree et al. (1999) shown in figure 2.2, heterogeneous nucleation (surface) and homogeneous nucleation (bulk). Homogeneous nucleation starts its first development with the formation of a cluster of atoms that forms a small seed crystal that grows by ions adsorbing onto imperfections of the crystal surface, hence increasing the crystal size, large crystals favor the crystal growth, and crystals encourage scale deposition. Heterogeneous nucleation takes place on a preexisting fluid boundary surface such as pipe surface roughness, perforations in production liners or even joints and seams in production pipelines [3].

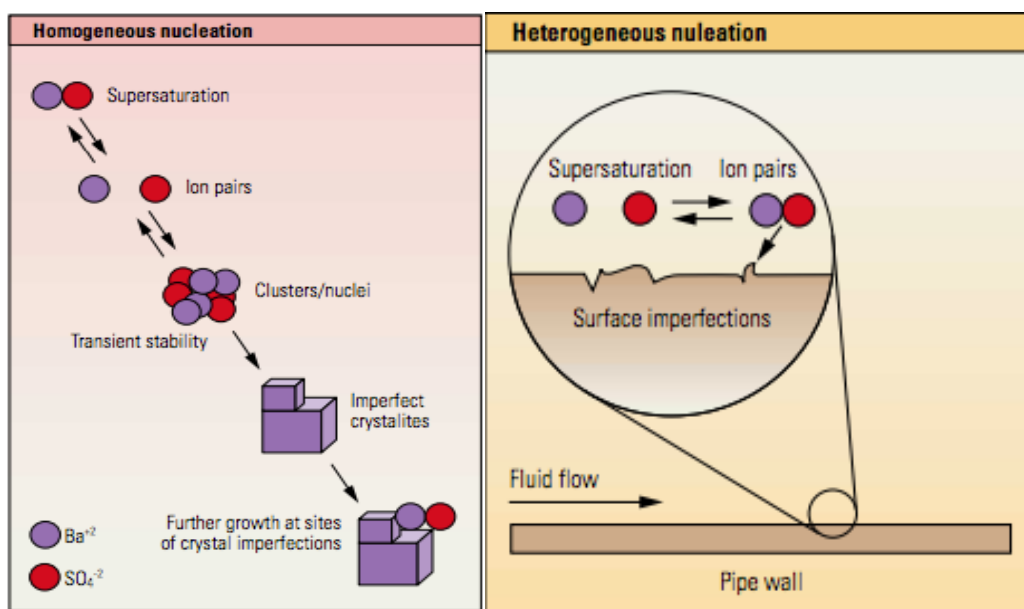


Figure 2.2 Homogeneous and Heterogeneous nucleation [1]

Location of scale:

Scale can have many different effects depending on the location;

- Scale in the near wellbore – can cause severe formation damage, it can block flow by clogging the pores hence reduce the production rate and it can disrupt downhole equipment such as the DHSV (downhole safety valve)[7].
- Scale in the production tubing - formed by a scale build up in the internal walls of production tubing, this scale is commonly formed in the roughness of the pipes, a scratch or a seam. The main effect is a decrease in the production rate caused from a reduction in the flowing area (figure 2.3). This can also lead to a pressure drop that can compromise the ability of the fluid to reach the top of the well, resulting in impaired productivity and can even choke the well.
- Scale in the topside process - may lead to insufficient separation and poor water quality. If not handled correctly, all this mechanisms may give significant production losses [1, 8].

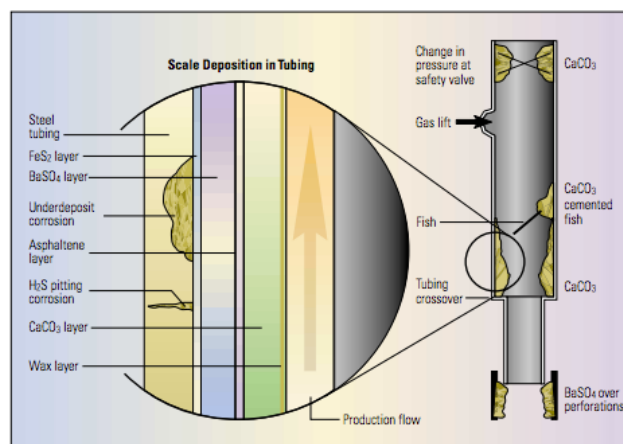


Figure 2.3 Shows scale deposition in a producing tubing [1]

Scale deposition can have many negative impacts and therefore it is important to continuously review and update the flow assurance management strategies for the protection and maintenance of the system and to extend the field lifetime. Scale management shows better results when handled in a preventive approach, considering the issues beforehand in the well and in the treatment design.

2.2 Types or scale

The most common types of scale in the oil industry are the following [1]:

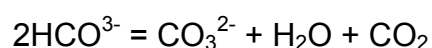
- Carbonates [Ca(II), Mg(II), and Fe(II)]
- Sulfates [Ca(II), Ba(II), Sr(II), and Ra(II)]
- Oxides and hydroxides [Fe(II), Fe(III), Mg(II) and Cu(II)]
- Sulfides [Fe(II), Cu(II) and Zn(II)]
- Sodium chloride (NaCl)

2.2.1 Carbonate Scales

Calcium carbonate scale is the most common type of scale found in the oil field well environment, and is one of the major problems encountered in North Sea oil production wells. In most cases the deposits consist of calcite, which is the most thermodynamically stable crystalline polymorph of CaCO₃. Aragonite and vaterite are next two polymorphs in order of decreasing thermodynamic stability[9]. The three crystals have the chemical formula CaCO₃, but they differ in crystal structure with calcite being the most common. Other known minerals are magnesite (MgCO₃) and iron carbonate siderite (FeCO₃) [1].

Formation water can have a concentration of 200,000 – 250,000mg/l TDS and the mineral composition has a complex dependence on mineral diagenesis. In carbonate and calcite cemented sandstone reservoirs, there is a high concentration of divalent calcium [Ca⁺] and magnesium [Mg⁺] ions[1]. However scale will not be formed until there is a change in the chemistry equilibrium. The interactions in the chemistry are complex, and in order to predict the scale deposition it is important to understand the following: [1]

1. Carbon dioxide dissolves in water to form carbonic acid.
2. Carbonic acid dissociates to form carbonate and bicarbonate, and by Le Chatelier's principle the reaction will move to the right with respect to the flowing equilibrium equation, in attempt to increase the pressure by forming more CO₂ gas [2].



3. As a result of this reaction the pH increases and the calcium carbonate gets supersaturated enough to precipitate (figure 2.4). The kinetics of the reaction is a function of temperature [10] All these chemical reactions are linked and each parameter can affect one another.

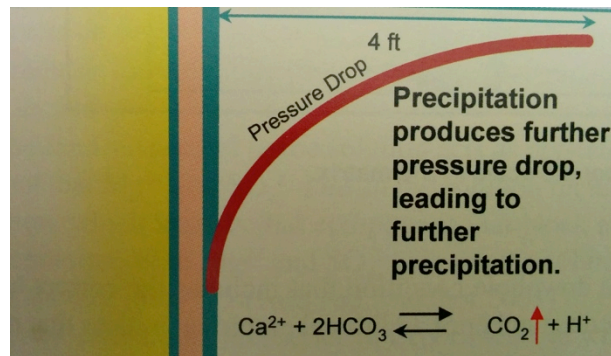
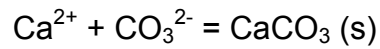


Figure 2.4 Carbonate scale precipitation by pressure drop [1]

Carbonate scale usually occurs at points where there is pressure drop; this can be at any point of the production system. It can be downstream in the pipeline, at topside, choke valves or safety valves. Calcium carbonate will not deposit in the well due to the CO_2 high concentration and hence low pH. However it may occur in a producing well, after several years, once the pressure has dropped [2].

2.2.2 Sulfate Scales

Sulfate scaling is usually a problem in seawater flooded reservoirs. Seawater is injected as a mechanism for upholding the pressure in the reservoir, especially in mature oil fields with increasing water cut [11]. In cases where the seawater is used for waterflood medium, group II metal ions (except magnesium) from the formation water and the high concentration of sulfate ions from the seawater, are readily to combine to form sulfate scale [12].



Sulfate scales have a wide range of solubility depending upon which divalent cation is present (figure 2.5), calcium sulfate is slightly soluble in water and soluble in many scale dissolvers, in a production operation where barium is present, it becomes the main flow assurance risk due to its low solubility relative to calcium carbonate, strontium sulfate (SrSO_4) and calcium sulfate (CaSO_4) [14].

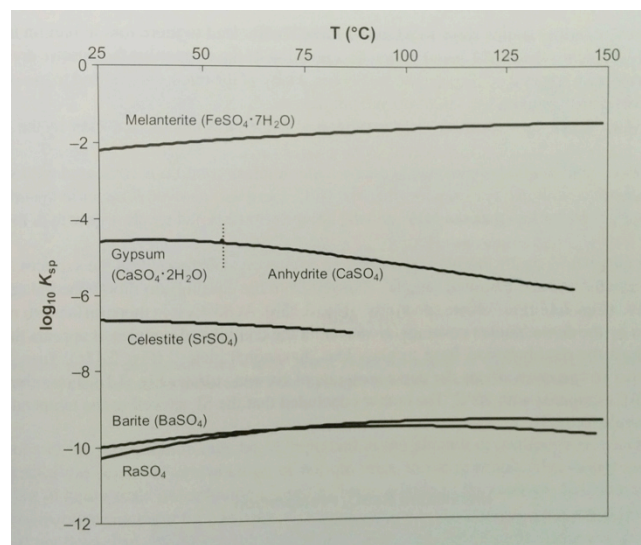
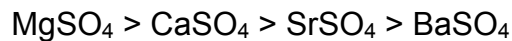


Figure 2.5 Sulfate minerals solubility as function of Ksp values [1]

Barium sulfate scale has very low solubility and, can only be dissolved only in the top dissolvers. Due to its low solubility it does not require a high concentration of barium ions in the formation water for the scale to deposit barite [2].

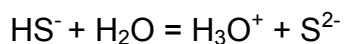
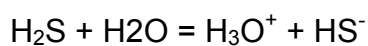
The situation is complicated by the fact that sulfate scales commonly co-precipitate with radioactive radium 226 and 228 (Ra^{++}). This results in naturally occurring radioactive material (NORM), resulting in restrictions, operational problems, and downtime, on top of the expense of removal and disposal of these scales [12].

The hardness of the sulfate scale depends on the ratio of FW to SW. Thus in the early stages of a field, when the seawater is first injected, the severity of the

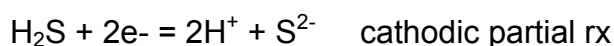
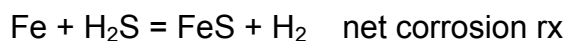
sulfate scale can be dramatic. However, in the late stages of the field there may be little or no sulfate scale as the PW is mainly SW [2].

2.2.3 Sulfide scales

The most common type of scales in the oil industry are calcium carbonate and sulfate scales. Over the recent years sulfide scales have become increasingly common, where the main sulfide scales are iron, zinc and lead, with the latter two often occurring together [15]. This kind of scale is formed mainly by the interaction between hydrogen sulfide and iron, zinc or lead, the most common among them is iron sulfide, originated mainly from corrosion of steel in producing wells. The majority of the of hydrogen sulfide comes from the activity of sulfate reducing bacteria (SRBs) on the sulfate ions from SW, the bacteria reduce sulfate ions to hydrogen sulfide as shown in the next reactions [2]:



Iron sulfide scales can be formed when the conditions are sour and corrosion is present, leading to the next reactions [1]:



2.2.4 Sodium chloride scales

In recent years there has been an increase with Halite scale (NaCl) related problems due to the increased development in hotter and deeper gas and gas condensate fields[16]. High sodium chloride concentrated water is normally present in HPHT reservoirs, even in wells with low water cut (< 0.5%) [2]. To produce scale this way the well must be producing a mixture of saline water and a permanent gas such as carbon dioxide or methane. The kinetics of this reaction are very fast in the main cause is a evaporation caused by a pressure drop [1].

Halite is easy to remove due to its high solubility in water, the most common method for counteracting the deposition of halite scale is with the injection of fresh water or by washing it periodically with fresh water [16].

2.3 Scale Inhibitors

As mentioned in 2.1, a preventive scale management strategy is preferred, considering additional to the cost of overdue or impaired production, the direct cost of removing scale from a well can be as high as \$2.5M [3]. In most cases chemical inhibition is the selected method of maintaining well productivity[17]. The main used mechanisms are crystal growth inhibition, nucleation inhibition and even scale dispersion.

“An inhibitor is defined as any chemical agent that reduces the rate of formation of a fouling scale”[1]; their basic function is to prevent the formation of scale by adsorbing onto the crystal nuclei as the scaling mineral precipitates, causing deformation of the normal crystal growth pattern and block the formation of larger crystals [17]. Studies have shown that in the case of a stable nuclei (crystal seed) with as little as 4 – 5% surface coverage of the total surface area of the nuclei, complete crystal growth inhibition can be achieved [18].

Inhibitors are different from chelating agents, because inhibitors act on scaling surfaces and by hindering the crystal formation and chelating agents tie up all scale forming ions.

In order for a scale inhibitor to work properly a minimum concentration of scale inhibitor (MIC) in the solution is needed, this is usually between 1 to 5 ppm depending on the conditions, however concentrations below 1ppm are difficult to detect through chemical analysis [17].

Two very essential properties for a scale inhibitor are the surface adsorption and the chemical binding at the nuclei surface or with a scale-forming ion in a solution [18]; for instance carbonates (CO_3^{2-}) and sulfates (SO_4^{2-}) mostly bind

with group II metal cations. In order to bind with a scale molecule the scale inhibitor must interact either with the produce water cations or anions, usually many interactions are required to hold the inhibitor to the surface. A good way to put several cations in a molecule is with a quaternary group, including these groups into anionic SI can be beneficial for adsorption, highly needed in the scale squeeze treatment[2].

These are some of the most important anionic groups attached to an organic molecule [2]:

- Phosphate ions ($-\text{OPO}_3\text{H}^-$)
- Phosphonate ions ($-\text{PO}_3\text{H}^-$)
- Phosphinate ions ($-\text{PO}_2\text{H}^-$)
- Carboxylate ions ($-\text{COO}^-$)
- Sulfonate ions ($-\text{SO}_3^-$)

Scale inhibitors are usually chosen depending on the predominant type of scale in the well to be treated. Figure 2.6 and 2.7 are examples of molecules, there are hundreds of chemicals available and in many cases the molecule can be tailored through testing for specific scaling conditions[1]. This is the list of the most relevant classes of SI[2]:

- Polyphosphates
- Phosphate esters
- Small, nonpolymeric phosphonates and aminophosphonates
- Polyphosphonates
- Polycarboxylates
- Phosphino polymers and polyphosphinates
- Polysulfonates

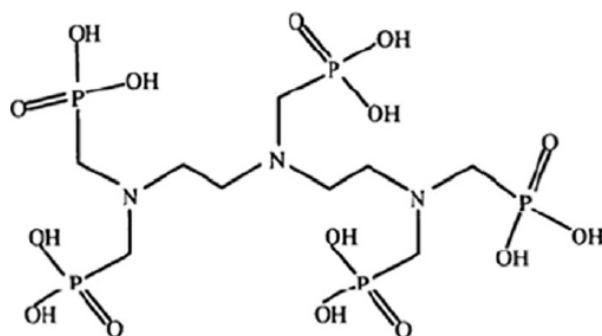


Figure 2.6 Diethylenetriaminepenta (methylene phosphonic acid) (DETPMP) common commercial scale inhibitors[11]

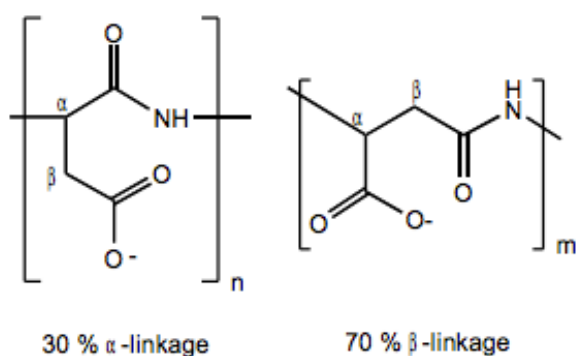


Figure 2.7 Polyaspartate molecule [19]

Nowadays with ever more restrictive environmental regulations and explorations in more vulnerable environments, there is a need for “greener” chemicals with lower toxicity, higher biodegradability and lower nutrient content. Polyaspartates are highly biodegradable alternatives to polyacrylate based scale inhibitors and have shown good efficacy in scale control. However the performance is still not as good as other compounds such as phosphonates[18].

2.4 Effect of scale in production and its economic impact

Scale related problems represent one of the highest economical costs of the operation and it can lead to severe production losses if not handled properly. In the Miller field in the UK North Sea sector, the production decreased from

30,000 bpd to zero in 24 hours [2]. From the flow assurance point of view, any scale build up in the tubular can reduce the diameter available for flow and choke the production, or cause a pressure drop that can impede the ability of the fluid to reach the sales point [1].

The economic impact of scale has been estimated at more than USD 1.4 billion (Frenier, 2002) each year, illustrated in figure 2.8 and figure 2.9.

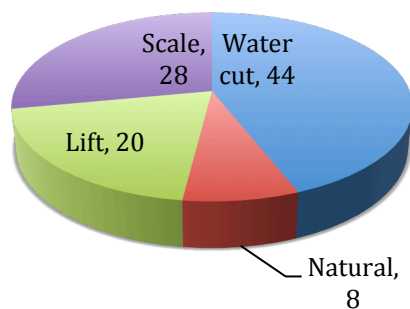


Figure 2.8 Percentage of lost production from each process [1]

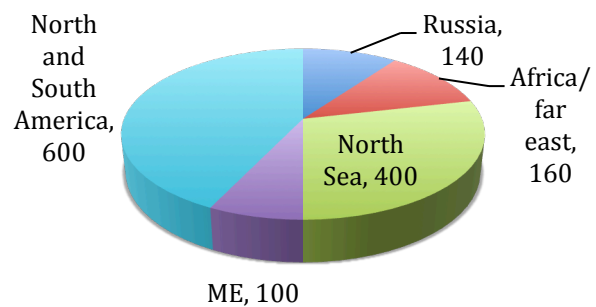


Figure 2.9 Cost of scale in million USD [1]

2.5 Scale squeeze

Scale squeeze is one of the most common and efficient methods for treating inorganic scale in the oil industry [20], and it is widely used to apply treatments of scale inhibitors for protecting the reservoir, near wellbore region, perforations and production tubing, it maintains well production by minimizing scale related downtime and protects safety valves from scaling [21]. Commonly the treatment uses a water based scale inhibitor solution usually a 5–20% solution in KCl or seawater [2, 22]. The treatment commonly includes the following steps [2, 5]:

1. Preflush which is used to clean and condition the near well-bore for the scale inhibitor.
2. Main treatment with concentrated scale inhibitor.
3. An overflush can be used to push the chemicals deeper in the formation.

4. Finally a shut-in period, typically 12-24 hours, such that the chemical is provided with sufficient contact time to adsorb onto the reservoir.
5. Production is restarted and the scale inhibitors provides protection to the region by desorbing into the produced water such that enough scale inhibitor concentration is maintained in the fluids to inhibit scale deposition for a period of time[13].

As soon as production starts again, there will be high concentration of scale inhibitor up the pipeline, it is common for a (25-35%) to be backproduced immediately. Over a longer period of time the concentration of the returned chemical gradually decreases until it reaches a concentration below the MIC (minimum inhibitor concentration that prevents scale deposition)[2], at this point the chemical is no longer efficient at inhibiting scale formation and it is necessary to stop production and re-squeeze the well in order to stop the formation of scale. Needless to say the amount of SI retained has an important bearing on the potential lifetime achieved by the treatment, therefore the economic importance in squeeze lifetime enhancers [23].

In Figure 2.10 is illustrated an schematic representation of the three main scale squeeze treatment stages being displaced radially in a single layer, homogeneous permeability, evenly pressured well.

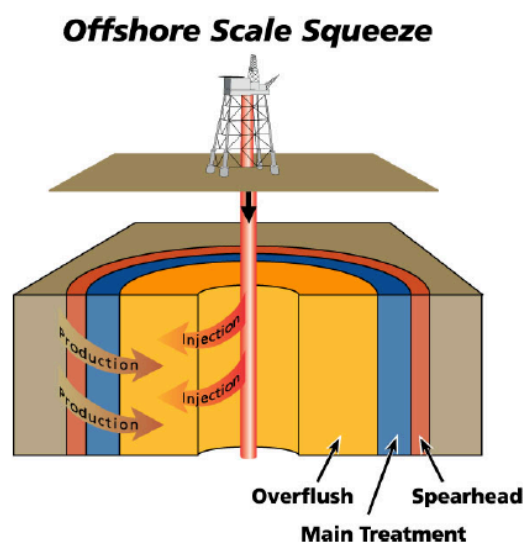


Figure 2.10 Schematic of the scale squeeze treatment stages [24]

Naturally, squeeze lifetime varies from well to well depending on a variety of factors such as production rate, watercut, and the geology of the reservoir. Squeeze lifetime has been evaluated based on inhibitor return concentration and cumulative water treated[8]. Reducing cost and prolonging the squeeze lifetime is essential; empirical data from each field and laboratory studies should be used to design and determine specific criteria for re-squeezing each well. Any shutdown of well caused by squeeze treatment has a significant impact on asset-revenue generation. Therefore one of the main objectives of the present downhole scale management strategies has to be maximizing squeeze lifetime through development and deployment of new technology [13].

There are a number of techniques, which have been developed to increase scale inhibitor retention on the rock formation, thus enhancing the lifetime of a squeeze treatment. These include [2]:

- Precipitation squeeze treatment
- Use of some transition metal ions and Zn^{2+} ions
- Raising the pH in situ
- Mutual solvents to change the rock wettability
- Blends with cationics polymers
- Incorporating cationic monomers in the scale inhibitor polymer structure
- Crossed-linked scale inhibitors.
- Use of kaolinite or other clay that enhances inhibitor adsorption
- Scale inhibitor microparticles

For the purpose of this research the focus will be on scale squeeze treatment with the use of a surfactant to change the rock wettability hence increasing the inhibitor adsorption to the rock [25]. It is believed that a cleaning of the rock surface extends the treatment lifetime, by removing organic material and therefore increasing the surface available for the inhibitor to adsorb to [13].

2.6 Rock Properties and petrophysics

2.6.1 Porosity and permeability

“The specific definition of porosity is the ratio of the pore volume (or void space) in a reservoir rock to the total volume (bulk volume) and is expressed as a percentage” (Dandekar, 2006). Porosity is the measure of the void space within the rock and it is considered in reservoir rocks as its storage capacity (figure 2.11). The more open space the rock has, the higher capacity it has to contain oil, making porosity one of the most important parameters from the reservoir engineering point of view [26].

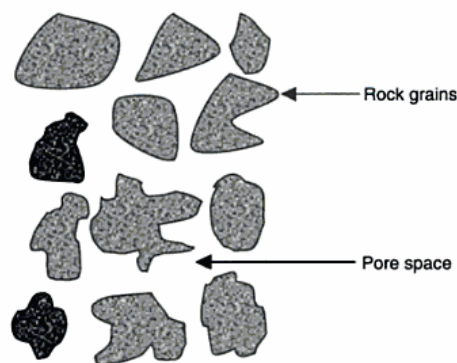


Figure 2.11 Representation of porosity [27]

2.6.2 Permeability and Darcy's law

“Permeability is the ability of a porous rock to transmit a fluid under the pressure gradient” [28], it is represented by k and is one of the most significant parameters in determining the production potential in a producing formation (figure 2.12). Contrary to porosity, permeability is a dynamic property that needs to be tested to be characterized by flow experiments [27].

Permeability is divided into three categories: absolute, relative and effective permeability. Absolute permeability is when the rock is 100% saturated with a single fluid (oil, water or gas) in the rock pore space with that fluid[28]. Effective permeability is the ability of the rock to conduct another fluid phase, in the presence of more than one fluid, and implies that all but one phase is immobile (gas, oil or water, represented by the K_g , K_o , and K_w respectively) [26].

Relative permeability is a measure of the ease of flow for two or more immiscible phases in a porous medium, and it is the ratio of effective permeability to the absolute permeability of the rock, hence relative to that phase permeability k_r [29, 30].

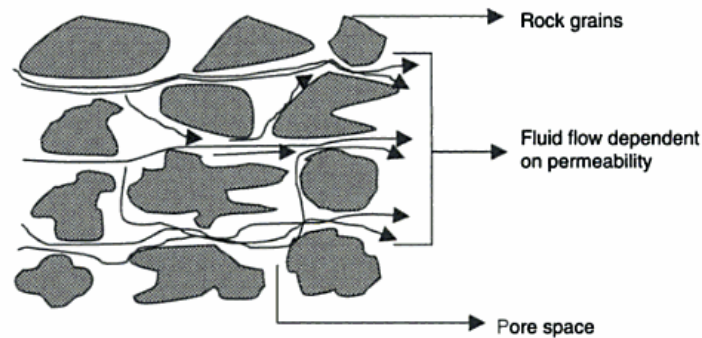


Figure 2.12 Representation of Permeability [27]

Permeability is primarily a property of the medium properties, it shows different behaviors with different fluids, as it depends on the rock wettability. This means if the mobile phase does not wet the rock surface, then it will be situated in the central parts of the pores. On the other hand, if the immobile phase wets the rock surface, then the central parts of the pores will be free for the mobile phase to flow through, hence the distribution, amount and properties of the immobile phase have an effect on the effective permeability [28].

Henry Darcy, a French engineer developed a method for measuring permeability in the 1850's which we now call Darcy's law, it is a fluid flow equation that even now is very relevant for a petroleum engineer. The equation is formulated in differential form as follows[26]:

$$u = \frac{q}{A_c} = -\frac{k}{\mu} \frac{dp}{dl}$$

Where:

u = fluid velocity, cm/s

q = flow rate, cm³/s

k = permeability of the porous rock, Darcy (0.986923 μm^2)

μ = viscosity of the fluid, centipoises (cP)

l = length of the rock sample, cm

$\frac{dp}{dl}$ = pressure gradient in the direction of the flow, atm/cm

Permeability is measured in an arbitrary unit called Darcy. One Darcy is relatively high permeability because in most of the reservoir rocks the permeability is lower than 1 Darcy, to avoid using fractions, a smaller unit, the millidarcy (mD) is used (1D = 1000 mD) [26]. "One Darcy is 1cm³ per second of a fluid having viscosity of 1 cP flowing through a 1 cm³ cross section of rock under a pressure gradient of 1 atm/cm"[28].

From Darcy's equation[27]:

$$1 \text{ darcy} = \frac{(cm^2/sec)(cP)}{(cm^2)(atm/cm)}$$

Where:

$$1cP = 1.0 \times 10^{-7} \text{ N sec/cm}^2$$

$$1 \text{ atm} = 10.1325 \text{ N/cm}^2$$

$$1D = \frac{(cm^3/sec)(1.0 \times 10^{-7} \text{ N sec/cm}^2)}{(cm^2)(10.1325 \text{ N cm}^2/cm)}$$

$$= 9.869 \times 10^{-9} \text{ cm}^2$$

$$= 0.986923 \mu\text{m}^2$$

2.6.3 Relative Permeability

Relative permeability is defined as "the ratio of the permeability to a fluid at a given saturation divided by the permeability to the same fluid at 100 percent saturation of that fluid" [31]. Darcy's law was originally formulated to measure permeability in a porous medium with a 100% saturated single phase fluid, however petroleum reservoirs with these characteristics very seldom exist. Under these circumstances when more than one fluid phase is flowing through a porous medium that the flow of one phase interact with the other, this interaction is a competition for the flow paths and therefore the importance of accurately describe it [27].

The quantification of relative permeability allows comparison of the ability of different fluids to flow in the presence of each other, since the presence of more than one fluid generally hinders flow. Thus in the case of two immiscible and mobile phases, flowing through a porous medium, the flow behavior is described by two phase relative permeability [31].

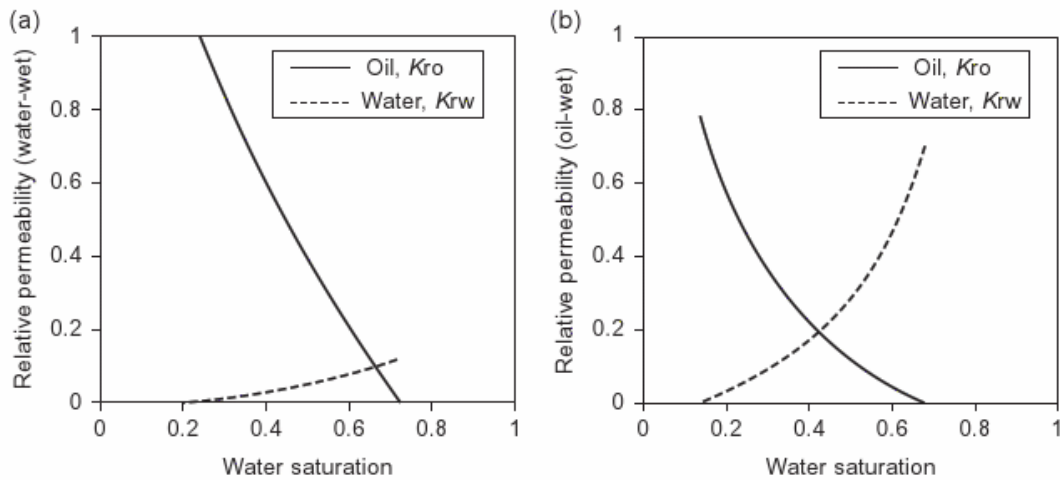


Figure 2.13 Typical oil-water permeability curves for a (a) water-wet and (b) oil-wet systems [32]

2.6.4 Permeability – Porosity relationships

There is no direct relationship between porosity and permeability; porosity refers to the magnitude of a void or a pore space whereas permeability is about the continuity of those pores. The only quantitative relationship is at both extremes, that is when porosity is zero then permeability is zero and when porosity is 100% then permeability is infinite [27].

However despite this relationship there is no fundamental trendline between these two properties. It has been shown that the correlation between them can be very useful, particularly when it is from the same type of formation[32] (figure 2.14).

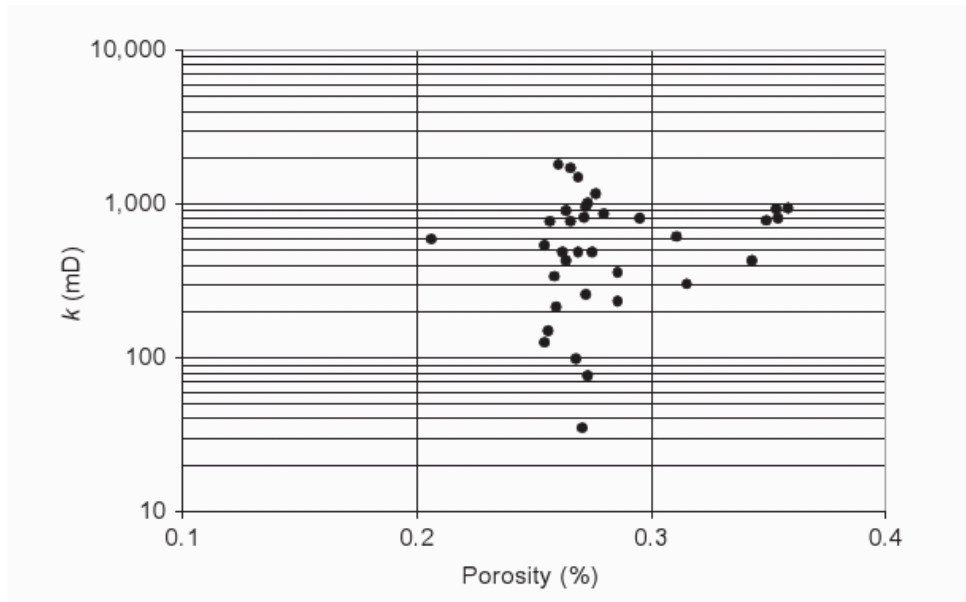


Figure 2.14 Permeability-porosity correlation in sandstone reservoir [27]

In 1927 Josef Kozeny derived one of the most relevant equations to correlate permeability as a function of porosity and specific surface area [28]. The modified Carman-Kozeny equation can be used for the two-phase k_r of porous media with arbitrary wettability [30].

2.6.5 Formation resistivity and water saturation

Fluid saturation or pore space saturation quantifies from the available pore space, how the three phases (gas, water, oil) are distributed or partitioned between them [27]. It is considered to be a very relevant factor because it is key in determining the actual amount of oil in a reservoir. A miss calculation can result in an over or underestimation of the amount of oil having potentially elevated economic losses, e.g. investment in a field where the production is not economically feasible due to the low extraction potential [33].

Fluid saturation also has important influence on flow properties due to the strong impact it has on relative permeability. It is “generally defined as the ratio of the volume of a fluid phase in a given reservoir rock sample to the pore volume of the sample” (Dandekar, 2006), and it can be expressed by the next equation [27]:

$$\text{fluid saturation} = \frac{\text{total volume of the fluid phase}}{\text{pore volume}}$$

The equation can be used to find the desired phase where S_g , S_o and S_w represent gas, oil and water saturation respectively. The fluid saturation should be reported either as the effective or a fraction of the total pore volume[27] as noted in the next equation[28]:

$$S_o + S_w + S_g = 1$$

$$V_o + V_w + V_g = 1$$

Residual oil saturation

Denoted by S_{or} the residual oil saturation can be approached by reservoir engineers in two different ways: one is the remaining oil in a reservoir after primary production and the other is the final oil saturation in a reservoir rock sample at the end of a laboratory gas or water displacement test [28], for the scope of this research, focus will be solely on the latter.

If a core plug 100% saturated with oil is injected with another phase (water, gas), the remaining or trapped oil left behind in the core is the residual oil saturation, which means that even with further injection of the fluid, it will flow through bypassing the remaining oil [34] (figure 2.15).

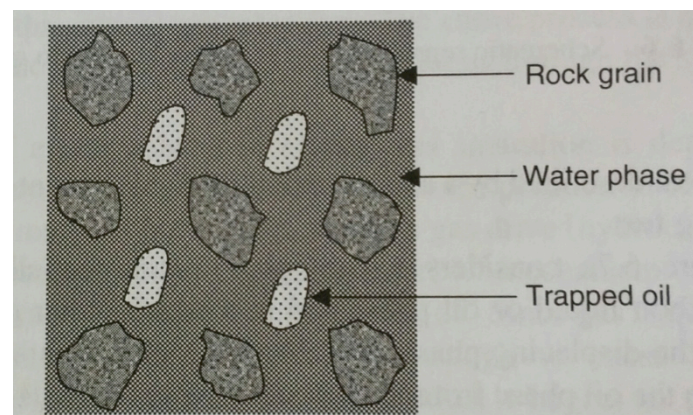


Figure 2.15 Oil trapped inside the pores of a core plug [27]

The main techniques for determination of residual oil are the following [35]:

1. Core measurements taken with pressure core barrel in a depleted section of the reservoir.
2. In-situ measurement via logging.
3. Measurements on non-pressured cores.

Irreducible water saturation

“Irreducible water saturation, denoted by S_{wi} , is defined as the minimum water saturation or the least water value of water saturation in a porous medium” (Dandekar, 2006). The amount of water present varies from 100% to close to zero, and even considering that fluids are usually arranged according to density and gravity, connate water is distributed throughout the reservoir, this is mainly due to capillary forces, rock wettability and lithology [36].

Irreducible water saturation can be measured by coreflood and centrifuge tests; in the coreflood test, the core is placed in a coreholder then is filled with brine, next oil is injected to displace the water until no more water is produced, then the final stabilized water saturation obtained is defined as the S_{wi} , the numerical value can be achieved with a simple equation. The centrifuge (figure 2.16) test consists of a series of coreholders positioned in a centrifuge, the cores to be tested are placed in this coreholders and set to spun, at different specific speed throughout the test. The centrifugal force pushes the water out of the core into a measuring device, this process keeps going until the amount of water expelled is zero, then the amount of water is noted and used to calculate the S_{wi} . In this test, the centrifugal force serves as a substitute for the gravity forces that exist in the reservoir[34].



Figure 2.16 Centrifuge used for Swi

The most accurate test is the one that reflects the true capillary forces that exist in the reservoir prior to production. Centrifuge tests have been established as the preferred method of measuring capillary pressure on individual core plugs [34].

2.7 Surfactants and wettability

2.7.1 What is a surfactant?

A surfactant describes a group of compounds known as amphiphiles or amphipathic compounds that are surface active (surface active agent). They are molecules that contain a part that has affinity for non-polar media (hydrophobic) and one part that has affinity for polar media (hydrophilic). The proportion between the hydrophilic and hydrophobic section can lead to molecules that are very soluble in water or ones that are very insoluble, this known as the hydrophilic-lipophilic balance or HLB [37].

Surfactants are surface active agents that have the ability to form oriented monolayers at interfaces, and strongly adsorb at surfaces, or are located at interfaces, thereby altering the physical properties of those interfaces. At the interface they can lower the interfacial tension[38]. They can form what is

known as Gibbs monolayers, which is when the molecules form a film at the air-aqueous solution interface with the hydrophobic tail oriented towards the air and the hydrophilic part portion immerse in the water as in figure 2.17 [39].

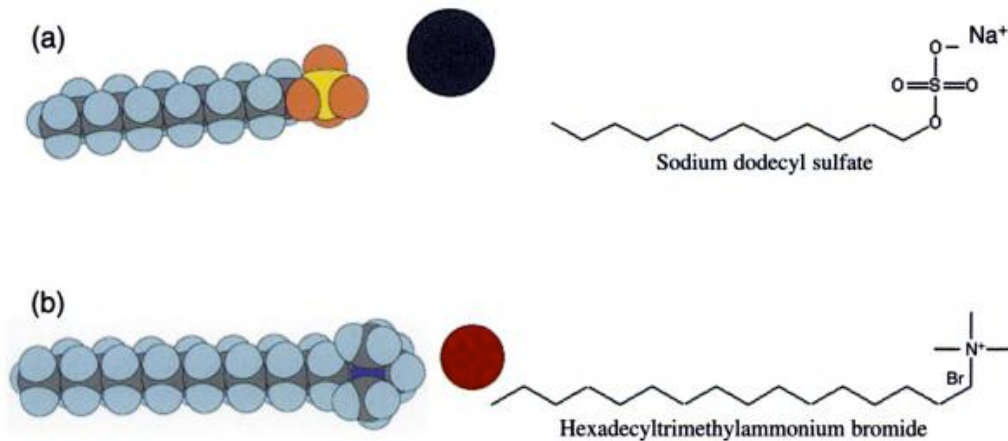


Figure 2.17 Representation of a surfactant (a) anionic (b) cationic [40]

The most helpful classification of surfactants is based on the nature of the hydrophile, with subgroups based on the nature of the tail or hydrophobe, the four basic classes are as follows[41]:

- Anionic: the hydrophile is a negatively charged group, such as carboxyl, sulfonate, sulfate of phosphate
- Cationic: the hydrophile is positively charged, such as the quaternary ammonium halides
- Nonionic: the hydrophile has no charge
- Amphoteric (and zwitterionic): the molecule has the potential to have both charges a negative and a positive

A surfactant can generate ultralow interfacial tension between oil and water, a surface and by reducing the interfacial tension reduces the capillary pressure and residual oil saturation, which then results in an increase in the water relative permeability [42, 43]. However different types of surfactants can give very different results, hence the need for a customized and detailed study [44].

CMC value

The critical micelle concentration (CMC) is the point where above it, surface tension becomes independent from concentration. This is an indication of the formation of aggregates. In fact many of the solution properties show a drastic change at this point Figure 2.18. The CMC value is defined by as “the concentration of maximum solubility of the monomer in that particular solvent” [45].

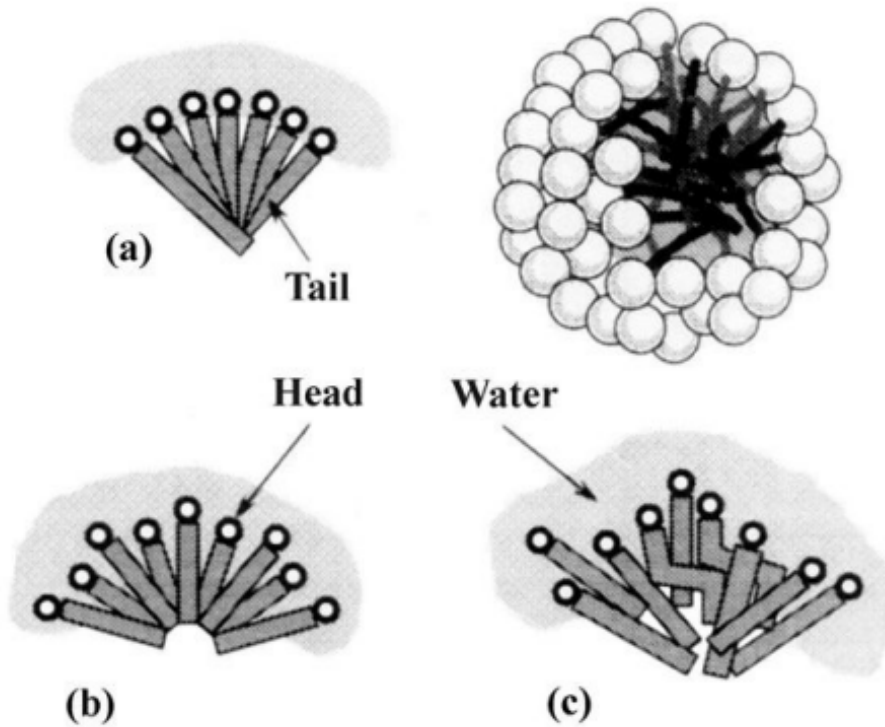


Figure 2.18 Schematic representation of a micelle (a) overlapping tails in the center (b) water penetrating to the center (c) chains bending [46]

It is important to know the CMC value because the surfactant must be at concentration higher than the CMC to show the best effect on the required objective, i.e. change in wettability, foam stability, etc. The two most common methods of finding the CMC value is to plot some of the physic chemical properties of the solution against the concentration and observe the sudden change in the plot [45] (Figure 2.19), or because the non-associated surfactant concentration no longer increases above the CMC [47].

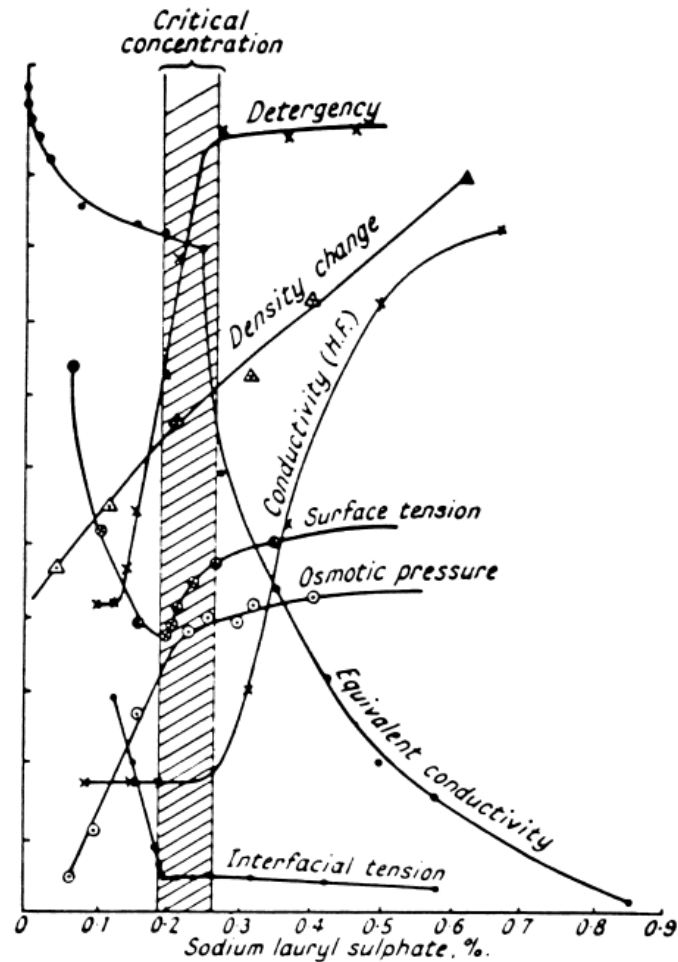


Figure 2.19 Representation of the changes in physical properties at the CMC [45]

Krafft and cloud point

The krafft point (T_k) is a certain temperature at which ionic surfactants have an abrupt rise in solubility, and it is considered as the lowest temperature at which the solubility is above the CMC [39]. In other words, as the temperature rise so does the solubility until at T_k it reaches the CMC, and above this point is when the maximum reduction in interfacial tension or surface occurs [45].

On the other hand, nonionic surfactants don't have a krafft point. Instead their solubility decreases as the temperature rise, then at a certain temperature known as the cloud point, the micelles from the surfactant solution separate out, and the solution face a marked increase in turbidity. The process is reversible once the temperature is lowered below the cloud point [39, 45].

Interfacial tension

An interface may be described as the boundary between at least two miscible phases[41]. The interfacial region can be very important due to the many chemical reactions taking place there; in addition many processes in the oil industry include the use of emulsions, foams and suspensions all of which have large interfacial areas.

Surface tension can be explained by Van der Waals attractive forces, all of the molecules in a liquid are attracted in the same magnitude except for those in the interfacial region[39]. Atoms or molecules at the interface will experience an asymmetric force field due to their interaction with adjacent units, this means they will have a higher energy level than identical molecules in the bulk [41]. This will pull these molecules to the interior in order to maintain equilibrium and comply with the minimum energy rule, these conditions lead to a contracting force at the surface known as interfacial tension[45].

Reduction of surface or interfacial tension is probably one of the most required properties in a surfactant solution. Surfactants have a tendency to contract spontaneously in order to minimize the surface area [48]. “When present in relatively low concentrations, such materials will preferably adsorb at available interfaces, replace the higher energy bulk phase molecules, and result in a net reduction in the free energy of the system as a whole” (Myers, 2006).

The surface tension or interfacial tension reduction of a liquid is determined by the energy of the molecules in the interfacial region, and it depends on the exchange of solvent molecules at the interface by surfactant molecules. It is the relationship between the amount of an adsorbing molecule and the rate of adsorption under certain circumstances that indicates the different surfactants effectiveness in applications where surface tension lowering is of importance [41, 48].

In aqueous solutions the relation between packed, polar water molecules, and relatively sparse, nonpolar phases, explain the action of surfactants in lowering the surface and interfacial tension of aqueous solutions, and why it is not so effective when it comes to affect the surface tension of organic liquids. This is because the molecular nature of the organic liquid and the surfactant are not sufficiently different to make adsorption satisfactory [45].

Wettability

“Wettability is the term used to describe the relative adhesion of two fluids to a solid surface” (Donaldson, 2011), it is a property that in a porous medium such as a reservoir rock can give a measure of the preference of one of the fluids (oil or water) to “wet” or spread to the surface [32]. At the point of intersection between two fluid phases and the solid surface a contact angle is produced (Figure 2.20). If the system is in equilibrium, then the fluids are not moving and are thermodynamically stable. Young’s equation denotes the equilibrium relationship [45]:

$$\gamma_{so} - \gamma_{sw} = \gamma_{wo} \cos\theta$$

Where:

γ_{so} = interfacial tension between a solid and oil

γ_{sw} = interfacial tension between a solid and water

γ_{wo} = interfacial tension between water and oil

θ = contact angle

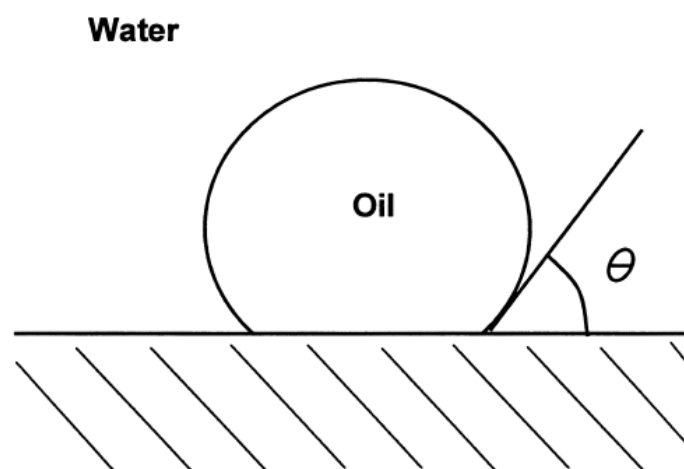


Figure 2.20 Contact angle measured through the water phase [45].

In a water-wet system, water will take over the smaller pores and spread over the majority of the surface of the larger pores, on the other hand if the rock surface is “oil wet” the rock will imbibe oil into the smaller pores. An example of a water-wet is: in oil saturated system water displaces the oil from the surfaces and imbibes into the smaller pores (this is when the system is in contact with water), thus when the two fluids are present in water wet system, the core will imbibe water, conversely in oil wet core will imbibe oil [32].

Wettability is easily determined by the way in which a surface shapes the droplets of a liquid situated on this surface, where the interfacial forces of the three phases interact with each other [39]. Measuring the contact provides direct macroscopic measurement of the wettability of a surface. One of the most used techniques to measure the wettability is by contact angle between the surface and the liquid. It is customarily measured through the water phase.

Contact angles can be static or dynamic, and dynamic can be advancing or receding. The spreading coefficient is the change of the free energy due to the spontaneous spreading of the wetting fluid, in terms of interfacial tensions can be written as [49]:

$$S_{ws} = \gamma_{so} - \gamma_{wo} - \gamma_{sw}$$

Where:

S_{ws} = spreading coefficient

A surfactant is a tool that can be used to change the wettability of a surface. This is obtained by lowering the interfacial tension between liquid and solid and consequently lower the contact angle and increase the tendency of the liquid to spread over the solid. In a porous rock, the surfactants can be used to improve the permeability or to change the distribution of fluids in the reservoir. However much remain unknown about the interactions between a rock reservoir and surfactants[50].

3 Experimental

The objective of this thesis is to test the effect of a surfactant as a preflush on scale inhibitor adsorption for increasing squeeze treatment lifetime. A common way to test this is through a coreflood test. For this there were three steps required beforehand. Those tests are a static adsorption test to select the scale inhibitor, then a static adsorption test to perform a quick screening of the surfactants and an ageing of the cores in order to change their wettability. These three steps will be explained in more detail further in this chapter.

A phosphonate was chosen as scale inhibitor because is analytically easier to handle, the results may be only applicable to scale inhibitors with the same functional group, more tests would be required in order to determine if the results are applicable to other type of SI.

3.1 Core Ageing

3.1.1 Theory

Many return permeability tests are performed on extremely water-wet cores, this can lead to a reduction in permeability and that can be interpreted as core/formation damage. Unrepresentatively high wettability alteration in the laboratory may lead to wrong conclusions [51].

The material used for the experiments was an initially extremely water-wet berea outcrop sandstone material. The need for ageing the cores in order to change their wettability was considered necessary to get more representative results.

3.1.2 Materials and equipment

Core

Extremely water wet Berea Outcrop Sandstone was used of approximately 100mD absolute permeability. Berea sandstone is the rock most frequently

used in coreflood experiments, they are extracted in Amherst, Ohio by Cleveland Quarries Company[52].

The material used for tests was a single 30cm long 1.5” diameter section of Outcrop Berea was cut into 6 approximately 5cm long cores.

Brine Composition

A simulated formation water from the North Sea was used (composition table 3.1). Bi-carbonate and sulphate were not added to the brine to prevent scaling from occurring in the core, as this was not the objective of the tests.

Table 3.1 Synthetic Brine Compositions

Ion	Formation Water (mg/l)
Sodium	14500
Calcium	400
Magnesium	100
Potassium	120
Barium	50
Strontium	44
Sulphate	0
Bi-carbonate	0
Chloride	23914
pH	6.0

Synthetic Oil

Isopar L synthetic oil was used for all stages at ambient temperature (figure 3.1). Dead crude oil was not used at ambient temperature to prevent wax and/or asphaltine plugging. Prior to use, the Isopar L oil was prepared as follows:

- Filtered to 0.45µm
- At T = Ambient, measured viscosity of 1.06cP.
- At T = 60°C, measured viscosity of 0.616cP.

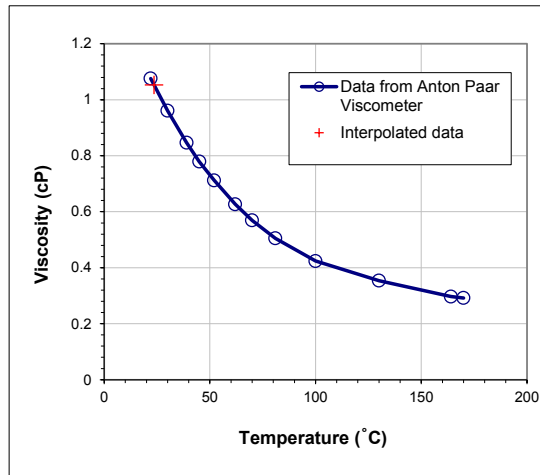


Figure 3.1 Measured Isopar L Viscosity, Anton Paar

Crude Oil

Dead crude oil from a North Sea production system was used for all stages at increased temperature. Prior to use, the dead crude oil was prepared as follows:

- Stirred
- Heat to $T = 60^{\circ}\text{C}$
- Stirred
- Filtered to $5\mu\text{m}$ into heated glassware
- Stored at $T = 60^{\circ}\text{C}$ until required

At a temperature of $T = 60^{\circ}\text{C}$, the dead crude oil had estimated viscosity of 4.6cP. Crude oil viscosity at $T = 60^{\circ}\text{C}$ was estimated by assuming that the effective oil permeability at S_{wi} measured to Isopar L and crude oil were equal at $T = 60^{\circ}\text{C}$.

Equipment

- M-I SWACO Custom Made Dual Coreflood Rig
- URC-628 ULTRA ROCK CENTRIFUGE
- Ageing Cell

3.1.3 Procedure

1) Core Preparation & Basic Measurements

The objective of this stage is to:

- Solvent clean & saturate cores with brine
- Measure absolute permeability

Test conditions

Table 3.2 Core Preparation Test Conditions

Overburden Pressure, P_o Bar	Pore Pressure, P_p Bar	Temperature °C
30	10	Ambient

1. Trim cores to maximum 5cm length for future use in rock ultra-centrifuge.
2. Measure core dimensions & weight.
3. Mount cores into coreholder.
 - Rather than performing measurements on all 6 cores individually, two composite cores were made comprising of Cores 1 - 3 & 4 - 6.
 - Absolute permeability of each individual outcrop Berea core was assumed to be equal and therefore the composite permeability was equal to the permeability of each individual core.

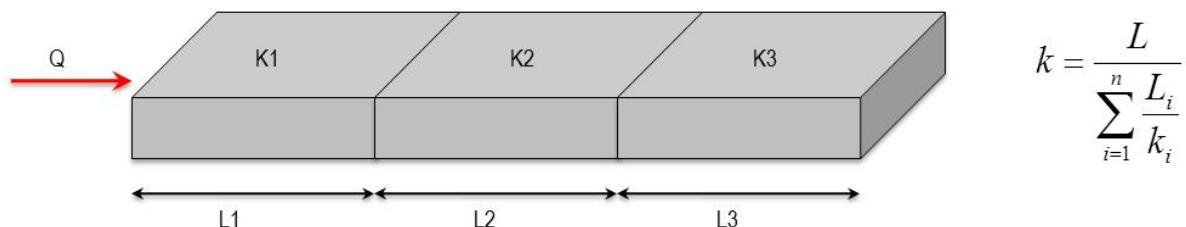


Figure 3.2 Representation of composite cores 1 - 3 & 4 - 6

4. Increase overburden pressure.
5. Set system pore pressure.
6. Displacement of methanol with FW at $Q = 1\text{ml/min}$ for $\sim 10\text{PV}$.

7. Absolute Brine Permeability at 100% S_w , $Q = 1, 2, 3, 4$ & 1ml/min.
8. Dismount cores from coreholder.
9. Weigh saturated cores.
10. Store individual cores in FW.

2) Core Preparation to Irreducible Water Saturation (S_{wi})

The objective of this step is to:

- Take cores to Irreducible water saturation.

Table 3.3 Centrifuge Test Conditions

Capillary Pressure, P_c Bar	Rotation Speed RPM	Equilibrium Time Hours	Invading Oil	Oil Density sg	Brine Density sg
5	6100	20	Isopar L	0.763	1.023

1. The cores were placed into individual sample containers.
2. Mineral oil (Isopar L) was filled up to the designated level.
3. O-rings were added with grease to seal the core-holders.
4. The distribution-header and sieves were placed in the bottom of the core-container before inserting the core.
5. The distribution header was placed at the bottom, the thin metal sieve on top of the header and then the rubber sieve.
6. The core was then covered with Isopar L oil.
7. The lid was placed on top and more oil added through the lid using a syringe.
8. Finally the whole assembly was sealed with a screw.
9. The core-holders were then placed into the rotor.
10. The core-holders must have the same weight (within $\pm 0,1$ gram) to prevent the ultracentrifuge from wobbling.
11. The weight was adjusted by modifying the amount of oil with the syringe or by placing small pieces of lead on top of the core.
12. The weight-difference is a result of different core sizes.

13. The rotor was then put into the centrifuge and the speed adjusted based on the core parameters, oil & water density and the required capillary pressure.
14. The cores were spun with a rotational speed of 6100 RPM to generate 5 bar capillary pressure.
15. While spinning, the amount of water displaced from the cores by Isopar L oil can be seen in the small windows of the rotor (with the help of a narrow, collimated light-beam which is passed through cell).
16. The amount of water released when spinning the cores for 24 hours served to calculate the irreducible water saturation.
17. Once constant expelled water volume was recorded, the cores were deemed to be at S_{wi} (irreducible water Saturation) i.e. no free water in the core.
18. The cores were removed from the centrifuge and stored under Isopar L oil.

3) Isopar L Permeability at Irreducible Water Saturation (S_{wi}) & Displacement of Isopar L with Crude Oil

The objective is:

- Measure effective permeability to Isopar L Oil at Irreducible Water Saturation (S_{wi}) at both Ambient and $T = 60^{\circ}\text{C}$.
- Miscible displace Isopar L oil with Crude Oil at $T = 60^{\circ}\text{C}$ & measure effective permeability to Crude Oil at Irreducible Water Saturation (S_{wi}).

Table 3.4: Test Conditions at measuring S_{wi} & Displacement of Isopar L with Crude Oil

Overburden Pressure, P_o Bar	Pore Pressure, P_p Bar	Temperature $^{\circ}\text{C}$
62	10	Ambient & 60

Procedure

1. Mount cores into coreholder.

- Rather than performing measurements on all 6 cores individually, two composite cores were made comprising of Cores 1 - 3 & 4 – 6.
 - Based on relatively equal water saturation, oil permeability at S_{wi} of each individual outcrop Berea core was assumed to be equal and therefore the composite permeability was equal to the permeability of each individual core.
2. Increase overburden pressure at max. 50Bar per hour.
 3. Set system pore pressure.
 4. Effective Isopar L Oil Permeability at S_{wi} at ambient temperature, $Q = 1, 2, 3, 4$ & 1ml/min.
 5. Increase system temperature to $T = 60^{\circ}\text{C}$ & allow 3 hours equilibrium.
 6. Effective Isopar L Oil Permeability at S_{wi} at $T = 60^{\circ}\text{C}$, $Q = 1, 2, 3, 4$ & 1ml/min.
 7. Displacement of Isopar L with filtered crude oil at $T = 60^{\circ}\text{C}$, $Q = 1\text{ml/min}$, ~3PV.
 8. Effective Crude Oil Permeability at S_{wi} at $T = 60^{\circ}\text{C}$, $Q = 0.25, 0.5, 0.75, 1$ & 0.25 ml/min.
 9. Cool system.
 10. Carefully release system pressures.
 11. Dismount from coreholder.
 12. Cores were then stored under crude oil.

4) 45 Day Core Ageing under Crude Oil at $T = 90^{\circ}\text{C}$

Objectives

- Age the highly water wet Berea outcrop cores to “non-water wet” conditions.

Table 3.5: Test Conditions Core Ageing under Crude Oil

Ageing Time Days	System Pressure Bar	Temperature $^{\circ}\text{C}$	Core Saturation Condition
45	20	90	S_{wi}

1. Set the piston of the ageing cell to the correct position to allow all cores to fit inside.
2. Fill the back of the piston with water.
3. Mount cores front section of ageing cell.
4. Fill dead space in front section with dead crude oil.
5. Insert ageing cell into heating cabinet.
6. Pressure to required pressure.
7. Set pump limiter and operating mode to hold required pressure.
8. Leak check.
9. Increase temperature to $T = 90^{\circ}\text{C}$.
10. Leave for 45 days.

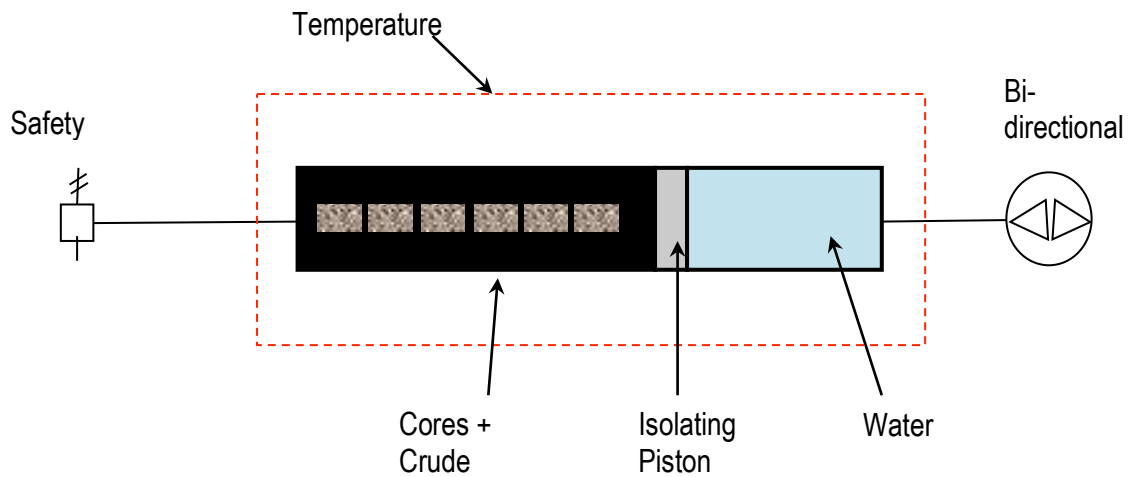


Figure 3.3 Ageing Set Up

3.2 Static Adsorption Test - Scale Inhibitor Adsorption

3.2.1 Theory/ objective

Static adsorption tests are used as a method for selecting the scale inhibitor by adsorption measurement for further coreflooding tests. The method consists on placing crushed formation rock into plastic bottles flooded with scale inhibitor solution, and measuring the scale inhibitor adsorption to the rock.

It is a test meant for a rapid screening, the information gathered from this tests is valuable but it not always show all the possible factors affecting the performance of the scale inhibitor [53].

3.2.2 Equipment and Materials

Equipment

- Oven
- Balance
- ICP-OES ICAP 6300 Duo

The ICP-OES, inductively coupled plasma optical emission spectroscopy, is technique to determine the elements based on measuring the characteristic emission of electromagnetic radiation from the element excited atoms and ions. The unknown sample was pumped to a nebulizer where the sample atomized to form a fine aerosol.

The sample is transported through the plasma (about 6000-8000 ° C), and the high temperature causes the sample components atomized and ionized. A small number of atoms / ions are excited, giving characteristic electromagnetic radiation as they return to their ground states.

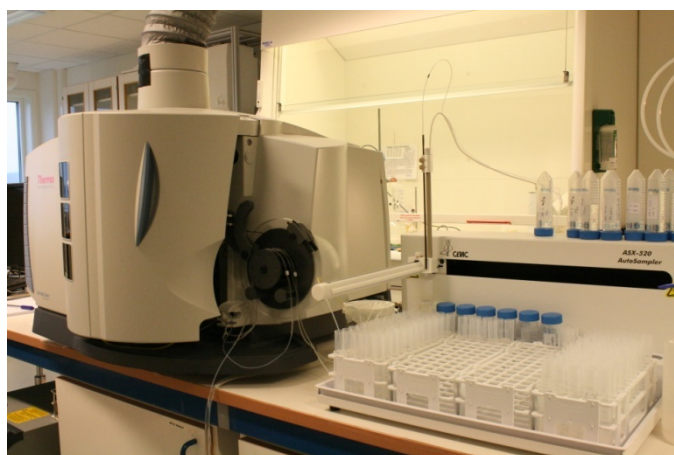


Figure 3.4 ICP-OES ICAP 6300 Duo

Chemicals:

- SI methylene phosphonic acid.
- SI methylene phosphonic acid with adjusted pH at 3.7.
- SI Bishexamethylenetriamine Penta (Methylenephosphonic Acid).

Sands:

As an adsorption medium two different types of sands were used: one collected from a separator in an offshore platform (Gulfaks), the other is clean sand from a beach (Bai Dao).

3.2.3 Procedure

1. Prepare 1.02sg NaCl (28.5g/l NaCl).
2. Prepare stock solution with 25000 mg/l of scale inhibitor in 1.02sg NaCl containing 100 mg/l Lithium.
3. Weigh 5 g of the sands into plastic bottles (glass bottles should not be used as scale inhibitor may be adsorb onto the quartz surface).
4. Make up duplicates (sample A and B) with 10 ml of the stock scale inhibitor solution to the bottles with sand.
5. Shake well and place them in the oven at 90° C.
6. Sample at 0 and 24 hours: extract about 3 – 4 ml and filter through a 0.45 μ filter into a 10 ml test tube.
7. Collected samples should be analyzed for P, Li, Ca, Mg, Sr, Ba, Fe, Na by ICP.

3.3 Compatibility Test

When selecting a scale inhibitor is an important prerequisite to perform a compatibility test with the SI and the brine and with any liquids that they will come in contact with [21]. The reason for this is to prevent deployment of chemicals into the formation that could cause formation damage due to precipitation, flocculation, emulsification or destabilization.

3.3.1 Theory/Objective

The test is used to confirm that there are no adverse effects when mixing two fluids.

3.3.2 Equipment and Materials

- Clear glass sample bottles.
- Scale Inhibitor.
- Formation water.

3.3.3 Procedure

The test was performed at ambient temperature and following the next steps:

1. Place the fluids in the clear glass sample bottles a ratio of: 50:50, 75:25 and 90:10 formation water and scale inhibitor respectively.
2. Shake the bottles and leave them for observation.
3. Observation was conducted for a period of 96 hours and observations were made at 0, 1, 2, 4, 24 and 96 hours.

3.4 Static Adsorption Test – Surfactant wash followed by Scale Inhibitor

3.4.1 Theory/Objective

The objective of this series of tests was to perform a quick screening of the surfactants to be used further in the coreflood tests. Literature shows contradictive information whereas an anionic or cationic are the best options [44], hence the need for this step previous to a coreflood.

3.4.2 Equipment and Materials

- Oven
- Balance
- ICP-OES ICAP 6300 Duo

The next surfactants solutions were tested, in table 3.6 are listed their main characteristics and properties:

Table 3.6 Surfactants Properties

Product ID	Chemical name/ group	Characteristics/ properties
H	Potassium Oleate Sulfonate - Sulfonates	- Anionic surfactant - Good wetting and low foaming properties
F	Tridecyl Alcohol Ethoxylate.	- Nonionic surfactant - Effective emulsifiers and emulsifier blend - Used as HLB variables
B	polyalkylene oxide block copolymer - Block Copolymers	- Nonionic surfactant - Good dispersing and wetting properties
E	Sodium Laureth sulfate, 3EO - Alkyl Ether Sulfates, Sulfates	- Anionic surfactant - Good foam and viscosity characteristics.
D	Sodium C14-C16 Olefin Sulfonate - Alpha Olefin Sulfonate, Sulfonates	- Anionic surfactant - Excellent viscosity and foam characteristics
G	Tridecyl Phosphate Esters, 6EO - Ethoxylated Phosphate Ester, Phosphate Ester	Provides particle size control, low coagulum, shear and freeze-thaw stability
A	Polysorbate 80 ethoxylated sorbitan ester based on a natural fatty acid (oleic acid).	- Non ionic - Effective at forming O/W emulsions
C		- Blend of non- ionic surfactants and water wetting agents

3.4.3 Procedure

1. Prepare relevant concentration of surfactant in 1.02sg NaCl (28.5g/l NaCl).

2. Prepare stock solution with 5000 mg/l of scale inhibitor in 1.02sg NaCl containing 200 mg/l Lithium
(higher concentration to account for dilution with surfactant).
3. Weigh 5 g of the sands into plastic bottles (glass bottles should not be used as scale inhibitor may be adsorb onto the quartz surface).
4. Prepare surfactant solution at required concentration.
5. Make up duplicates (sample A and B) with 10 ml of the surfactant solutions to the bottles with sand, and place them at 50°C.
6. Age for 2 hours with surfactant.
7. Remove 5 ml of surfactant solution.
8. Add 5 ml of scale inhibitor stock solution, shake well and place them at 90° C.
9. Sample at 0 and 24 hours: extract about 3 – 4 ml and filter through a 0.45 μ filter into a 10 ml test tube.
10. Collected samples should be analyzed for P, Li, Ca, Mg, Sr, Ba, Fe, Na by ICP.

3.5 Corefloods to Evaluate Scale Inhibitor Adsorption and Wettability Change on Aged & Non-aged Cores

3.5.1 Theory/objective

These corefloods tests were performed on 6 different Berea cores samples as indicated in table 3.7, to determine baseline differences in adsorption / desorption profiles based on wettability, the treatment used on each is also on table 3.7.

In order to produce “non-water wet surfaces”, Berea cores at S_{wi} (by ultra-centrifuge) were treated as specified in point 3.1 in this chapter. Coreflood number 1 was not submitted to this process as it was used as control of the water conditions.

3.5.2 Materials and equipment

Chemicals:

The squeeze products evaluated are shown in Table 3.6, 2Wt.% SI was selected so that the core was not oversaturated during treatment injection.

Table 3.7 Products Evaluated

Coreflood Number	Core	Pre-Flush	Main Scale Inhibitor Treatment
1	Unaged Extremely Water Wet Berea	1.02sg NaCl	2Wt.% BHPMP in 1.02sg NaCl + 500ppm LiCl
2	Aged Non-Water Wet Berea	1.02sg NaCl	2Wt.% BHPMP in 1.02sg NaCl + 500ppm LiCl
3	Aged Non-Water Wet Berea	500 ppm Product A	2Wt.% BHPMP in 1.02sg NaCl + 500ppm LiCl
4	Aged Non-Water Wet Berea	500 ppm Product B	2Wt.% BHPMP in 1.02sg NaCl + 500ppm LiCl
5	Aged Non-Water Wet Berea	10%wt. solvent	2Wt.% BHPMP in 1.02sg NaCl + 500ppm LiCl
6	Aged Non-Water Wet Berea	500 ppm Product C	2Wt.% BHPMP in 1.02sg NaCl + 500ppm LiCl

Table 3.8 Core Material

Coreflood Number	Core	Condition	Length (cm)	Diameter (cm)	Composite Absolute Permeability $K_w 100\%S_w$ (mD)	Unaged Initial Composite Effective Permeability $K_o S_{wi}$ (mD)	Porosity (Frac.)	Pore Volume (ml)
1	Berea 7	Unaged Extremely Water Wet	4.81	3.81	64.4	56.0	0.169	9.27
2	Berea 1	Aged Non-Water Wet	4.96	3.81	63.9	51.8	0.169	9.56
3	Berea 2	Aged Non-Water Wet	4.87	3.81	64.4	2.65	0.169	9.38
4	Berea 3	Aged Non-Water Wet	4.77	3.80	64.4	2.65	0.169	9.14
5	Berea 4	Aged Non-Water Wet	4.83	3.78	59.9	2.65	0.169	9.16
6	Berea 5	Aged Non-Water Wet	4.91	3.80	59.9	2.65	0.169	9.41

Test Fluids:

Oil:

Given that all core samples (both aged and unaged) were at S_{wi} at the start of each coreflood, Isopar L synthetic oil was used for all stages at ambient and

reservoir temperature. Previous studies have shown that synthetic Isopar L oil is an acceptable replacement for crude oil when using aged core samples.

Brine:

A simulated formation water from the North Sea was used, the composition is indicated in Table 3.1. Bi-carbonate and sulphate were not added to the brine to prevent scaling from occurring in the core, as this was not the objective of the tests. The brine was filtered to 0.45µm, degassed and pH adjusted before use. At the test temperature of $T = 90^{\circ}\text{C}$, the formation water had an estimated viscosity of 0.35 cP. Brine viscosity was estimated by assuming that the absolute brine permeability measured at ambient conditions and reservoir conditions were equal.

Equipment

- ICP-OES ICAP 6300 Duo
- M-I SWACO Custom Made Dual Coreflood Rig

The tests were performed in a specially designed “dual” coreflood apparatus (figure3.5), where two corefloods were conducted simultaneously, and where each core shares the same overburden pressure, pore pressure and temperature control system. All flow lines were Alloy 600 to limit corrosion by low pH fluids. HPLC pumps were used to pump oil, brine and chemical solutions. All transducers and transmitters were externally calibrated to ensure the accuracy of permeability data generated. All pressures and temperatures were continuously logged via a LabView system.

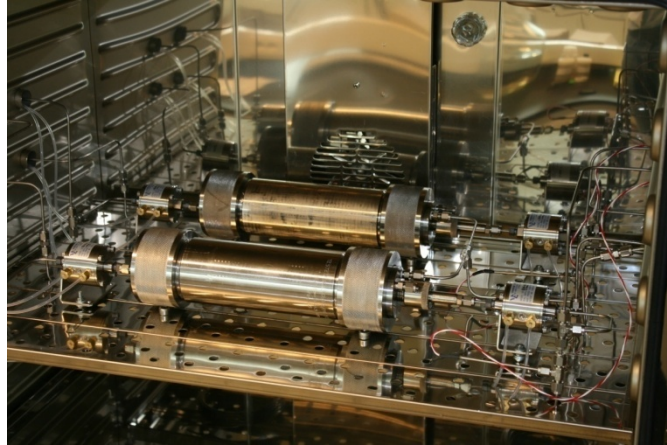


Figure 3.5 Formation damage lab dual core rig simulator

The coreflood test conditions are shown Table 3.9

Table 3.9 Test Conditions

Overburden Pressure, P_o Bar	Pore Pressure, P_p Bar	Reservoir Temperature $^{\circ}\text{C}$	Main Treatment Temperature $^{\circ}\text{C}$
100	20	90	50

3.5.3 Procedure

1) Ambient Stages (Formation to Wellbore Direction)

1. Add protective Teflon layers.
2. Mount core into coreholder.
3. Increase overburden pressure at max. 50Bar per hour.
4. Set system pore pressure.
5. Isopar L at $Q = 1\text{ml/min}$ for $\sim 10\text{PV}$ to Displace Crude Oil from Aged Core
6. Ambient Effective Isopar L Permeability at S_{wi} , $Q = 0.5, 1, 1.5, 2,$ & 0.5ml/min .
7. Increase system temperature to **$T = 90^{\circ}\text{C}$** .

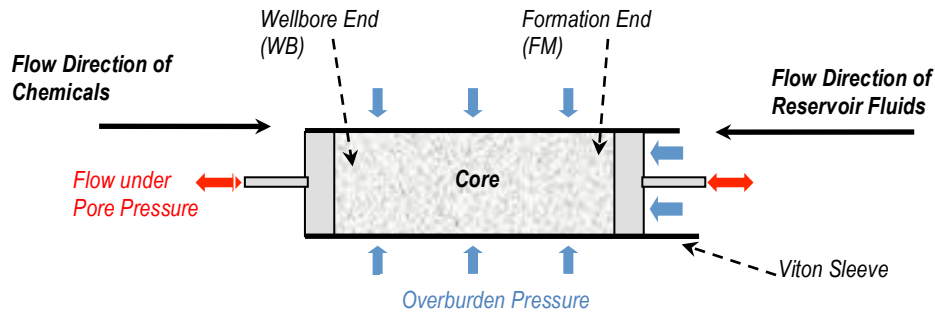


Figure 3.6 Schematic of Core Sample showing Flow Directions and Pressures

2) Pre-Treatment Stages (Formation to Wellbore Direction)

1. Isopar L Saturation at S_{wi} , $Q = 4\text{ml/min}$ (to displace any residual crude oil).
2. Effective Isopar L Permeability at S_{wi} , $Q = 1, 2, 3, 4 \ \& \ 1\text{ml/min}$.
3. Brine Saturation to S_{or} , $Q = 2 \rightarrow 4 \rightarrow 8\text{ml/min}$ (until stable).
 - Measure expelled oil volume for saturation control.
4. Pore Volume (Li tracer) at S_{or} , $Q = 1\text{ml/min}$.
 - 30 x 2ml Effluent Samples.
5. Effective Brine Permeability at S_{or} , $Q = 1, 2, 3, 4 \ \& \ 1\text{ml/min}$.

3) Treatment Injection (Wellbore to Formation Direction)

1. **Pre-Flush:** $Q = 1\text{ml/min}$, $T = 90^\circ\text{C}$, $\sim 3\text{ PV}$, 2ml Effluent Samples for Ca, Mg, Fe, Ba, Sr, pH & photography.
2. Cool System to $T = 50^\circ\text{C}$ (representing near wellbore cooling by pre-flush).
3. **Scale Inhibitor Treatment:** $Q = 1\text{ml/min}$, $\sim 5\text{ PV}$, $T = 50^\circ\text{C}$, 2ml Effluent Samples for "SI", Li, Ca, Mg, Fe, Ba, Sr, pH & photography.
4. Heat System to $T = 90^\circ\text{C}$.
5. Shut in core overnight ($\sim 18\text{ hours}$), $T = 90^\circ\text{C}$.

4) Post-Flush / Desorption (Formation to Wellbore Direction)

1. Post-Flush (chemical desorption) with brine, $Q = 1\text{ml/min}$, 1 Day, Effluent Samples for "SI", Li, Ca, Mg, Fe, Ba, Sr, pH & photography.

- Collect 60 x 2ml samples at the start of post-flush then switch to 18ml samples for remainder of post-flush.
2. Effective Brine Permeability at S_{or} , $Q = 1, 2, 3, 4$ & 1ml/min.

5) Post-Treatment Stages (Formation to Wellbore Direction)

1. Isopar L Saturation at S_{wr} , $Q = 2 \rightarrow 4 \rightarrow 8$ ml/min (until stable).
 - Measure expelled water volume for saturation control.
2. Effective Isopar L Permeability at S_{wr} , $Q = 1, 2, 3, 4$ & 1ml/min.
3. Brine Saturation to S_{or} , $Q = 2 \rightarrow 4 \rightarrow 8$ ml/min (until stable).
 - Measure expelled oil volume for saturation control.
4. Effective Brine Permeability at S_{or} , $Q = 1, 2, 3, 4$ & 1ml/min.

3.6 SQUEEZE 8 prediction software

The use of modeling software is a commonly used tool to design and optimize scale squeeze treatments. “Modelling is used at the core flooding stage to identify and quantify the degree of retention of the specific scale inhibitor on the rock substrate in question”(Mackey, 2003) [54]. Inhibitor retention can be assessed by the use of laboratory data from core flood tests, and scale squeeze prediction software. Information such as the effluent concentrations during postflush/ desorption can be used in to derive an inhibitor-rock interaction function, or isotherm. “The isotherm may be used to evaluate how the inhibitor will perform on a given well system. The performance of different inhibitors may be compared by using their respective isotherms to model the same basic treatment. The inhibitor that gives the longest squeeze life to its own MIC will usually be selected, everything else being equal” (Mackey, 2001) [55].

Freundlich Isotherm

A Freundlich isotherm is curve that relates the concentration of a solute on the surface of an adsorbent with respect to the concentration of the solute in the liquid with which it is in contact [54].

The constant k is mostly responsible for determining the maximum adsorbed concentration. The higher the value of k , the more mass is adsorbed at a given solution concentration, also at low concentrations gives a steeper isotherm. K tends to define the slope of the isotherm [55].

$$\Gamma_{eq} = K \cdot C^{\frac{1}{n}}$$

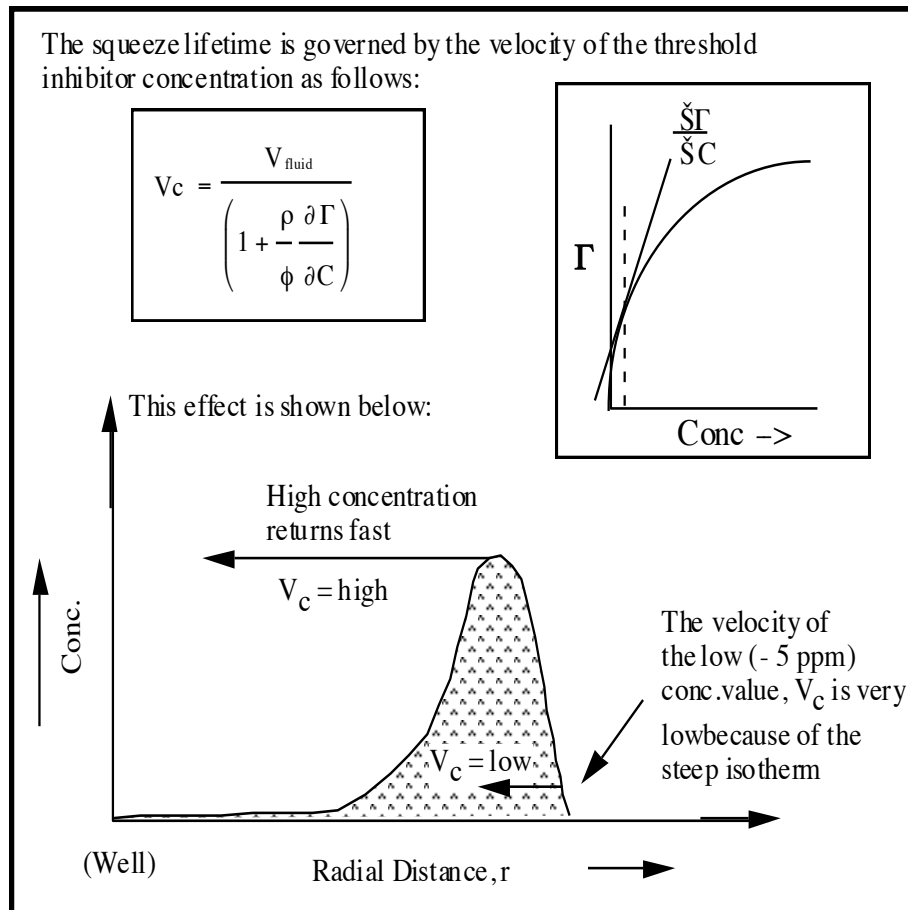


Figure 3.7 Representation of threshold velocity concentration in squeeze lifetime

The following information is needed to use the SQUEEZE 8 modelling program:

Procedure

1. Fill in all the information required by the software program (core length, core diameter, Volume of Inhibitor injected [ml], injected pore volumes, effluent concentration, etc)

2. Inset laboratory obtained effluent scale inhibitor concentrations vs pore volumes
3. Derive Isotherm
4. Center isotherm to match the lab data. This may be done manually, or by requesting an automatic extrapolation of the first two points in the derived isotherm.
5. Once an isotherm has been derived, it may be validated by using the derived isotherm to model the amount of inhibitor retention in the core, then match it with the experimental values, if the model is accurate, must represent the inhibitor retention

4 Results and Discussion

In the following chapter discussion and results about the experimental work will be presented. The main objective of these experiments is to test the effect of surfactants on improvement of scale squeeze treatment lifetime, and as mentioned in the previous chapter this was tested by simulating the well conditions in a rig simulator. Other tests were needed to get to the point of testing in the rig. Results are arranged according to the objective of each series of tests. Description and scope is indicated on each section.

4.1 Core Ageing

The cores were kept under ageing for a total time of 45 days, when they were taken out from the device a drop test was performed with the aim of verify if any change in wettability had taken place in them. According to literature assessing wettability by contact angle is a good indication of the wettability of a fluid over a given surface [56].

The objective of the “Drop Test” is to see approximate contact angle and dissipation time, hence give a qualitative indication of the wetting conditions of the material and a fluid.

To perform the “**Drop Test**” on both a non-aged core (extremely waterwet) and an aged, the following steps were taken:

- Lay core at S_{wi} in plastic weighing boat
- Remove any surface oil
- Place a single drop of brine on the core surface, photograph and start timer
- Record time until the droplet of brine has fully dissipated

Figure 4.1 to 4.6 show the drop test performed on both, an extremely water-wet Berea and a core that went through the process of ageing. The results show a relevant difference with contact angle and imbibition time. For the water wet core it took 30 seconds for the drop of brine to imbibe into the core, while for the

aged (non water-wet) the same drop took 10 minutes, giving a clear indication of the wettability change.

Non aged berea

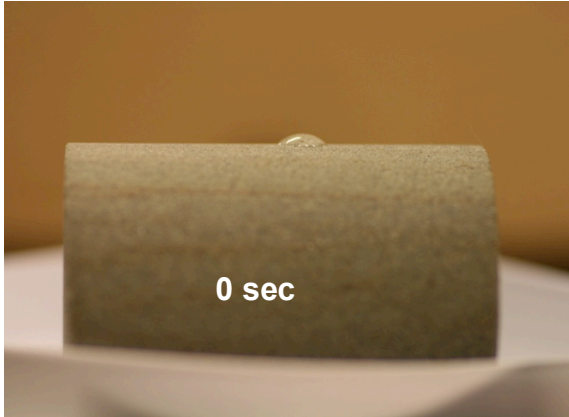


Figure 4.1 0sec

Aged berea

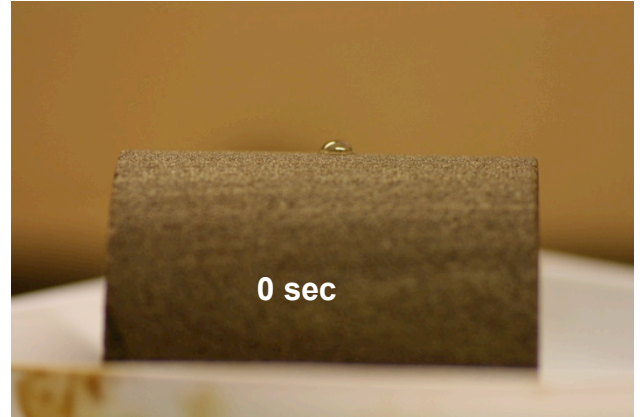


Figure 4.2 0sec

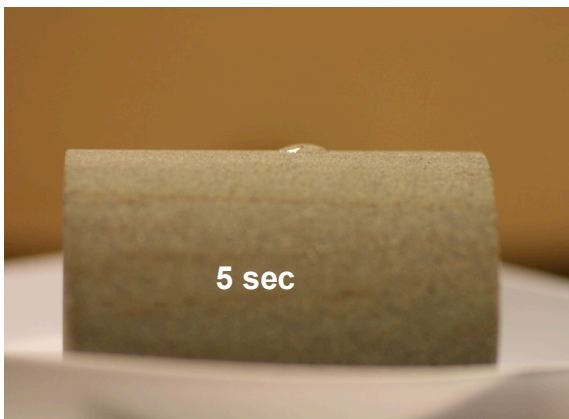


Figure 4.3 5sec

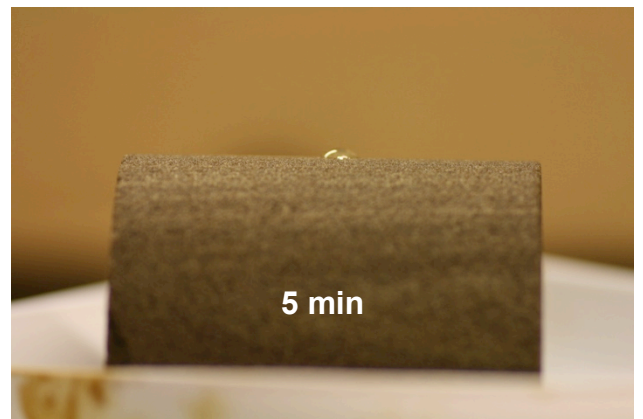


Figure 4.4 5min

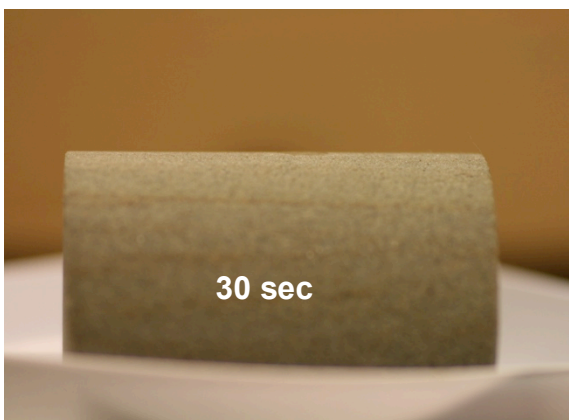


Figure 4.5 30sec

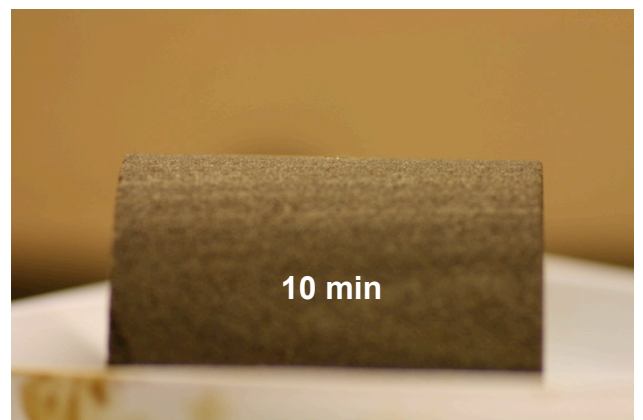


Figure 4.6 10min

4.2 Static Adsorption Test - Scale Inhibitor Adsorption

The objective of the test was to choose the optimal SI for the coreflood tests. It was performed with 2 different type of phosphonate SI, with different pH, two different sands and in duplicate. Figure 4.7 illustrates the adsorption of scale inhibitor to the sand.

During the test, the pH was adjusted using NaOH to limit the adsorption of scale inhibitor and be able to see more subtle changes in the adsorption. Test number 1, was performed using two different sands and a scale inhibitor solution of a Hydroxyethylamino-di (methylene phosphonic acid) with a pH of 4.

The results show insufficient Scale inhibitor adsorption to the sand; with the Bai Dao sand showing no adsorption.

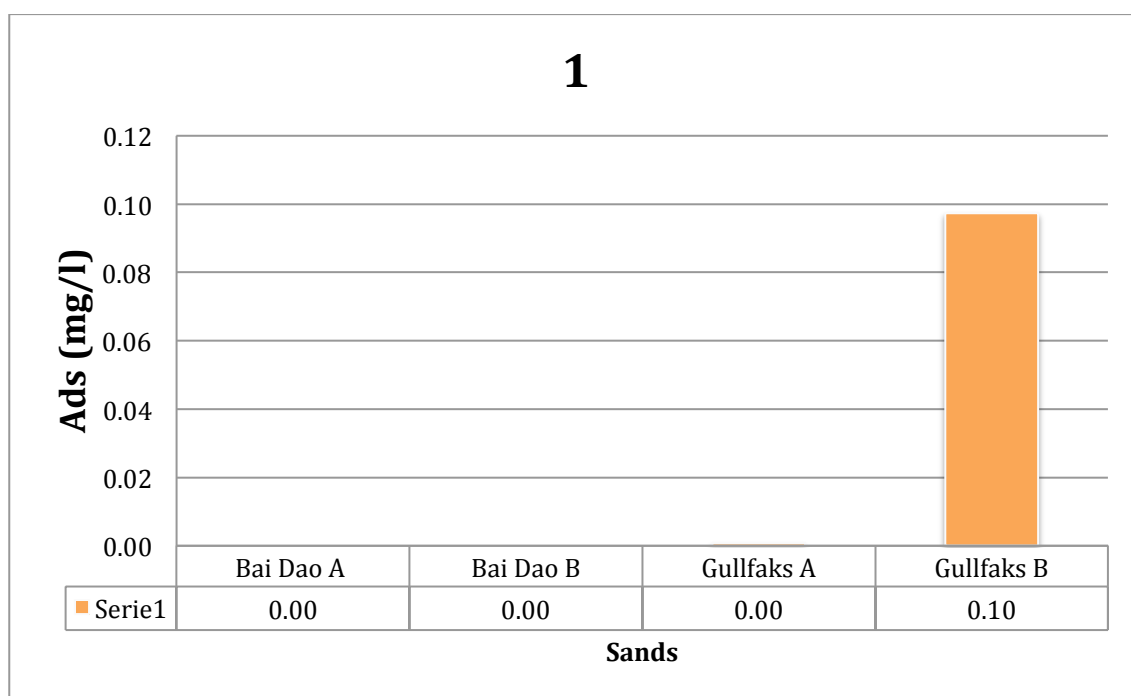


Figure 4.7 Static adsorption test #1

In test number 2, the same Hydroxyethylamino-di (methylene phosphonic acid) was used, in this case the ratio of scale inhibitor solution to sand was changed from 40 ml of SI to 5 g of sand to 10 ml of SI to 5g of sand.

The results illustrated in graph 4.8 show an improvement in the scale inhibitor adsorption with respect to test#1 for Gullfaks sands. However the results are still not relevant for Bai Dao sands. This could be due to the fact that Bai Dao sands lack of several clays and minerals.

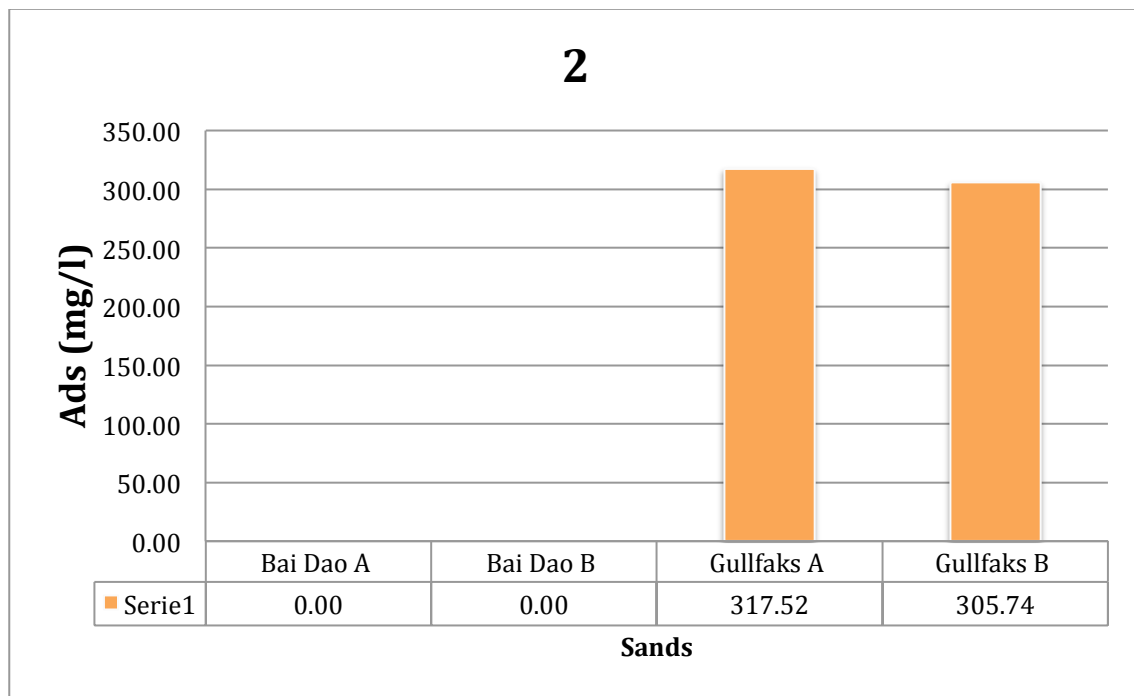


Figure 4.8 Static adsorption test #2

Static adsorption number 3 was performed using a Hydroxyethylamino-di (methylene phosphonic acid) with a pH of 3.5, it was done in duplicate and using two different sands. The difference with test number 2 is the change in the scale inhibitor pH.

The results of adsorption of scale inhibitor to the rock from this test are slightly under the results from test number 2, which are considered insufficient for the coreflood test; hence the next step will be test a different scale inhibitor. Results illustrated in figure 4.9.

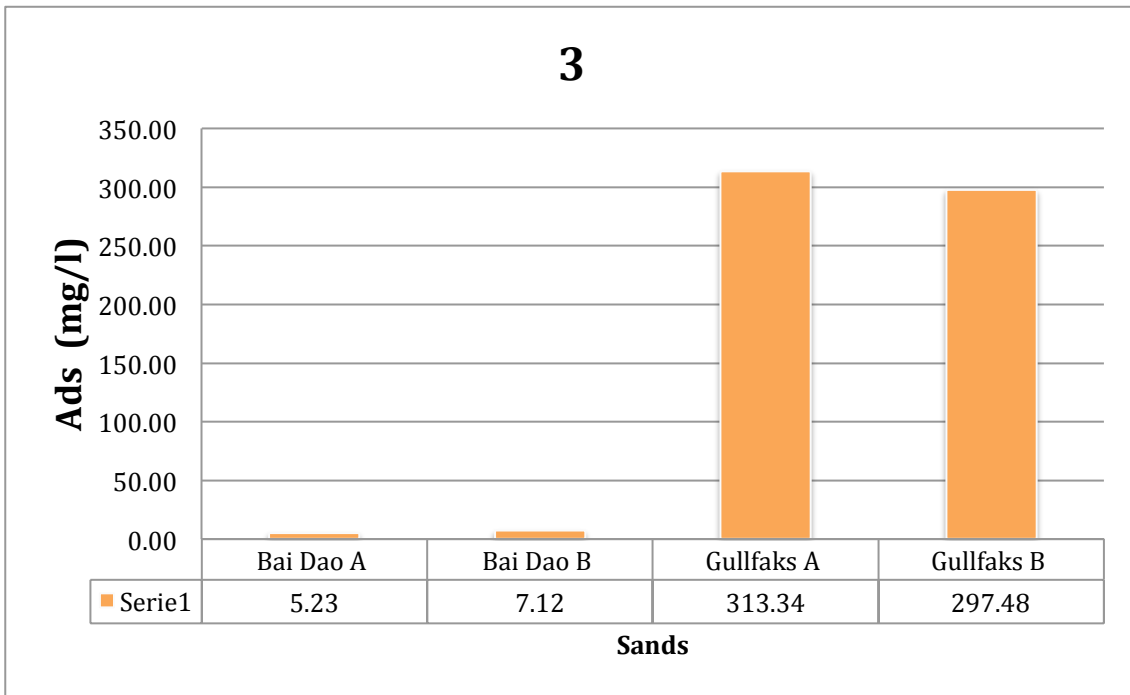


Figure 4.9 Results static adsorption test#3

Static adsorption number 4 was performed using a Bishexa methylene triamine Penta (Methylenephosphonic Acid) (BHPMP) as scale inhibitor, with a pH of 3.7, it was performed on duplicate and using 2 different sands. The results are illustrated in figure 4.10.

The results show a significant improvement in scale inhibitor adsorption in comparison with the previous tests, hence it was decided to use this SI for further coreflood tests.

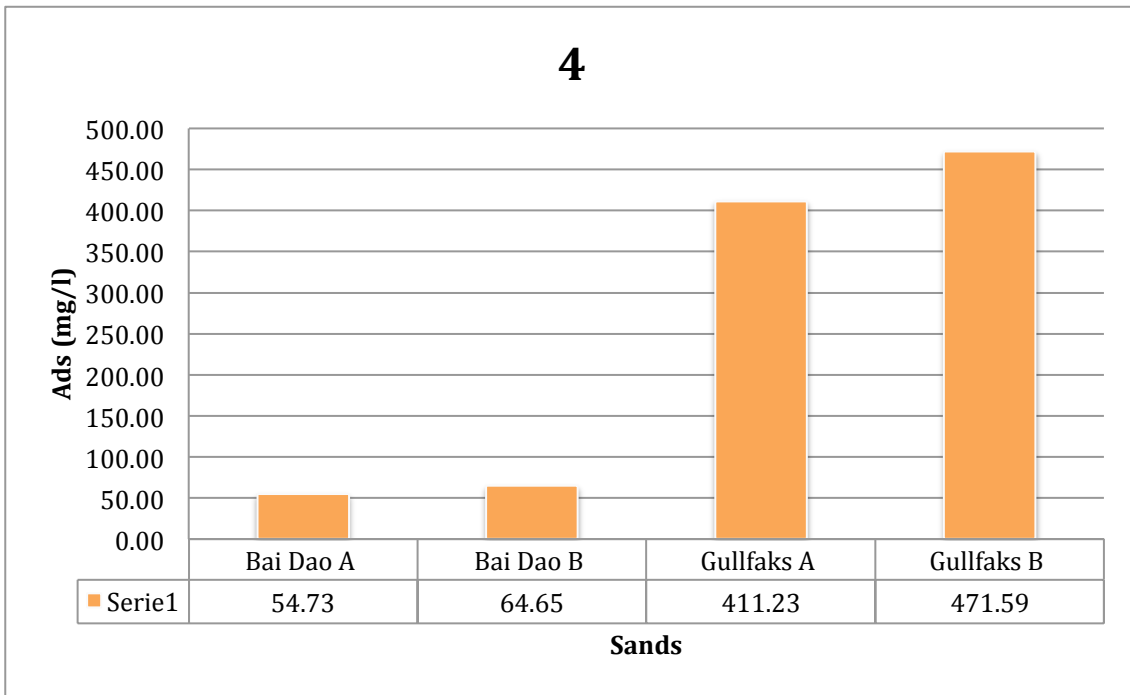


Figure 4.10 Results static adsorption test#4

4.3 Compatibility Test

A compatibility test was carried out to confirm no adverse effect between the formation water and the scale inhibitor. The following pictures figure 4.11 and 4.12 were taken at 0 and 96 hours respectively.

In the first periods of observation (0, 1, 2, 3, 4 and 24 hours) no relevant change in the solution was noticed. The observation at 96 hours presented slightly turbidity in the 50:50 ratio, no precipitation was observed. In the bottles with 75:25 and 90:10 ratios, no noticeable change was perceived.

The turbidity in the first bottle can be due to a slight incompatibility over the 24 hour test period at 90°C, however no negative outcome is expected due to the much lower ratio at which the formation water and scale inhibitor will be at the coreflood tests, and also because no precipitation was observed.

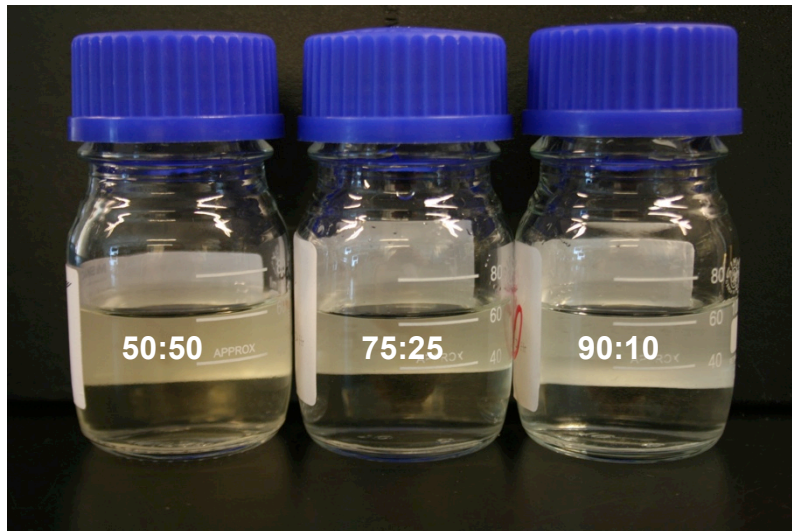


Figure 4.11 Compatibility test before ageing

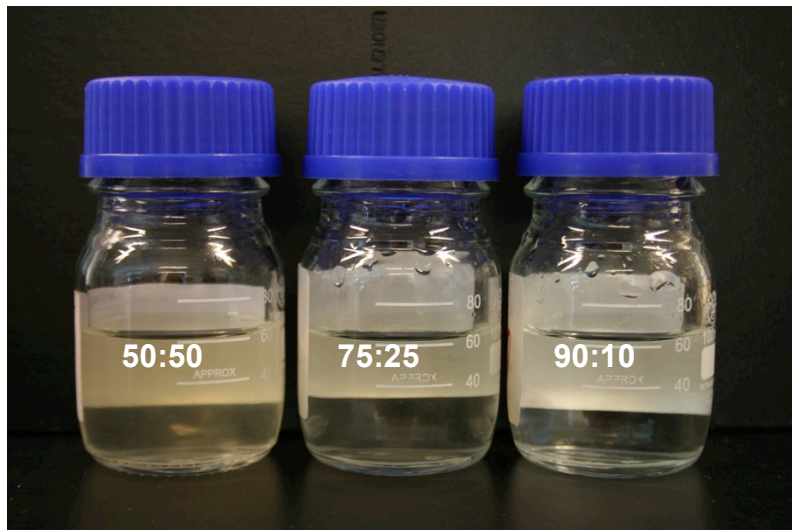


Figure 4.12 Compatibility test after ageing

4.4 Static Adsorption Test – Surfactant/ solvent wash followed by Scale Inhibitor

The tests were performed at different concentrations and with a duplicate. From all the tests, the duplicates were averaged and compiled in figure 4.13 to show in a sensitive scale the effect that different preflushes have on scale inhibitor adsorption in static adsorption tests. Two bottles with only sand and NaCl The solvent were included on each test as a 'control'; also the 10% solvent blend was included on each test on duplicate to have a point of reference for the adsorption.

The figure illustrates a non significant change in adsorption when a surfactant is used as a preflush; the reasons for this can be the fact that this is a static test where the lack of sensitivity does not necessarily reflect the dynamic conditions of a reservoir/ coreflood test, where a dynamic test is a more accurate representation of the conditions at which the chemical would be subject to.

The objective of this test was to perform a fast surfactant screening for further tests in the coreflood. Therefore the test was considered unsuccessful by not showing relevant adsorption. The surfactants will be chosen based on their chemical characteristics and functions.

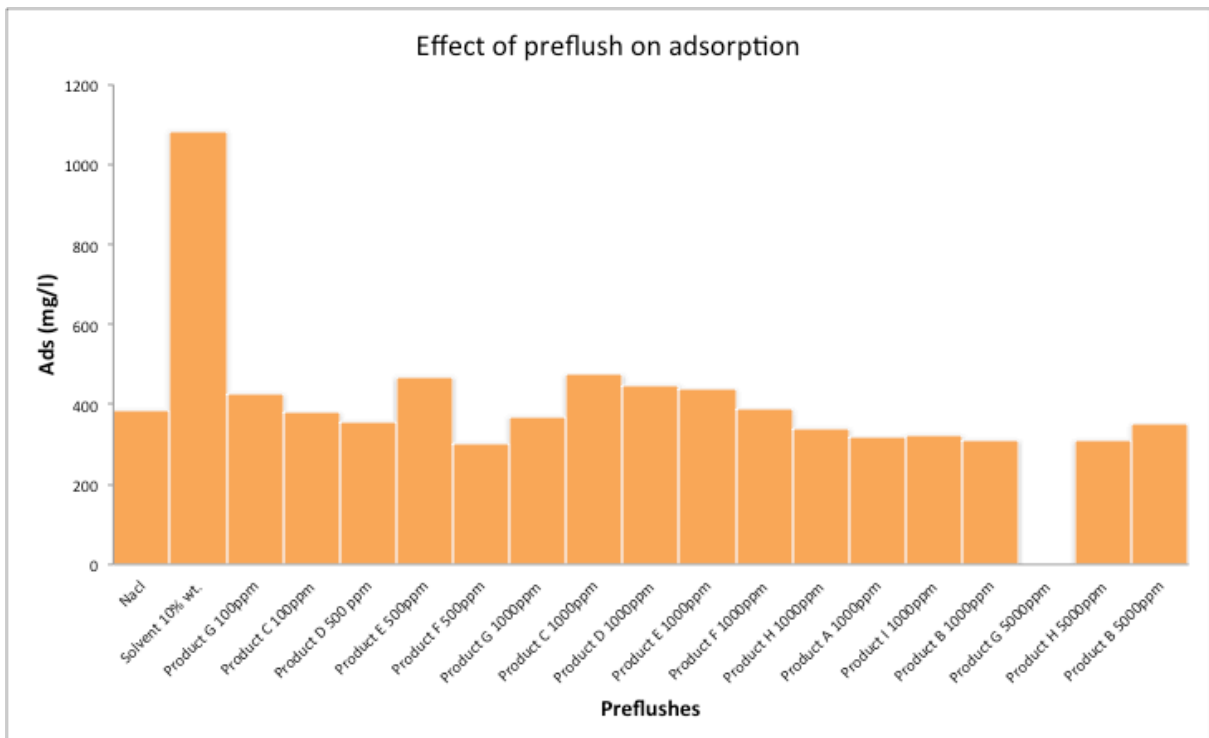


Figure 4.13 Scale inhibitor adsorption with different surfactants as preflush

The chemical groups for the products mentioned in figure 4.13 are listed as follows:

- A Polysorbate 80
- B Polyalkylene oxide block copolymer
- C Blend of non- ionic surfactants and water wetting agents

- D Sodium C14-C16 Olefin Sulfonate
- E Sodium Laureth sulfate, 3EO
- F Tridecyl Alcohol Ethoxylate.
- G Tridecyl Phosphate Esters, 6EO
- H Potassium Oleate Sulfonate
- I Ethoxylated Phosphate Ester

4.5 Corefloods to Evaluate Scale Inhibitor Adsorption and Wettability Change on Aged & Non-aged Cores

4.5.1 Scale Inhibitor Return

Figures 4.14 – 4.19 show the normalized SI and Li concentration during main treatment injection, shut in and early post-flush (desorption). The interpretation of these Figures is as follows:

Main Treatment Stage:

Offset / delay in normalized SI relative to normalized Li indicates the amount of SI retention during injection. The larger the offset, the higher the retention.

Post-Flush after Shut In

Reduction in normalized SI relative to normalized Li indicates the amount of SI retention during shut in. The larger the reduction, the higher the retention.

The observations from Figures 4.14 – 4.19 are summarized as a manual mass balance determination in Figure 4.22.

1) Coreflood 1: Unaged Extremely Water Wet, preflush 1.02 sg NaCl

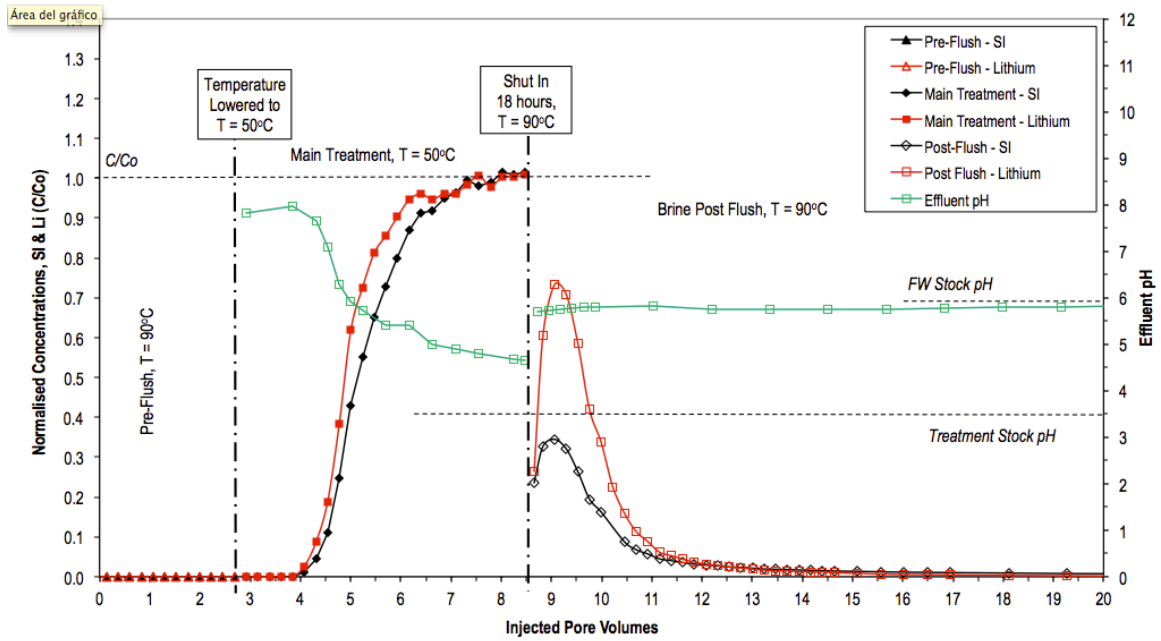


Figure 4.14 Scale Inhibitor and L (C/Co) in coreflood 1 (injection, shut-in, post-flush and desorption)

2) Coreflood 2: Aged Non-Water Wet, preflush 1.02 sg NaCl

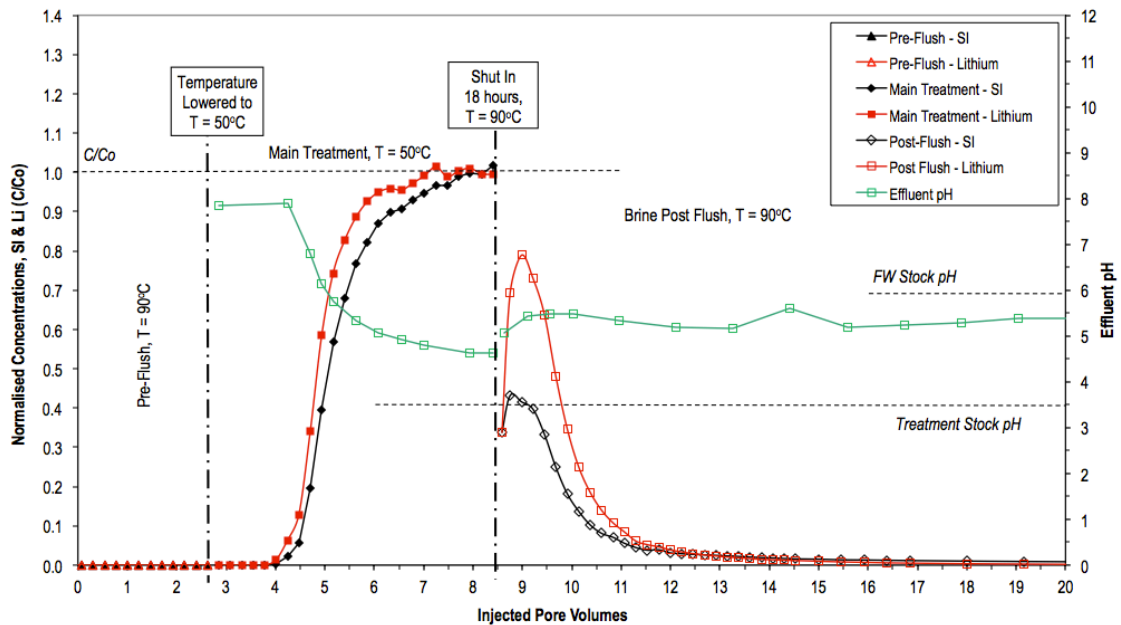


Figure 4.15 Scale Inhibitor and L (C/Co) in coreflood 2 (injection, shut-in, post-flush and desorption)

3) Coreflood 3: Aged Non-Water Wet, preflush Product A

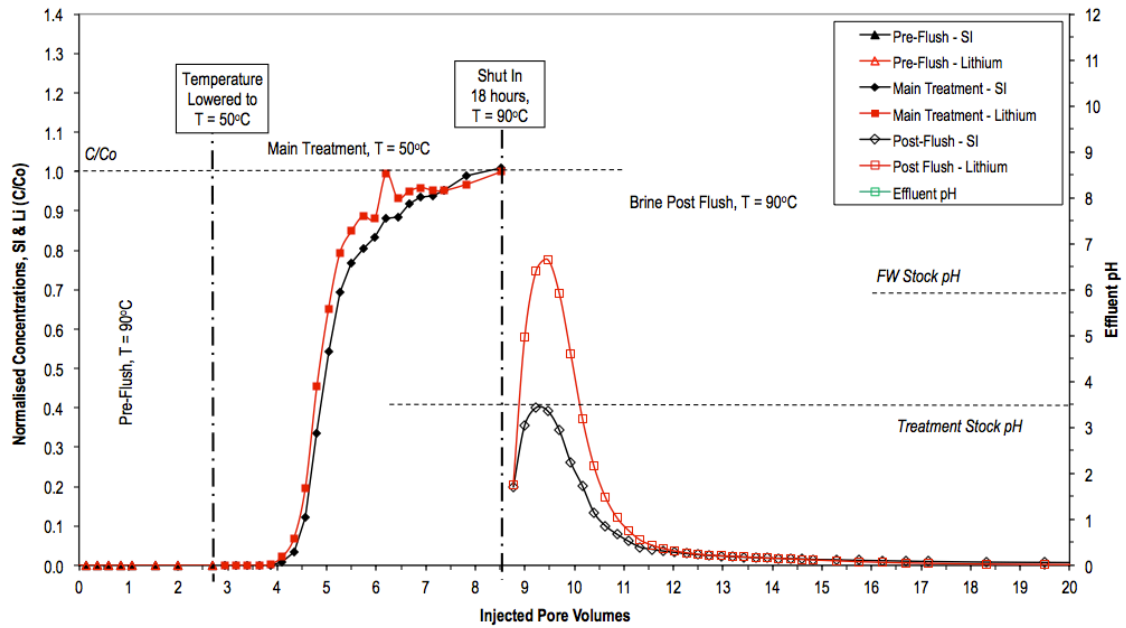


Figure 4.16 Scale Inhibitor and L (C/Co) in coreflood 3 (injection, shut-in, post-flush and desorption)

4) Coreflood 4: Aged Non-Water Wet, preflush Product B

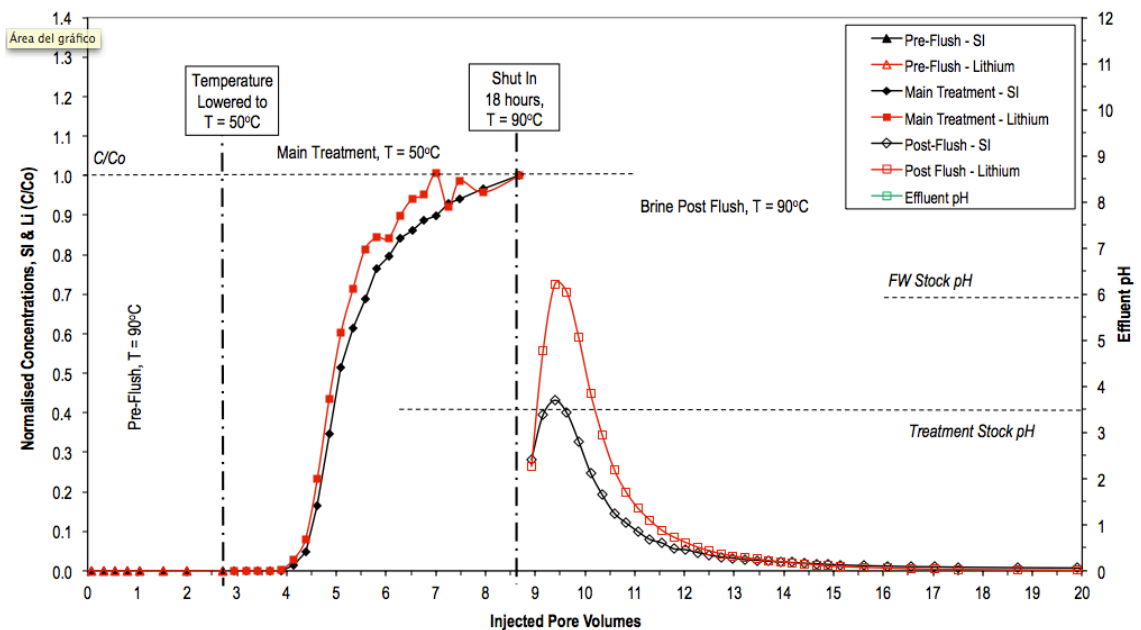


Figure 4.17 Scale Inhibitor and L (C/Co) in coreflood 4 (injection, shut-in, post-flush and desorption)

5) Coreflood 5: Aged Non-Water Wet, preflush 10% wt. solvent blend

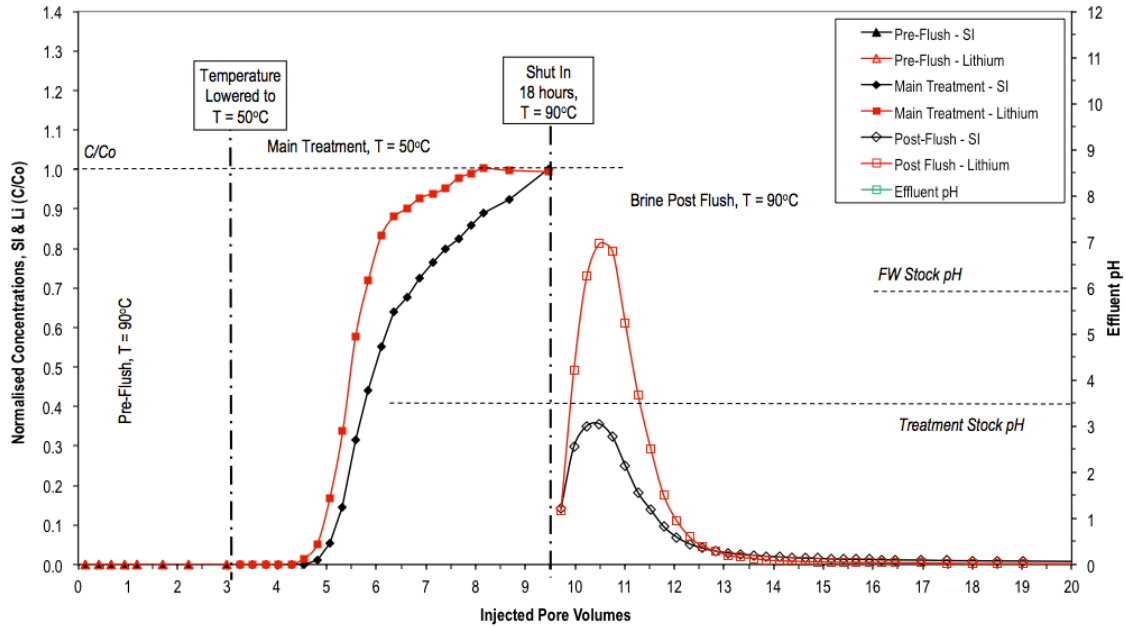


Figure 4.18 Scale Inhibitor and L (C/Co) in coreflood 5 (injection, shut-in, post-flush and desorption)

6) Coreflood 6: Aged Non-Water Wet, preflush Product C

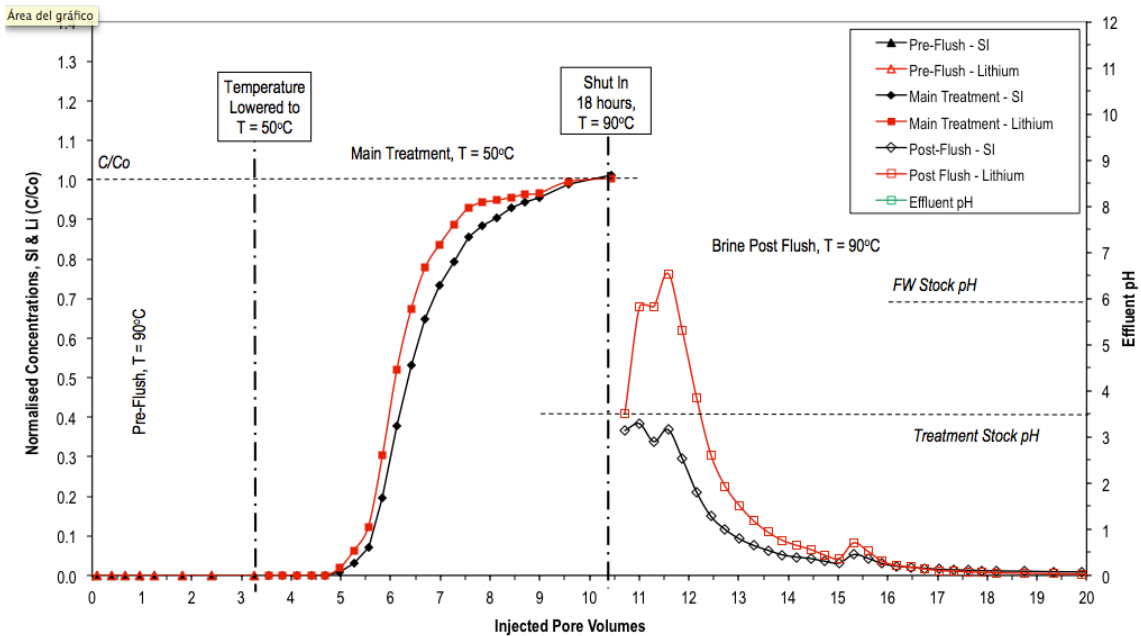


Figure 4.19 Scale Inhibitor and L (C/Co) in coreflood 6 (injection, shut-in, post-flush and desorption)

4.5.2 Scale inhibitor return profile for the 6 coreflood tests

Desorption or scale inhibitor return, is the phase that allows the inhibitor to be displaced from the formation slowly over a period of time [57]. The scale inhibitor return data, obtained from all 6 coreflood tests is illustrated in figure 4.20, The logarithmic scale shows the number of injected pore volumes with respect to scale inhibitor concentration.

During the experimental part of this project the desorption stage was stopped after 18 hours when the concentration was still relatively high (10 ppm in the post flush stage), yet it is possible to appreciate the different effluent scale inhibitor concentrations for each of the corefloods.

It is believed that the amount of scale inhibitor retained in the rock, in one of the factors directly related to the scale squeeze lifetime, with that assumption it is possible to infer from the graph which of the preflush solution have been the most effective. In this case, the data suggest that the surfactant Product C is the one shaping the conditions with the best outcome for scale inhibitor adsorption.

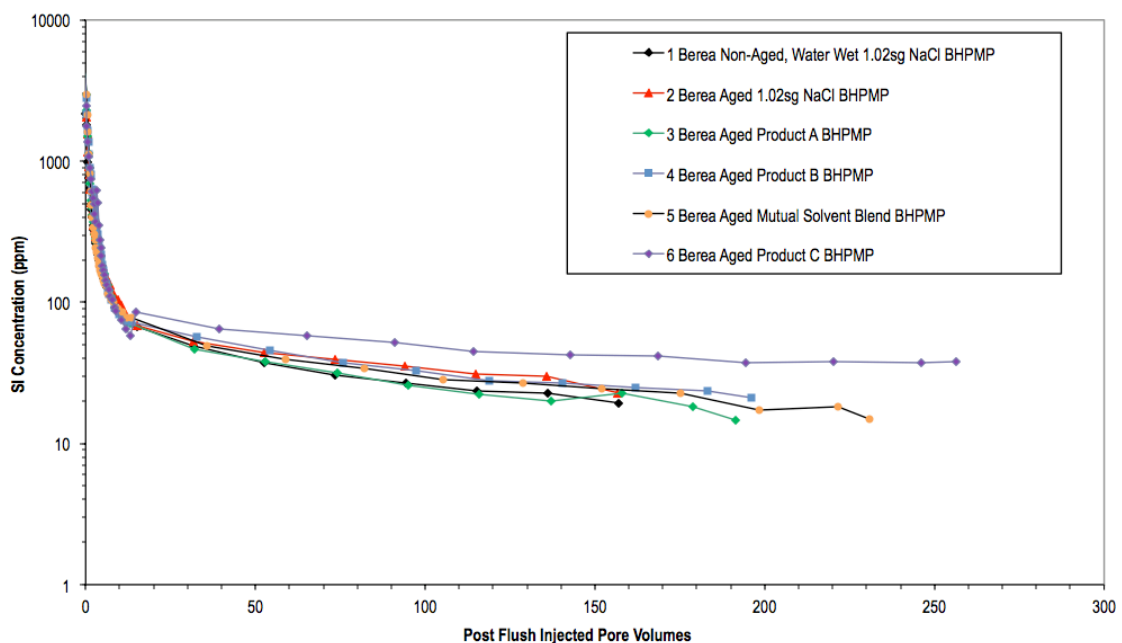


Figure 4.20 Scale inhibitor postflush/ desorption profile

Figure 4.21, as well as figure 4.20, shows the scale inhibitor return profile from all 6 corefloods test. In this graph the scale is linear, where the first part of desorption stage is illustrated in a better way. At this point the (first pore volumes of postflush) Product C is presenting a more particular behavior in respect with rest, showing a lower scale inhibitor concentration and right after higher than the rest. This can be an indication of a longer squeeze lifetime.

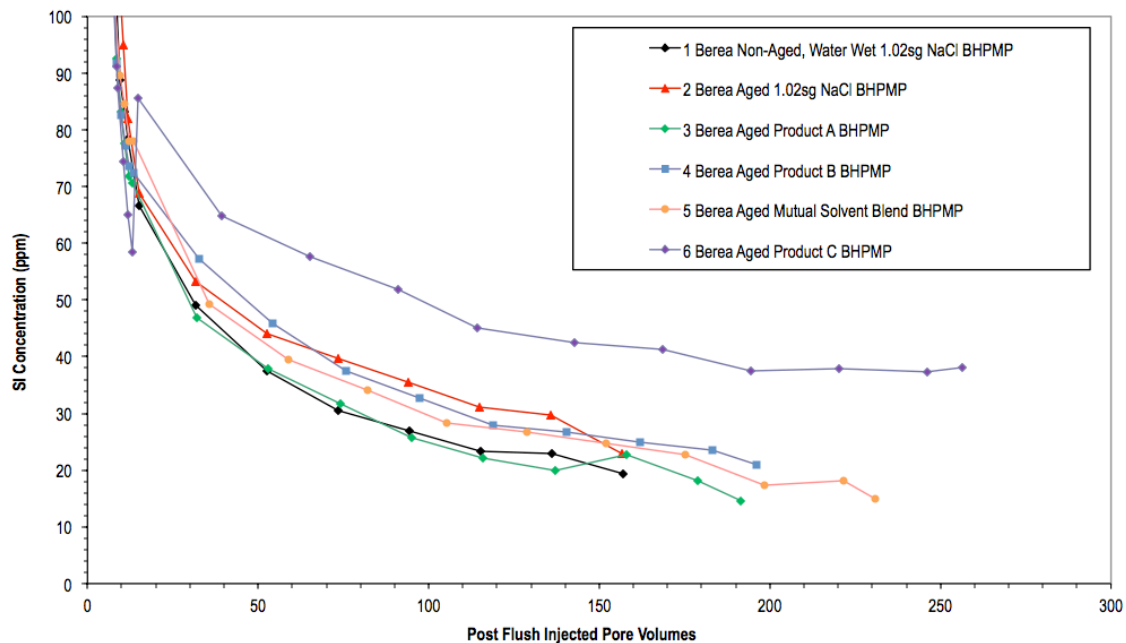


Figure 4.21 Scale inhibitor postflush/ desorption profile (linear scale)

4.5.3 SI Retained in Core during injection, Postflush and after Postflush (mass balance)

Figure 4.22 shows a manual mass balance of retained scale inhibitor during the injection, returned post-flush and remaining material in the core. The mass balance was performed with the purpose of analyzing how the adsorption is affected on each of test stages with the different preflushes.

The result illustrated in figure 4.22 shows a notable improvement of adsorption when the 10 wt.% solvent blend is used, particularly during the injection and the after postflush, however the amount of retained scale inhibitor is only one of the

factors and does not necessarily is a proof of a longer squeeze lifetime. The mechanics of how the SI is adsorbed to rock is equally if not even more relevant than how much it is adsorbed in quantity.

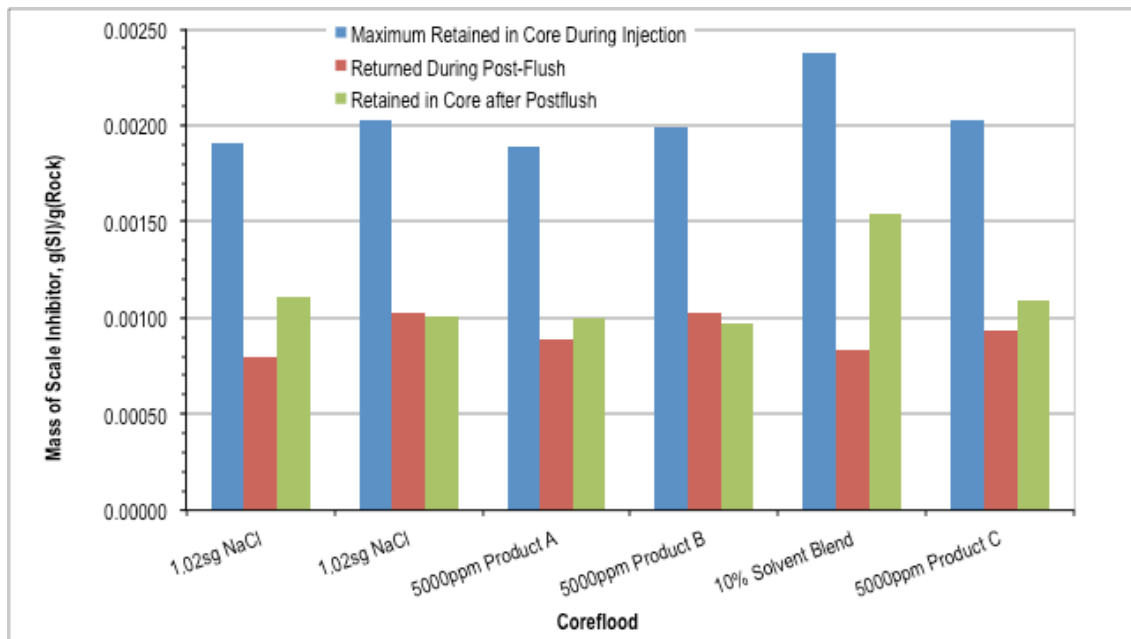


Figure 4.22 Scale Inhibitor retained in the core.

The manual mass balance has the possibility of uncertainty in the different stages of acquiring the analytical data:

The ICP analysis has a 10% error, then when analyzing concentrations of 2Wt.% (20,000 ppm) can result in high margin of error, whereas when analyzing concentrations of 10ppm the possible error is much less (1 ppm).

Concentration of SI injected is lower (relative to a squeeze treatment), in addition in order to centrifuge the cores, a max 5cm length was used which is smaller than normally experiments.

4.5.4 Permeability Data Analysis

Oil return permeability (mD)

The oil return permeability in mD is illustrated in figure 4.23, where it shows consistent initial oil permeability at irreducible water saturation ($K_{o1} Sw_i$), this

means all 6 cores are at fairly the same conditions at the beginning of the test, showing whether they are water wet or oil wet, when the saturation is at S_{wi} , the location of the 20% irreducible water does not impair significantly on the flow of oil.

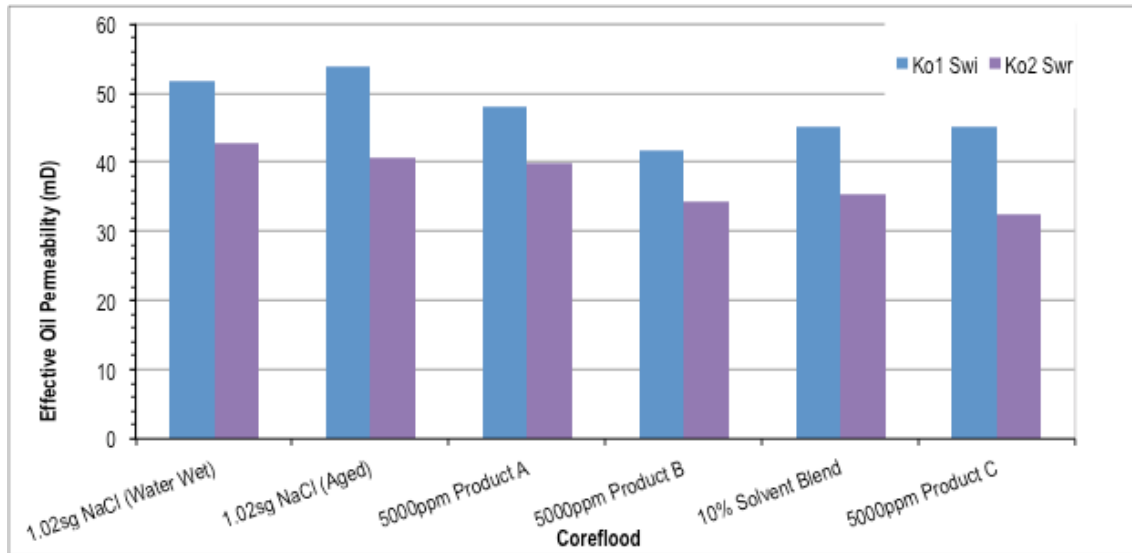


Figure 4.23 Oil return permeability (mD)

Oil Return Permeability (%)

The oil return permeability ($K_{o2} S_{wi}$) in % is expressed in figure 4.22, where it illustrates a reasonably consistent return permeability to oil (72 - 83%), suggests all preflush fluids are largely non-damaging to oil permeability in this type of rock, under these test conditions. Some contribution to the observed reduction in oil permeability will come from a likely relative increase in water saturation compared with the initial conditions, this means that low water saturation is obtained via the centrifuge (capillary forces), but it is not possible to get the same S_{wi} value at the end of the corefloods when using flooding (viscous forces). Hence the relative permeability to oil will be lower at slightly higher water saturation.

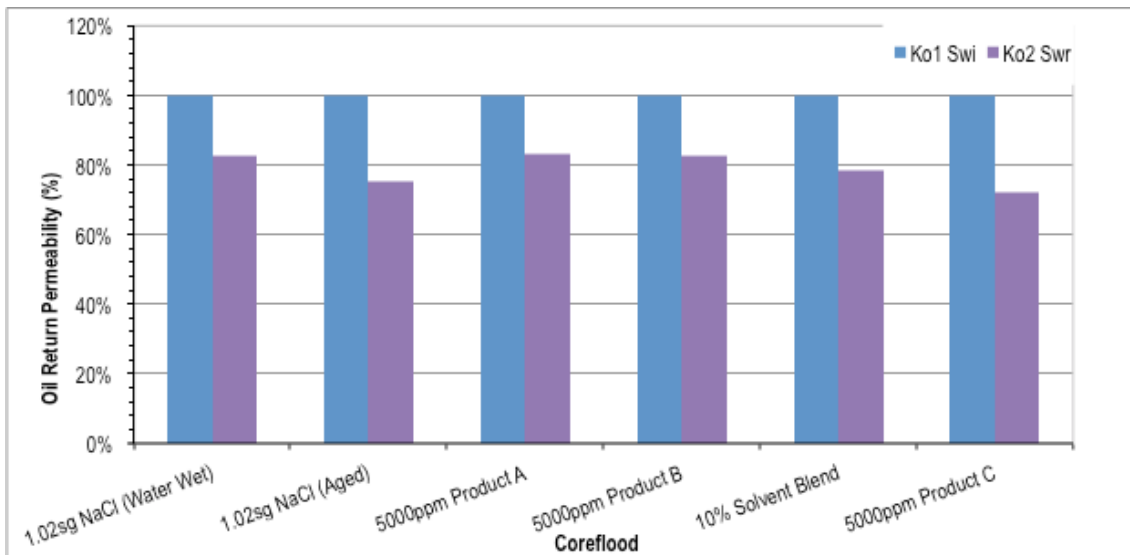


Figure 4.24 Oil Return permeability

Effective brine permeability (mD)

Figure 4.25 shows the effective brine permeability where:

Kw1 = Initial effective brine permeability at Sor.

Kw2 = Effective brine permeability at Sor after desorption period.

Kw3 = Final effective brine permeability at Sor after re-injecting oil to Swr followed by brine to Sor.

The difference in initial brine permeability at Sor between corefloods 1 & 2 is the changing in wetting caused by ageing i.e. Less water wet / Higher effective permeability to brine.

In this graph is very well illustrated the difference in wettability between the cores, where the coreflood 1 (1.02 sg NaCl water-wet) shows very low value at initial brine permeability (kw1Sor), than for the rest of the cores (the aged cores) where the permeability the values are similar and present good consistency.

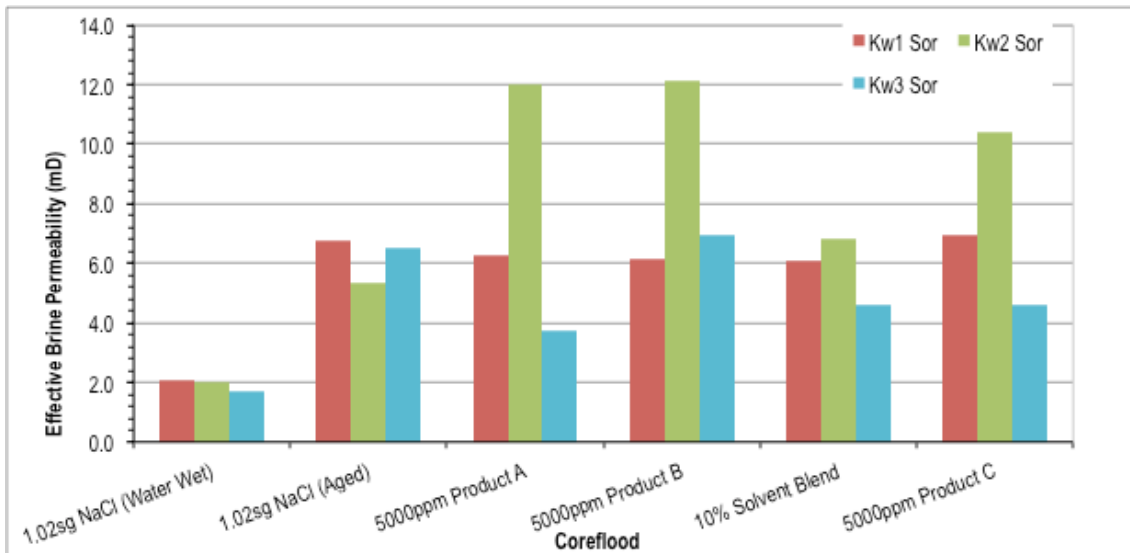


Figure 4.25 Effective brine permeability (mD)

Brine return permeability (%)

Brine return permeability (%), is illustrated in figure 4. 26. Increases in % return permeability to brine after the desorption stage (Kw2) are interpreted as the result of a lowering of residual oil saturation as a result of surfactant / solvent injection. After re-injection of oil to Swr and re-injection of brine to Sor, any reductions in final % return permeability (Kw3) are interpreted as a change to more water wet conditions.

Product A, Product B and Product C are interpreted as being able to displace residual oil from the core during injection hence larger % return permeability to brine after post-flush / desorption (Kw2Sor).

The solvent blend does not show the same behavior, whereby only a small increase in Kw2 was recorded.

Product A has the lowest final % return permeability to brine (Kw3 Sor) suggesting the largest wetting change (towards water wet). The solvent blend and Product C also show a reduction in final brine permeability but to a lesser extent compared with Product A.

The Product B does not show the same Kw3 behavior suggesting wetting has not been changed, and the improvement in adsorption shown might be due to “bridging properties” of the surfactant.

In summary the brine permeability results are interpreted as follows:

1. Product A displaces residual oil and changes wettability.
2. Product C displaces residual oil and changes wettability.
3. Solvent blend changes wettability but does not displace much residual oil.
4. Product B displaces residual oil but does not change wettability.

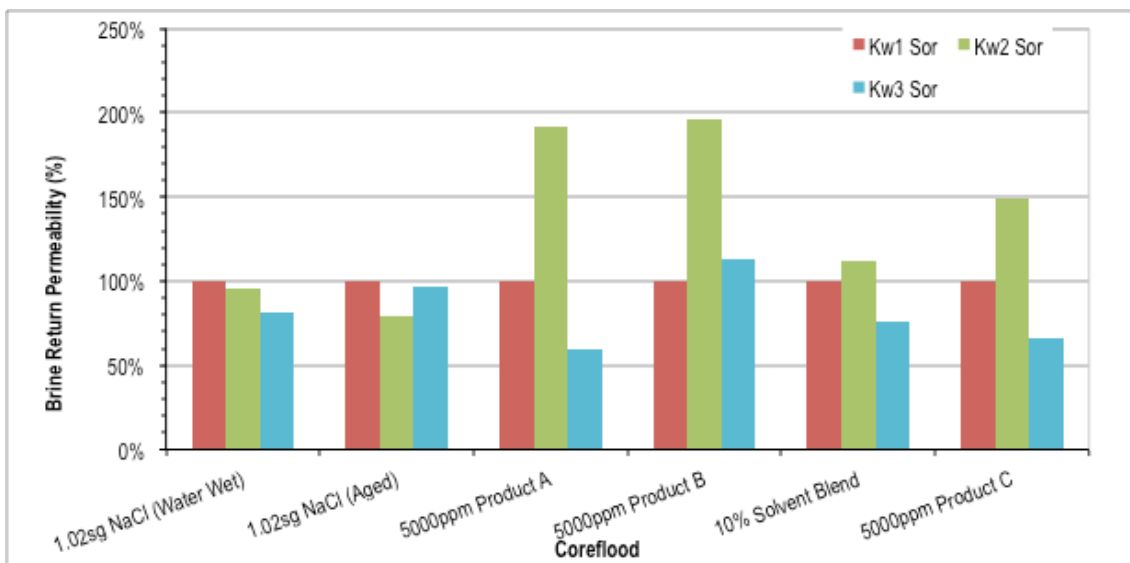


Figure 4.26 Brine return permeability (%)

4.6 SQUEEZE 8 prediction software

As mentioned in 3.6, modeling software SQUEEZE 8 (SQUEEZE 8, FAST, HWCH, 2012), was used to predict the different lifetimes of each of the corefloods. The postflush/ desorption time was on average 18 hours for each of the corefloods, after that period of time the concentration of scale inhibitor was still relatively high (approx. 10 ppm).

The software use properties of the core injected inhibitor volumes, effluent SI return concentration data vs volume to derive and validate an isotherm for each coreflood. The chemical analysis data from the return scale inhibitor profile for each coreflood was used to form an isotherm it was possible to obtain the post-flush volume to predict the number of pore volumes to 20, 15, 10, 5 & 1ppm.

Figure 4.27 shows the predicted post flush/ desorption pore volumes done to a concentration of 1 ppm minimum. It includes data from the 6 coreflood tests. Where coreflood number 1 and 2 are the base reference for a water wet and a non water wet core with only NaCl as a preflush (no surfactant/solvent as used).

Coreflood number 1 is the unaged extremely water wet berea core, which would be the ideal wetting conditions that provide the clean water wet surface for the SI to adsorb, and according to the prediction is the coreflood with the fourth longest predicted lifetime.

Corefloods number 4, 5 and 6 (product B, the solvent blend and Product C) are predicted to have a longer squeeze lifetime than the extremely water wet core meaning that they have a beneficial effect over the predicted treatment lifetime.

Product A show an improvement over the aged core with no surfactant or solvent at all, but it shows the least improvement from the rest and even less than the water wet with only NaCl as a preflush. In graph 4.26 is illustrated how Product A is the one showing the biggest changing in wetting, however Product B, Product C and the solvent blend are showing the best improvement in squeeze lifetime even if these products are not the ones showing the biggest change towards water-wet. This validates what mentioned 4.5.3, the amount of SI retained in the core is a factor, but also the mechanics of the adsorption to the rock.

The graph is also showing a good reproducibility in the data particularly in the first stage where all the bulk is at the same numbers, then at threshold levels is presumably the difference in desorption from each,

The assumption was that the larger the wetting change, then the larger the lifetime, however this prediction model is showing that there are other potential mechanisms improving the lifetime.

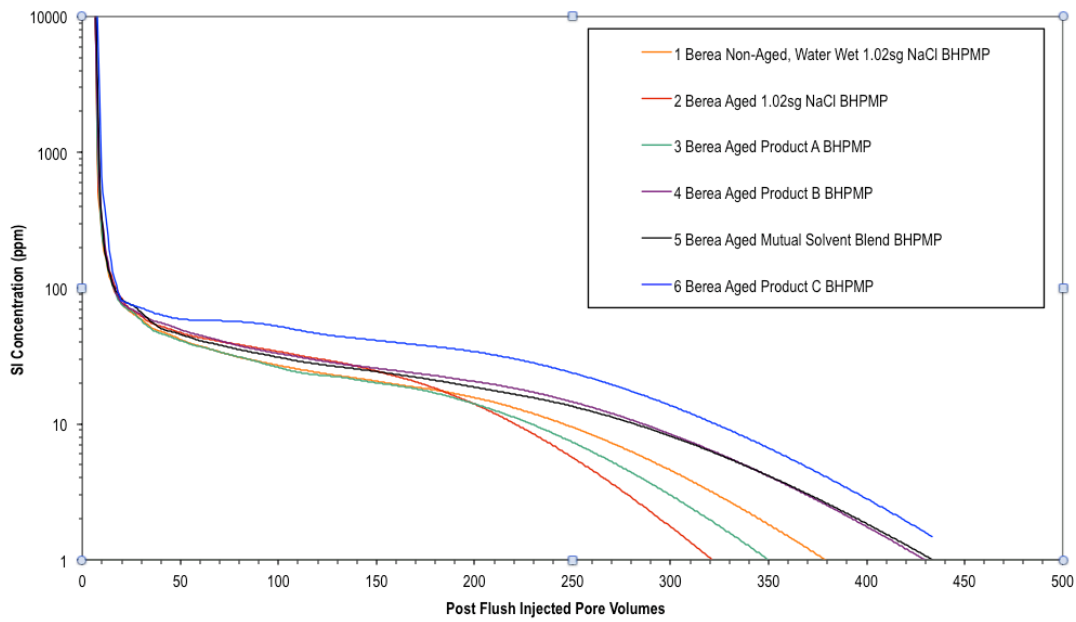


Figure 4.27 Predicted post flush injected pore volumes.

Predicted Inhibitor Lifetime (PV) to MIC Concentration (ppm)

The predicted scale inhibitor lifetime at different concentrations (1, 5, 10, 15, 20) is expressed in figure 4.28

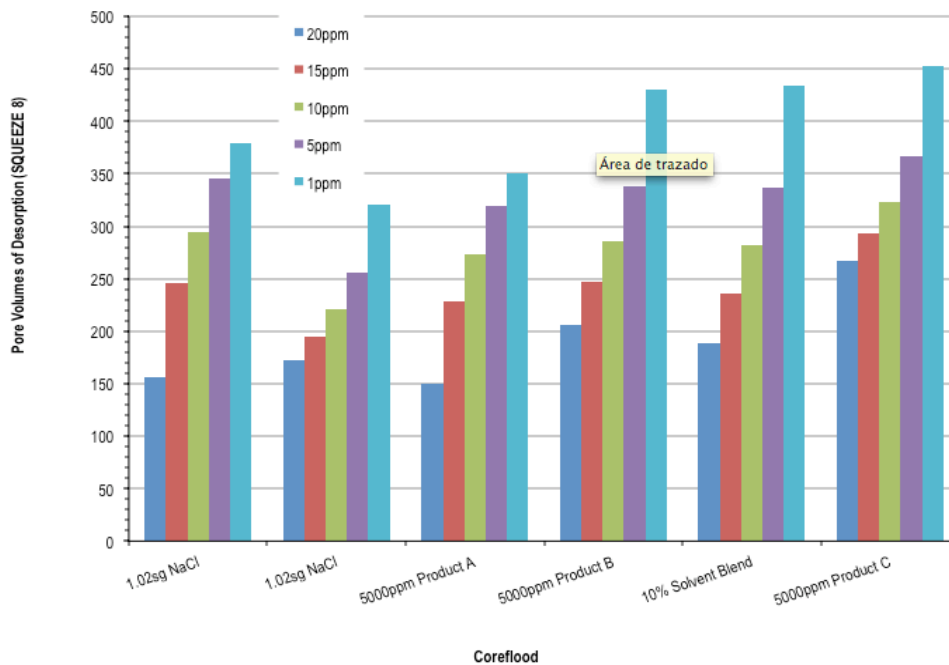


Figure 4.28 Predicted Scale Inhibitor at different concentrations

Conclusion

The main objective of this thesis was to research the use of surfactants to change the rock wettability and act as enhancers on squeeze lifetime. In this work experiments with corefloods to simulate the field conditions were performed. Numerical results based on several experiments are presented and analyzed. Each test was performed following base line procedure and at identical operating conditions.

The following observations were made:

- The treatment life was significantly extended when using a surfactant/ solvent preflush.
- When comparing a water wet core and oil wet core, both with only NaCl as a preflush, the water wet core shows significantly better treatment lifetime, indicating that water wet conditions are beneficial in increasing scale squeeze lifetime.
- The use of Surfactants/ solvent changed the wettability of the rock towards more water-wet conditions. The changed was clearly observed with all four used preflushes.
- Surfactants/ solvent were beneficial in the improvement of the treatment lifetime. This was proven by showing larger treatment lifetime than the extremely water wet core with only NaCl as preflush
- The data showed that the change in the wettability was not the only mechanism involved in increasing the treatment lifetime.

In summary, the results showed a clear improvement of the potential treatment lifetime when a surfactant/ solvent was used as a preflush.

It is recommended for further work to go deeper in the mechanics behind the improvement of the treatment lifetime. And compare if the same results are given when using a scale inhibitors with different functional groups.

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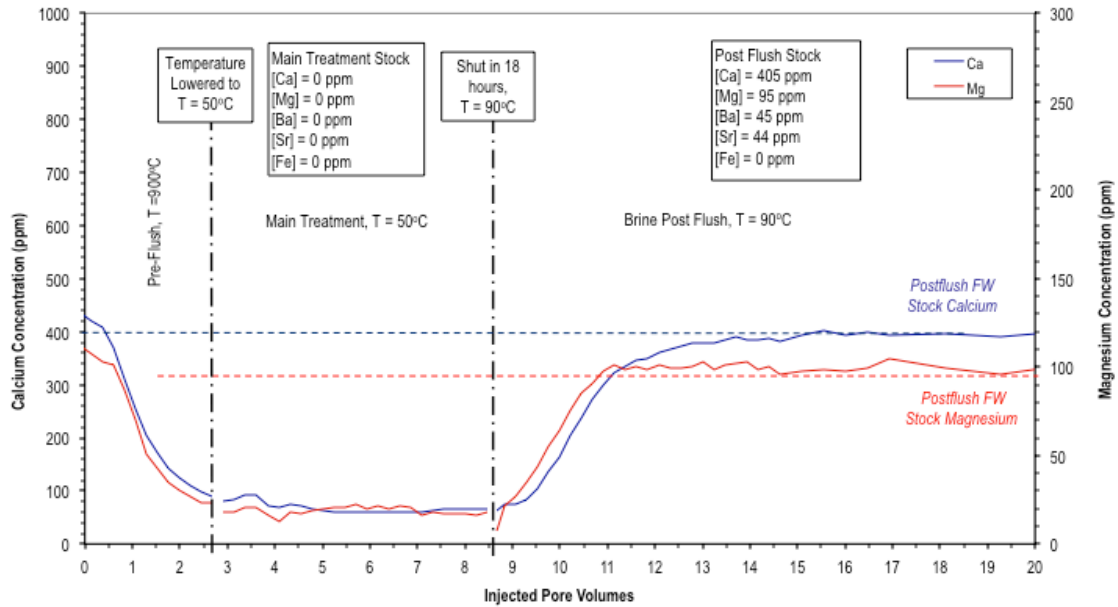
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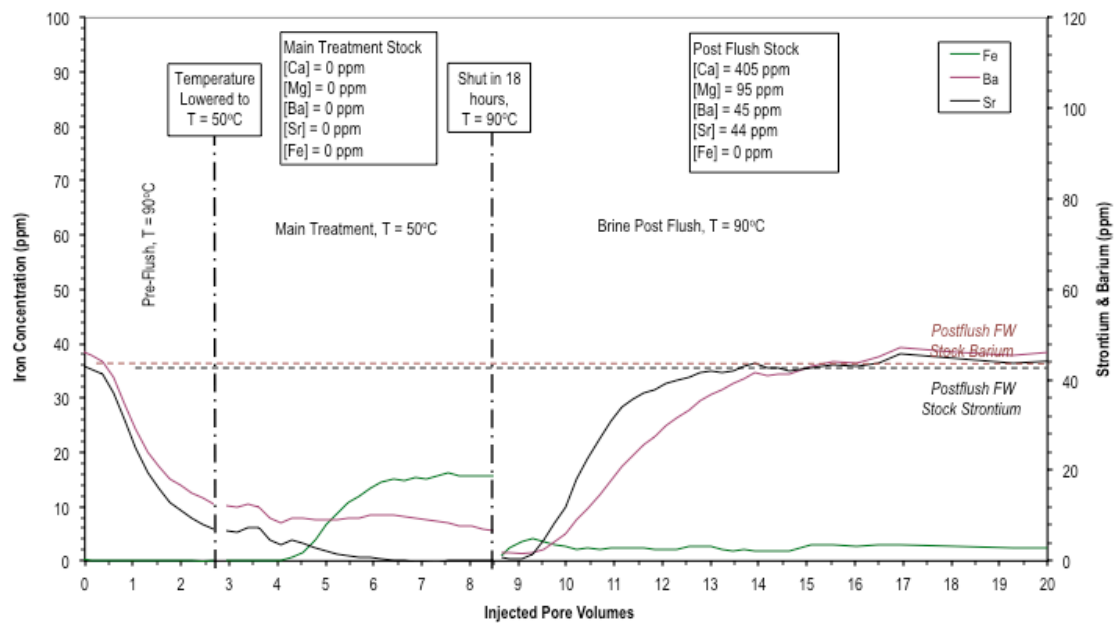
Appendix

The next graphs show the analytical results from the effluent during the coreflood tests, a cation analysis was performed to verify the nothing unusual happened.

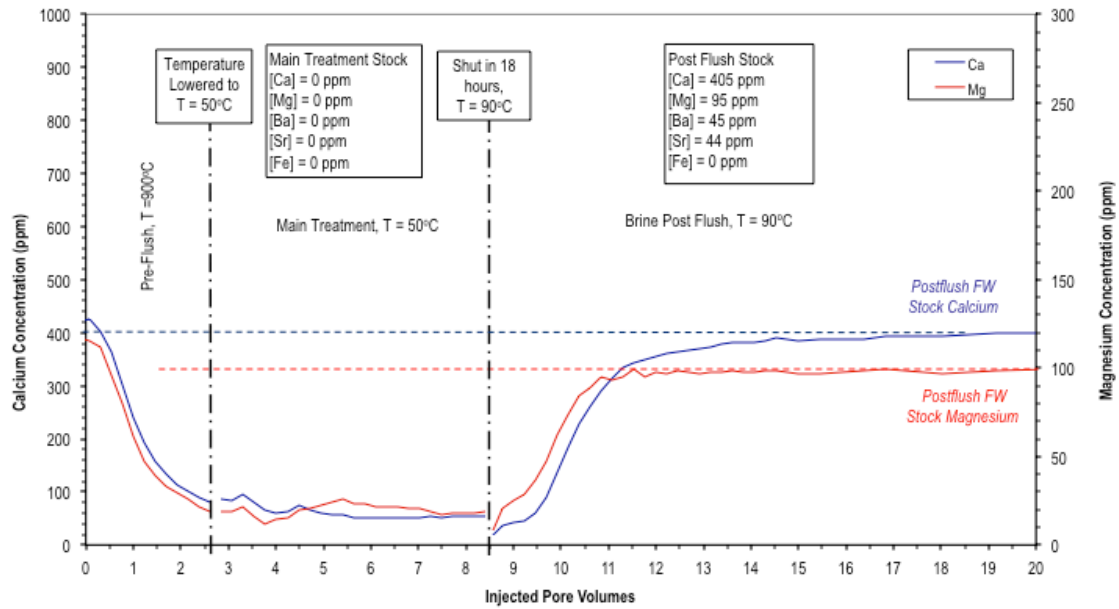
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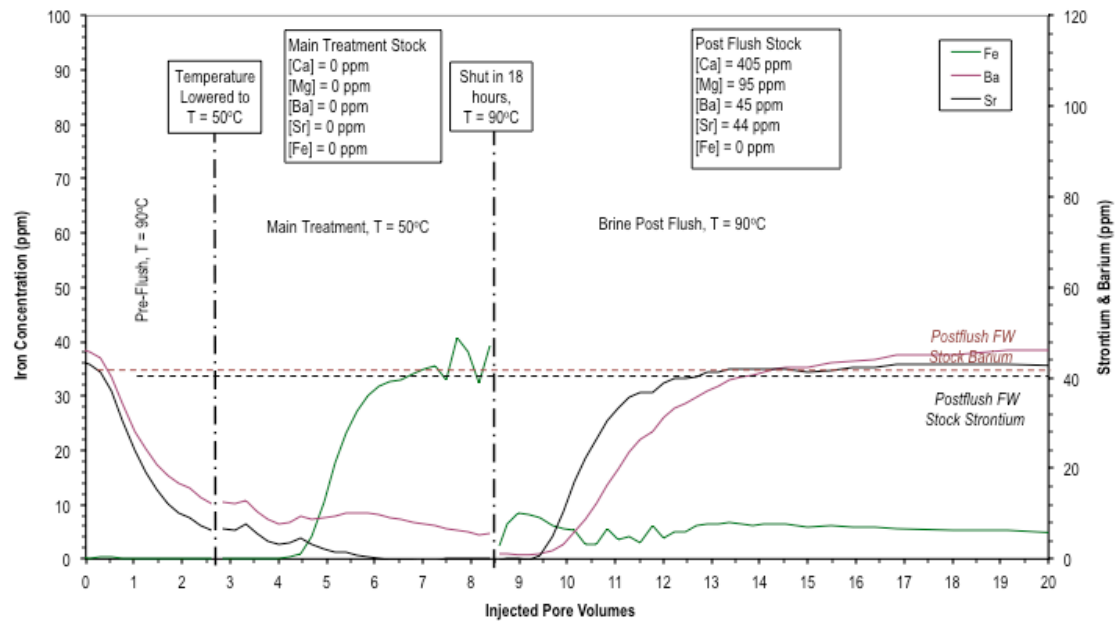
Strontium, barium and iron



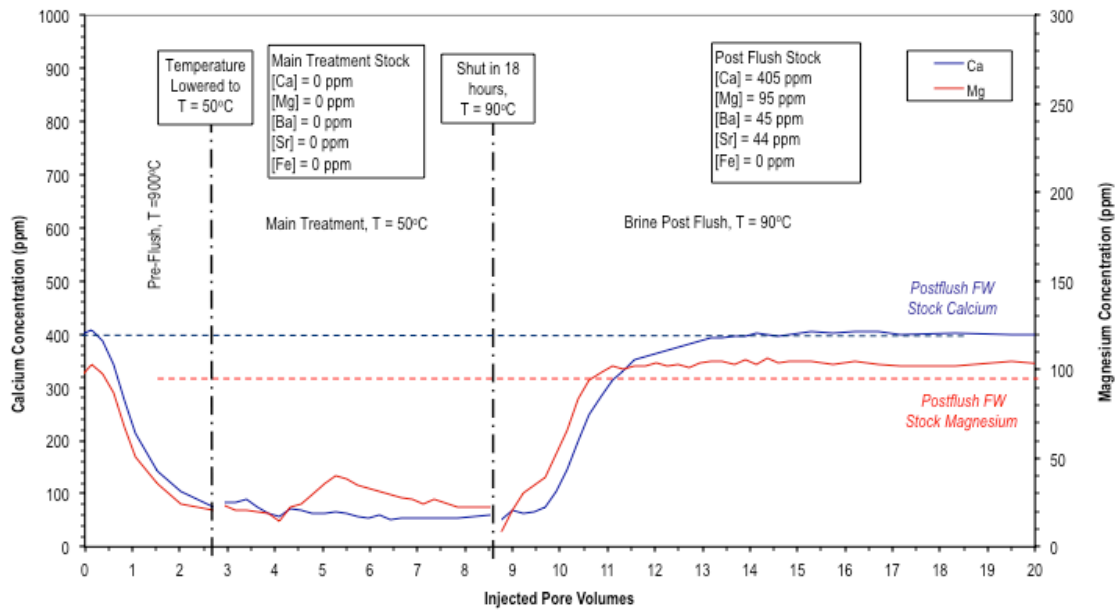
Coreflood #2 Magnesium and calcium



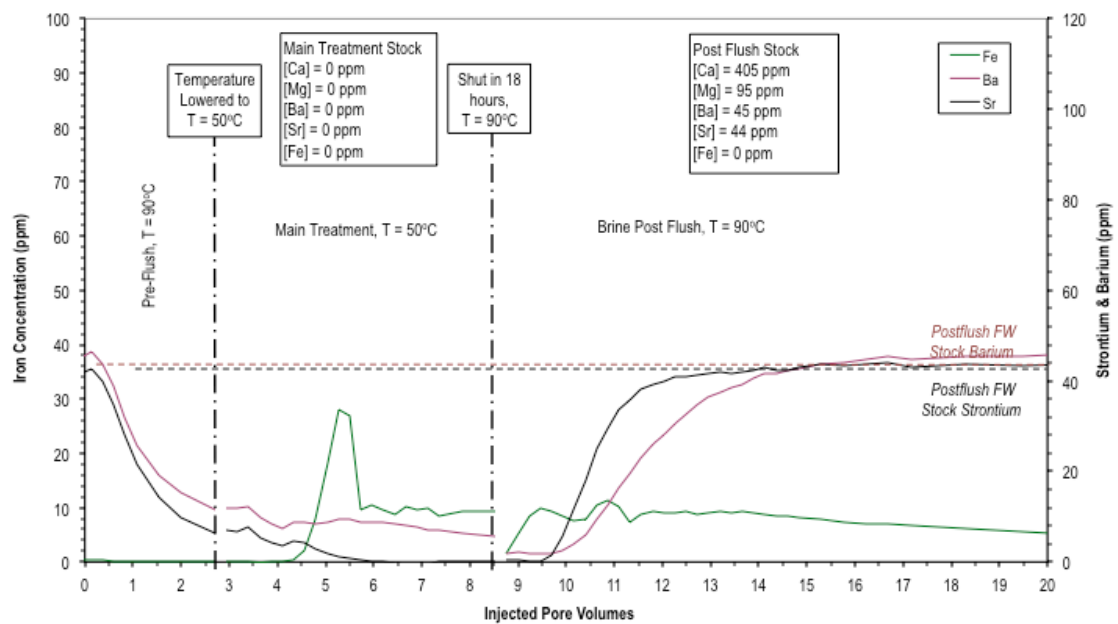
Strontium, barium and iron



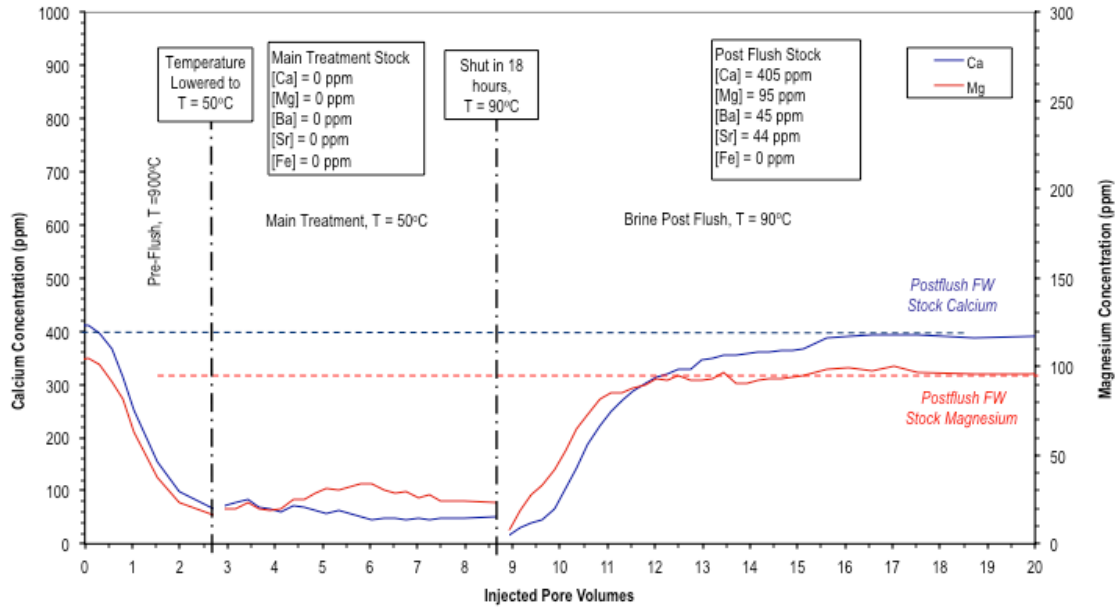
Coreflood #3 Magnesium and calcium



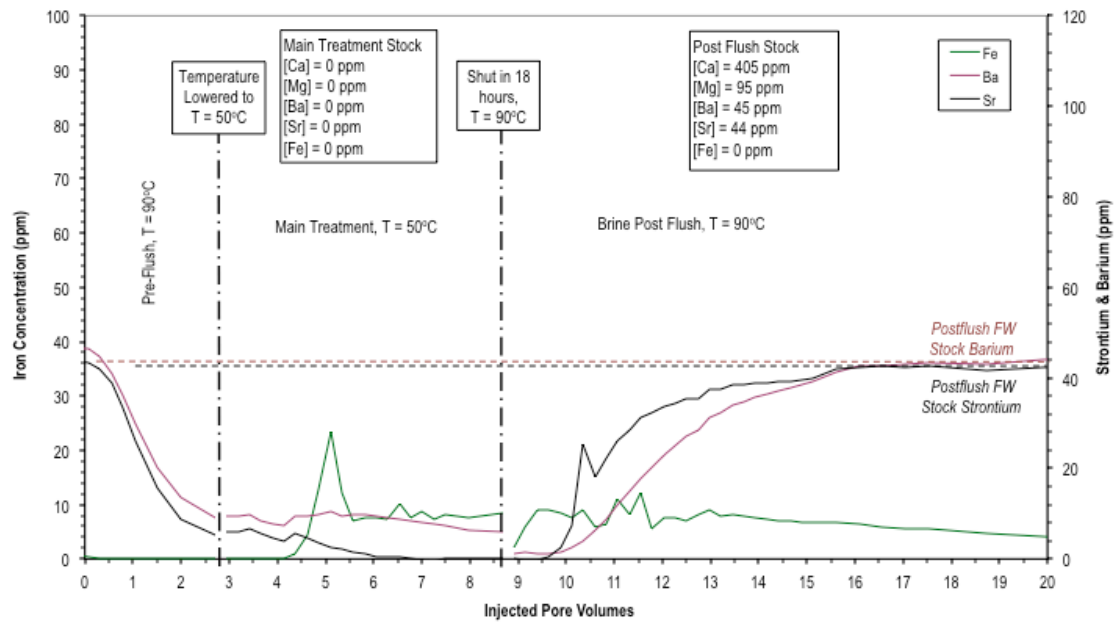
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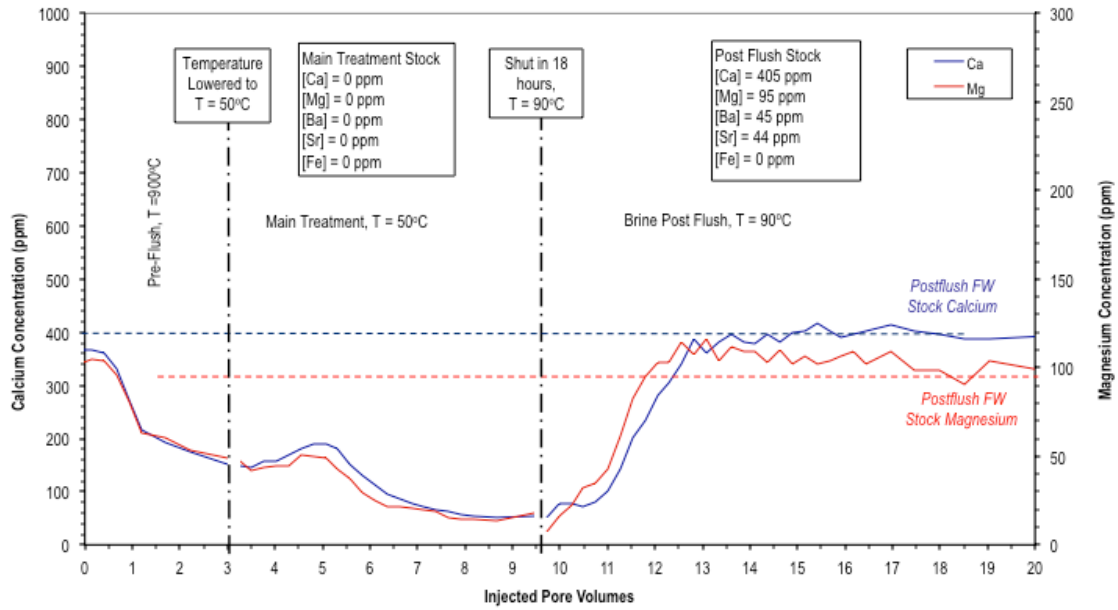
Coreflood #4 Magnesium and calcium



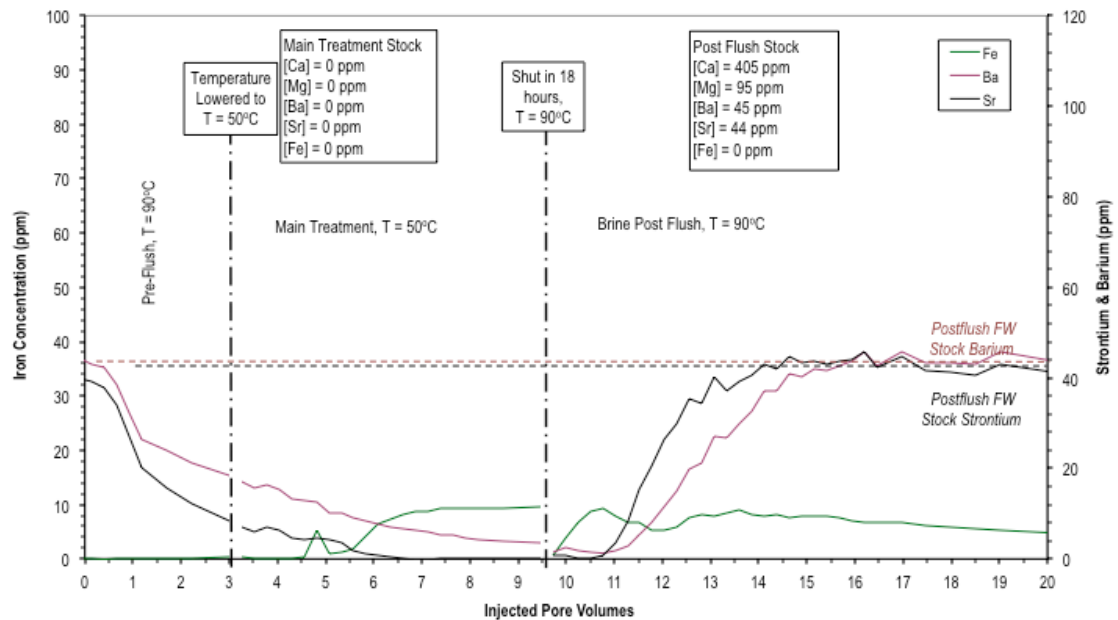
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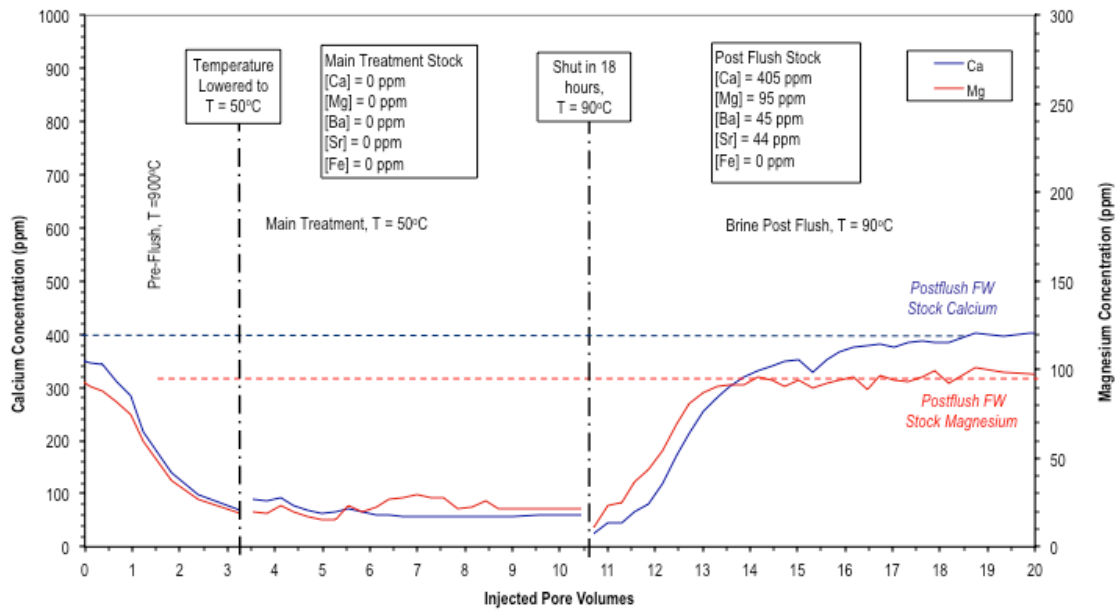
Coreflood #5 Magnesium and calcium



Strontium barium and iron



Coreflood #6 Magnesium and Calcium



Strontium, barium and iron

