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Faculty of Science and Technology

Study of Novel Polymeric Aminomethylenephosphonates as Oilfield Scale Inhibitors

by

Parya Bayat

University of
Stavanger

Faculty of Science and Technology

Department of Chemistry, Bioscience and Environmental Engineering

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Abstract

Scaling is one of the most frequently stated problems with the oil industry and scale inhibitors (SI) are applied to prevent the formation of the scale layers on the surface of the field facilities or the formation rocks. Examples of the well-known types of SIs are organophosphonic acid compounds and their salts, which can be found as both non-polymeric and polymeric molecules with attached phosphonate groups. However, the performance of phosphonate base SIs is limited by their poor compatibility with calcium ions. Therefore, there is still a need to develop SIs with reliable calcium compatibility and thermal stability at high temperature and high-pressure formations along with being environmentally acceptable.

The specific objective of this study was to design phosphonate base SIs applicable in high temperature and high-pressure formations with characteristics including high calcium compatibility, thermal stability and biodegradability. In the present study, several novel phosphonated polyetheramines were synthesized from Jeffamine polyetheramines due to their known biodegradability, biocompatibility and non-toxic characteristics. The final products were evaluated for their carbonate and sulfate scale inhibition performance using a high-pressure dynamic tube blocking rig at approximately 80 bar and 100 ^{o}C. The compatibility with calcium ions, thermal stability and the biodegradability (in seawater) of these products were also examined.

This study showed that the phosphonated polyetheramines had a significant positive performance on both barite and calcite scale formation, in comparison of the findings with those of other studies on commercial aminophosphonate SIs such as diethylenetriaminepentakis- (methylenephosphonic acid) (DTPMP). For example, the results from this thesis revealed that Phosphonated Jeffamine EDR-176 (P.EDR-176) was found to be the most potent scale inhibitor with a fail inhibitor concentration at 2 ppm for sulfate scale and no formation of the calcite scale even at 1 ppm (the lowest concentration of the injected SI). The second major finding was that all the synthesized SIs showed significant compatibility with calcium ions. Moreover, the investigation of thermal aging test indicated a small decay of scale inhibition performance in this study. However, the poor biodegradability for some of the tested SIs in seawater, according to OECD 306, is the main challenge.

Therefore, this study makes a major contribution to research on phosphonated polyetheramine as potential scale inhibitors with significant calcium compatibility for the oilfield applications.

Accomplishment

Poster presentation at “IOR NORWAY 2019” Conference, UiS, Stavanger.

- Phosphonated Polyetheramine Scale Inhibitors - Powerful Calcium Compatibility for Oilfield Applications. (APPENDIXES A)

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Parya Bayat

Stavanger, Norway

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Abbreviations

AIBN - Azobisisobutyronitrile

ATMP - Aminotris methylenephosphonic acid

BCF - Bioaccumulation Factor

BHMTMP - Bis (Hexamethylenetriaminepenta- (Methylenephosphonic Acid))

BOD - Biological Oxygen Demand

C.EDR-176 - Carboxylated Jeffamine EDR-176

DOC - Dissolved Organic Carbon

DTPMP - Diethylenetriaminepentakis methylenephosphonic acid

EDTMP - Ethylenediamine Tetra- (Methylenephosphonicacid)

EO - Ethylene Oxide

ESA - Epoxysuccinic Acid

HDTMP - Hexamethylenediaminetetra (Methylenephosphonic Acid)

ISO - International Organization for Standardization

MIC - Minimum Inhibitor Concentration

Na_4EDTA - Tetrasodium Ethylenediaminetetraacetate

NMR - Nuclear Magnetic Resonance

P.D-230 - Phosphonated Jeffamine D-230

P.EDR-148 - Phosphonated Jeffamine EDR- 148

P.EDR-176 - Phosphonated Jeffamine EDR-176

P.T-403 - Phosphonated Jeffamine T-403

P.XTJ-568 - Phosphonated Jeffamine XTJ-568

PEG - Polyethylene glycol

PESA - Polyepoxysuccinic Acid

PLONOR - Pose Little or No Risk to the Marine Environment

PO - Polyoxy

POE - Polyoxyethylene

SI - Scale Inhibitor

ThOD - Theoretical Oxygen Demand

1 Introduction

Inorganic scaling is considered as a significant flow assurance obstacle in the oil industry. Water-Soluble inorganic salts will deposit as scale under supersaturation conditions. The deposition of the mineral salts will cause damages through the production system and therefore, loss of well productivity. Scaling can occur on almost any surface so that once a scale layer is first formed it will proceed to grow thicker unless treated. Calcium carbonate (calcite and aragonite) and sulfate salts of calcium (gypsum), strontium (celestite), and barium (barite) are the most common types of scales in the oil industry. The use of scale inhibitors (SIs) is the most popular and useful scale control method.

Phosphonated base chemicals are a major class of SIs used for oilfield scale control. Commercial SIs for carbonate and sulfate scaling are generally polymeric, polyphosphonates, polycrylates, polymaleates, polysulphonates, and copolymers while some are non-polymeric molecules with only a few phosphonate groups. Placing phosphonate groups in the SI can be helpful to detect and determine the concentration of the SI in the produced water. Phosphonates also adsorb strongly to formation rocks, giving long squeeze lifetimes, which saves the operator time and money by reducing the downtime for well treatments. Phosphonates can also be introduced in one chemical as an aminomethylenephosphonate group. The $-N-CH_2-PO_3H_2$ group presumably enhances the metal binding capabilities of the molecule via both the amine and phosphonate interactions, which will improve the chelating potential of the SI. The disadvantages of the phosphonate groups are their poor biodegradability and calcium compatibility.

Many inhibitors are known, but only a few show good biodegradation to make them environmentally acceptable in areas with strict regulations, such as offshore Norway.[1] The main issue with the current biodegradable SIs that they are stable at low temperatures (>100 °C).

In this thesis, two class of SIs are studied. The first objective of this study is to synthesize and modify the commercial SI Polyepoxysuccinic acid in-house (PESA which claimed to be easily biodegradable). The second objective of this project is to synthesize and introduce new phosphonated polyetheramine SIs, which have good calcium compatibility for oilfield applications and are stable at high temperature and pressure formations compare to commercial SIs. SIs in the second study are linear and branched polyetheramines (from Huntsman Corp.) which were phosphonated using the Moedritzer-Irani reaction. This study therefore set out to assess the calcium compatibility, thermal stability and biodegradability of SIs with regard to potential application in high temperature and pressure formation.

This study would have possible benefits in the development of SIs regarding their efficiency for giving long squeeze lifetimes which saves the operator time and money by reducing the downtime for well treatments. The results not only enable a more accurate understanding of the thermal degradation of the SIs but also facilitate the selection and placement of the SIs for high-temperature oil and gas production.

1.2 References

1. Mady, M. F.; Charoensumran, P.; Ajiro, H.; Kelland, M. A., Synthesis and Characterization of Modified Aliphatic Polycarbonates as Environmentally Friendly Oilfield Scale Inhibitors. *Energy & Fuels* **2018,** *32* (6), 6746-6755.

2 Background and State of the Art

2.1 Scale

2.1.1 *What is Scale*

Scale formation is the precipitation and adhesion of sparingly soluble inorganic salts on the surface of equipment.[1] The impurity of water where industrial water processing is required results in scale formation; This accounts for major maintenance problem in many industries.[2] Figure 1 shows the scale formed in oilfield equipment and its severity.

Figure 1. formation of scale a) in the pipeline, b) on separator surface and c) on clean separator surface.[3]

In the petroleum industry, water is considered an unwanted by-product produced with crude oil. The produced water contains several inorganic salts. The scale formation depends on various factors such as temperature, pressure, pH, partial pressure of CO_2 etc. under the condition in which the salts are soluble in water scaling is not encountered as a problem. The salts start to precipitate when the condition changes and water is in supersaturated condition.[2]

Damage and blockage of wells and topside flow lines are the consequences of scale formation.[4] The scale can deposit on almost any surface so that once a scale layer is formed, it will continue to get thicker unless treated.[.5]

The coarseness of the surface of the equipment has an essential effect on the tendency of scale formation.[2] Many formation damages are the result of the scale formation, where the deposition can occur depending on the characteristics of the scale and the fluid composition.[6, 7] Also, the blockage in production facilities can cause critical operational problems. In the oilfields, the carbonate and the sulfate scales are the two main varieties of scale. The principal candidates for deposition of scale are the internal surface of the equipment such as pipeline, choke, underground pumps and other equipment, also surface facilities such as separators and heat transfers. If the formed scale is not treated it can cause severe issues regarding the flow channels, which will finally result in total loss of production.[8, 9]

Under favorable conditions, homogeneous and heterogeneous nucleation results in the formation of scales. Nucleation starts if the solution contains both cationic and anionic species, and supersaturation condition occurs. Supersaturation is the function of temperature and pressure.

If solution temperature is increased then due to evaporation, the unsaturated solution may become saturated and eventually supersaturated, resulting in exceeding the solubility limit and it may start the formation of scales. This kind of scaling can be termed as “autoscaling”. The carbonate and sulfate scales can be formed as a result of pressure change in the system. Halite can also form in a similar way from highly saline water. Figure 2 displays conditions and different areas of potential scaling in a typical waterflood operation.

The degree of supersaturation leads to the degree of scaling potential of the water. Several factors affect the scaling tendencies of the water.[10, 11]

i. Excess concentration of minerals

ii. Condition of temperature, pressure and pH of the solution

iii. Mixing of incompatible water such as injection water for pressure

maintenance and formation water

iv. Change in thermodynamic conditions, i.e. pressure and temperature

v. Agitation and velocity (hydrodynamics)

vi. Particle size

vii. The environment of deposition

viii. Roughness of surface

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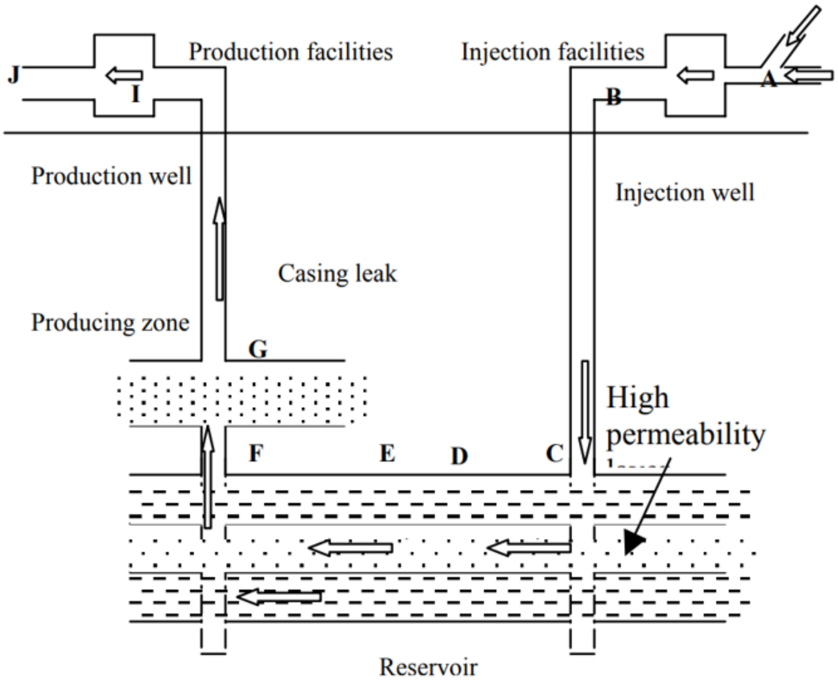


Location	Mixing of produced brine with brine from casing leak
A to B	Mixing of brines for injection
B to C	Pressure and temperature increase
C to D	Pressure decline and continued temperature increase
C to F	Solution composition may be adjusted by cation exchange, mineral dissolution or other reactions with the rock
D to F	Mixing of brines in the reservoir
E to J	Pressure and temperature decline. Release of carbon dioxide and evaporation of water due to the pressure decline if a gas phase is present or forms between these locations.
F	Mixing of formation water and injection water which has “broken through” at the base of the production well
G	Mixing of brines produced from different zones
H	Mixing of produced brine with brine from casing leak

Figure 2. Responsible factors for scale formation at different locations during water flooding.[12]

The equivalence in the ratio of the present cation and anions in the aqueous solution is another requirement for scale formation if the equivalence is not correct, then no scale will form. Water tests show that the formation water is abundant of cations such as Ca^{2+}, Ba^{2+} etc., while the seawater is onion-rich (SO_4^{2-}).[13] Water flooding process and enhanced oil recovery methods are two examples of operations in which the seawater is introduced into the reservoir, and there it might mix with the formation water (Figure 3). If the condition in the reservoir is supersaturated, the incompatible water mixes will form sulfate scale. “incompatible mixing” is the terms for this process.[12]

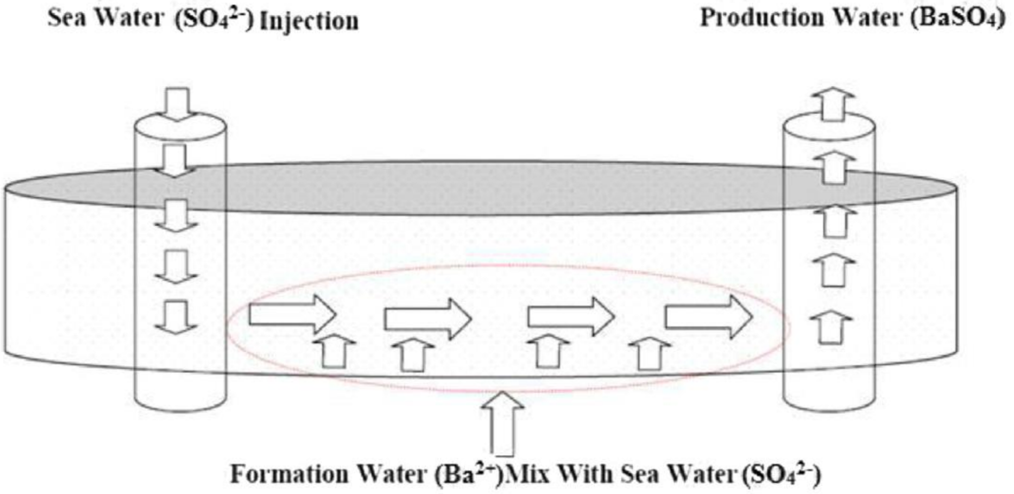


Figure 3. Mixing of the seawater with the formation water. [14]

2.1.2 *Scale Formation Mechanisms*

Oil gas and water are the three major presented and produced fluids in the reservoirs. Mineral salts are dissolved in the produced water in under-saturated condition. However, as a result in changes in of temperature, pressure, pH, partial pressure of CO_2, etc., inorganic salts precipitate and form scales.[11, 13] Scale deposits tend to adhere to solid surfaces. Once the first layer is formed, the next layers have a higher tendency to deposit and gradually more scale layers are formed on the surface of the equipment. In an oil well, choking of the net diameter of flow conduits can result in losing the total loss of production. The internal surface of pipelines, choke, underground pumps, separators and heat treater are the most vulnerable parts of the system regarding the scale formation.[8, 9] Scaling is a complex phenomenon and involves crystallization mechanisms.

Once the activity of cations and anions in the solution surpasses their saturation limit and the solution shifts supersaturated, the crystallization and following deposition of scales takes place. Also, the kinetics of the reaction plays a key role in the degree of scaling.[15] Both surface and bulk crystallization are the two mechanisms which will cause scale formation.[16, 17] Heterogeneous nucleation and homogeneous nucleation mechanisms are the foundations of surface and bulk crystallization, respectively.[14]

In homogeneous nucleation there is no role of foreign material and the nucleation occurs in bulk solution in liquid phase. Thus, in this case formed scale particle may flow through the system and do no deposit or in the other way they may get deposited as sediments to form cake layer. On the other hand, heterogeneous nucleation occurs in the presence of foreign substances which act as trigger for the deposition of formed scales on the solid surface of equipment encountered. The foreign substance can be suspended solids, scale nuclei, welds/stress joint on the metals, corrosion site present on metal surface etc.[14] One of the factors responsible for scaling is corrosion. It is often ignored but the fact is that the corroded metal provides Fe^{2+} and Fe^{3+} cations in flowing fluid which results is formation of iron sulfides, iron oxides and iron carbonate scales.[18] The scale formation steps are shown in Figure 4:

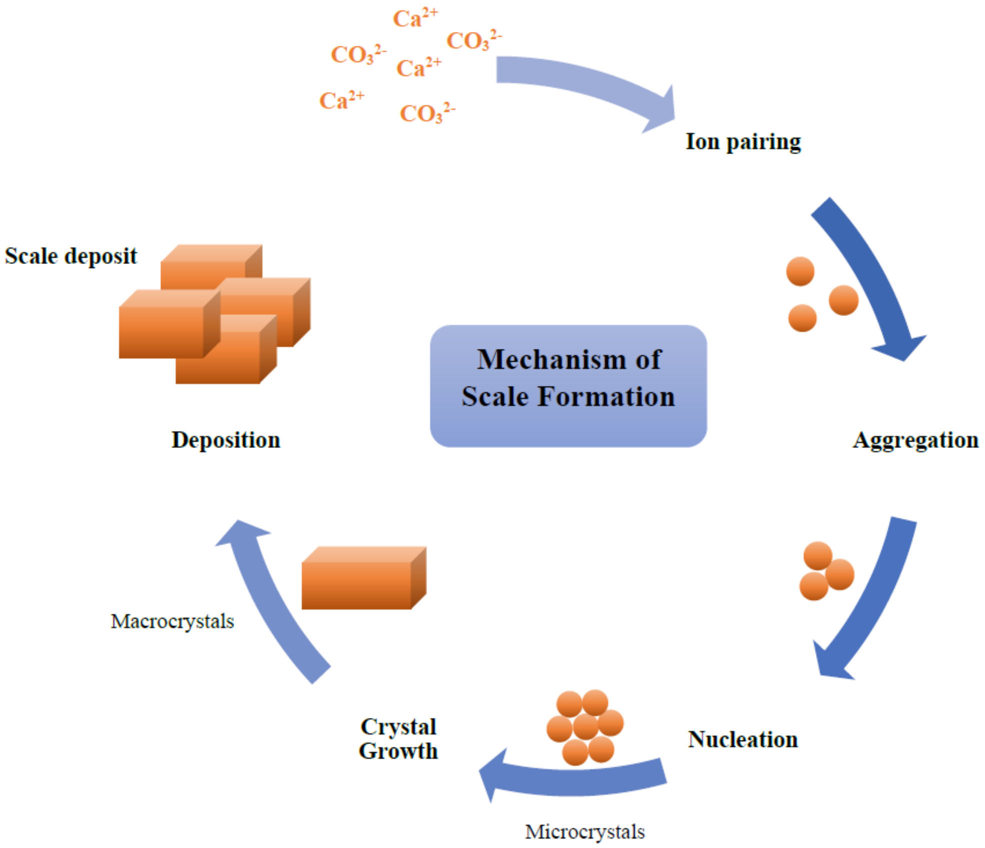


Figure 4. Schematic of calcium carbonate scale formation mechanisms.

Aggregation: Ion pairs are formed as the result of the collision of the cations (e.g. Ca^{2+}) and anions (e.g. CO_3^{2-}/SO_4^{2-}) under supersaturation conditions. The ion pairs can attach and make micro-aggregates, which could be the core of crystals, embryo, and micronuclei.[15]

Nucleation: The formation of the micro-aggregates leads to the formation of micro-crystals. Substrate and in some cases the bulk fluid are the areas where the nucleation might occur at approximately higher saturation ratio.[15]

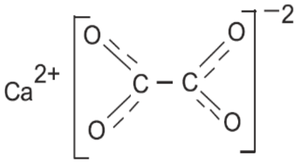
Crystal growth: The agglomerates and adsorption of the produced microcrystals on to the surrounding surfaces will create bigger microcrystals. The large microcrystals will then continue to grow, and finally, they form depositional microcrystals.

Agglomeration: The surface will be covered by the scale layers when the Formed micro crystals expand by adsorbing further cations and anions in the mixture. The formed scale converts to deposit.[15]

2.2 Different Types of Oilfield Scales

The solubility of minerals will decrease as the temperature declines (although calcium carbonate is an exception). From the sea-surface to the seabed, the temperature will decrease significantly. Therefore, this will enhance pipeline scale problems. Another factor affecting the deposition of inorganic salts is the presence of organic thermodynamic hydrate inhibitors (THIs). Methanol and small ethylene glycols are examples of THIs and methanol are the worst.[19] These compounds have less polarity than water. Consequently, the solubility of common scaling salts will decrease. On the other hand, the deeper and colder the fields are developed the need for using THIs will increase. The challenges facing scale control in deep-water fields have been reviewed.[20] The most common oilfield scales are listed in Table 1 :

Table 1. Common oilfield scales.[14]

Name	Chemical formula	Mineral
Calcium carbonate	$CaCO_3$	Calcite, aragonite, or rarely vaterite
Calcium sulfate	$CaSO_4$	Anhydrite, hemihydrate ($CaSO_4 \cdot 5H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$)
Calcium oxalate		Beerstone
Barium sulfate	$BaSO_4$	Barite
Magnesium hydroxide	$Mg(OH)_2$	Brucite
Magnesium oxide	MgO	Periclase
Silicates	$Me(SinO_x)\ yH_2O$	Serpentine, acmite, gyrolite, gehlenite,amorphous silica, quartz, cristobalite, pectolite
Aluminum oxide Hydroxides	AlO(OH)	Boehmite, gibbsite, diaspore, corundum
Aluminosilicates	Al_xSiyO_z	Analcite, cancrinite, noselite
Copper	Cu	Metallic copper, cuprite (Cu_2O), tenorite (CuO)
Phosphates	$Ca_{10}(PO_4)6(OH)_2$	Hydroxyapatite
Magnetite or nickel Ferrite	NiFe2O4	Trevorite

These scales are sulfates such as calcium sulfate (anhydrite, gypsum), barium sulfate (barite), and strontium sulfate (celestite) and calcium carbonate. Other less common scales have also been reported such as iron oxides, iron sulfides and iron carbonate and calcium naphthenate scale from acidic crudes.[21]

2.2.1 *Calcium Carbonate Scale*

Calcium carbonate is one of the most common scales in the oil field. In nature, three types of this scale, namely Aragonite, Calcite and Vaterite, can be found.[22] Among these, calcite is the most stable polymorph of calcium carbonate. Water solubility as a function of temperature for all three forms of calcium carbonate is illustrated in Figure 5:

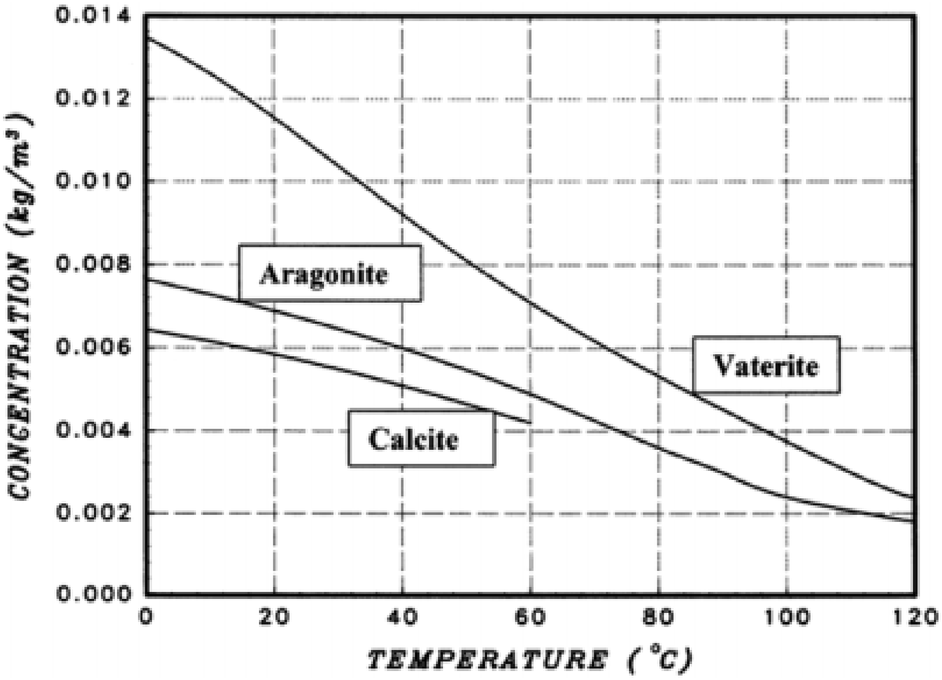


Figure 5. The water solubility of three different forms of calcium carbonate as a function of temperature.[23]

Calcium carbonate ($CaCO_3$) is poorly soluble in pure water. However, calcium bicarbonate ($CaHCO_3$) is very water soluble. The produced water from the oil field usually carries considerable amounts of both bicarbonate and calcium ions. The changes in pressure during the oil extraction process will result in changes in pH and consequently, scale formation. The following equilibrium explains the calcium carbonate deposition when a drop in the pressure occurs:[24]

$$2HCO_3^- \leftrightarrow CO_3^{2-} + H_2O + CO_2$$

According to Le Chatelier's principle, this equilibrium will move to the right due to the pressure drop. As the pressure decreases, more CO_2 gas will be formed in order to increase the pressure. The formation of carbonate ions causes pH levels to rise.[25] If the concentration of carbonate ions is high enough, calcium carbonate scale will form. The following equation shows calcium carbonate formation:

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

This equation is the combined form of the following equilibrium equations as shown below: [2]

$CO_2(g) \leftrightarrow CO_2(aq)$

$H_2O + CO_2(aq) \leftrightarrow HCO_3^- + H^+$

$HCO_3^-(aq) \leftrightarrow CO_3^{2-} + H^+$

$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$

$H_2O \leftrightarrow H^+ + OH^-(water)$

The formation of calcium carbonate scale occurs when the production system experiences the critical drop in pressure. In an oil field, the first calcium carbonate scale may form after several years.

2.2.2 *Sulfate Scales*

Seawater-flooded reservoirs usually face the problem of sulfate scale formation. As it is shown below, Group II metal ions, except magnesium, can form sulfate scales when mixed with sulfate ions:

$$M^{2+} + SO_4^{2-} \rightarrow MSO_4\ (s)$$

2.2.2.1 Calcium Sulfate

One of the frequently occurring mineral scales is calcium sulfate. The three primary forms of this scale are: i) Dihydrate ($CaSO_4.2H_2O, gypsum$); ii) hemihydrate ($CaSO_4.\frac{1}{2}\ H_2O, plaster\ of\ Paris$); and iii) anhydrite ($CaSO_4$).[2] Figure 6 shows the water solubility of these three forms of calcium sulfate as a function of temperature.

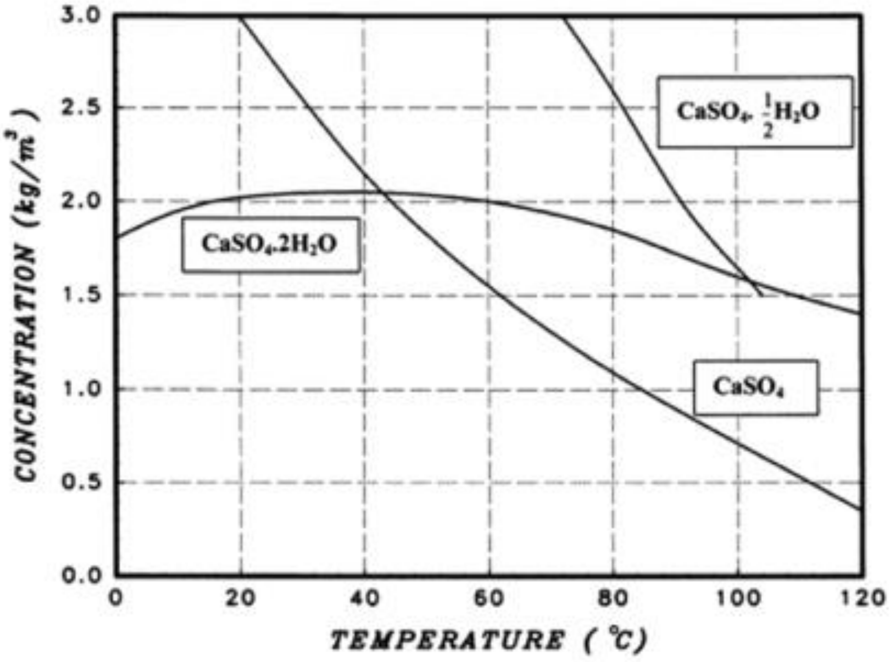


Figure 6. The water solubility of different forms of calcium sulfate as a function of temperature.[24]

As it is shown in Figure 6, most deposited calcium sulfate form under below 40 °C is gypsum. Hemihydrate and anhydrite are frequently occurring scales on heat exchangers in distillation column.[11, 26]

2.2.2.2 Barium Sulfate

Barium sulfate is known as one of the toughest and most stable scales compared with other kinds of scale. Despite calcium carbonate, the water solubility of barium sulfate increases with increase in temperature of the system and it has the least water solubility among other scales. In offshore fields, the injected seawater contains significant SO_4^{2-} at the same time, the formation water is rich in Ba^{2+}, consequently the formation of insoluble $BaSO_4$ is problematic.[2] The following equation illustrates the formation of barium sulfate:

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)\Delta_r H^o = \text{-}\ 858.56 \cdot \text{KJ/mol}$$

The methods performed to remove the existing scales are scale removal methods which differ from the scale inhibition methods. According to various factors, such as the nature and site and severity of the scale, chemical or mechanical methods could be implied.[27] Another method for managing the scale issue in the industry is to prevent scale formation. In this study, prevention management will be discussed.

Scale prevention refers to the management of the scale formation in production facilities primarily. Studies show that efficient scale management is to make an early decision in the progress of development and maintenance of the industrial fields.[5] This method suggests that as the first layer of the scale tends to form, the mechanism of scale formation should be disrupted. In oilfields, injection of seawater and reinjection of produced water demands scale formation management.

Different methods have been applied for mitigating scaling issues:

- Desulfation of injected seawater
- Scale control/inhibition
- Mechanical and chemical removal of existing scale

2.3 Scale Inhibitors

2.3.1 *What is a Scale Inhibitor*

Scale inhibitors are the chemicals that prevent inorganic scale nucleation, precipitation and deposition on equipment surfaces. Several factors affect the performance of Scale inhibitors, which include pH, temperature, the presence of divalent cations and other oilfield chemicals such as corrosion inhibitors in the brine. Scale inhibitor's threshold level for a specific level of inhibition is called minimum inhibitor concentration (MIC). For the effectiveness of scale inhibitors evaluation tests are being conducted. Two tests are particularly adapted in the oil industry. These tests are static bottle test and dynamic tube blocking tests.[28] The static bottle test evaluates the effectiveness of the scale inhibitors in the prevention of scale deposition in the bulk phase of the surface. This is the most widely used test method due to low cost and quick to measure inhibitor's effectiveness on scaling control in bulk phase. On the other hand, dynamic tube blocking test evaluates the effectiveness of scale inhibitors on preventing scaling in a capillary tube in a flowing condition.[29] Inhibitor's efficiency can be calculated as the ratio of the time needed to tube blocking in the presence of inhibitor and the time required to tube blocking in the absence of inhibitor.[30]

The composition of the compounds can differ considerably in various regions. For example, the levels of barium ions deviate from a few mgL-1 to gL-1, and the pH varies from 4.4 to 7.5 in the Central North Sea Province. While high salinity and high concentration of sulfate and acidic compounds are the characteristics of the formation water in the southern zone of the North Sea. The ideal scale inhibitor should have the following properties:[31]

- Effective scale control at low inhibitor concentration,
- Compatibility with sea and formation water,
- Balanced adsorption-desorption properties, allowing the chemicals to be slowly and homogeneously released into the production water,
- High thermal stability,
- Low toxicity and high biodegradability, and
- Low cost.

Scale Inhibitor should work slowly and steadily for longer times. It is desirable for scale inhibitors to get releases in optimum level for several months for a successful job. Most used method for inhibitor placement is squeeze treatment. It is a costly process. Thus, retention of inhibitor for maximum life of production is very desirable. Scale inhibitors normally required in ppm level in produced fluid for a successful job. Any greater level of the dose will not be further effective and only cause wastage of the inhibitors. Thus, Scale inhibitors must be chemically active yet compatible with reservoir conditions. Thus, reservoir temperature, pressure and brine composition critically affect the stability of the inhibitors. The primary mechanism for the inhibitor release is hydrolysis. In the different class of Inhibitors, phosphonates are most stable having half-life more than one year at 300 °F over the pH and salinity range found in the reservoir.[32]

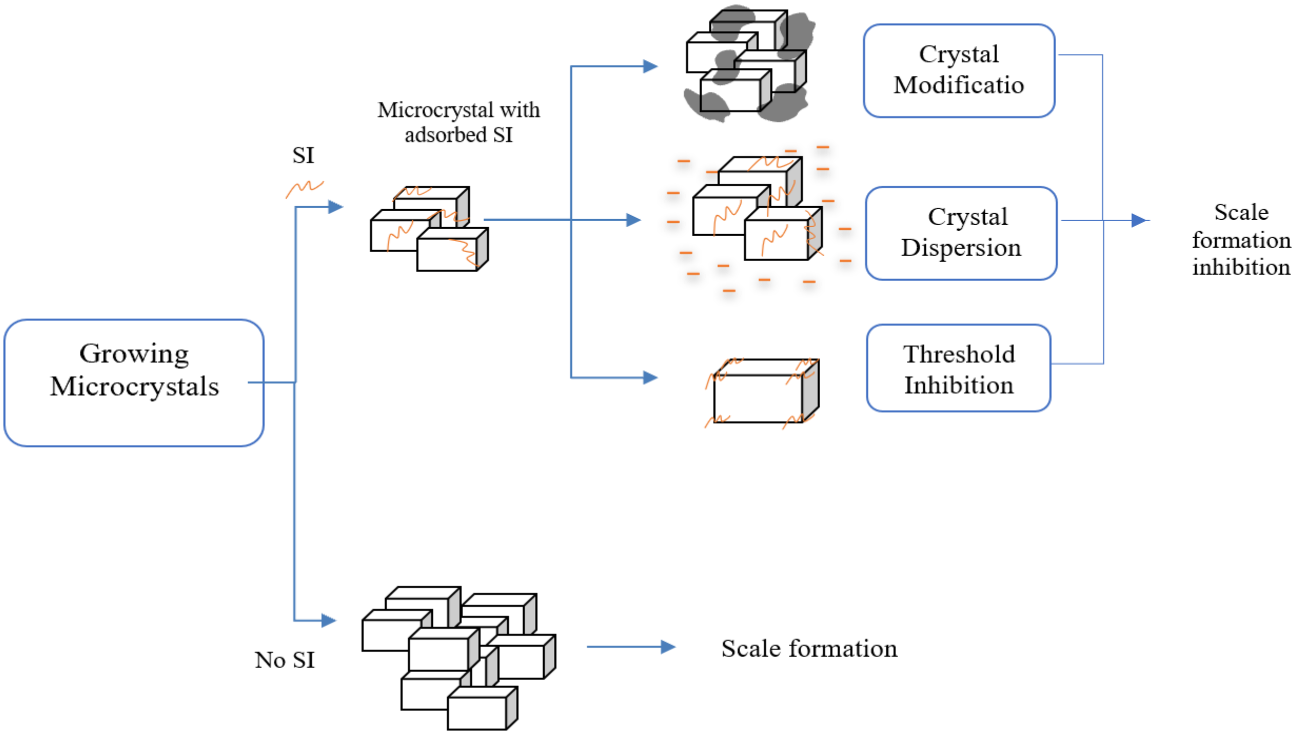


Figure 7. Pathways of scale inhibition.

There are several potential mechanisms for inhibition of scale formation for polymeric SIs; threshold inhibition, dispersion, and crystal modification are the examples of the possible mechanisms. As illustrated in Figure 7, the SI adsorbs on the developing crystal surface as a microcrystal of scale starts to build. In this step, three pathways for scale prevention can happen.[33]

Generally, polymers are known as suitable nucleation inhibitors and dispersants. When the polymers are examined under their threshold levels, they slow down the speed of crystallization. The mechanism that polymers deploy to inhibit the crystallization is by adsorption onto the crystal surface when the crystallization starts and they are used in the lattice.[3, 34, 35] The amino phosphonates are an example of the famous non-polymeric SIs. This type of inhibitors will hinder the active growth sites of the formed crystals, and therefore, they will prevent the crystal growth; however, the nucleation prevention is not possible if these SIs are tested under their threshold level. In order to assure that the aminophosphonate will stop the nucleation, the concentration of the SI must be increased. In the same way, the increase in the test dose rate of the polymer will assure crystal growth prevention. In summary, nucleation inhibition, crystal growth inhibition, and even scale dispersion are the mechanism which will allow the SI to reach its critical purpose.[36] Previous studies have established that 3%-5% coverage of the surface of the carbonate or sulfate scale crystal by the polymeric SI is enough for the desired inhibition performance.[37] Also, according to studies, 16 % of the surface of the barite scale must be covered by small aminophosphonate for sufficient inhibition.[38]

In recent years, there have been improvements in the patterns and mechanisms by which the capability of the SIs against scale formation is determined.[39] Among all sulfate scale inhibitor types, the mechanism for inhibition of sulfate scale by aminophosphonates is suggested to be more complicated. The prevention of scale growth for calcium scale inhibitor complex starts with the addition of the calcium in the lattice, which leads to changes in the lattice. As a result, aminophosphonates have been proved to be weak sulfate scale inhibitors at deficient concentrations of the calcium ions.[35, 40]

Several methods are conducted to apply the SIs in the field, which will be discussed later. In the following, the different types of SIs and their usage against different classes of scales will be discussed. As mentioned earlier, the oilfield scales such as carbonates and sulfates are rich in cations and anions (CO_3^{2-} and SO_4^{2-}), along with the high concentration of divalent metal cations. Both nucleation inhibition and crystal growth prevention depend on the attachment of the SI particle to the surface of the scale. Therefore, the scale inhibitor must be able to combine with the anions or cations in the produced water. Regularly to keep the inhibitor attached to the surface, a number of these interactions are needed. The presence of molecules with various similar functional groups will help to increased interaction with the lattice ions on the crystal surface.[5]

There are several anionic groups attached to an organic molecule that can interact well with group II cations on the scale crystal surface. The most important of these are:[5]

- Phosphate ions ($–OPO_3H^–$)
- Phosphonate ions ($–PO_3H^–$)
- Phosphinate ions ($–PO_2H^–$)
- Carboxylate ions ($–COO^–$)
- Sulfonate ions ($–SO_3^–$)

The efficient SIs are the molecules which contain two or more of these ions, or mixtures of these ions in their structure. However, the most effective SIs are the ones that are in the anionic dissociated form they can also be provided in the acid form. The examples for acidic form are carboxylic acid and phosphonic acid while sodium, potassium, or ammonium salts are the representatives of the anionic dissociated form. Except for polyphosphates, the anionic groups are all attached through carbon atoms to the main backbone of the molecule.[5]

Below is a list of the most common classes of scale inhibitors containing these ions or acids: [5]

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

2.3.2 *Methods of Deploying Scale Inhibitors*

In recent years, there have been improvements in the structure and the performance of the scale inhibitors. Specifically, there has been an increasing interest in producing more biodegradable Scale inhibitors. However, the application of the SI is a common condition which has a considerable impact on its performance, and more advances are required for this process. For inhibiting the scale accumulation, the scale inhibitor must be put into the formation. Origin of scaling occurs in the formation and eventually, it coats subsurface facilities and processing equipment. SIs could be introduced to the field with different methods. The most common methods are as below: [41]

- Continuous injection
- Squeeze treatment
- Solid, slow-release scale inhibitor compositions

The most widely and favor mechanism is squeeze treatment.[3]

2.3.2.1 Scale Inhibitor Squeeze Treatments

For the purpose of inhibiting the scale formation in producing wells and in the near well-bore area, scale inhibitor squeeze treatment is employed. As illustrated in Figure 8, to begin this process, a mixture of the SI is introduced to the well. By injecting the mixture of SI in a higher pressure than the formation pressure, the SI will be launched into the near-well. The required time for the absorption of the SI to the formation rock is provided by shutting down the well for hours. Prior to starting the production, the produced water will be injected to the well and will cross the pores. After that some of the pre-injected SIs are dissolved in the produced water, sufficient amount of the SI will be present in the produced water for the inhibition of the scale.[5]

Squeeze treatments follow these five stages, which is illustrated in Figure 9:[5]

1. A pre-flush stage

2. The primary treatment where the chemical SI (usually aqueous) solution is introduced into the formation with a concentration range of 2.5%-20%

3. An over-flush, intended to push the main slug to the required depth into the formation off from the wellbore

4. A shut-in, a period to enable the SI to attach on the rock surface

5. The well is put back on production

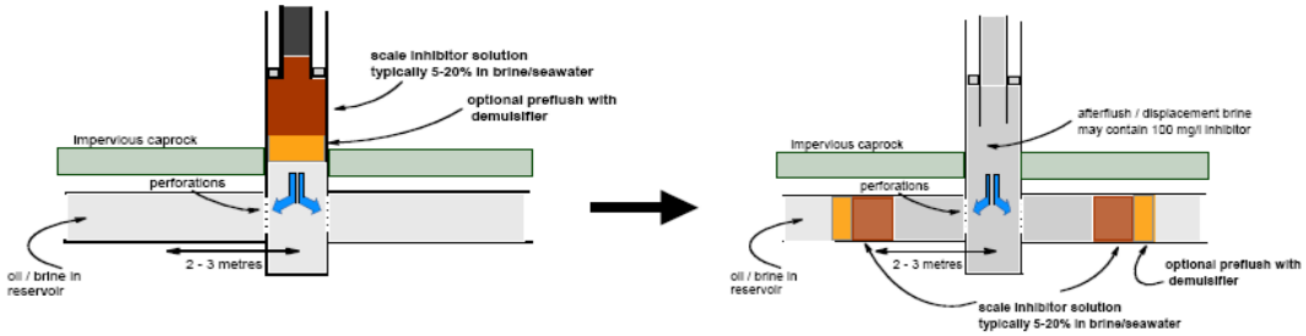


Figure 8. Scale inhibitor squeeze treatment illustration.[5]

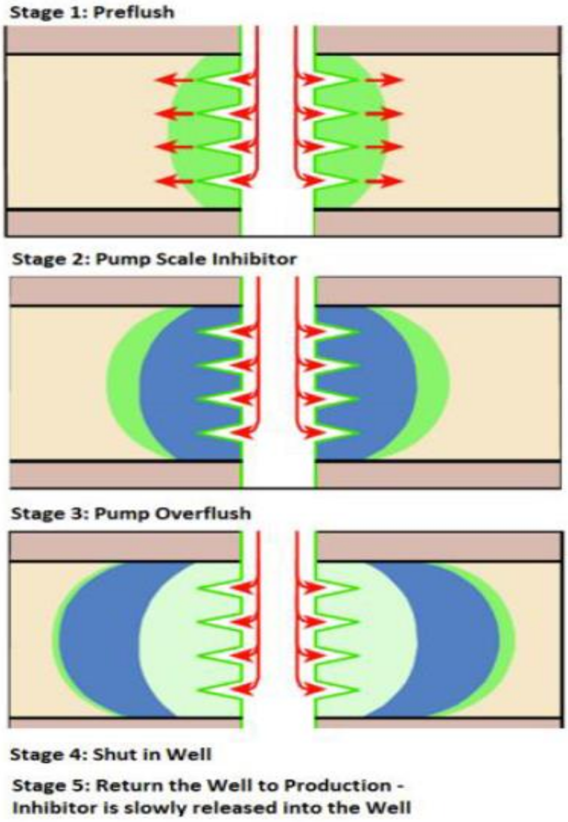


Figure 9. The five steps in squeeze treatment.

The inhibition of the scale formation continues until the concentration of the SI in the well is over a specific concentration. The limiting concentration of the SI in the well is known as minimum inhibitory concentration (MIC). There are varieties of the circumstances that will influence the lifetime of the squeeze treatment. The examples of these factors are production rate, water cut, and the reservoir geology/mineralogy of the reservoir. The example of a situation where the concentration of the inhibitor decreases under the MIC (2ppm) after approximately 92 days is shown in Figure 10.[5]

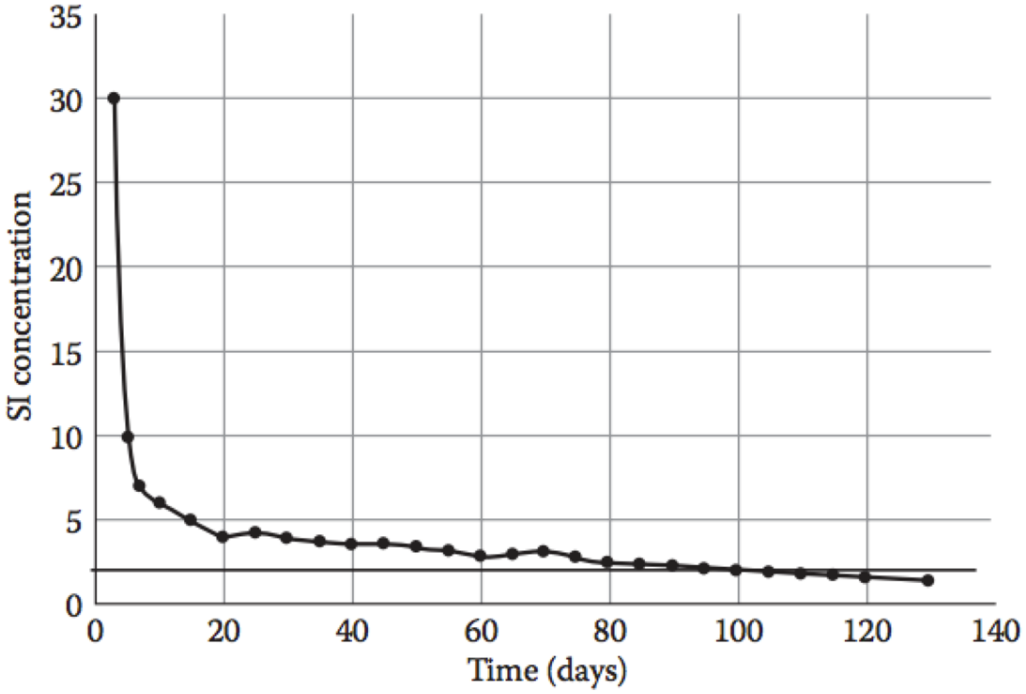


Figure 10. The SI concentration (ppm) vs time showing the drop below MIC (2 ppm) after about 92 days of squeeze treatment.[5]

Several techniques have been improved to enhance scale inhibitor maintenance on the rock formation and therefore improve the continuance of a squeeze treatment. They include [5]:

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

Precipitation squeeze treatment has been suggested to be useful for enhancing the retention of the scale inhibitor in the near wellbore. Incompatibility of the SIs with high concentrations of calcium or magnesium is one of the critical issues at the formation temperature and pH. In the precipitation squeeze treatment, the injection of cations or Fe (II) ions with scale inhibitor will improve the retention time of the SI in the reservoir by precipitation of the inhibitor-cation complex in the near wellbore.[5, 42-45]

Thus far, previous studies have confirmed notable effectiveness of the addition of Zn^{2+} ions in the squeeze treatment solution.[5, 46] Synergistic impacts on barite scale inhibition was also evident in data from laboratory experiences for specific scale inhibitors. Also, corrosion inhibition can be improved by phosphonate and Zn^{2+} additions. The increase in the pH of the scale inhibitor is another practical factor in the precipitation squeeze method. Higher pH will change the acidic groups to anionic groups, which will result in the easier formation of complexes with cation ions. Therefore, calcium/magnesium complexes will precipitate.[5]

Mutual solvent, small non-ionic amphiphile, is a method to increase the squeeze lifetime. This technique enhances inhibitor retention by making rocks more water wet.[47, 48] They also remove trapped water, water blocks, caused by an all-aqueous squeeze treatment. The mutual solvent is therefore used in the pre-flush, and in combination with the pH-modifying technique.

2.3.3 *Environmental Regulations*

In the new global environmental attitude, applying less hazardous chemicals has become a central issue. Environmentally unacceptable chemicals which are present in produced water are a significant problem in the oil industry. ‘Green Chemicals’ can broadly be defined as the readily biodegradable chemicals that do not cause adverse consequences on the environment. The harsh conditions for the fields that are in deep and cold waters grow the need for more efficient chemicals. Nevertheless, it is proved that designing green chemicals with high-performing characteristics is not simple.[5] There have been regulations in different parts of the world against the application of hazardous chemicals to reduce the application of the oilfield chemicals.

OSPAR

“OSPAR is the agreement by which 15 Governments & the EU cooperate to protect the marine environment of the North-East Atlantic”.[49] Oslo convection against dumping in 1972, followed by the Paris convection in 1974 resulted in foundation of OSPAR which stands for ‘OS’ for Oslo and ‘PAR’ for Paris. The OSPAR guidance for the North-East Atlantic presents the required regulatory for the ecotoxicological examination of the applied chemicals in offshore drilling in the North Sea. In 2001, OSPAR guidelines were fulfilled with the purpose of harmonizing the compulsory control policies for marine chemicals. OSPAR requirements for the three classes of tests are:[8]

• **Acute toxicity**: The term "Acute toxicity" refers to the harmful impacts of a substance that appear either from a single exposure or from multiple exposures in a short period (typically less than 24 hours).[50]

• **Bioaccumulation**: Bioaccumulation is associated with the relative solubility of a chemical in lipids (found in fatty tissues) and water. It can be determined based on relative solubility in octanol (representing fatty tissue) and water. This is shown as the logarithm of the octanol-water distribution coefficient: log Pow. If the coefficient is larger than or equal to three, the substance is considered to be a bioaccumulation risk unless the experimental examination of a bioaccumulation factor (BCF) shows the opposite.[8]

• **Seawater biodegradation (persistence):** Biodegradability testing is specified in the OECD 306 protocol using either the shake-flask dissolved organic carbon (DOC) method or the closed bottle biological oxygen demand (BOD) method. Biodegradation is calculated as the ratio of the amount of oxygen consumed during the degradation period to the calculated theoretical oxygen demand (ThOD). The test is normally carried out over a 28-day period.[8]

Chemical additives related by obligations in emission/discharge permissions are broken into four classifications (green, yellow, red and black) regarding the distribution in the activity's guidance:[51]

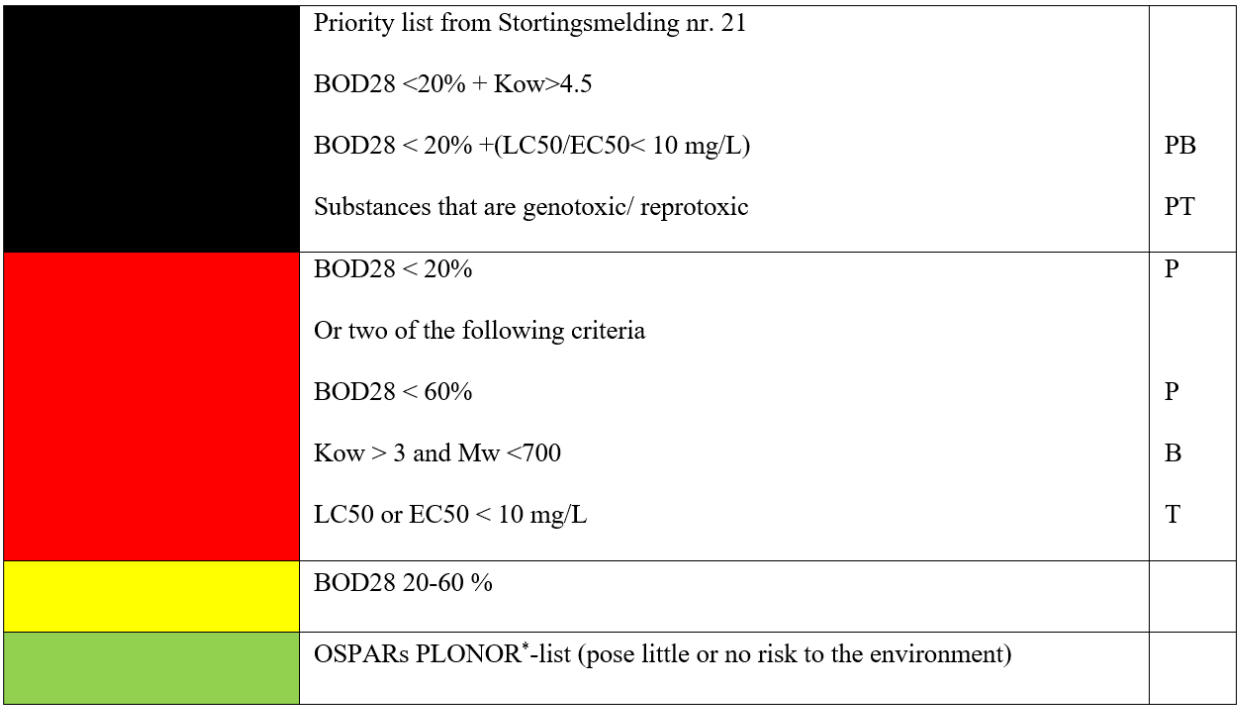
1) GREEN Chemicals granted having no or minimal environmental impact. No specific conditions are required for their discharge.

2) YELLOW Chemicals in use, but not included by any of the other classes. Can generally be discharged without specified conditions.

3) RED Chemicals which must be prioritized for replacement, but which can be discharged with government approval.

4) BLACK Chemicals which the government can allow to be discharged in exceptional condition – where this is essential for safety, for example.

Table 2. The classification of the utilized chemicals in oilfield industries. (The last column refers to the properties that impact P: persistence, B: bioaccumulation, T: toxicity).



⬛	Priority list from Stortingsmelding nr. 21 BOD28 <20% + Kow>4.5 BOD28 < 20% +(LC50/EC50< 10 mg/L) Substances that are genotoxic/ reprotoxic	 PB PT
🟥	BOD28 < 20% Or two of the following criteria BOD28 < 60% Kow > 3 and Mw <700 LC50 or EC50 < 10 mg/L	P P B T
🟨	BOD28 20-60 %	
🟩	OSPARs PLONOR*-list (pose little or no risk to the environment)	

s

**"Pose little or no risk to the marine environment", a list from OSPAR of chemical compounds considered to have little or no impact on the marine environment if discharged.*

2.4 Earlier Studies

2.4.1 *Phosphonates and Aminophosphonates*

Phosphonoacetic acid and 2-aminoethylphosphonate are considered as natural phosphonic acids. Previous studies have suggested some of the anthropogenic phosphonic acids as useful complexing and chelating agents.[52, 53] For instance, the effectiveness of phosphonic acids against apatite nucleation and crystal growth has been proved.[54] Moreover, among different types of SIs that are used in oilfields, organophosphonic acid compounds and their salts are well-known.[55-58]

Organophosphonic acid compounds are designed in different types such as small non-polymeric SI molecules with only a few phosphonate groups or polymeric compounds that contain several joined phosphonate groups.[5] A common way of introducing the phophonate to the main structure is with an aminomethylenephosphonate group. The existing amine group in the structure of the chemical will benefit the SI by operating as a Lewis base ligand in the inhibition process. Also, phosphonate groups will facilitate the measurements for the concentration of the SI in the produced water. Therefore, the presence of the phosphonate group can result in a better understanding of the minimum inhibitory concentration (MIC). Finally, the proper time for re-squeezing the well can be determined using the (MIC).[59]

2.4.2 *Synthesis of Aminomethylenephosphonic Acids*

Moedritzer−Irani Reaction

Kurt Moedritzer and Riyad R (1966), discovered the Moedritzer−Irani reaction.[60] This reaction has been deployed for synthesizing producing various commercial aminomethylenephosphonic acid SIs.[1, 61] The general equation for the synthesis of aminomethylenephosphonic acids by the Moedritzer−Irani reaction is shown in Figure 11:

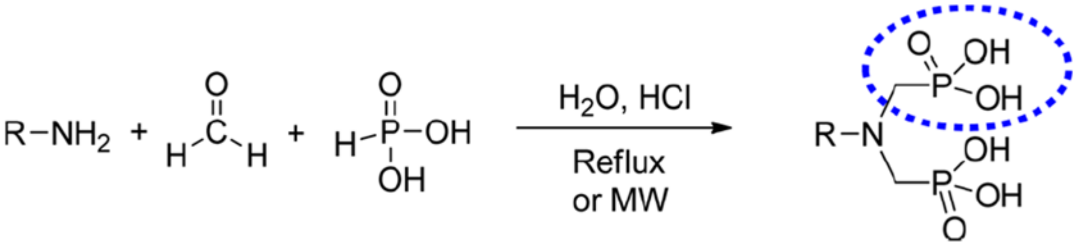


Figure 11. General equation for the synthesis of aminomethylenephosphonic acids by the Moedritzer−Irani reaction.[62]

Figure 12 displays the structures of common oilfield SIs with this functional group. They include aminotris- (methylenephosphonic acid) (ATMP), ethylenediamine tetra-(methylenephosphonicacid) (EDTMP), Diethylenetriaminepentakis methylenephosphonic acid (DTPMP), hexamethylenediaminetetra (methylenephosphonic acid)(HDTMP), and bis(hexamethylenetriaminepenta- (methylenephosphonic acid)) (BHMTMP).

Phosphonomethylated polyamines are good barite scale inhibitors, and they also can be applied in squeeze treatments. An N-phosphonomethylated amino-2- hydroxypropylene polymer (molecular weight of around 300 - 5000), can be produced by the reaction of a small polyalkyleneamine, such as triethylenetetramine, with epichlorohydrin later reacting the amine groups with formaldehyde and phosphorous acid.[63]

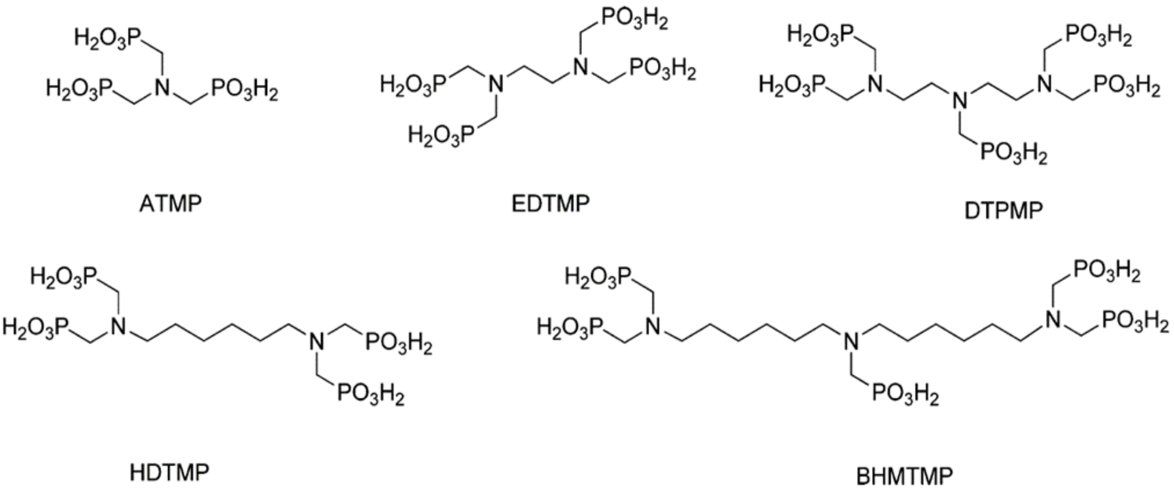


Figure 12. Examples of the commercial oilfield SIs containing aminomethylenephosphonate groups.

2.5 New Idea

Biodegradable and biocompatible polymers have gained attention and have been proposed for different applications. Polyethylene glycol (PEG) is a water-soluble polymer that contains easy end group modification. Biodegradability and biocompatibility are the known properties of this polymer.

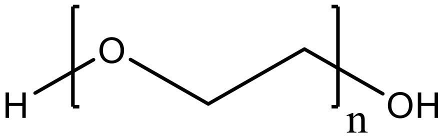
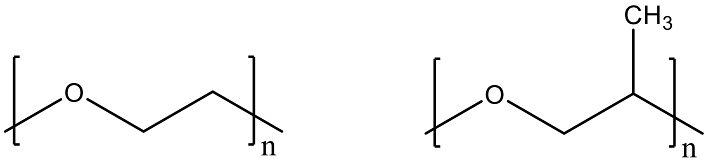


Figure 13. Polyethylene glycol (PEG).

Jeffamine is a polyetheramine made of varying ratio of diamino terminated triblock copolymers of polyoxyethylene (POE) and polyoxypropylene and is one of PEG compounds.[64] Jeffamine polytheramines refers to the chemicals that are made from propylene oxide (PO), ethylene oxide (EO), or mixed PO/EO backbone. The backbone of these chemicals contains attached primary amino groups. Jeffamine polytheramines are a part of an expanding group of Huntsman products.

The reaction of the amines in the backbone of the Jeffamine polyetheramines can give rise to their flexibility, toughness, while it could lower their viscosity and colour. A number of factors play a role in the capability of designing new compounds or mixtures from Jeffamine family.[65] The broad variety of molecular weight, amine functionality, repeating unit model, and distribution are the main features of Jeffamine poletheramines. The formation of urea, imide, epoxy opening, amide and imine bonds (Schiff base), are the examples of the different reactions that result in diverse molecular modifications of Jeffamine compounds.[66]

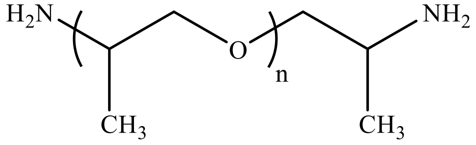


(a) (b)

Figure 14. Molecular structure of (a) ethylene oxide (EO), (b) propylene oxide (PO).

JEFFAMINE® D Series

Jeffamine D series products are amine terminated PPGs with the following representative structure (Figure 15):

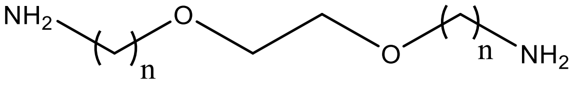


JEFFAMINE®	n	Mw
D-230	~2.5	230

Figure 15. Jeffamine D series chemical structure.

JEFFAMINE® EDR Series

Jeffamine EDR-148 and Jeffamine EDR-176 amines are considered as the most reactive compounds among other Jeffamine diamines and triamines. These products can be used for many purposes as they are unhindered diamines with the ability to be miscible in a broad class of solvents. Their structure is represented in Figure 16:

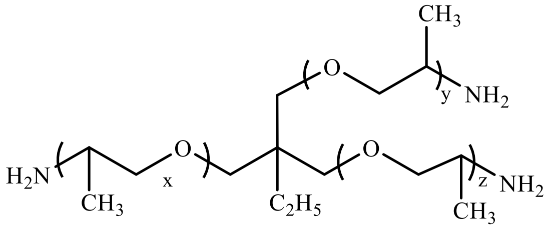


JEFFAMINE®	n	Mw
EDR-148	2.0	148
ECR-176	3.0	176

Figure 16. Jeffamine EDR series chemical structure.

JEFFAMINE® TRIAMINES (T series)

Another group of Jeffamines are Jeffamine T series, which are the result of the reaction of PO with a triol initiator, followed by functionalizing the terminal hydroxyl groups with amines. They are illustrated by the following structure (Figure 17):



JEFFAMINE®	Moles PO (x+y+z)	Mw
T-403	5-6	440

Figure 17. Jeffamine T series chemical structure.

In the present study, the water soluble Jeffamine, a commercial PEG-containing diamino terminated triblock copolymers (polyoxypropylene(POP)-poly-oxyethylene(POE)-polyoxypropylene (POP)) was used to prepare SIs. Jeffamine family includes different series of compounds which are biodegradable, biocompatible and non-toxic with great applications in biomedicine and adsorption of contaminants from industrial effluents.[66] Jeffamine has also proven to be significant due to its easy end group modification via different reactions such as formation of urea, imide, epoxy opening, amide and imine (Schiff base) bonds.[67, 68]

Although phosphonate base SIs can offer several advantages in squeeze treatments over other SI classes, one downside is that they are not readily biodegradable. Recently, there have been several attempts to provide environmentally acceptable biodegradable SIs but rarely phophonate base.

The biodegradable, biocompatible and non-toxic characteristics of Jeffamine group encouraged us for a study to design and synthesize a series of methylenephosphonated polyetheramines (Jeffamine) as new SIs. The methylenephosphonate group was introduced onto the amines by the Moedritzer−Irani reaction to improve their inhibition performance. All synthesized compounds were also evaluated for calcium compatibility, thermal stability and their biodegradability.

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3 Experimental Procedures

3.1 Chemicals

All the chemicals used in this thesis were purchased from VWR, Nippon Chemical Industrial Co., Ltd., Tokyo Chemical Industry Co., Ltd., Sigma-Aldrich and Huntsman Corporation. The solvents were used without further purification.

3.2 Characterization of Scale Inhibitors (SIs)

To characterize the target chemicals, and to verify the reactions, NMR spectroscopy was used. The NMR spectra were recorded on a 400 MHz Bruker NMR spectrometer in deuterium oxide (D_2O) with two drops of sodium deuteroxide solution. ^1H NMR and ^{31}P NMR chemical shifts were obtained in D_2O.

3.3 Syntheses

In this study, two series of chemical experiments were conducted. The first series included synthesis of polepoxysucicinc acid according to patent.[1] The other set of synthesis was phosphonation of linear and branched polyetheramines (from Huntsman Corp.) using the Moedritzer-Irani reaction.[2]

3.3.1 *Synthesis of Polyepoxysuccinic Acid (PESA)*

The synthesis of PESA was conducted in two steps. The first step consists of synthesizing epoxysuccinic acid (ESA), and the second step was polymerization of ESA to produce polyepoxysuccinic Acid (PESA). The procedure is described below.

Step1, Synthesis of Epoxysuccinic Acid (ESA):

Maleic anhydride (2 gr, 20 mmol) and deionized water (15 ml) were charged into a 250 ml one neck flask equipped with a mechanical stirrer in an ice batch. Using a dropping funnel, NaOH (50 %, 2.62 gr, 32 mmol) was added to the flask dropwise over 30 minutes, and a solid compound was formed. By transferring the flask from ice batch to a heating batch and increasing the temperature to 80 ℃ the solid was totally dissolved and then it followed by cooling to 55 °C and the reaction was held overnight (Figure 18). After completion of the previous reaction, H_2O_2 (2.9 gr, 20 mmol) was then added to the solution dropwise over 0.5 hours followed by the addition of sodium tungstate (0.035 gr, 0.1 mmol). The mixture was slowly warmed up to 90 ° C until a clear solution was observed and then cooled down to 60 °C and had a pH of approximately 3. Sodium hydroxide was added to the mixture to raise the pH to around 6. The temperature was maintained at 60 °C for 1 hour. Then, more sodium hydroxide was added to increase the pH of the solution to 8 and to remove excess peroxide. After 0.5 hours of heating and reflux of the mixture, the pH was adjusted back to 7 with the addition of sulfuric acid (Figure 19).

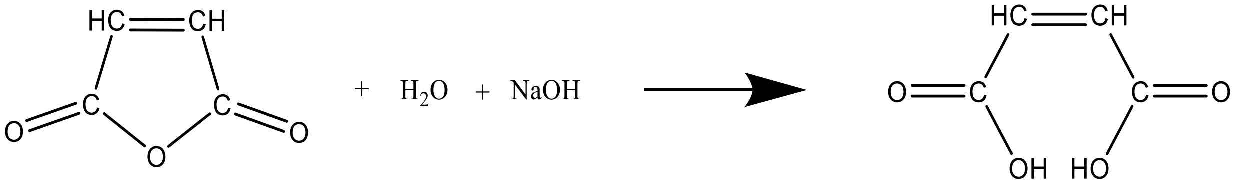


Figure 18. Synthesizing Maleic acid with maleic anhydride and sodium hydroxide.

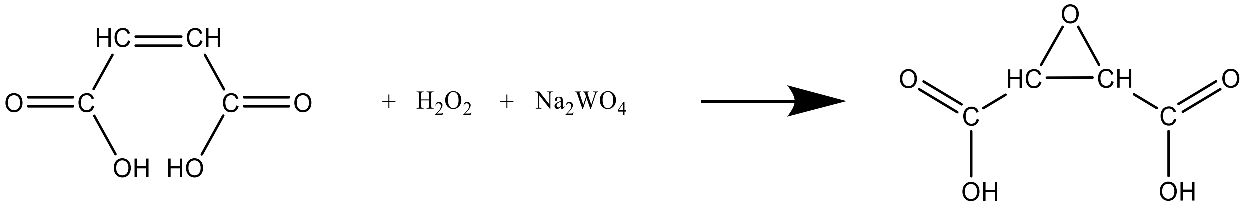


Figure 19. Synthesizing Epoxy Succinic Acid (ESA) with maleic acid, hydrogen peroxide and sodium tungstate.

Step 2, Polymerization of ESA:

In this step, several initiators such as Azobisisobutyronitrile (AIBN) (2 % w/w and 4 % w/w), $Ca(OH)_2$ (2 % w/w), NaOH (2 % w/w) were tested in order to polymerize ESA. All the polymerization processes followed the same procedure. The process containing the addition of AIBN (4% w/w) is described below as an example.

As presented in Figure 20, AIBN (0.04 gr, 0.2 mmol) was added directly to the in-house ESA (1 gr, 7 mmol) solution and then heating the mixture to 80 °C and maintaining the temperature for 2 hours. Then the temperature of the reaction was increased to 100 °C and was held for 2 hours. Finally, the mixture was cooled down to room temperature. The solvent of the solution was removed under reduced pressure.

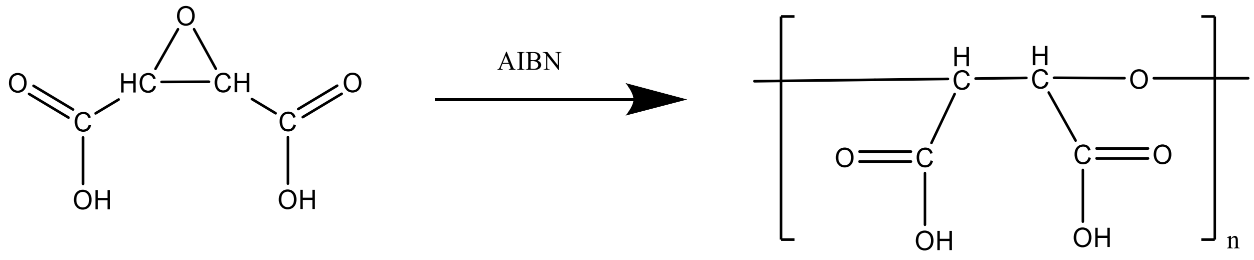


Figure 20. Polymerization of ESA with an initiator.

3.3.2 *Synthesis of Polyetheramines (JEFFAMINE®)*

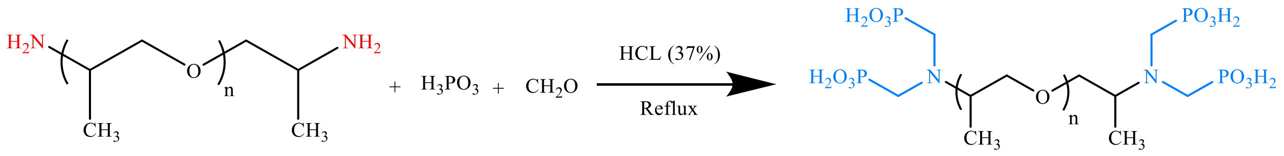
3.3.2.1 Functionalizing all amino groups with PO_3H_2

The Moedritzer-Irani reaction was invented in 1966 by Kurt Moedritzer and Riyad R. Irani.[2] This reaction is applied for the synthesis of N,N-disubstituted aminomethylphosphonic acids or N-substituted iminobis methylphosphonic acids. The Moeditzer-Irani reaction proceeds in very acidic solution. In this study, five polyetheramines were synthesized using Moedritzer-Irani reaction. The molecular weight and the amount of the chemicals used in these reactions can be found in Table 3. Figures 21 to 25 show the structure of Jeffamine polyetheramines synthesis. All synthesis followed the same procedure. The synthesis of jeffamine D-230 is described below as an example.

Jeffamine D-230 (2 gr, 8.6 mmol) was weighed and added to a 250 ml tow-neck glass flask fitted with a reflux condenser, a magnetic stirrer and a thermometer. Phosphorous acid (3.4 gr, 34.7 mmol) dissolved in water (10 ml) was charged to the flask dropwise, and then it followed by addition of HCl 37 % (3.4 gr, 34.7 mmol) to the mixture. The flask held in an ice batch due to an exothermic reaction. Next, the reaction mixture was heated up to 60 °C while N_2 was injected to the system using an N_2-filled balloon to have an anaerobic condition. At 60 °C, aqueous formaldehyde 37 % (2.8 gr, 34.7 mmol) was added dropwise over a thirty-minute period. The temperature of the reaction was increased to 110 °C to reflux for 72 hours. The reaction mixture was then cooled down to room temperature. The solvent of the liquid phase was removed under reduced pressure. The remained solid product of the reaction was washed with diethyl ether, and after removing diethyl ether by reduced pressure, the chemical was tested with NMR.

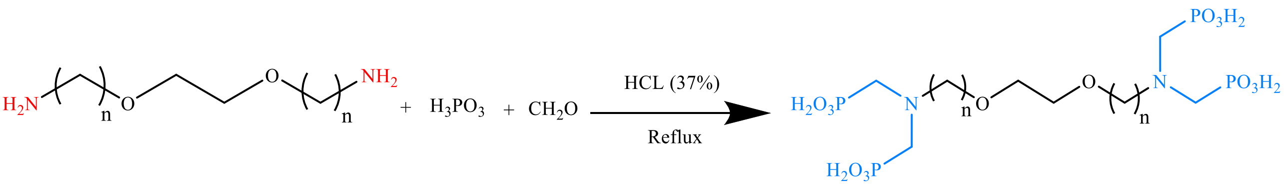
Table 3. The amount of the used compounds in synthesis of JEFFAMINE® polyetheramines.

ID	Molecular weight	Equivalent	Amount (g)	Amount (mmol)
Phosphonation of Jeffamine D-230, (See Figure 21)				
Jeffamine D-230	230	1	2	8.6
Phosphorous acid	98	4	3.4	34.7
Formaldehyde (37%)	30.03	4	2.8	34.7
Hydrogen chloride (37%)	36.46	4	3.4	34.7
Phosphonation of Jeffamine EDR-148, (See Figure 22)				
Jeffamine EDR-148	148	1	2	13.5
Phosphorous acid	98	4	5.29	54.05
Formaldehyde (37%)	30.03	4	4.387	54.05
Hydrogen chloride (37%)	36.46	4	5.326	54.05
Phosphonation of Jeffamine EDR-176, (See Figure 23)				
Jeffamine EDR-176	176	1	10	56
Phosphorous acid	98	4	22.27	227
Formaldehyde (37%)	30.03	4	18.44	227
Hydrogen chloride (37%)	36.46	4	22.4	227
Phosphonation of Jeffamine T-403, (See Figure 24)				
Jeffamine T-403	440	1	5	11.3
Phosphorous acid	98	6	6.68	68.18
Formaldehyde (37%)	30.03	6	4.35	68.18
Hydrogen chloride (37%)	36.46	6	6.71	68.18
Phosphonation of Jeffamine XTJ-568, (See Figure 25)				
Jeffamine XTJ-568	219	1	5	22
Phosphorous acid	98	4	8.94	91.2
Formaldehyde (37%)	30.03	4	7.41	91.2
Hydrogen chloride (37%)	36.46	4	8.99	91.2



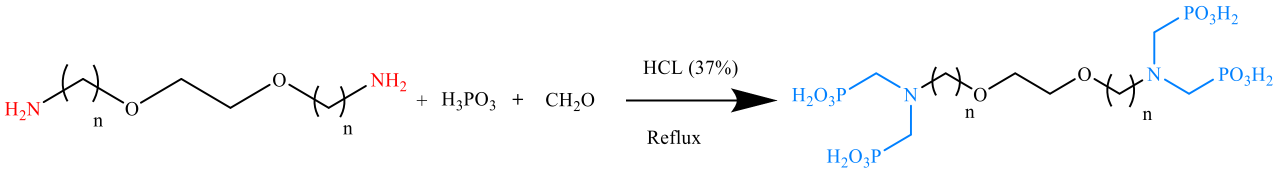
n= 2 Mw=230

Figure 21. Phosphonation of Jeffamine D-230 with phosphorous acid, CH_2O and HCl.



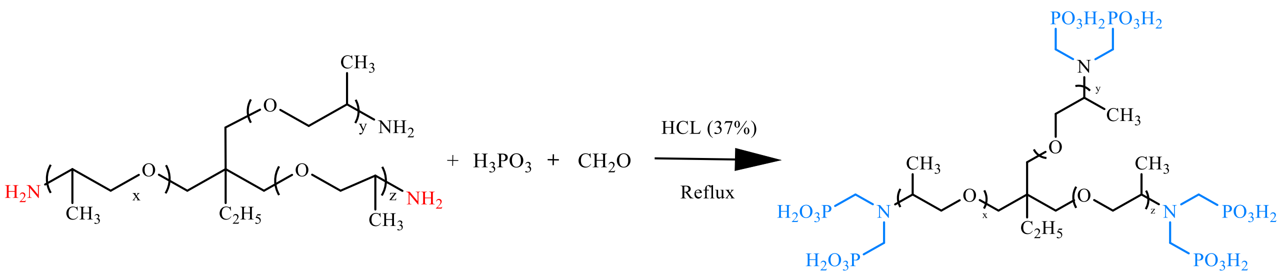
n= 2 Mw=148

Figure 22. Phosphonation of Jeffamine edr-148 with phosphorous acid, CH_2O and HCl.



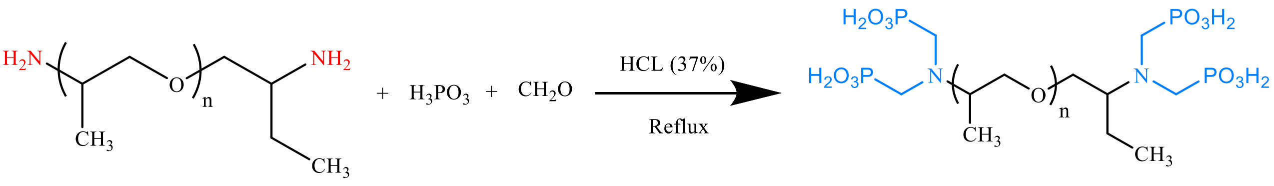
n= 3 Mw=176

Figure 23. Phosphonation of Jeffamine EDR-176 with phosphorous acid, CH_2O and HCl.



x+y+z = 5-6 Mw=440

Figure 24. Phosphonation of Jeffamine T-403 with phosphorous acid, CH_2O and HCl.

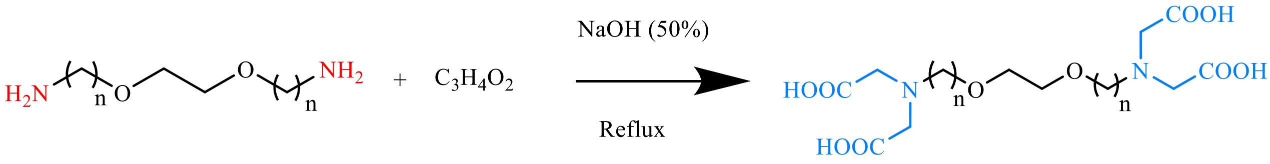


n= 2.25 Mw= 219

Figure 25. Phosphonation of Jeffamine XTJ-568 with phosphorous acid, CH_2O and HCl.

3.3.2.2 Functionalizing all amino groups with COOH

As shown in Figure 26, Jeffamine EDR-176 (10 gr, 56.81 mmol) was added in a round two-neck flask. Acrylic acid (16.37 gr, 227.17 mmol) was diluted in 40 ml deionized water and was added dropwise to the flask. The pH of the solution was measured 9. To increase the pH of the solution to 11, NaOH 50 % was added to the solution. The flask was then fitted with a reflux condenser, a magnetic stirrer and a thermometer. The temperature of the solution was increased to 80 °C and kept stirring under reflux for three days. The reaction mixture was then cooled down to room temperature. The solvent of the liquid phase was removed under reduced pressure. The remained solid product of the reaction was washed with diethyl ether, and after removing diethyl ether by reduced pressure, the chemical was tested with NMR.



n= 3 Mw=176

Figure 26. Functionalizing the amino groups of Jeffamine EDR-176 with COOH.

3.4 High-Pressure Dynamic Tube Blocking Test

A representation of high-pressure dynamic tube blocking rig is shown in Figure 27. As represented, the heart of the rig has three pumps that are capable of pumping fluids in a rate of 10 ml per min through a 316 micro bore coil. This coil is put in an already heated oven. The coil is 3 meters long and has a diameter of one millimeter. Records of the differential in pressure across the coil so as to measure the rate of scaling and the initiation are made. The data is collected on a computer by the help of Labview 8.0 software. The blocking rig is designed to withstand temperatures of up to 200 °C and pressures of 300 bars (ca.4200 psi). The experiments that are recorded here, are carried at 80 bar (pressure) and 100 °C (temperature).[3] The equipment was adjusted to run four different stages of the testing automatically. The tests were:

1. A blank test without a scale inhibitor.
2. Several tests with the scale inhibitor. Each test took an hour at a decreasing pressure.
3. A repeat test of the above test but this time starting at the previous concertation that had led to rapid scale formation in the first test.
4. Another test without scale inhibitor.

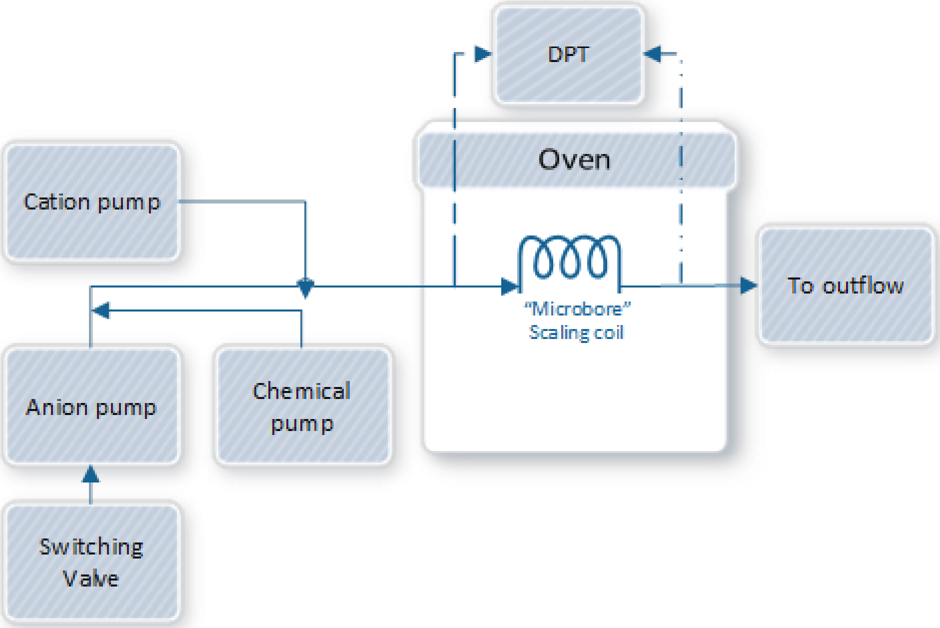


Figure 27. Schematic of the dynamic tube blocking equipment for scale inhibitor testing.

The first pump (pump 1) is used to inject brine 1 which is used for scaling cations, the second pump (pump 2) is used to inject scaling anions (brine two). The coil cleaning solutions are also injected in pump 2. Pump 3 is injected with scale inhibitor solution. The picture of the equipment can be found in Figure 28. The software can be set to automatically regulate the scale inhibitor concentration.

In this study, we regulated to reduce the scale inhibitor concentration for our experiments in every hour. The concentration of the injected SI started from at most 100 ppm and was decreased to 50, 20, 10, 5, 2 and finally down to 1ppm until there was a scale formation. The same procedure was followed for the commercial products.

For evaluating the inhibition capability of the in-house synthesized SIs for both carbonate and sulfate scales, the starting concentration of the injecting SI was chosen 100 ppm for the first tests. Sometimes there were random failures and so the rapid scale was taken at the point when the differential pressure increased to 0.5 bar (7 psi) and above. This is usually called fail concentration (FIC) of the scale inhibitor and not the minimum inhibitor concentration (MIC). This ensures that any confusion on the use of the term MIC which means minimum inhibitor concentration that prevents scale formation is avoided. The formed scale in the coil was cleaned between each and every stage using 5 wt% tetrasodium ethylenediaminetetraacetate solution that had a pH of between 12 and 13. After scale removal, the distilled water was injected for 10 min with a flow rate of 9 ml per second.

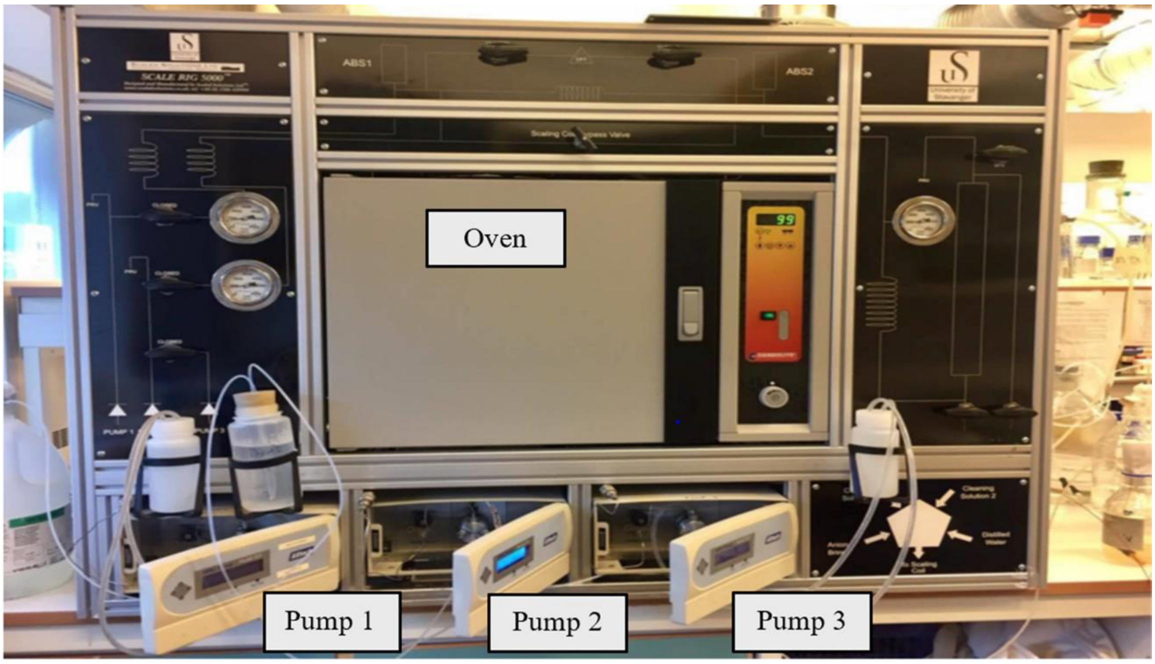


Figure 28. The scale Rig used for high-pressure tube blocking testing of SIs.

A graph in Figure 29 shows clearly the four stages of the experiments. Both carbonate and sulfate scaling test produce similar graphs. The information on the graph is from the absolute pressure in any of the side of scaling and the differential pressure across the coil. If no scale has been formed, the differential pressure is 1 psi at a flow rate of 10 ml per second.

As represented in the graph, in the first blank test the differential pressure rises above 10 psi after 14 min. In this stage, the coil was cleaned using the cleaning solution which caused a drop in differential pressure to 1 psi. Distilled water was used to clean the cleaning solution after a total time of 34 min the first test by injection of 20 ppm of the SI started. No scale was formed in this concentration of the SI. The test carried out by injecting 10 ppm of the SI. In this step, the first scale was formed after 42 min. The process of cleaning the coil by EDTA and distilled water was conducted automatically. In order to confirm the repeatability of the tests, the whole procedure was repeated. In the second scaling test. The scale was formed at 10 ppm and after 33 min. The test was finished by another blank test. The scale was formed after 13 min in the second blank test.

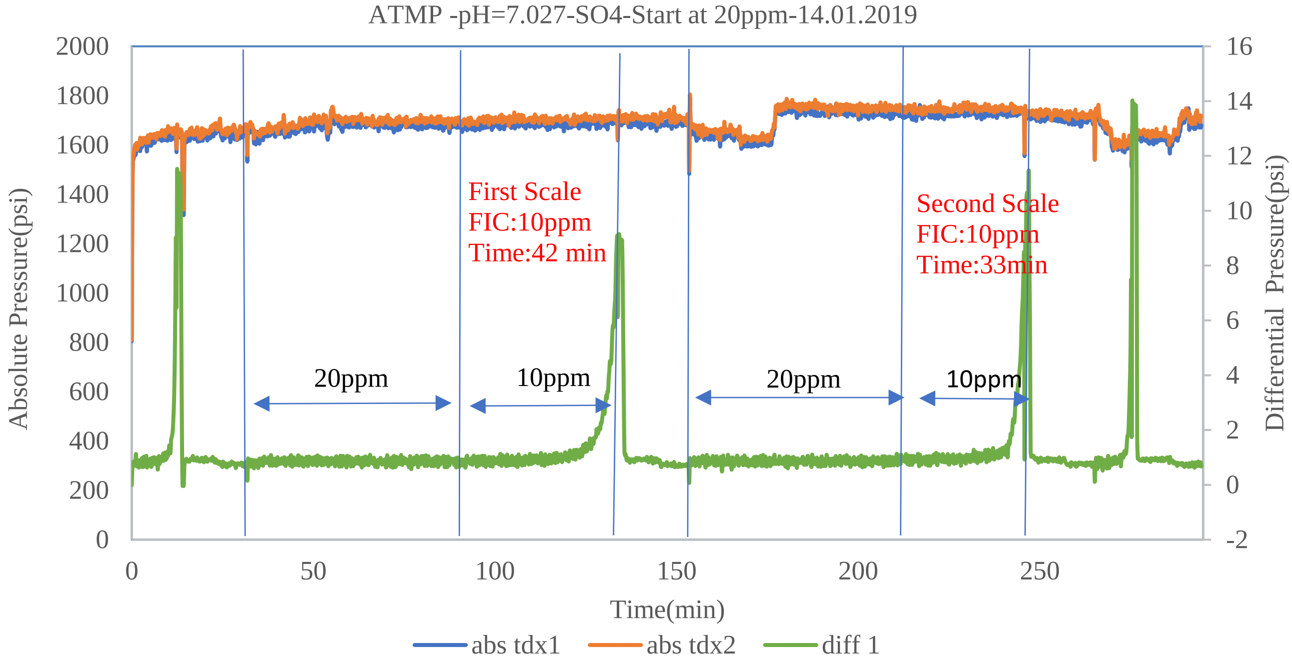


Figure 29. Example of logging data for a scale inhibitor test.

The brines that are in Table 4 and Table 5 , are mixed and stirred to ensure the salts are completely dissolved. They were then degassed for exactly 15 min using a vacuum pump to ensure the dissolved gas is removed. Bubbles in water can cause the pump to stop because they prevent the brine from flowing through the line. We used similar procedure to prepare EDTA following Table 6.

Table 4. The composition of carbonate brine 1 and brine 2 used in the scale-rig.

		Brine 1			
ion	ppm	Chemical formula	g/l	g/3L	g/5L
Na	19510	NaCl	49.59	148.77	247.97
Ca	2040	$CaCl_2 * 2H_2O$	7.48	22.45	37.42
Mg	530	$MgCl_2 * 6H_2O$	4.43	13.30	22.16
K	1090	KCl	2.0781	6.23	10.39
Ba	570	$BaCl_2 * 2H_2O$	1.0138	3.04	5.07
Sr	290	$SrCl_2 * 6H_2O$	0.8824	2.65	4.4122
Cl	0	Actual Cl ppm	35633.19		
		Brine 2			
ion	ppm	Chemical formula	g/l	g/3L	g/5L
Na	19510	NaCl	49.59	148.77	247.95
SO_4	2000	Na_2SO_4 Anhydrous	2.76	8.26	13.76
		Actual Cl ppm			

Table 5. The composition of sulfate brine 1 and brine 2 used in the scale-rig.

		Brine 1			
ion	ppm	Chemical formula	g/l	g/3L	g/5L
Na	19510	NaCl	38.640	115.93	193.2
Ca	2040	$CaCl_2 * 2H_2O$	5.3100	15.930	26.55
Mg	530	$MgCl_2 * 6H_2O$	13.660	40.980	68.30
K	1090	KCl	1.9200	5.7600	9.600
Ba	570	$BaCl_2 * 2H_2O$	0.5100	1.5300	2.550
Sr	290	$SrCl_2 * 6H_2O$	0.4400	1.3200	2.200
Cl		Actual Cl ppm	31166.40		

Brine 2					
ion	ppm	Chemical formula	g/l	g/3L	g/5L
Na	19510	NaCl	35.04	105.12	175.20
SO_4	2960	Na_2SO_4 Anhydrous	4.380	13.149	21.900
		Actual Cl ppm	30086.47		

Table 6. The composition of EDTA used for flushing in the scale-rig.

EDTA	
Dissolved in 2 L deionized water	
$Na_2EDTA*2H_2O$	120 g
NaOH	40 g

3.5 Compatibility with Calcium Test

The produced water contains divalent cations which will affect the inhibition efficiency of many scale inhibitors.[4] The barium sulfate saturation ratio (SR) of the brine mix and the presence of divalent cations Ca^{2+} and Mg^{2+} are the factors that affect the inhibition efficiency of phosphonate base barite scale inhibitors.[5, 6] Compatibility tests are necessitated to check that the scale inhibitor does not precipitate when combined with formation brines causing formation damage.

To examine the compatibility of the scale inhibitor with calcium ion, solutions with different calcium ion contents were mixed with various inhibitor concentrations to evaluate if precipitation occurs. Scale inhibitors of 100, 1000, 10 000, and 50 000 ppm were dissolved in 20 mL of deionized water in 50 ml glass bottles. Then, 30 000 ppm sodium chloride (3.0 wt %) and calcium chloride dihydrate in doses from 10 to 10 000 ppm were added. The bottles were shaken until everything was dissolved and the solution looked clear. The containers were placed in the oven at 80 °C; the test time was generally 24 h. The turbidity and/or precipitation of SIs complexed with calcium ion in the synthetic brine solution were checked after 30 min, 1, 4, and 24 h.

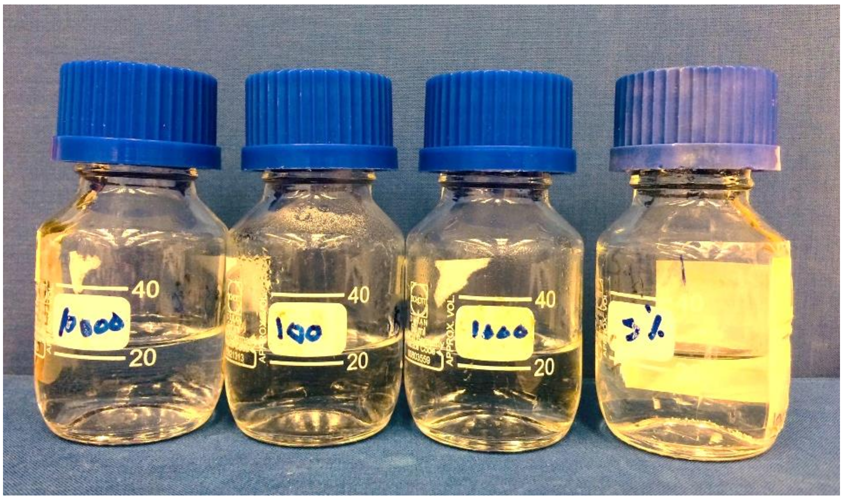


Figure 30. Compatibility test in 10000 ppm Ca^{2+} and 3% NaCl in 2 ml after 24 hours, all bottles with clear solutions.

3.6 Hydrothermal Stability Test

Thermal aging tests are required to assure that the inhibitor is stable at the high-temperature reservoirs for the anticipated squeeze lifetime. The inhibitor solution is aged in a static bottle, and then its scale inhibition performance is compared with a non-aged sample.[7]

A 2.5 wt % additive solution in deionized water is purged with nitrogen for one hour and placed in a pressure tube. It is then nitrogen-sparged to minimize the residual oxygen in the tube before heating at 130 °C for 1 week. The aged solution is then examined for its sulfate and carbonate inhibition performance in the dynamic scale loop test.

3.7 SI Seawater Biodegradability Test

The SI seawater biodegradability test was performed by Krista Michelle Kaster and linn Svendsen at the university of Stavanger. In this study, a method based on OECD 306 guidelines was employed to determine the biodegradability of the SIs of interest in the marine environment. In summary, OxiTop Control manometric system (WTW, Germany) was used for BOD measurements of each of the tested SIs over 28 days. The percentage of the biodegradability was assessed based on the comparison between the measured BOD with the calculated theoretical oxygen demand (ThOD) values. Also, in order to maintain the necessary conditions for microbial activity and growth, nutrients were added to the seawater samples.

Seawater sampling

The seawater was taken from a non-polluted fjord (salinity ≈ 3.5 %) (59° 1'N, 5° 37'E) located in Mekjarvik via a piping system and collected from the International Research Institute (IRIS). The temperature of the seawater obtained from a depth of 80 m was approx. 8°C. The sample was stored at 15 °C for 24 h prior to the start of the experiment in a 10-litre autoclaved glass vial for the first attempt. In experiment two, the sample was stored at 15 °C for one week prior to the trial start.

BOD analysis

1028 g of seawater was weighed in an autoclaved Schott bottle of 1 litre. 10 µl of vitamin and 10 µl of the amino acid were added to the seawater along with 1 ml of nutrients A, B, C and D (Appendix E and F). Approximately 308 g of the mixture was weighed and added to 500 ml of brown bottles with three parallels to each inhibitor. 310 g of blank, positive (sodium benzoate) and negative control were weighed and added to identical bottles of three parallels each. 1.8 ml of 1% solution of the inhibitors were added in each of their respective parallels. Two beads of sodium hydroxide were added to the rubber sleeve of each bottle. Then, the bottles were closed and activated with measurable OxiTop(P)-C bottle heads.

The OxiTop(P)- system was used to perform the BOD assay, which analyzed aerobic biodegradation of the inhibitors in seawater over 28 days with constant stirring at 20 °C. Measurable OxiTop(P)-C bottle heads and OxiTop(P) Control 110 were used to measure and read pressure changes in the bottles (WTW, 2014). The method used to determine the biodegradation of the inhibitors was based on the OECD 306 procedure.

Figure 31. OxiTop Control manometric system

3.8 References

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4 Results and Discussions

4.1 Syntheses

4.1.1 *Synthesis of Polyepoxysuccinic Acid (PESA)*

The synthesis of PESA was conducted in two steps.[1] The first step in this process was the synthesis of ESA. This step involved the reaction between maleic anhydride with sodium hydroxide followed with the addition of hydrogen peroxide and sodium tungstate, under reflux overnight. The second step was the polymerization of the obtained ESA. Different initiators were used for the polymerization procedure (see section 3.3.1). The synthesis of PESA was not successful. Although the procedure was repeated several times with changes in reflux periods and PH range, the desired product was not obtained, according to NMR. In particular, the pH adjustment during the process was problematic. So, this was not further investigated.

4.1.2 *Synthesis of Jeffamine Polyetheramines*

The synthesis of the in-house made SIs involved the reaction between linear and branched polyetheramines with phosphorous acid, formaldehyde and HCl, under reflux for three days to yield phosphonated polyetheramines. The syntheses were done according to the procedure of Moeditzer-Irani reaction.[2] In all the syntheses of the in-house SIs the desired products were gained, according to the NMR (APPENDIXES B). Table 7 presents the yield percentage of the syntheses in this study.

Table 7. The yield percentage of the syntheses.

SI	Yield%
P.D-230	88.47
P.EDR-176	78.57
P.EDR-148	83
P.T-403	95
P.XTJ-568	86.58

4.2 High-Pressure Dynamic Tube Blocking Test

The barite and calcite scale inhibition potential of different SIs was performed in a High-Pressure Dynamic Tube Blocking rig at 100 °C and 80 bars. In all the experiments, consistent results were obtained from the first and the second test. There is an undeniable relationship between pH and scale inhibition which is due to protonation of the SI. Previous studies found that a rise in the pH of the crystal growth medium over a pH limit of 4−9 gives an enhancement in inhibitor performance while the poor inhibitor performance is exhibited at pH < 4.27.[3] Therefore, in this study the pH of the SIs prepared in the 1000 ppm solution was adjusted to 5-7.

Table 8 shows the fail inhibitor concentration (FIC) for commercial and the in-house synthesized SIs for sulfate scale inhibition. The purpose of testing the commercial SIs was to compare the inhibition performance of these chemicals with the obtained results for the in-house synthesized SIs. Polyepoxysuccinic acid (PESA) is a commercially available biodegradable polycarboxylate SI. The sodium salts of two non-polymeric phosphonates, DTPMP and ATMP were also tested.

Inhibitors were injected at concentrations of 100, 50, 20, 10, 5, 2, and 1 ppm in the period of 1 h for each concentration until the scale was formed. Two blanks tests with no inhibitor were also performed in each run. In order to show the repeatability of the results, each row of Table 8 shows the results for two blank tests (with no injection of SI) and also two SI tests under the same conditions. For the barite tests (Table 8), the scale formation time for blank tests is 10-12 min. It can be seen from the data in Table 8 that PESA shows the best barite scale inhibition with FIC value of 2 ppm compared with the other commercial SIs. DTPMP and ATMP show good inhibition performance by FIC values of 5 and 10 ppm, respectively. The weakest barite scale inhibition belongs to Italmatch (SPE 1704) SI, which failed at 20 ppm and after 28 min.

The bottom half of Table 8 shows the FIC and time values for the in-house synthesized SIs. In this study, linear and branched polyetheramines (from Huntsman Corp.) were phosphonated using the Moedritzer-Irani reaction. The results obtained from the sulfate scale test shows that all products gave good barite scale inhibition compared to the commercial SIs. Among the in-house SIs, P.EDR-176 and P.EDR-148 are the chemicals that were synthesized from the linear polyetheramines. The difference between P.EDR-176 and P.EDR-148 is the length of their chain and therefore, their molecular weight. As can be seen from Table 8, P.EDR-176 showed the best results by failing at 2 ppm, after 5 and 14 min in the first and the second test, respectively. However, P.EDR-148 showed weaker inhibition performance by FIC value of 5 ppm after 19 and 27 min in the first and the second experiments, respectively. P.D-230 and P.T-403 Failed at the same concentration of 10 ppm. The weakest scale inhibition result for the sulfate test was obtained from testing P.XTJ-568, in which the scale was formed at 20 ppm concentration of SI and after 26 and 30 min.

Table 8. Fail inhibitor concentration (FIC) values for commercial and new scale inhibitors (SIs) for sulfate scale.

SI (1000 ppm)	**SO_4**					
	1stBlank	**First Scale Test**		**Second Scale Test**		**2ndBlank**
	Time (mins)	Conc. (ppm)	Time (mins)	Conc. (ppm)	Time (mins)	Time (mins)
PESA	10	2	1	2	8	10
Italmatch (SPE 1704)	12	20	28	20	24	10
ATMP	11	10	42	10	33	11
DTPMP	10	5	5	5	9	10
In- house Synthesized Scale Inhibitors						
P.D-230	10	10	9	10	9	10
P.EDR-148	10	5	19	5	27	10
P.EDR-176	12	2	5	2	14	10
P.T-403	10	10	21	10	29	10
P.XTJ-568	10	20	26	20	30	11

The experimental data on FIC for commercial and synthesized SIs for carbonate scale inhibition are present in Table 9. Data from this table can be compared with the data in Table 8, which shows that all the tested SIs showed better inhibition performance against calcite scale than the barite scale, except ATMP and DTPMP. What stands out for the test results for commercial SIs, comparing the results in table 7 with table 6, is that although Italmatch (SPE 1704) showed the weakest scale inhibition for sulfate scale, it had excellent performance for inhibition of the carbonate scale by the FIC values of 20 and 1 ppm, respectively. The FIC value for both calcite and barite scaling observed to be the same for PESA; for the calcite scale test PESA failed at 2 ppm, after 6 and 1 min in first and the second test, respectively. ATMP and DTPMP SIs failed at 20 and 10 ppm, respectively.

The results from the calcite scale test for the in-house SIs can be found in the bottom half of Table 9. As presented in the table (below), all the synthesized SIs showed excellent carbonate scale inhibition. The result from the P.EDR-176 test is outstanding in Table 9; it shows that no carbonate scale was formed even in the lowest concentration of this SI (1 ppm). Also, the carbonate scale test for P.EDR-148 failed at 1 ppm after 58 min in both tests, which is a remarkable result. It can be seen from the data in Table 9 that P.T-403 and P.XTJ-568 have the same FIC values of 2 ppm but with different FIC times, which are approximately 20 and 10 min, respectively. However, P.D-230 showed the weakest result by FIC of 5 ppm; it is also a very good inhibition performance compared with ATMP and DTPMP, the phosphonate base commercial scale inhibitors.

In another synthesis, the amines in Jeffamine EDR-176 were also functionalized with carboxylic groups. The final product, named as C.EDR-176 was tested for its carbonate scale inhibition performance. As it is shown in Table 9, C.EDR-176 showed very poor results by failing at 100 ppm and after 17 minutes for carbonate scale test. Therefore, it was no more investigated.

Table 9. Fail inhibitor concentration (FIC) values for commercial and new scale inhibitors (SIs) for carbonate scale.

SI (1000 ppm)	**CO_3**					
	1st Blank	**First Scale Test**		**Second Scale Test**		**2nd Blank**
	Time (mins)	Conc. (ppm)	Time (mins)	Conc. (ppm)	Time (mins)	Time (mins)
PESA	10	2	6	2	1	10
Italmatch (SPE 1704)	10	1	4	1	15	11
ATMP	11	20	26	20	26	12
DTPMP	10	10	20	10	20	12
In-house synthesized Scale Inhibitors						
P.D-230	10	5	4	5	6	10
P.EDR-148	12	1	58	1	58	14
P.EDR-176	10	< 1 *		< 1 *		10
P.T-403	12	2	20	2	20	12
P.XTJ-568	17	2	8	2	10	15
C.EDR-176	11	100	17	100	17	13

* *No scale was formed during the test.*

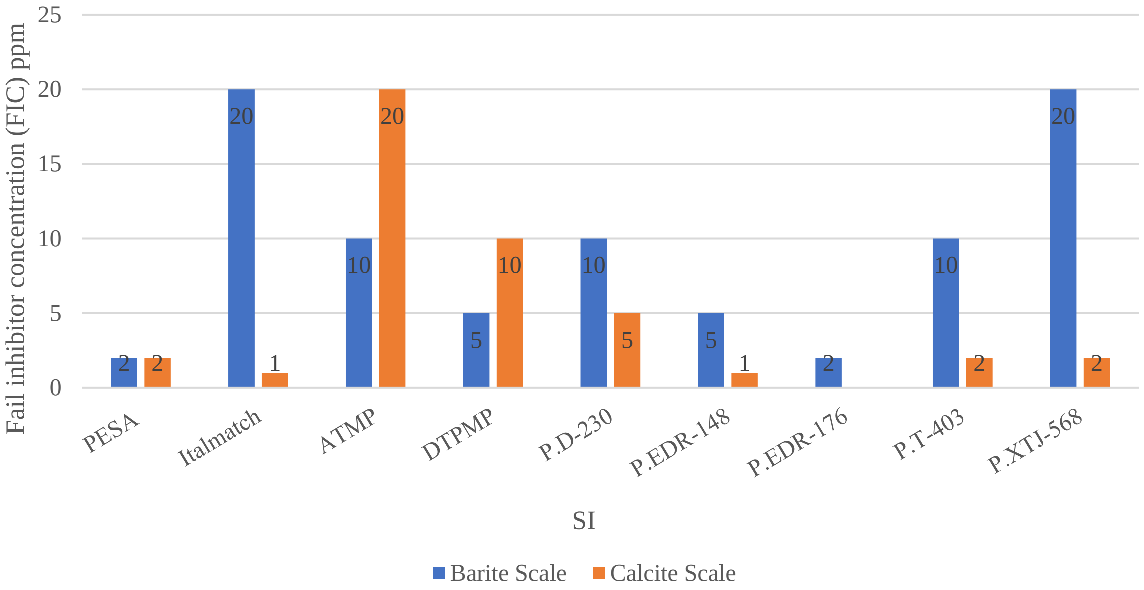


Figure 32. FIC results for the in-house synthesized and commercial SIs for sulfate and carbonate scale tests.

Figure 32 summarizes and compares the obtained FIC results for the in-house synthesized and commercial SIs for sulfate and carbonate scale tests. In summary, these results show that all the tested SIs showed better performance against calcite scale formation than the barite scale, except DTPMP and ATMP. The compatibility of the two classes of commercial phosphonates with divalent metal ions might be the reason for the poor performance of DTPMP and ATMP for carbonate scale. For example, the carbonate test contains a higher concentration of calcium ions than the sulfate test.[4]

Comparing the results for commercial SIs, PESA showed the best performance for the barite scale by failing at 2 ppm, and the best inhibition for the calcite scale belongs to Italmatch SI (SPE 1704) by FIC value of 1 ppm.

Earlier investigations have suggested that the amino phosphonate groups result in poor to moderate inhibition performance for sulfate and carbonate scale formation.[5] In this study, linear and branched polyetheramines were synthesized, and aminomethylenephosphonate groups were terminated into these molecules via the Moedritzer-Irani reaction. It is claimed that the $-N-CH_2-PO_3H_2$ group improves the metal binding capabilities of the molecule via both the nitrogen and phosphonate interactions.[4]

The results from in-house synthesized SIs suggest that the phosphonated linear polyetheramines are better SIs than the phosphonated branched polyetheramines. Both P.EDR-176 and P.EDR-148 are synthesized from the linear polyetheramines, which had the best scale inhibition capacity for both barite and calcite scale. FiguresFigure 33 to Figure 36 provide the experimental data for P.EDR-176 and P.EDR-148. As mentioned in the previous studies, the distance between the aminomethylenephosphonate groups appears to be positively related to scale inhibition performance.[6] The results, as shown in figures below, indicate that P.EDR-176 with a longer distance between aminomethylenephosphonate groups has better inhibition performance than P.EDR-148.

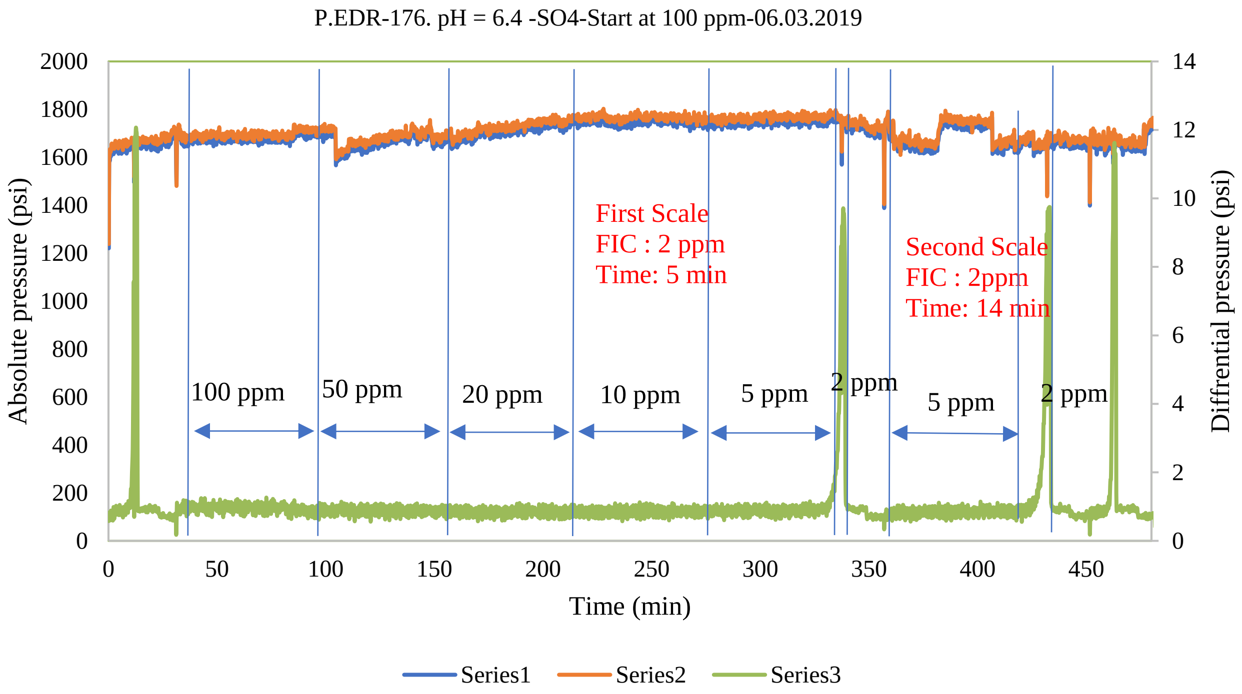


Figure 33. FIC and time values from high-pressure dynamic tube blocking experiments of P.EDR-176 for sulfate scale.

As it is shown in Figure 33, the sulfate scale in the first and the second blank test is formed after 12 and 10 min, respectively. The equipment is set to decrease the concentration of the injected SI each hour if no scale has formed. The injection of the SI stars from 100 ppm and it decreases to 2 ppm du to no formation of the sulfate scale. Finally, the first scale is formed at FIC value of the 2 ppm and after 5 min. The coil is washed with EDTA and distilled water automatically for 20 min. The second test starts at 5 ppm. After 60 min no scale is formed, so the concentration of the SI is decreased to 2ppm. The second scale is formed at 2 ppm and after 14 min.

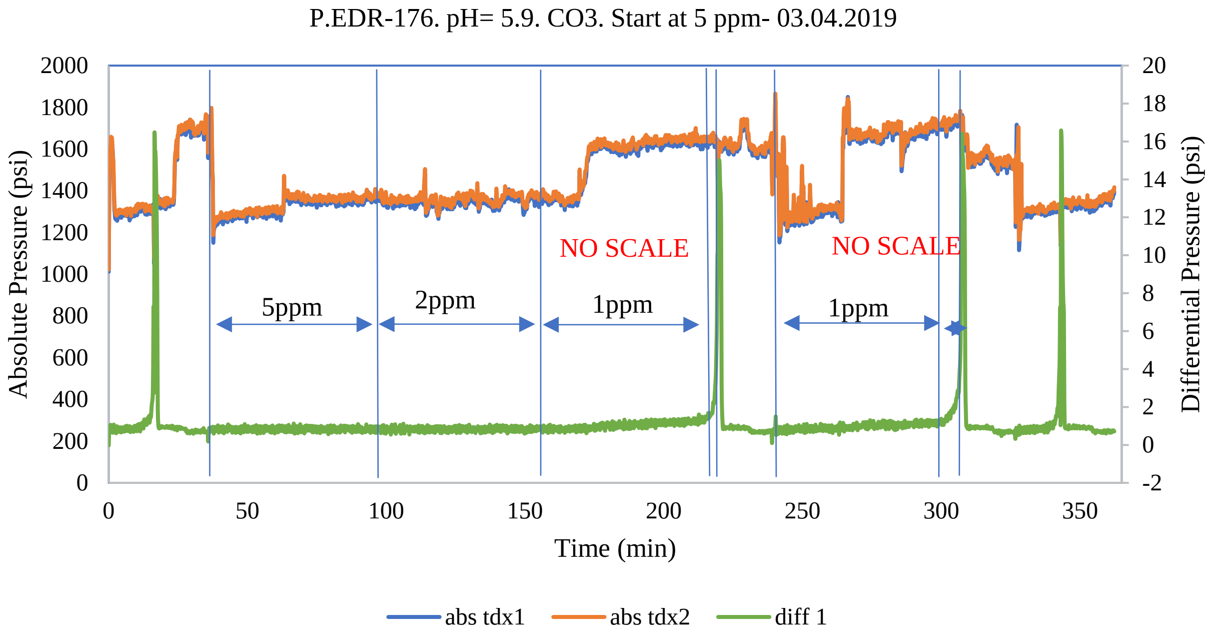


Figure 34. FIC and time values from high-pressure dynamic tube blocking experiments of P.EDR-176 for carbonate scale.

The FIC value for the P.EDR-176 SI was obtained 2 ppm. (Figure 33). It was predicted that the FIC value for the carbonate scale would not exceed from 2 ppm. As it is shown in Figure 34, the injection of the P.EDR-176 starts at 5 ppm. The test continues with no formation of the scale. The second tests stats from 1 ppm of the SI, and again no scale was formed. The present results are significant.

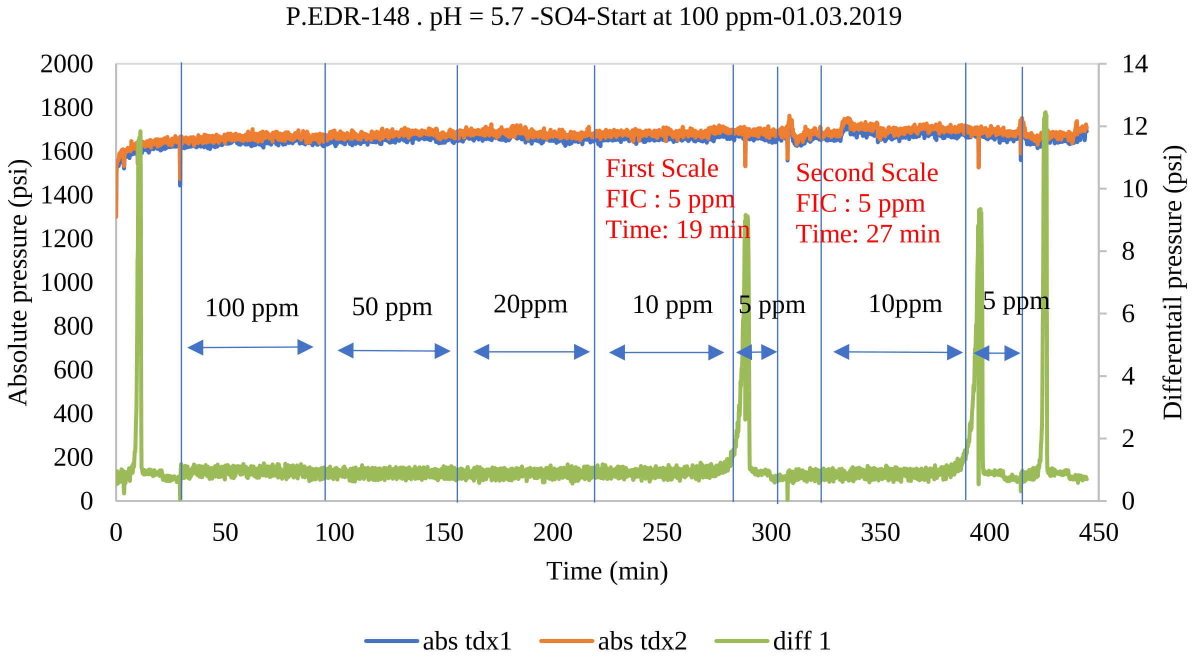


Figure 35. FIC and time values from high-pressure dynamic tube blocking experiments of P.EDR-148 for sulfate scale.

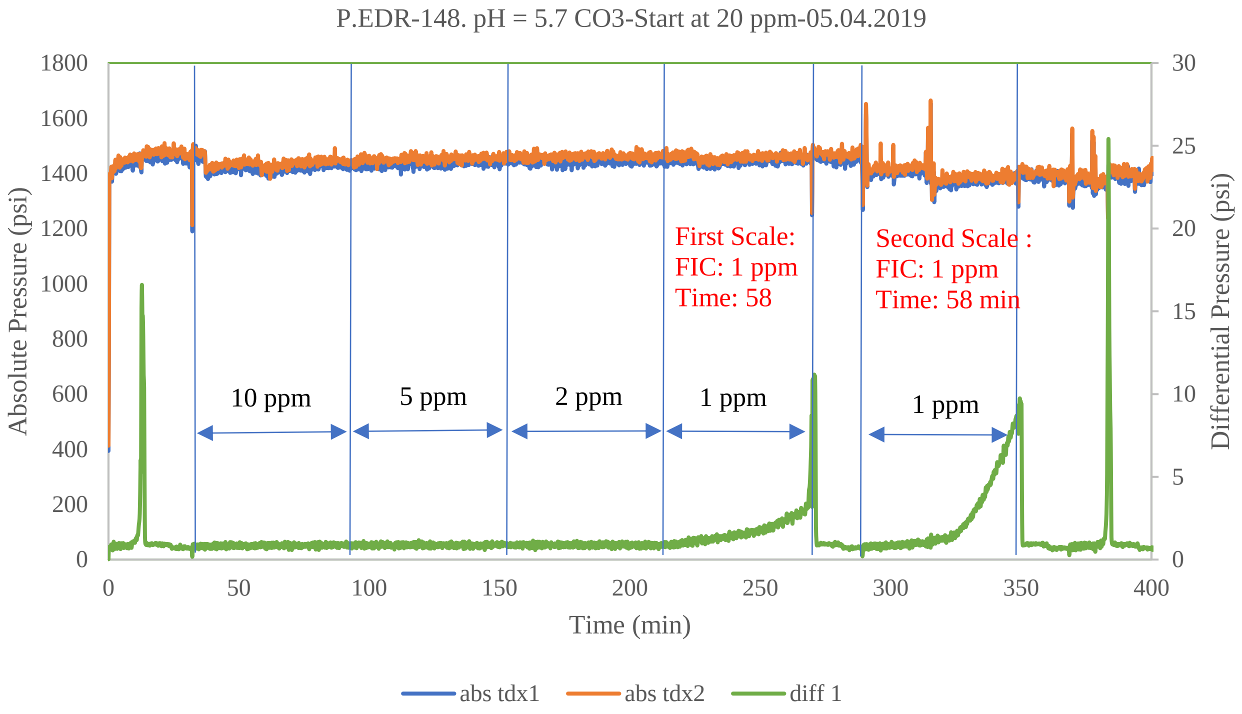


Figure 36. FIC and time values from high-pressure dynamic tube blocking experiments of P.EDR-148 for carbonate scale.

The pH of all the tested SIs in this project was adjusted to 4-6 using NaOH as pH adjuster. In order to study the effect of different pH adjusters on the SI performance, another test was performed. Table 10 compares the results from two tests of P.EDR-176 in the same conditions, except the used pH adjuster, for carbonate scale. As it is shown, there is no difference between using KOH or NaOH as the pH adjuster. In both experiments, no carbonate scale was formed during the whole time.

Table 10.The effect of different pH adjusters on fail inhibitor concentration (FIC) values for P.EDR-176 for carbonate scale.

pH Adjuster	**CO_3**					
	1st Blank	**First Scale Test**		**Second Scale Test**		**2nd Blank**
	Time (mins)	Conc. (ppm)	Time (mins)	Conc. (ppm)	Time (mins)	Time (mins)
P.EDR-176						
NaOH	10	< 1 *	-	< 1 *	-	10
KOH	14	< 1 *	-	< 1 *	-	15

* *No scale was formed during the test.*

4.3 Calcium Compatibility Test

One of the main effecting factors in squeeze treatment is the compatibility of the SI with calcium ions. The precipitation of SI complexes in the well area can contribute to severe formation damages. Data from several studies suggest that phosphonate base SIs show less calcium compatibility compared with polycarboxylate or polysulfonate base SIs.[6, 7] A series of compatibility tests were conducted at 80 °C to achieve a solid understanding of the compatibility of the in-house synthesized SIs with calcium ions. Some of the results are presented in Table 11to Table 16. In this series of tests, different concentrations of SI and calcium ions were tested against each other. As can be seen in the tables (below), the range for the SI concentration was from 100 to 50 000 ppm, and the calcium ion concentration varied from 100 to 10 000 ppm. In order to provide a typical salinity of the formation water, 30 000 ppm of $CaCl_2H_2O$ was also added to all the samples.

Previous studies consider the formation of calcium−SI complexes as a challenge for the application of phosphonate base SIs. These SIs are incompatible in high concentrations of calcium ions.[8] In contrast to earlier findings, it was found that the phosphonate base SIs showed excellent compatibility with Ca^{2+} at 1000 ppm over the 24 h test period, except from P.EDR 148 at 50 000 ppm. In other tests with calcium ion concentration of 100 and 10 000 ppm, all the samples were still clear after 24h. A possible explanation for this might be that these SIs benefitted from the oxygen molecule in their backbone.

Table 11. Compatibility test in 100 ppm of Ca^{2+} and 30000 ppm (3.0 wt.%) NaCl for P.EDR-176.

SI	Dose (ppm)	Appearance				
		At Mixing	30 mins	1 hour	4 hours	24 hours
SI-1	100	Clear	Clear	Clear	Clear	Clear
SI-1	1000	Clear	Clear	Clear	Clear	Clear
SI-1	10000	Clear	Clear	Clear	Clear	Clear
SI-1	50000	Clear	Clear	Clear	Clear	Clear

Table 12. Compatibility test in 1000 ppm of Ca^{2+} and 30000 ppm (3.0 wt.%) NaCl for P.EDR-176.

SI	Dose (ppm)	Appearance				
		At Mixing	30 mins	1 hour	4 hours	24 hours
SI-1	100	Clear	Clear	Clear	Clear	Clear
SI-1	1000	Clear	Clear	Clear	Clear	Clear
SI-1	10000	Clear	Clear	Clear	Clear	Clear
SI-1	50000	Clear	Clear	Clear	Clear	Clear

Table 13. Compatibility test in 10 000 ppm of Ca^{2+} and 30000 ppm (3.0 wt.%) NaCl for P.EDR-176.

SI	Dose (ppm)	Appearance				
		At Mixing	30 mins	1 hour	4 hours	24 hours
SI-1	100	Clear	Clear	Clear	Clear	Clear
SI-1	1000	Clear	Clear	Clear	Clear	Clear
SI-1	10000	Clear	Clear	Clear	Clear	Clear
SI-1	50000	Clear	Clear	Clear	Clear	Clear

Table 14. Compatibility tests in 100ppm of Ca^{2+} and 30000 ppm (3.0 wt.%) NaCl for P.EDR-148.

SI	Dose (ppm)	Appearance				
		At Mixing	30 mins	1 hour	4 hours	24 hours
SI-1	100	Clear	Clear	Clear	Clear	Clear
SI-1	1000	Clear	Clear	Clear	Clear	Clear
SI-1	10000	Clear	Clear	Clear	Clear	Clear
SI-1	50000	Clear	Clear	Clear	Clear	Haze

Table 15. Compatibility test in 1000 ppm of Ca^{2+} and 30000 ppm (3.0 wt.%) NaCl for P.EDR-148.

SI	Dose (ppm)	Appearance				
		At Mixing	30 mins	1 hour	4 hours	24 hours
SI-1	100	Clear	Clear	Clear	Clear	Clear
SI-1	1000	Clear	Clear	Clear	Clear	Clear
SI-1	10000	Clear	Clear	Clear	Clear	Clear
SI-1	50000	Clear	Clear	Clear	Clear	Haze

Table 16. Compatibility test in 10 000 ppm of Ca^{2+} and 30000 ppm (3.0 wt.%) NaCl for P.EDR-148.

SI	Dose (ppm)	Appearance				
		At Mixing	30 mins	1 hour	4 hours	24 hours
SI-1	100	Clear	Clear	Clear	Clear	Clear
SI-1	1000	Clear	Clear	Clear	Clear	Clear
SI-1	10000	Clear	Clear	Clear	Clear	Clear
SI-1	50000	Clear	Clear	Clear	Clear	Clear

4.4 Thermal Stability Test

The specific objective of this experiment was to investigate the thermal stability of the SIs at the reservoir temperature. Thermal stability is a key factor in the SI squeezing method. Therefore, P.EDR-176 and P.T-403 were thermally aged at 130 °C and at initial pH values of 2 and 5, respectively. Then, tested for performance against carbonate and sulfate scale.

As presented in section 4.2, P.EDR-176 showed the best inhibition performance (before thermal aging test) for the calcite and barite scale test, and it is was synthesized from a linear polyetheramine known as Jeffamine EDR-176 . Also, P.T-403, which is the product of the phosphonation of a branched polyetheramine named Jeffamine T-403, showed good scale inhibition performance in pre-aging inhibition tests. The molecular structure of the two SI is illustrated in Figure 37. In these experiments, 2.5 wt % solutions of the candidate SIs were heated in a sealed tube at 130 °C for 1 week under anaerobic conditions. The aged SIs were re-tested in dynamic tube-blocking scale inhibition tests for barite scaling and calcite scaling. The results are presented in Table 17 and Table 18 and also Figure 38 and Figure 39.

Table 17. Fail inhibitor concentration (FIC) values for the aged P. EDR-176.

Thermal Aging Test	**Scale Type**	**1st Blank**	**First Scale Test**		**Second Scale Test**		**2nd Blank**
		Time (mins)	Conc. (ppm)	Time (mins)	Conc. (ppm)	Time (mins)	Time (mins)
Before	Barite	12	2	5	2	14	10
	Calcite	10	< 1 *	-	< 1 *	-	10
After	Barite	10	10	31	10	35	10
	Calcite	10	1	20	1	20	14

* *No scale was formed during the test.*

Table 17 shows the experimental data on time and FIC values of the primary and the aged P.EDR-176 for barite and calcite scale inhibition. The results show that P.EDR-176 showed weaker performance by going from a FIC of 2 to 10 ppm for barite scaling. However, the thermal aging had less effect on its inhibition ability for calcite scale. In the pre-aging test, no scale was formed when P.EDR-176 was injected at its lowest concentration of 1 ppm, but in the after-aging test, the calcite scale was formed at FIC value of 1 ppm and after 20 min.

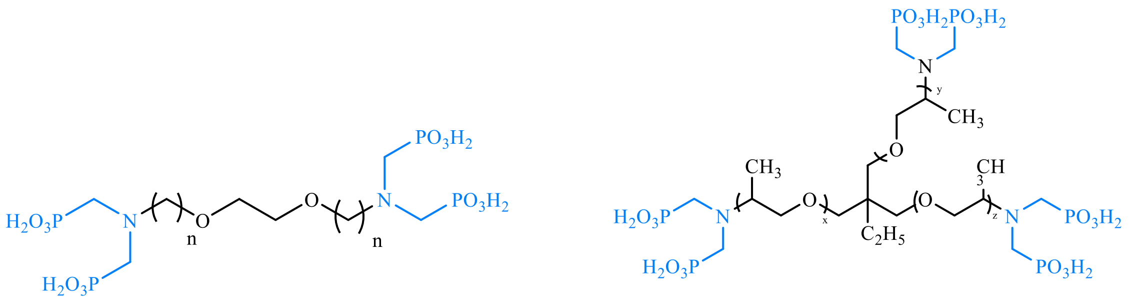
Comparing the results for two SIs, it can be observed that almost the same pattern happened for P.T-403. It can be seen from the data in Table 18 that P.T-403 performance worsened from 10 to 20 ppm for barite scale; however, the thermal aging did not affect its performance for calcite inhibition. The test failed at 2 ppm, which is the same as the pre-aging inhibition test.

Table 18. Fail inhibitor concentration (FIC) values for the aged P.T-403.

Thermal Aging Test	**Scale Type**	**1st Blank**	**First Scale Test**		**Second Scale Test**		**2nd Blank**
		Time (mins)	Conc. (ppm)	Time (mins)	Conc. (ppm)	Time (mins)	Time (mins)
Before	Barite	10	10	21	10	29	10
	Calcite	12	2	20	2	20	12
After	Barite	10	20	37	20	37	10
	Calcite	11	2	17	2	17	10

Figure 38 and Figure 39 summarize the results from the dynamic tube-blocking tests before and after the thermal aging test for both calcite and barite scales. These results suggest that the thermal aging test had more effect on the inhibition performance of the SIs for the barite scale than the calcite scale. For calcite scale tests (Figure 38), thermal aging showed no effect on the FIC value of P.T-403, while P.EDR-176 FIC changed from having no scale formation to FIC value of 1ppm. For barite scale tests (Figure 39), thermal aging showed a negative effect on SI performance by increasing the FIC from 2 to 10 ppm and from 10 to 20 ppm for P.EDR-176 and P.T-403, respectively.

This shows that the SI is not thermally stable, but it still has an inhibition effect. Prior studies that have noted the importance of the structure of the SIs on thermal stability. It is claimed that the number of the $-CH_2-$ groups between the amine groups affects the thermal stability of the SI. The fewer number of $-CH_2-$ linkages will enhance the steric ‘‘strain’’, which is a result of the repulsion between the phosphonate groups. Therefore, the thermal stability of the SI will decrease. It is also reported that the number of amine groups affects the repulsion between the phosphonate groups.[9] The results from the current study, match those observed in earlier studies. As it is shown in Figure 37 P.T-403, which contains more amine groups, showed more stability after thermal aging test specifically for calcite scale inhibition.



(a) (b)

Figure 37. The molecular structure of in-house SIs. (a) P.EDR-176, (b) P.T-403.

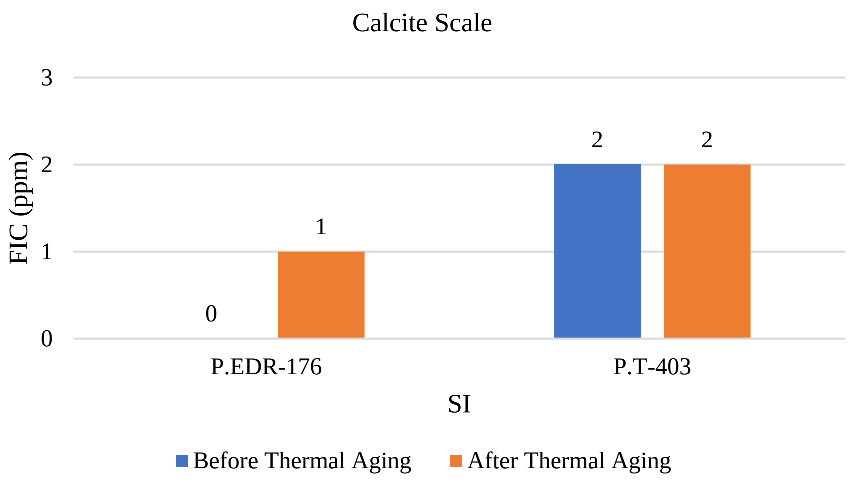


Figure 38. Comparison between FIC values before and after thermal aging test of the SIs for calcite scale.

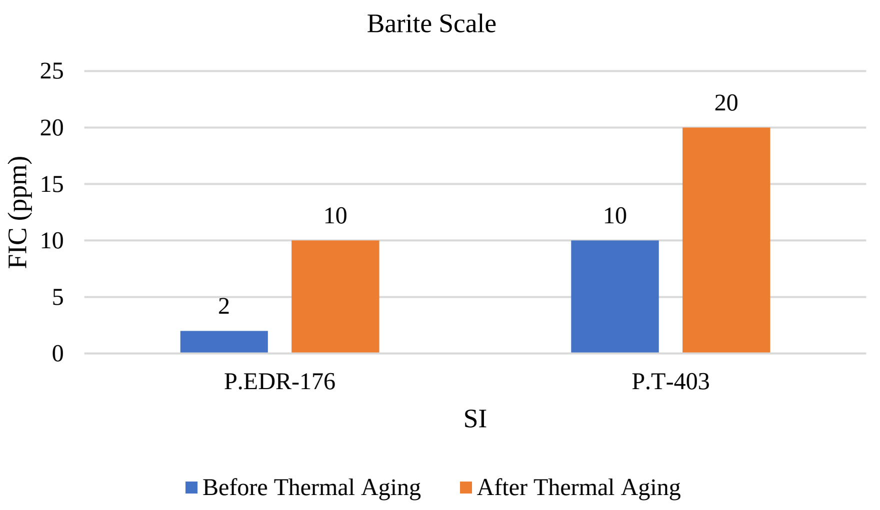


Figure 39. Comparison between FIC values before and after thermal aging test of the SIs for barite scale.

Figures 40 to 43 show the results obtained from a High-Pressure Dynamic Tube Blocking rig at 100°C and 80 bars for P.EDR-176 and P.T-403 after thermal stability test.

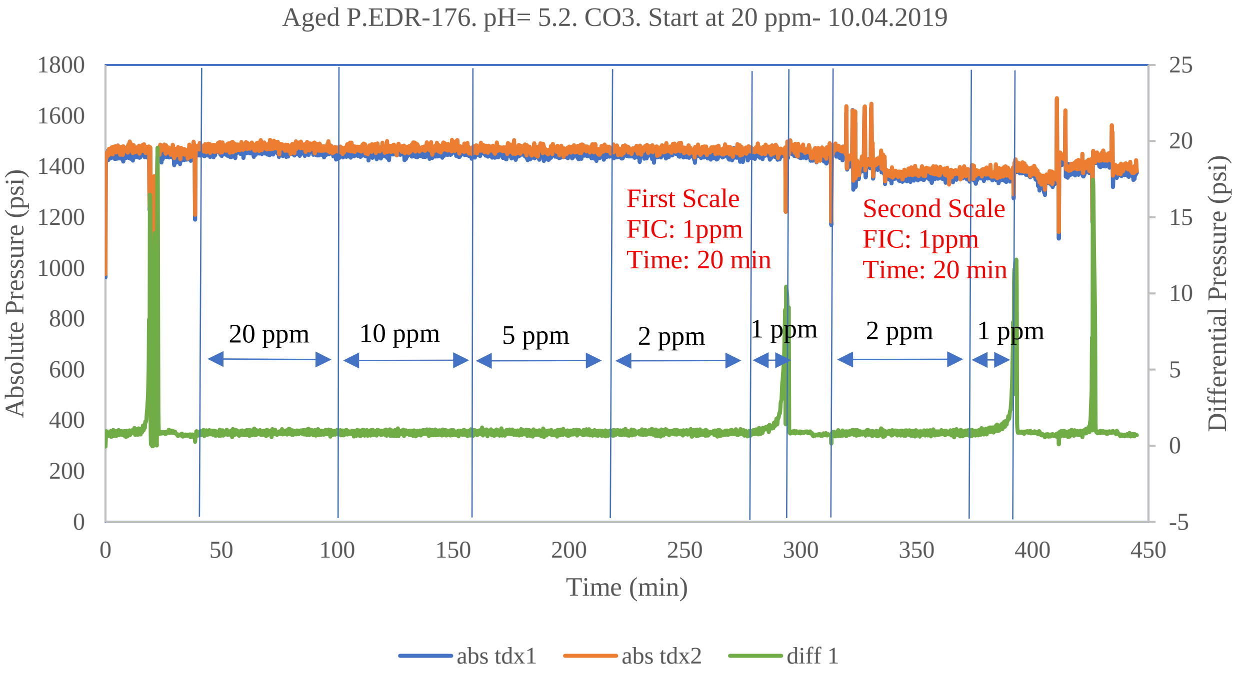


Figure 40. FIC and time values from high-pressure dynamic tube blocking experiments of aged P.EDR-176 for carbonate scale.

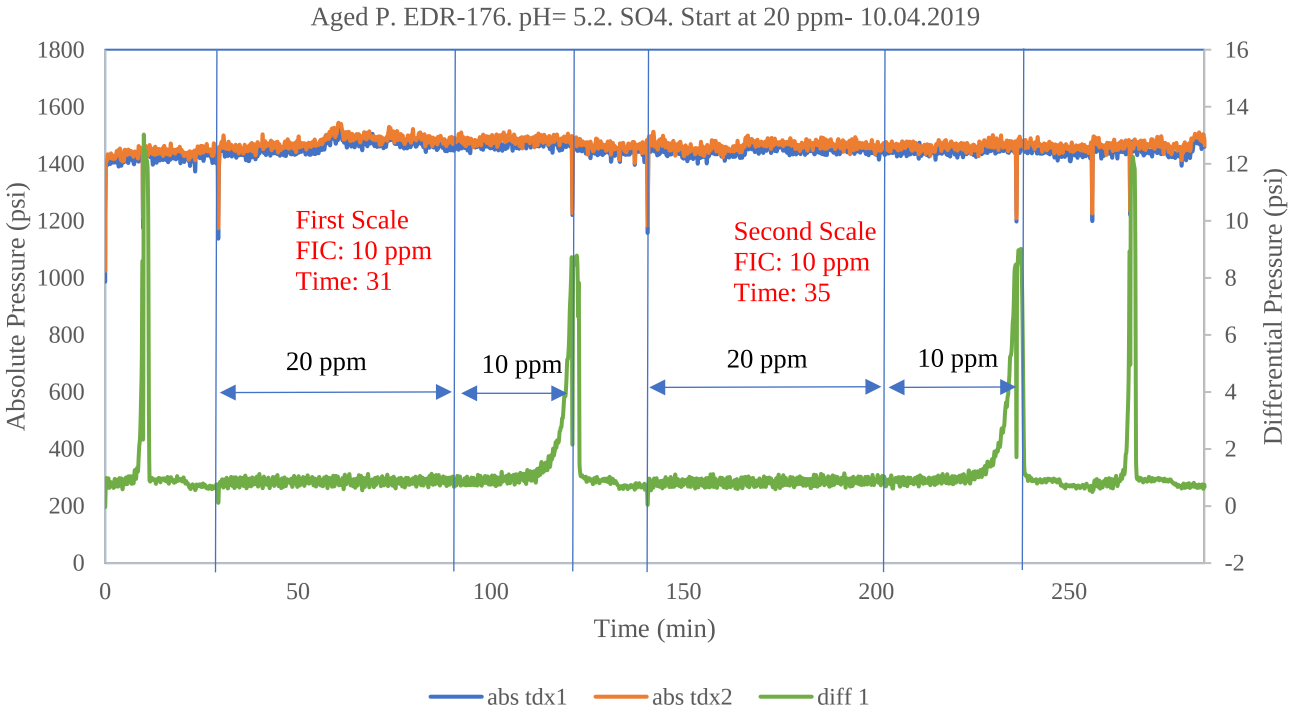


Figure 41. FIC and time values from high-pressure dynamic tube blocking experiments of aged P.EDR-176 for sulfate scale.

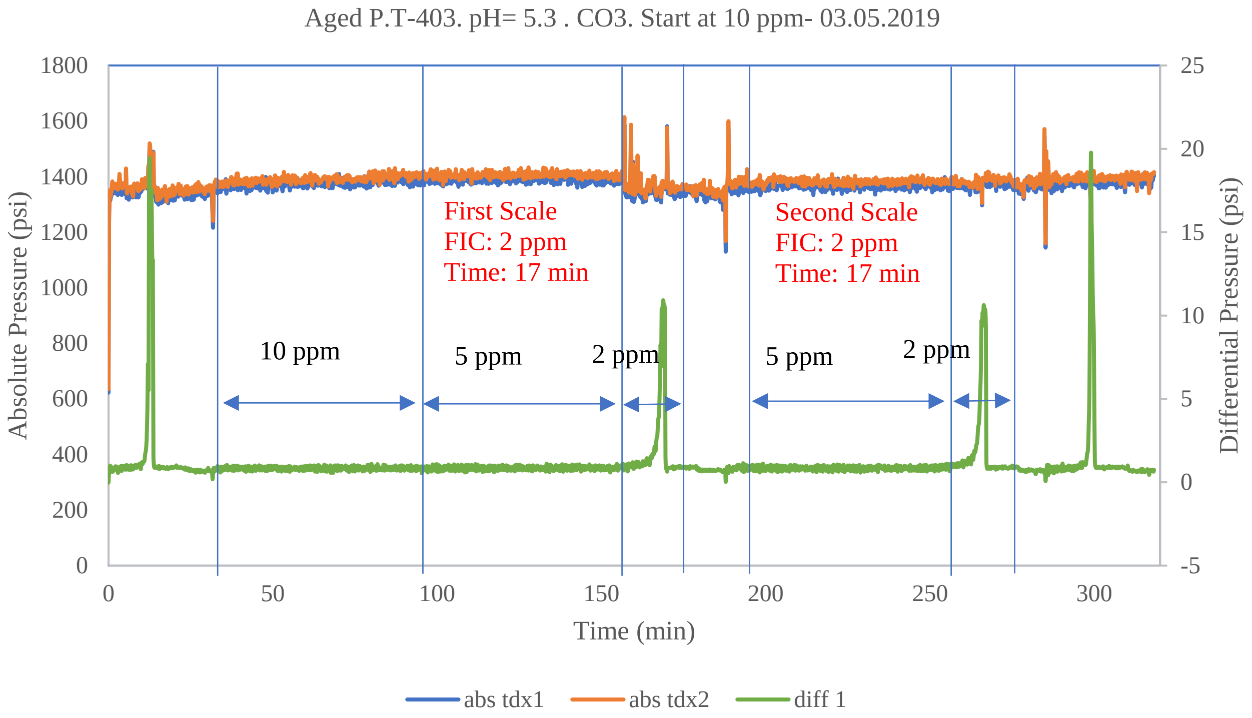


Figure 42. FIC and time values from high-pressure dynamic tube blocking experiments of aged P.T-403 for carbonate scale.

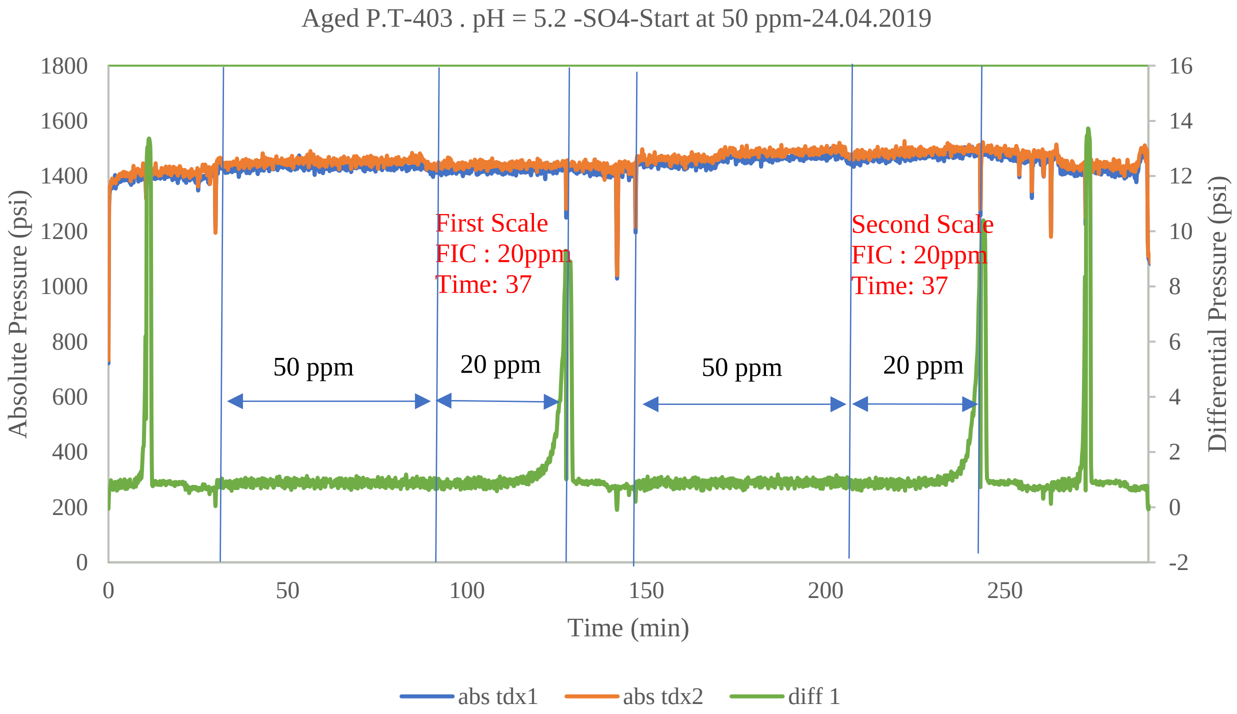
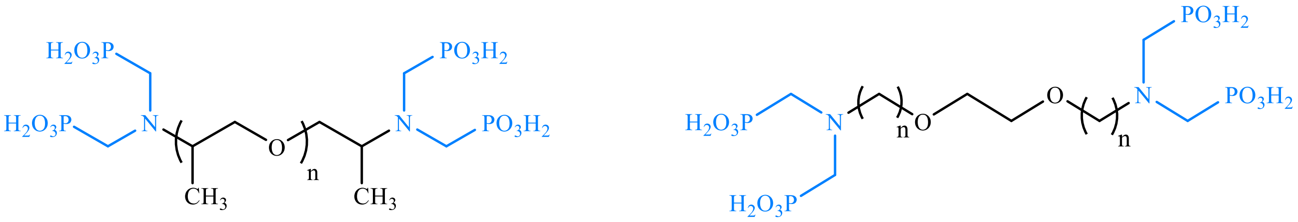


Figure 43. FIC and time values from high-pressure dynamic tube blocking experiments of aged P.T-403 for sulfate scale.

4.5 Biodegradation Tests

In this study, P.D-230 and P.EDR-148 were the candidates for the biodegradation test. Figure 44 shows the molecular structure of the tested in-house SIs.



(a) (b)

Figure 44. The molecular structure of in-house SIs. (a) P.D-230, (b) P.EDR-148.

Table 19 and Figure 45 presents the results obtained from the biodegradation tests according to OECD 306 over 28 days. Sodium benzoate is degraded very well with no notable lag time, giving 28-day biodegradation of about 84-94%; therefore, the BOD of sodium benzoate was measured as the reference. Previous studies showed a poor degradation of 15% in 28 days for DTPMP and moderate biodegradation of 34% for ATMP.[10] In comparison, P.D-230 gave only an average of 9.08% biodegradation and P.EDR-148 gave 20.27%. This finding was unexpected and suggested that the in-house SIs have poor biodegradability. However, this is contrary to previous studies which have suggested that the Jeffamine polyetheramines are biodegradable chemicals .[11] It is also expected that the existing nitrogen and phosphorus compound in aminomethylenephosphonate group, function as nutrients to the microorganisms and result in better biodegradability. Observational studies are subject to several potential problems that may bias their results. Future studies on the current topic are therefore recommended.

Table 19. Biodegradability activity measured by the OECD 306 procedure over 28 days.

Inhibitor	%BOD by OECD 306
Seawater	0
Sodium benzoate	93.4
DTPMP	15*
ATMP	34*
P.D-230	9.08
P.EDR-148	20.27

**The results are from previous studies.*[10]

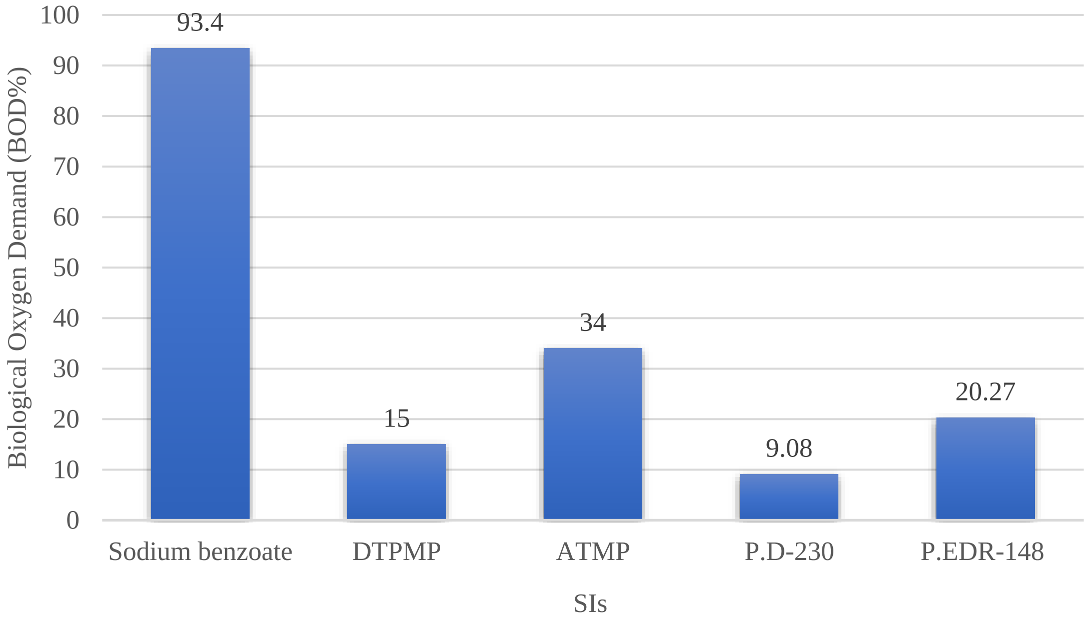


Figure 45. BOD test results for the commercial and in-house SIs.

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11. Erdem, A.; Ngwabebhoh, F. A.; Yildiz, U. J. J. o. e. c. e., Novel macroporous cryogels with enhanced adsorption capability for the removal of Cu (II) ions from aqueous phase: Modelling, kinetics and recovery studies. **2017,** *5* (1), 1269-1280.

5 Conclusion and Recommendations

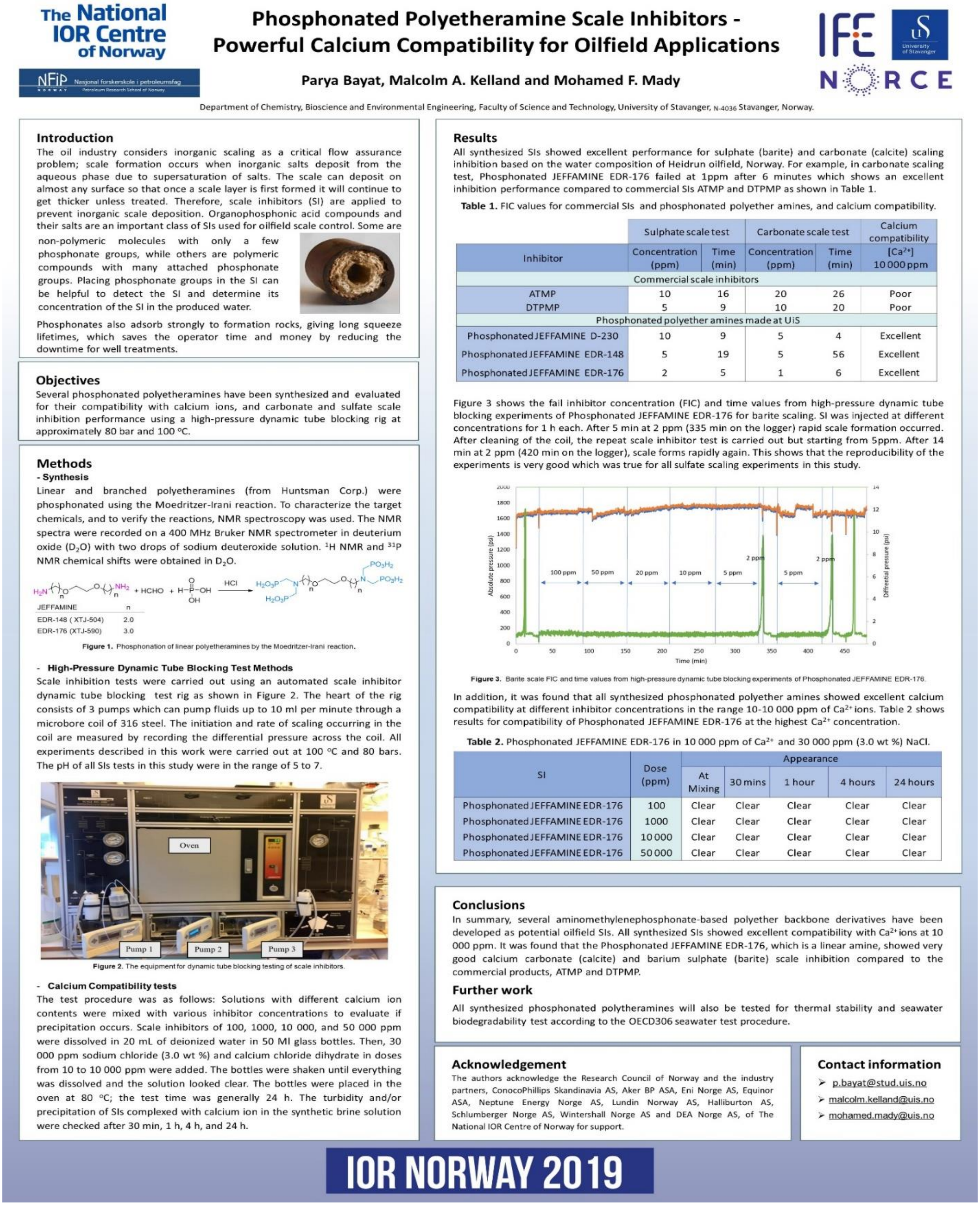
The present research aimed to examine a new class of branched and linear Jeffamine polyetheramines, functionalized with anionic functional group (phosphonate and carboxylate), as potential oilfield SIs. This study applied Moedritzer−Irani reaction to functionalize the amine compounds with methylenephosphonate groups. The calcite and barite scales inhibition performance of all the in-house synthesized SIs have been examined in a high-pressure dynamic tube blocking rig at approximately 80 bar and 100 °C. Moreover, the calcium compatibility, the thermal stability and the biodegradability of the synthesized SIs were screened. To have a better understanding of the performance of the newly synthesized SIs, some of the results from this study were compared with the results from previous studies on some phosphonate base commercial SIs such as ATMP and DTPMP.

The results of this study concluded that all the in-house phosphonated SIs showed high inhibition capability against both calcite and barite scale, compared with the commercial SIs. For example, P.EDR-176, synthesized from the linear polyetheramines, showed excellent barite inhibition by FIC value of 2 ppm, and excellent calcite scale inhibition by no formation of the scale at the lowest concentration of the injected SI (1 ppm). However, functionalizing the polyetheramines with carboxylic groups gave poor scale inhibition for carbonate scales, with FIC at 100 ppm. Therefore, it was not investigated for more analyses. Further tests revealed that the in-house phosphonate base SIs showed excellent compatibility with Ca^{2+} at 100, 1000 and 10 000 ppm over the 24 h test period. Besides, the anaerobically thermal aging of the SIs for one week at 130 °C showed good thermal stability by giving just a small decline of scale inhibition performance. Two of the in-house SIs P.D-230 and P.T-403 were screened for their biodegradability and they showed 9.08 and 20.27 BOD%, respectively, in 28 days in seawater by the OECD 306 test.

This study would have possible benefits in the development of scale inhibitors regarding their efficiency for giving long squeeze lifetimes which saves the operator time and money by reducing the downtime for well treatments. Further research should be carried out to report other characteristics such as their adsorption properties on formation rock for application in squeeze treatment.

6 APPENDIXES

APPENDIX A- Poster Presentation IOR-2019



Phosphonated Polyetheramine Scale Inhibitors - Powerful Calcium Compatibility for Oilfield Applications

Parya Bayat, Malcolm A. Kelland and Mohamed F. Mady

Department of Chemistry, Bioscience and Environmental Engineering, Faculty of Science and Technology, University of Stavanger, N-4036 Stavanger, Norway.

Introduction

The oil industry considers inorganic scaling as a critical flow assurance problem; scale formation occurs when inorganic salts deposit from the aqueous phase due to supersaturation of salts. The scale can deposit on almost any surface so that once a scale layer is first formed it will continue to get thicker unless treated. Therefore, scale inhibitors (SI) are applied to prevent inorganic scale deposition. Organophosphonic acid compounds and their salts are an important class of SIs used for oilfield scale control. Some are non-polymeric molecules with only a few phosphonate groups, while others are polymeric compounds with many attached phosphonate groups. Placing phosphonate groups in the SI can be helpful to detect the SI and determine its concentration of the SI in the produced water.

Phosphonates also adsorb strongly to formation rocks, giving long squeeze lifetimes, which saves the operator time and money by reducing the downtime for well treatments.

Objectives

Several phosphonated polyetheramines have been synthesized and evaluated for their compatibility with calcium ions, and carbonate and sulfate scale inhibition performance using a high-pressure dynamic tube blocking rig at approximately 80 bar and 100 °C.

Methods

- Synthesis

Linear and branched polyetheramines (from Huntsman Corp.) were phosphonated using the Moedritzer-Irani reaction. To characterize the target chemicals, and to verify the reactions, NMR spectroscopy was used. The NMR spectra were recorded on a 400 MHz Bruker NMR spectrometer in deuterium oxide (D_2O) with two drops of sodium deuteroxide solution. ^1H NMR and ^{31}P NMR chemical shifts were obtained in D_2O.

JEFFAMINE	n
EDR-148 (XTJ-504)	2.0
EDR-176 (XTJ-590)	3.0

Figure 1. Phosphonation of linear polyetheramines by the Moedritzer-Irani reaction.

- High-Pressure Dynamic Tube Blocking Test Methods

Scale inhibition tests were carried out using an automated scale inhibitor dynamic tube blocking test rig as shown in Figure 2. The heart of the rig consists of 3 pumps which can pump fluids up to 10 ml per minute through a microbore coil of 316 steel. The initiation and rate of scaling occurring in the coil are measured by recording the differential pressure across the coil. All experiments described in this work were carried out at 100 °C and 80 bars. The pH of all SIs tests in this study were in the range of 5 to 7.

Figure 2. The equipment for dynamic tube blocking testing of scale inhibitors.

- Calcium Compatibility tests

The test procedure was as follows: Solutions with different calcium ion contents were mixed with various inhibitor concentrations to evaluate if precipitation occurs. Scale inhibitors of 100, 1000, 10 000, and 50 000 ppm were dissolved in 20 mL of deionized water in 50 Ml glass bottles. Then, 30 000 ppm sodium chloride (3.0 wt %) and calcium chloride dihydrate in doses from 10 to 10 000 ppm were added. The bottles were shaken until everything was dissolved and the solution looked clear. The bottles were placed in the oven at 80 °C; the test time was generally 24 h. The turbidity and/or precipitation of SIs complexed with calcium ion in the synthetic brine solution were checked after 30 min, 1 h, 4 h, and 24 h.

Results

All synthesized SIs showed excellent performance for sulphate (barite) and carbonate (calcite) scaling inhibition based on the water composition of Heidrun oilfield, Norway. For example, in carbonate scaling test, Phosphonated JEFFAMINE EDR-176 failed at 1ppm after 6 minutes which shows an excellent inhibition performance compared to commercial SIs ATMP and DTPMP as shown in Table 1.

Table 1. FIC values for commercial SIs and phosphonated polyether amines, and calcium compatibility.

	Sulphate scale test		Carbonate scale test		Calcium compatibility
Inhibitor	Concentration (ppm)	Time (min)	Concentration (ppm)	Time (min)	[Ca^{2+}] 10 000 ppm
Commercial scale inhibitors					
ATMP	10	16	20	26	Poor
DTPMP	5	9	10	20	Poor
Phosphonated polyether amines made at UiS					
Phosphonated JEFFAMINE D-230	10	9	5	4	Excellent
Phosphonated JEFFAMINE EDR-148	5	19	5	56	Excellent
Phosphonated JEFFAMINE EDR-176	2	5	1	6	Excellent

Figure 3 shows the fail inhibitor concentration (FIC) and time values from high-pressure dynamic tube blocking experiments of Phosphonated JEFFAMINE EDR-176 for barite scaling. SI was injected at different concentrations for 1 h each. After 5 min at 2 ppm (335 min on the logger) rapid scale formation occurred. After cleaning of the coil, the repeat scale inhibitor test is carried out but starting from 5ppm. After 14 min at 2 ppm (420 min on the logger), scale forms rapidly again. This shows that the reproducibility of the experiments is very good which was true for all sulfate scaling experiments in this study.

Figure 3. Barite scale FIC and time values from high-pressure dynamic tube blocking experiments of Phosphonated JEFFAMINE EDR-176.

In addition, it was found that all synthesized phosphonated polyether amines showed excellent calcium compatibility at different inhibitor concentrations in the range 10-10 000 ppm of Ca^{2+} ions. Table 2 shows results for compatibility of Phosphonated JEFFAMINE EDR-176 at the highest Ca^{2+} concentration.

Table 2. Phosphonated JEFFAMINE EDR-176 in 10 000 ppm of Ca^{2+} and 30 000 ppm (3.0 wt %) NaCl.

SI	Dose (ppm)	Appearance				
		At Mixing	30 mins	1 hour	4 hours	24 hours
Phosphonated JEFFAMINE EDR-176	100	Clear	Clear	Clear	Clear	Clear
Phosphonated JEFFAMINE EDR-176	1000	Clear	Clear	Clear	Clear	Clear
Phosphonated JEFFAMINE EDR-176	10 000	Clear	Clear	Clear	Clear	Clear
Phosphonated JEFFAMINE EDR-176	50 000	Clear	Clear	Clear	Clear	Clear

Conclusions

In summary, several aminomethylenephosphonate-based polyether backbone derivatives have been developed as potential oilfield SIs. All synthesized SIs showed excellent compatibility with Ca^{2+} ions at 10 000 ppm. It was found that the Phosphonated JEFFAMINE EDR-176, which is a linear amine, showed very good calcium carbonate (calcite) and barium sulphate (barite) scale inhibition compared to the commercial products, ATMP and DTPMP.

Further work

All synthesized phosphonated polytheramines will also be tested for thermal stability and seawater biodegradability test according to the OECD306 seawater test procedure.

Acknowledgement

The authors acknowledge the Research Council of Norway and the industry partners, ConocoPhillips Skandinavia AS, Aker BP ASA, Eni Norge AS, Equinor ASA, Neptune Energy Norge AS, Lundin Norway AS, Halliburton AS, Schlumberger Norge AS, Wintershall Norge AS and DEA Norge AS, of The National IOR Centre of Norway for support.

Contact information

- p.bayat@stud.uis.no
- malcolm.kelland@uis.no
- mohamed.mady@uis.no

APPENDIX B- NMR Figures

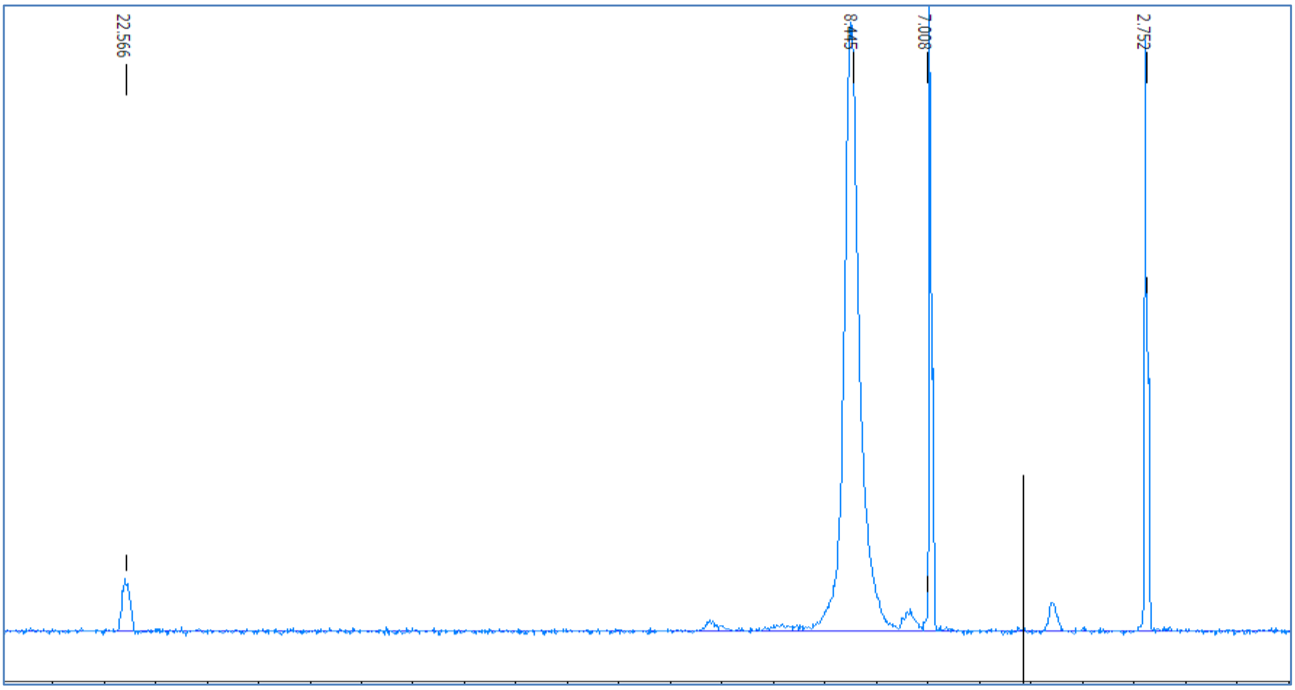


Figure 1. 31P NMR for P.D-230.

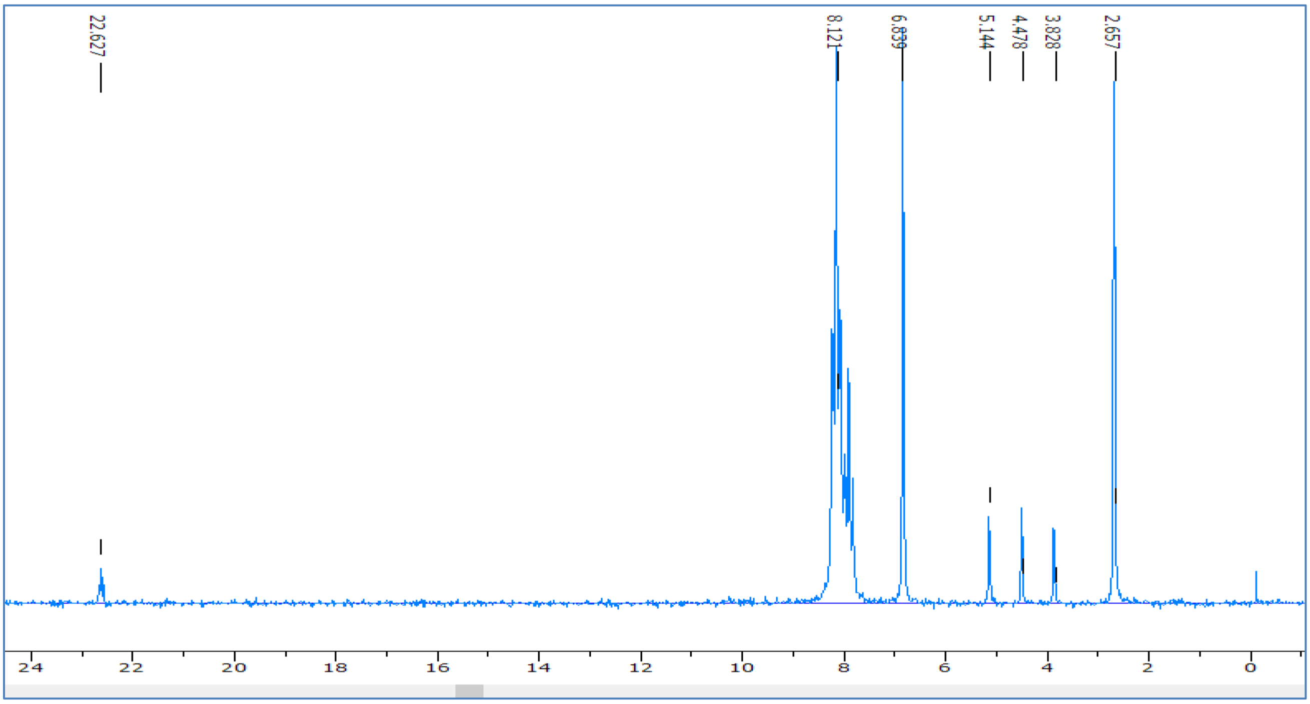


Figure 2. ^{31}P NMR for P.EDR-176.

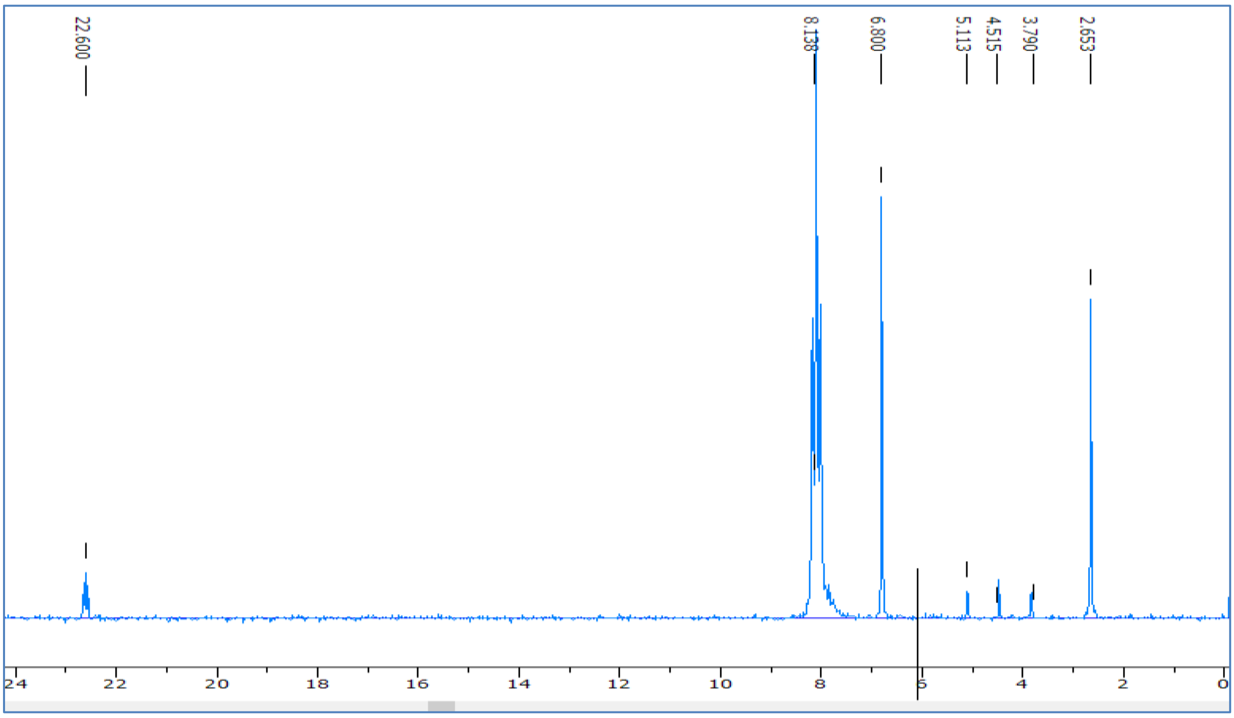


Figure 3. ^{31}P NMR for P.EDR-148

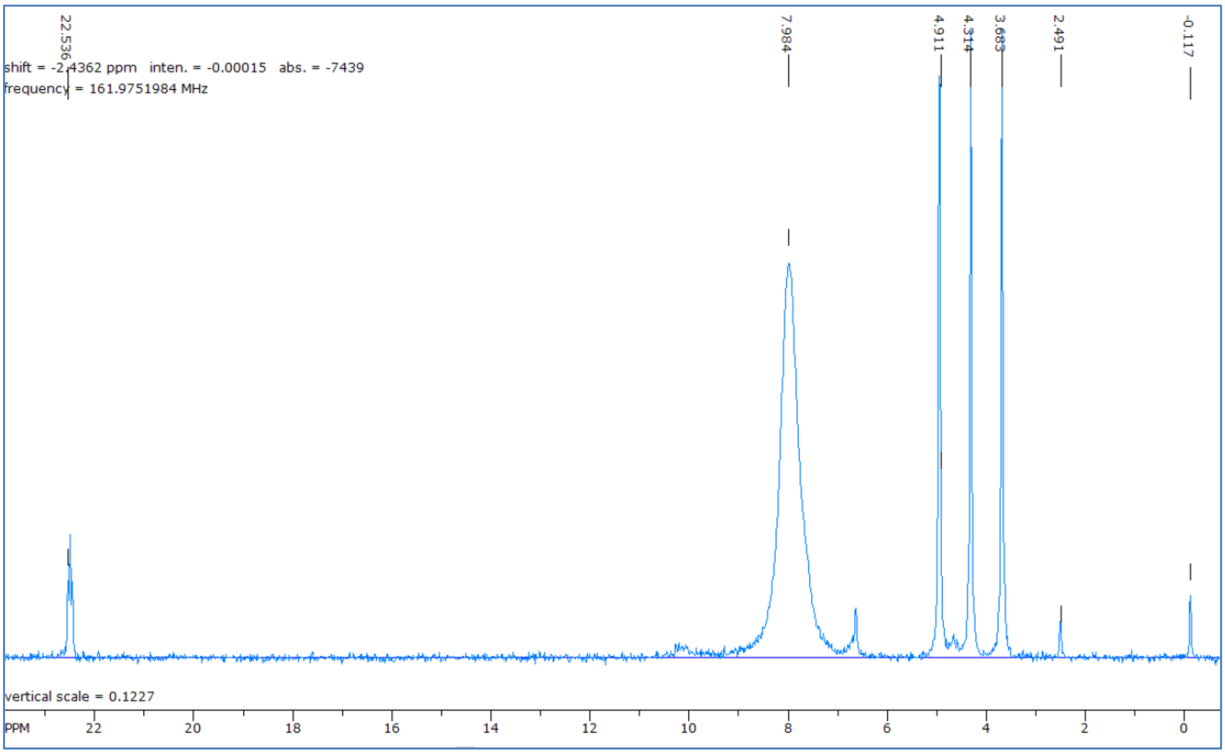


Figure 4. ^{31}P NMR for P.T-403.

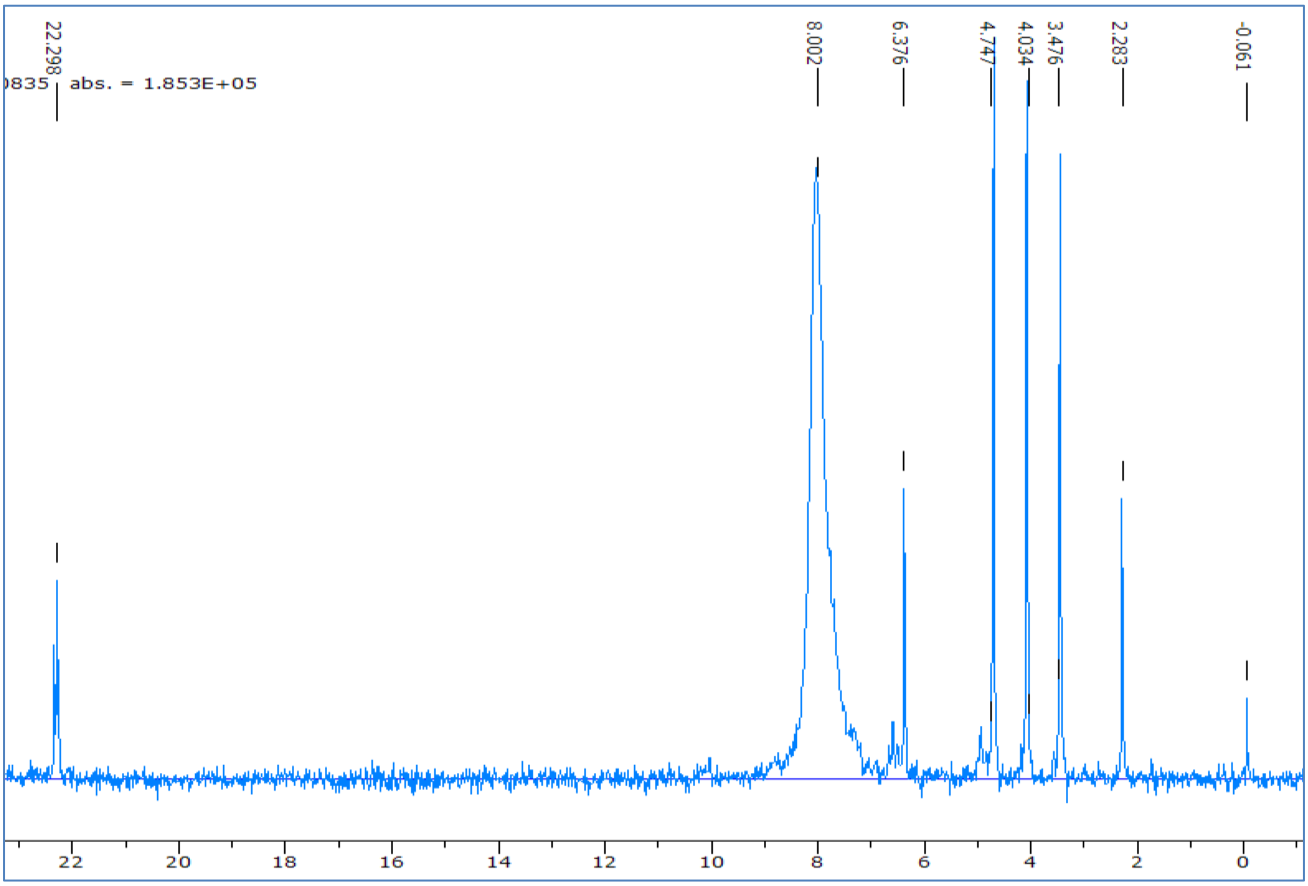


Figure 5. ^{31}P NMR P.XTJ-568.

APPENDIX C- High-pressure Dynamic Tube blocking graphic test results

Commercial Scale Inhibitors

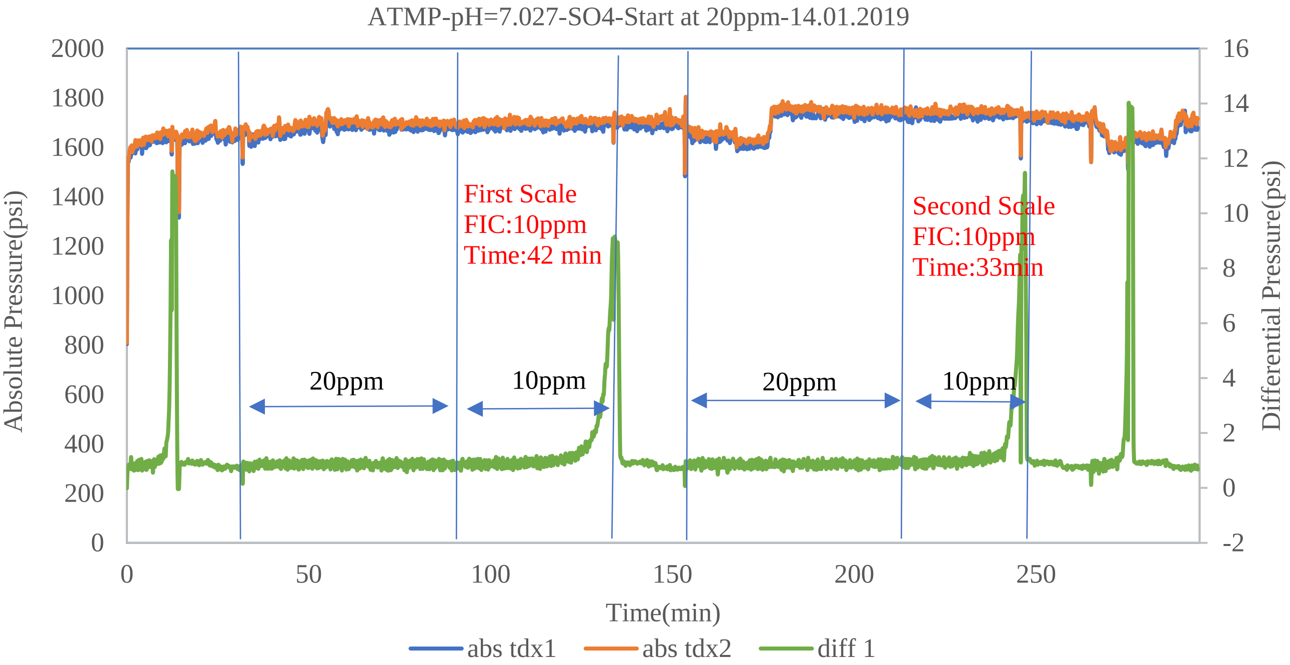


Figure 6. FIC and time values from high-pressure dynamic tube blocking experiments of ATMP for sulfate scale.

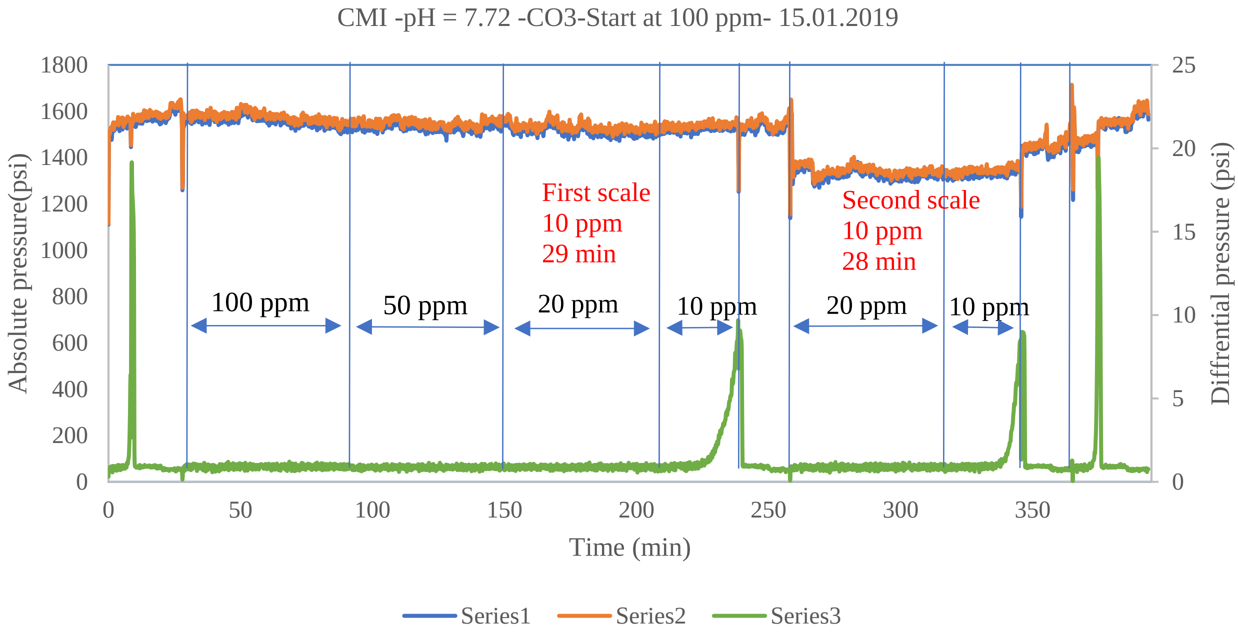


Figure 7. FIC and time values from high-pressure dynamic tube blocking experiments of CMI for carbonate scale.

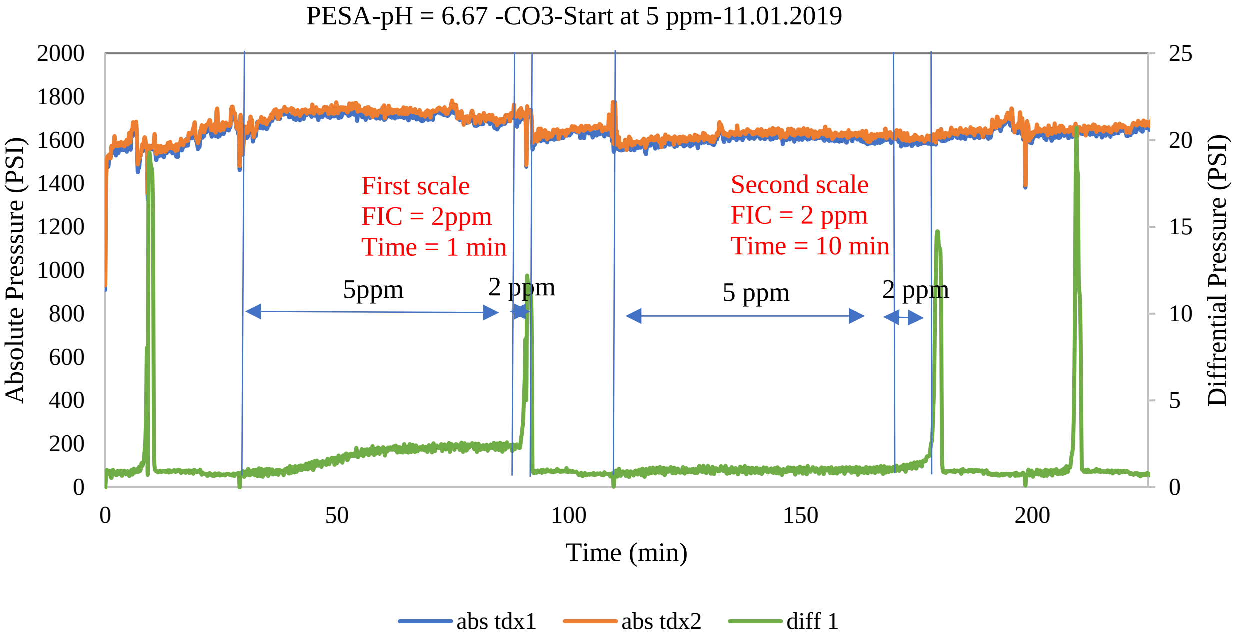


Figure 8. FIC and time values from high-pressure dynamic tube blocking experiments of PESA for carbonate scale.

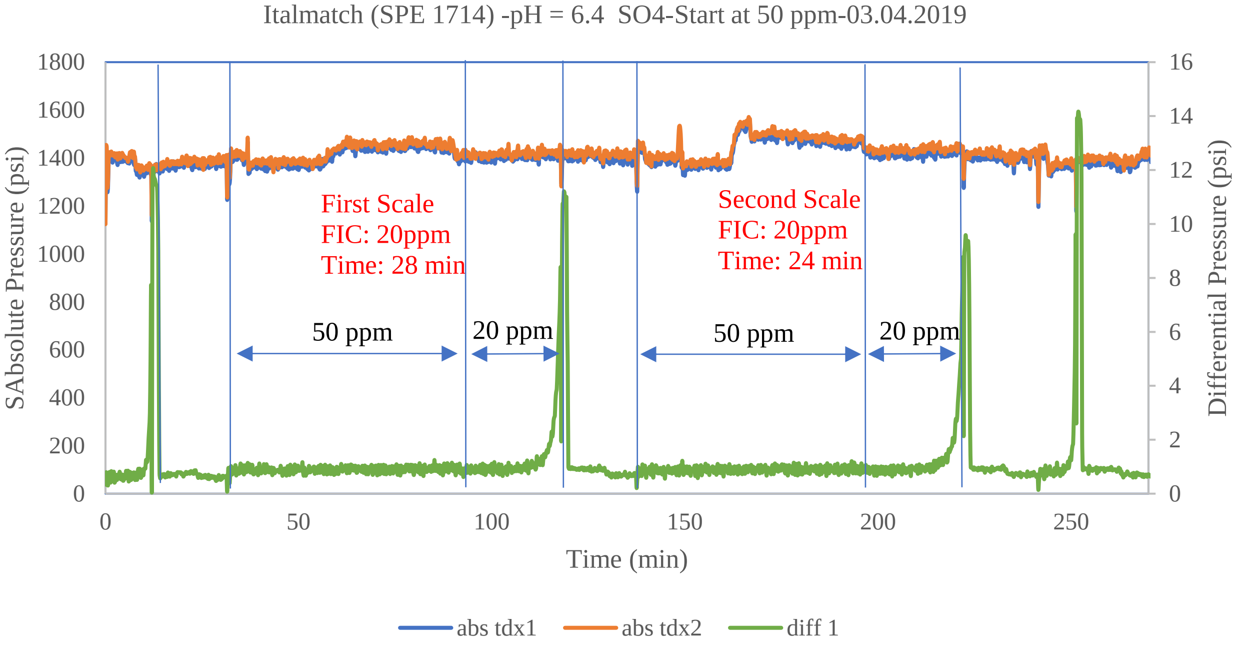


Figure 9. FIC and time values from high-pressure dynamic tube blocking experiments of Italmatch for sulfate scale.

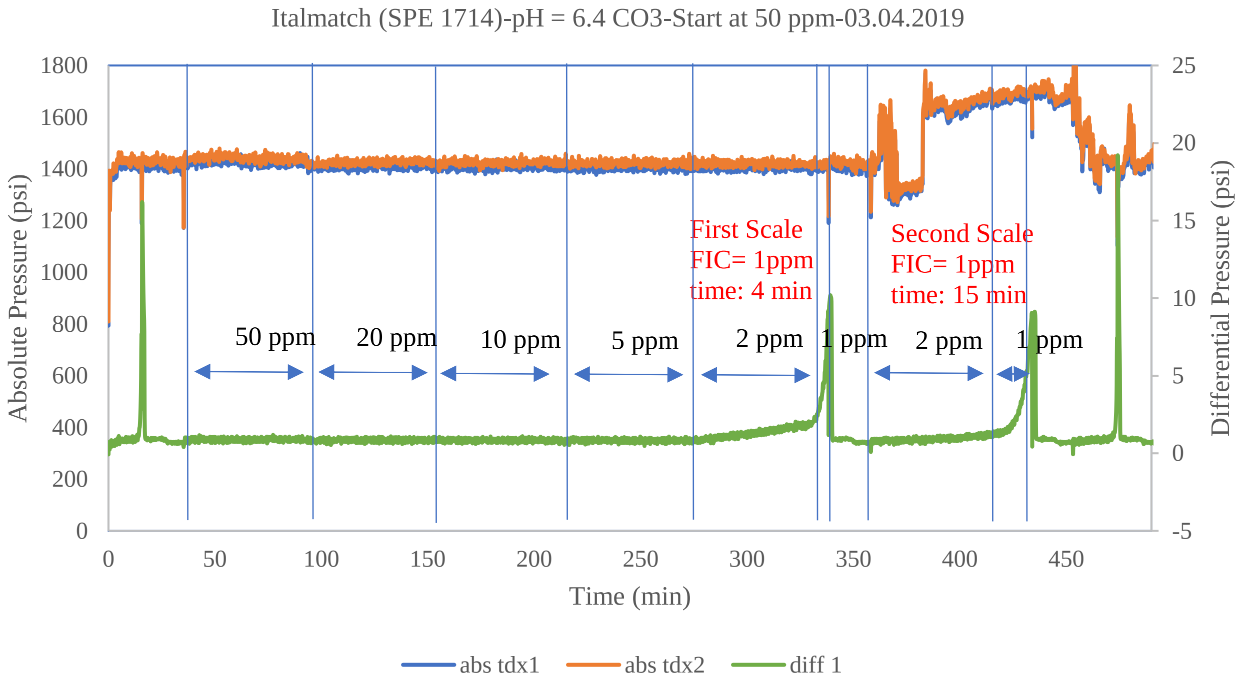


Figure 10. FIC and time values from high-pressure dynamic tube blocking experiments of Italmatch for carbonate scale.

Phosphonated Polyetheramines Made at UiS

Sulfate (Barite) Scaling Tests

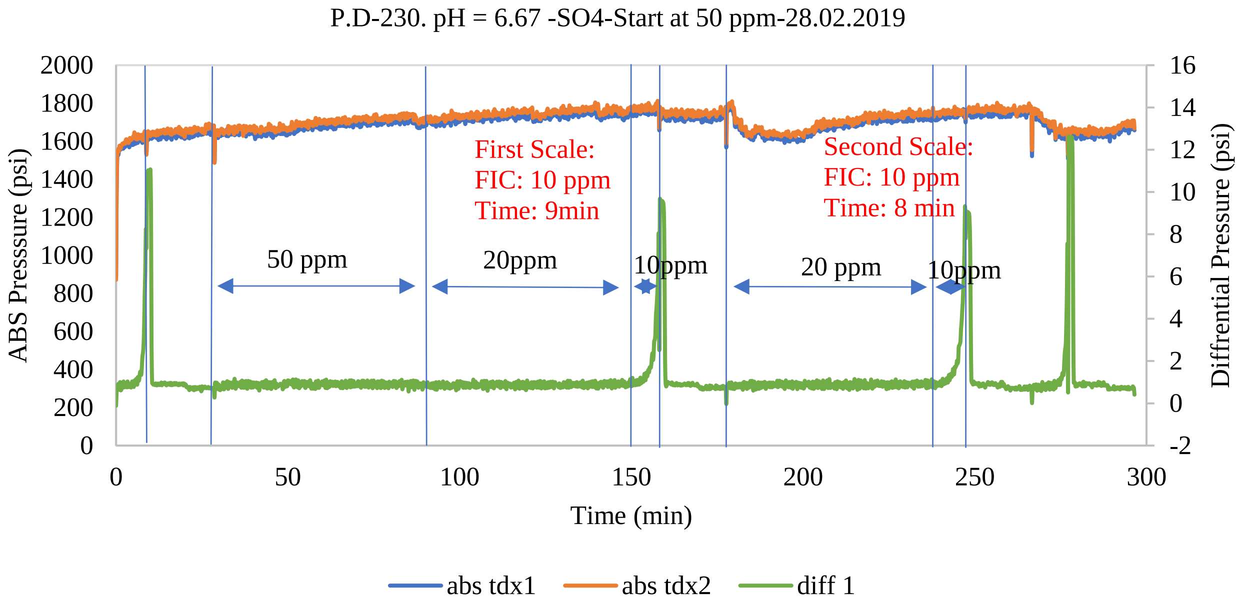


Figure 11. FIC and time values from high-pressure dynamic tube blocking experiments of P.D-230 for sulfate scale.

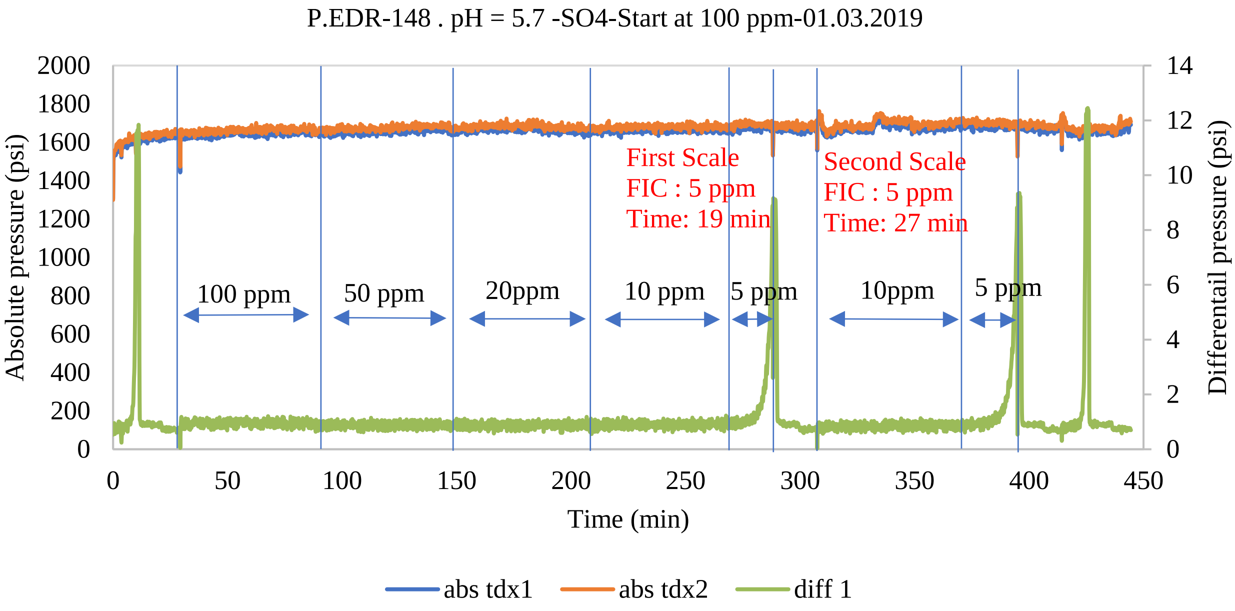


Figure 12. FIC and time values from high-pressure dynamic tube blocking experiments of P.EDR-148 for sulfate scale.

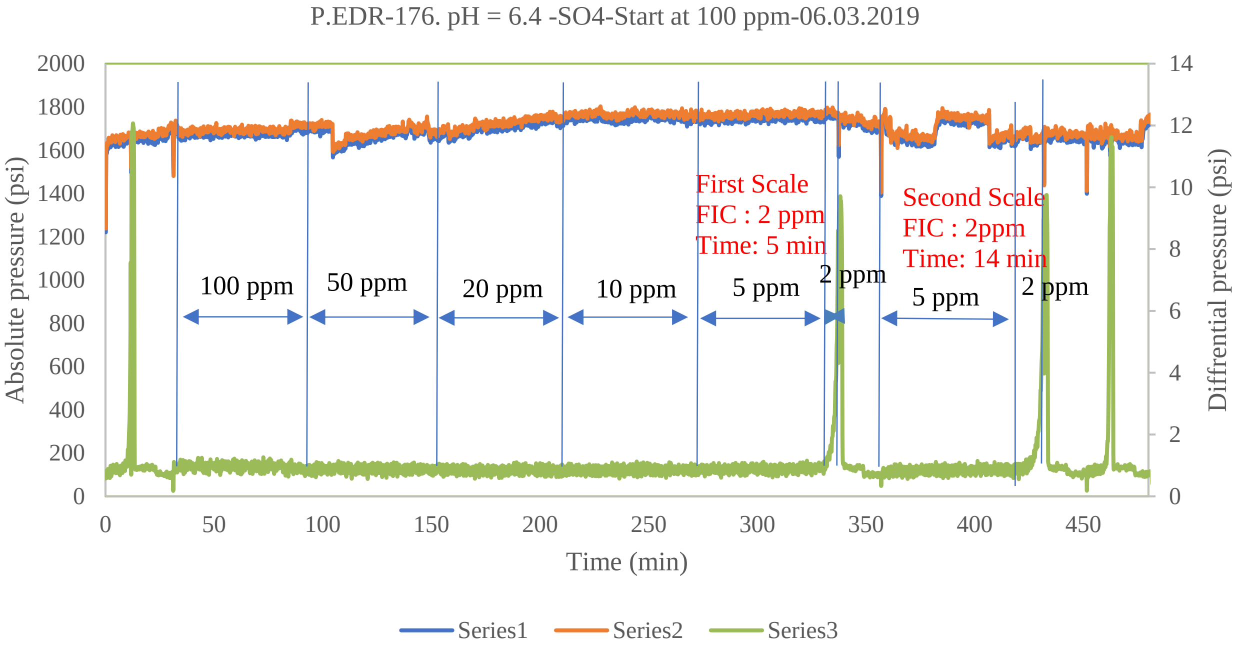


Figure 13. FIC and time values from high-pressure dynamic tube blocking experiments of P.EDR-176 for sulfate scale.

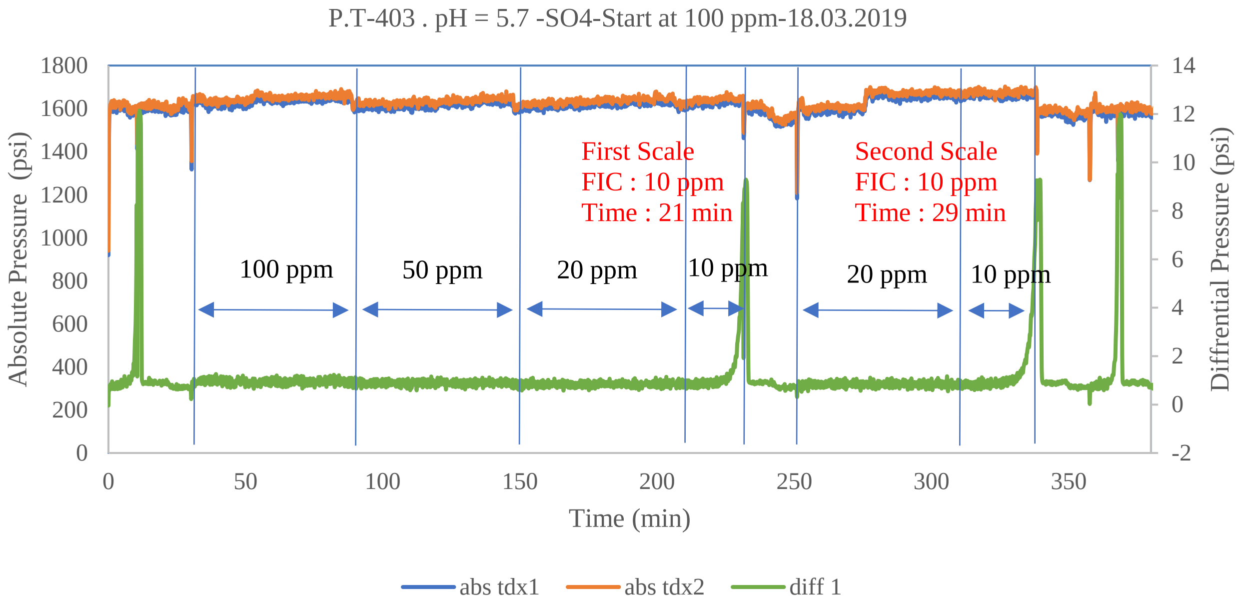


Figure 14. FIC and time values from high-pressure dynamic tube blocking experiments of P.T-403 for sulfate scale.

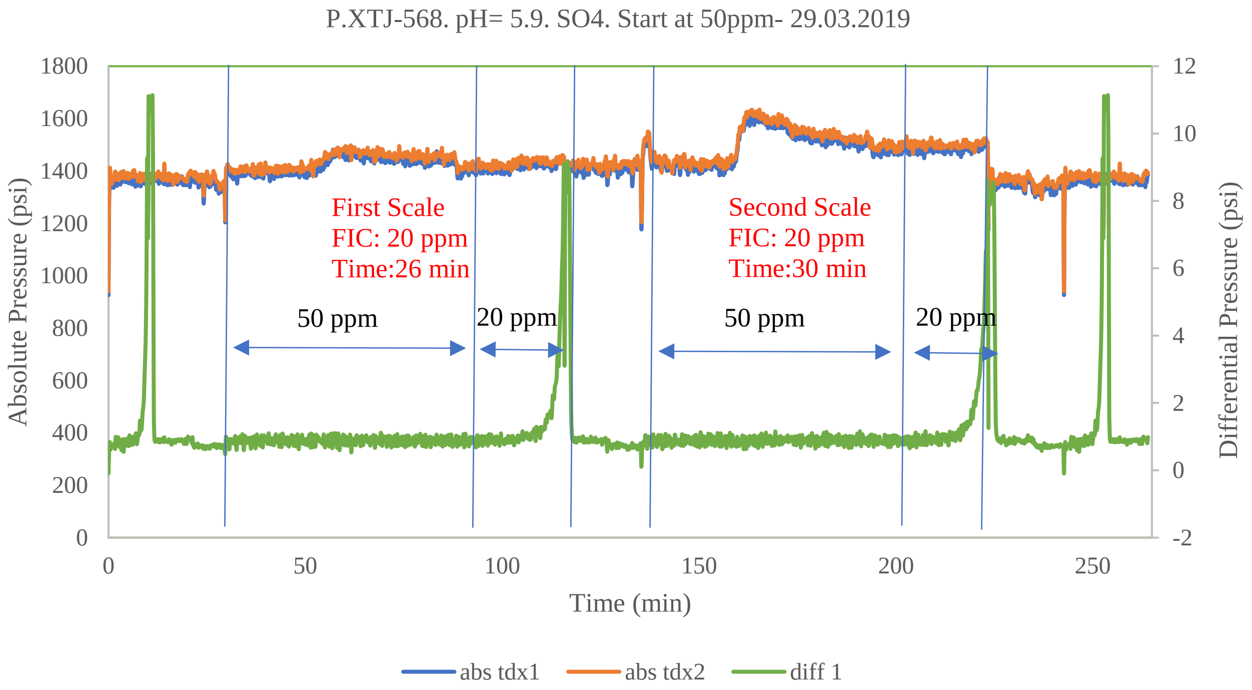


Figure 15. FIC and time values from high-pressure dynamic tube blocking experiments of P.XTJ-568 for sulfate scale.

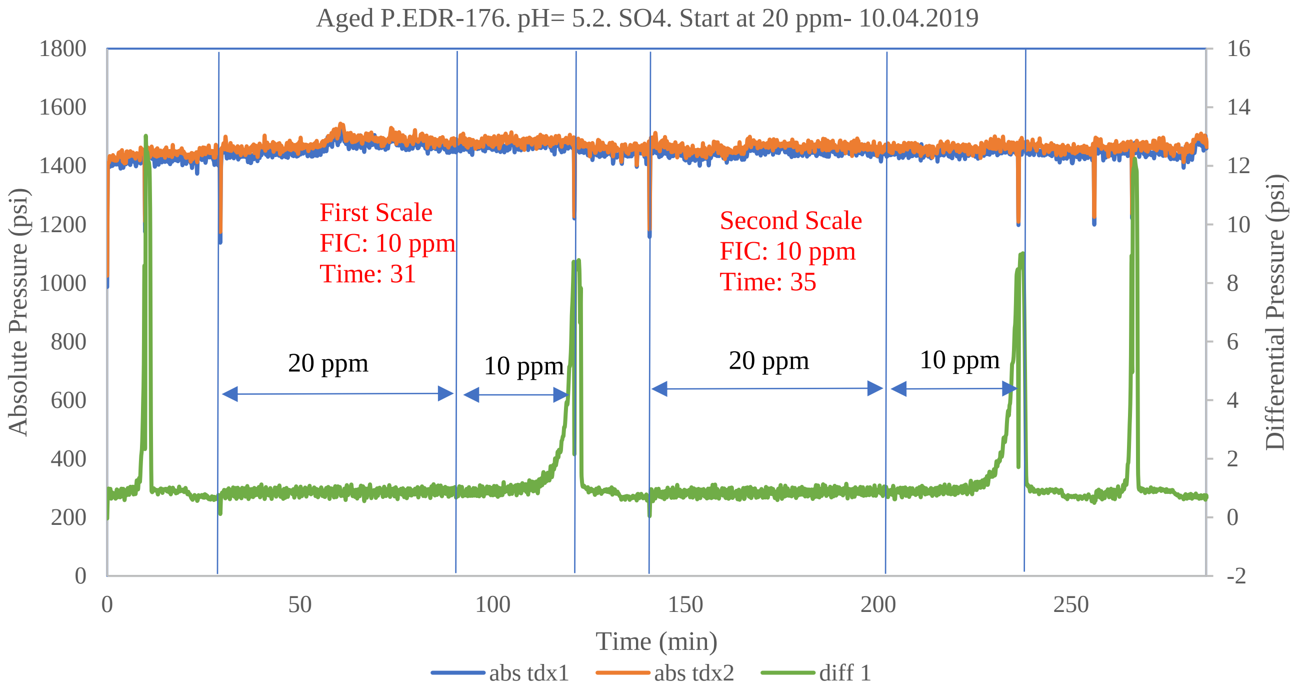


Figure 16. FIC and time values from high-pressure dynamic tube blocking experiments of aged P.EDR-176 for sulfate scale.

Carbonate (Calcite) Scaling Tests

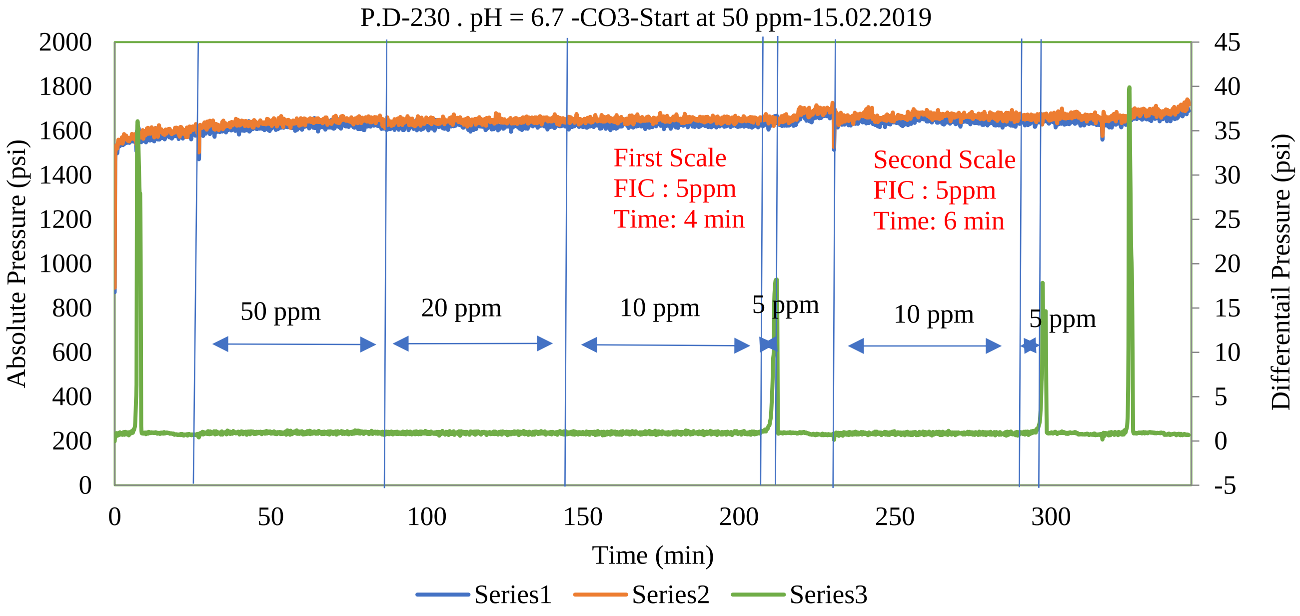


Figure 17. FIC and time values from high-pressure dynamic tube blocking experiments of P.D-230 for carbonate scale.

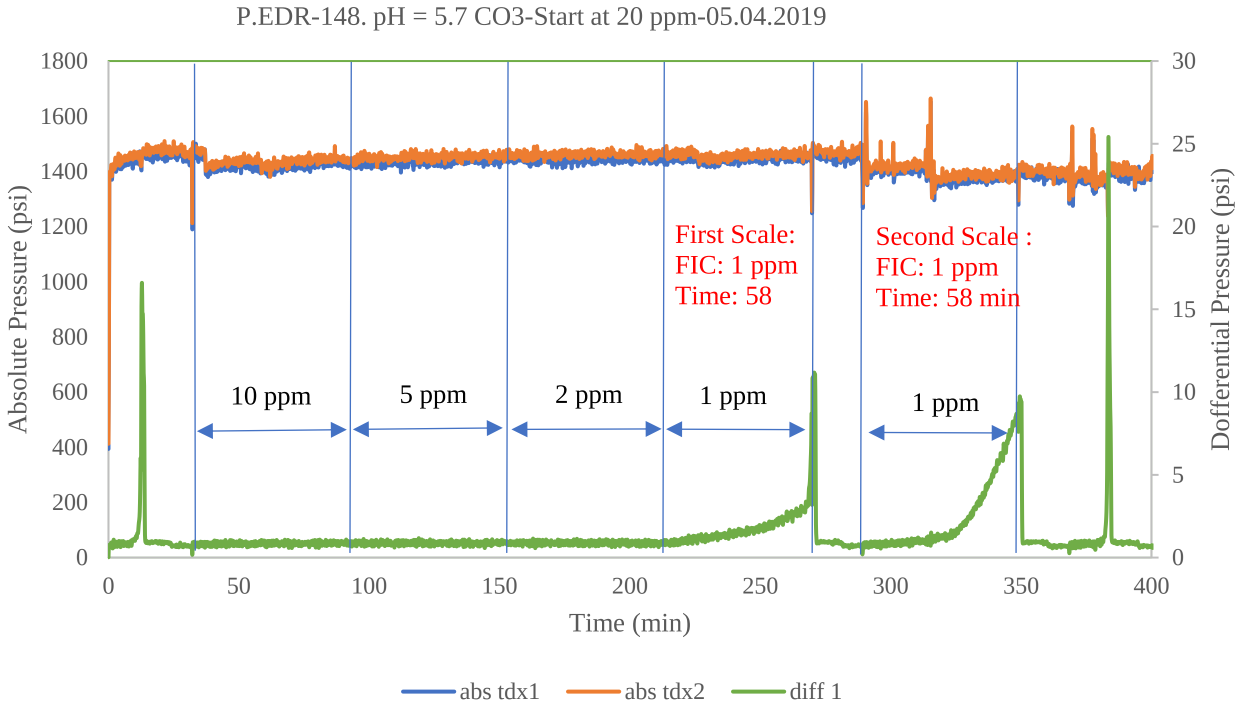


Figure 18. FIC and time values from high-pressure dynamic tube blocking experiments of P.EDR-148 for carbonate scale.

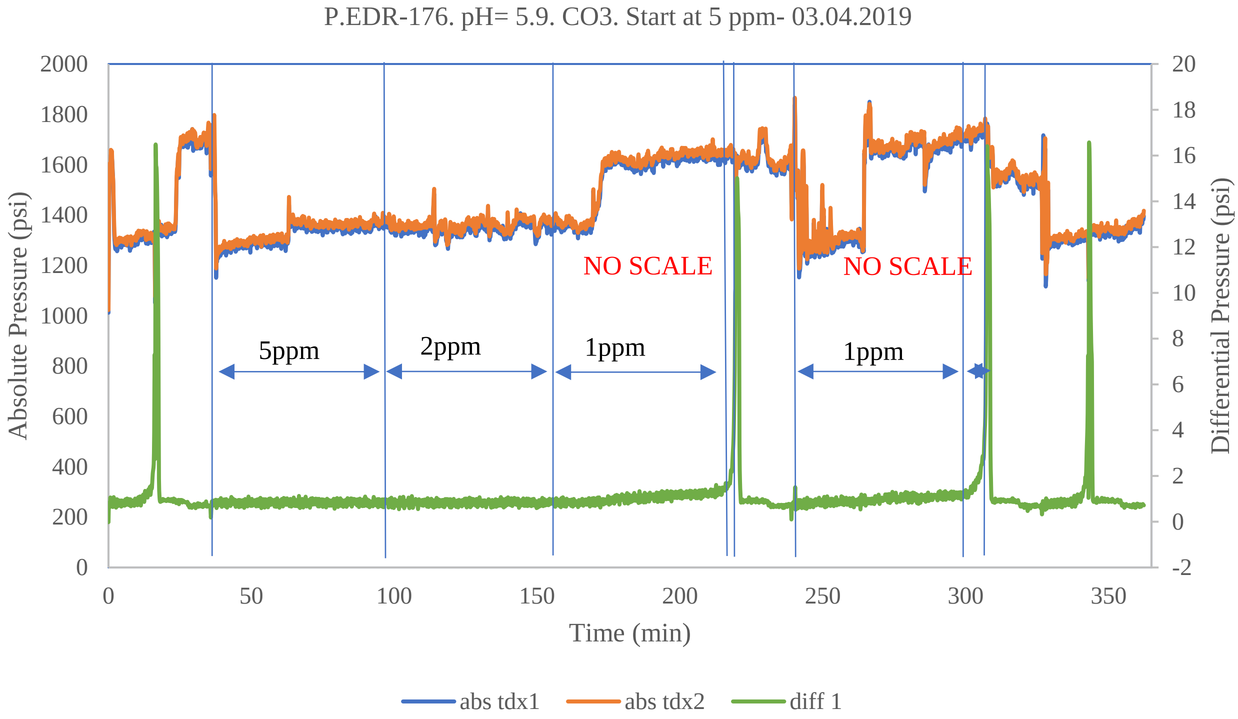


Figure 19. FIC and time values from high-pressure dynamic tube blocking experiments of P.EDR-176 for carbonate scale.

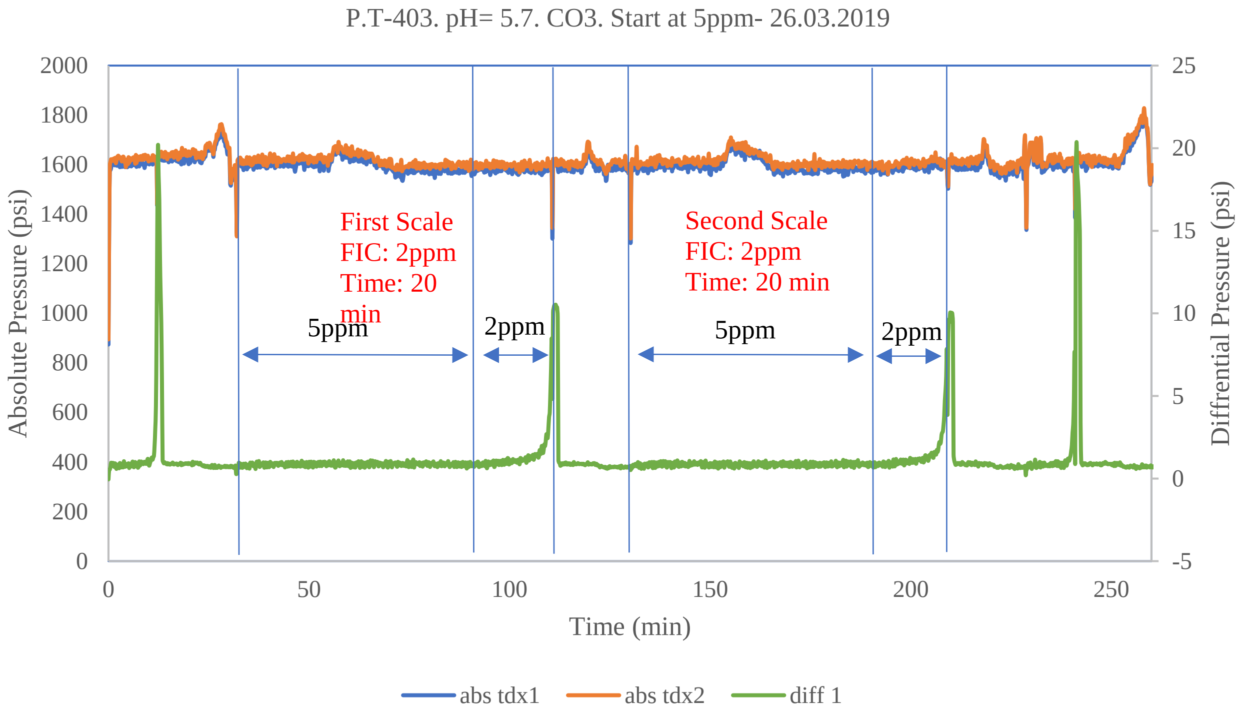


Figure 20. FIC and time values from high-pressure dynamic tube blocking experiments of P.T-403 for carbonate scale.

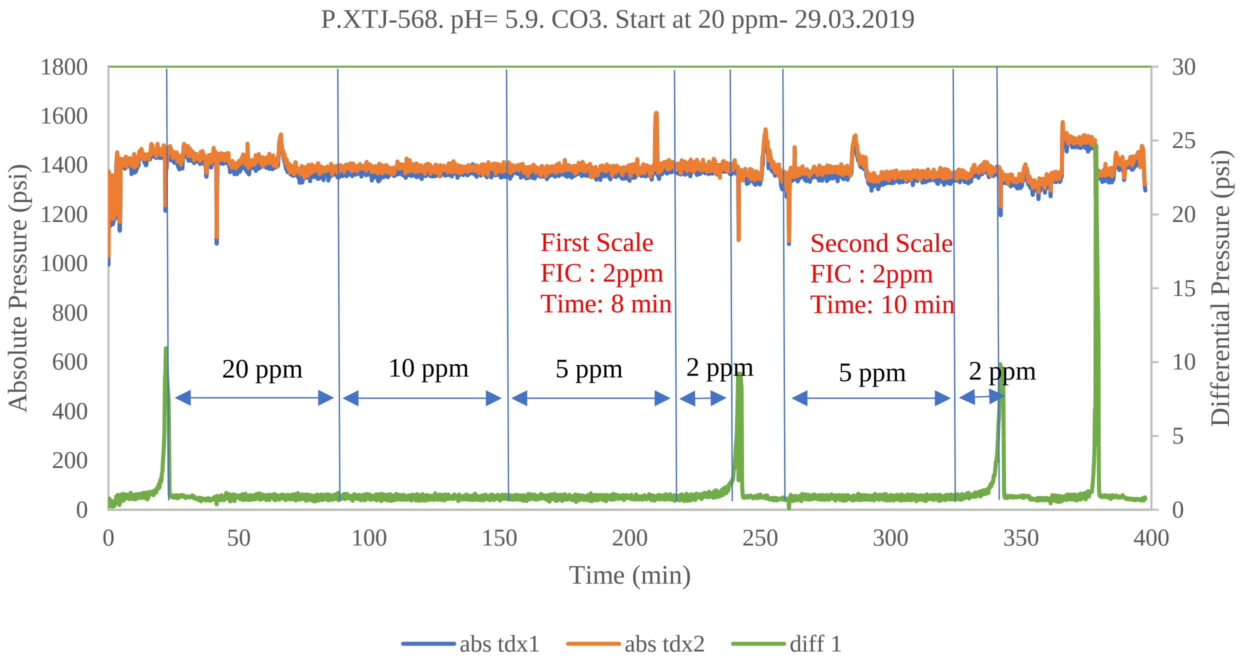


Figure 21. FIC and time values from high-pressure dynamic tube blocking experiments of P.XTJ-568 for carbonate scale.

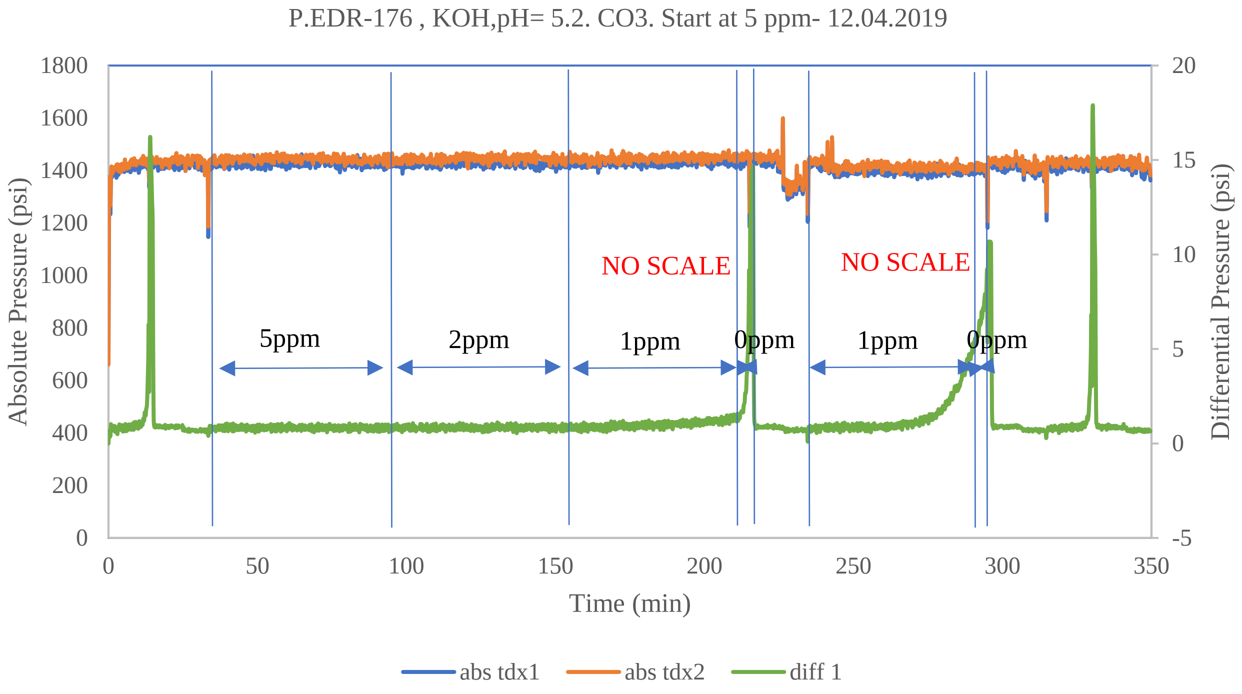


Figure 22. FIC and time values from high-pressure dynamic tube blocking experiments of PEDR-176 for carbonate scale. (KOH as the pH adjuster)

Jeffamine EDR-176 functionalized with COOH

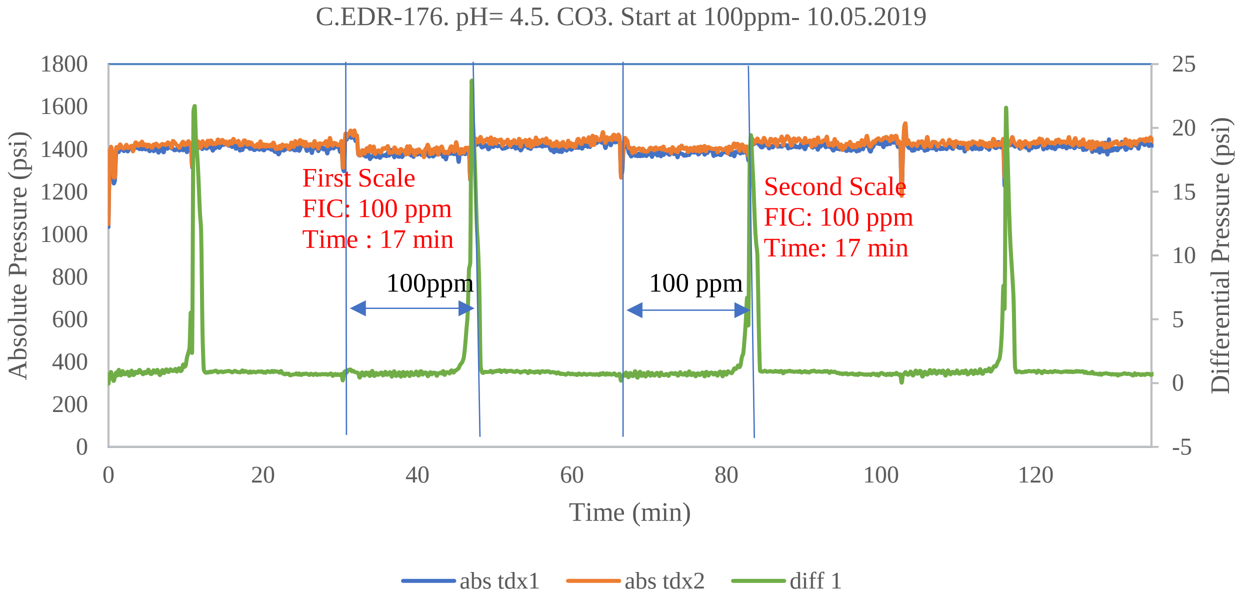


Figure 23. FIC and time values from high-pressure dynamic tube blocking experiments of C.EDR-176 for carbonate scale.

APPENDIX D- Calcium compatibility test

Table 20. Compatibility tests in 1000 ppm of Ca^{2+} and 30000 ppm (3.0 wt.%) NaCl for P.D-230.

SI	Dose (ppm)	Appearance				
		At Mixing	30 mins	1 hour	4 hours	24 hours
SI-1	100	Clear	Clear	Clear	Clear	Clear
SI-1	1000	Clear	Clear	Clear	Clear	Clear
SI-1	10000	Clear	Clear	Clear	Clear	Clear
SI-1	50000	Clear	Clear	Clear	Clear	Clear

Table 21. Compatibility tests in 10 000 ppm of Ca^{2+} and 30000 ppm (3.0 wt.%) NaCl for P.D-230

SI	Dose (ppm)	Appearance				
		At Mixing	30 mins	1 hour	4 hours	24 hours
SI-1	100	Clear	Clear	Clear	Clear	Clear
SI-1	1000	Clear	Clear	Clear	Clear	Clear
SI-1	10000	Clear	Clear	Clear	Clear	Clear
SI-1	50000	Clear	Clear	Clear	Clear	Clear

Table 22. Compatibility test in 1000 ppm of Ca^{2+} and 30000 ppm (3.0 wt.%) NaCl for P.T-403.

SI	Dose (ppm)	Appearance				
		At Mixing	30 mins	1 hour	4 hours	24 hours
SI-1	100	Clear	Clear	Clear	Clear	Clear
SI-1	1000	Clear	Clear	Clear	Clear	Clear
SI-1	10000	Clear	Clear	Clear	Clear	Clear
SI-1	50000	Clear	Clear	Clear	Clear	Clear

Table 23. Compatibility test in 10 000 ppm of Ca^{2+} and 30000 ppm (3.0 wt.%) NaCl for P.T-403.

SI	Dose (ppm)	Appearance				
		At Mixing	30 mins	1 hour	4 hours	24 hours
SI-1	100	Clear	Clear	Clear	Clear	Clear
SI-1	1000	Clear	Clear	Clear	Clear	Clear
SI-1	10000	Clear	Clear	Clear	Clear	Clear
SI-1	50000	Clear	Clear	Clear	Clear	Clear

Table 24. Compatibility test in 1000 ppm of Ca^{2+} and 30000 ppm (3.0 wt.%) NaCl for P.XTJ-568.

SI	Dose (ppm)	Appearance				
		At Mixing	30 mins	1 hour	4 hours	24 hours
SI-1	100	Clear	Clear	Clear	Clear	Clear
SI-1	1000	Clear	Clear	Clear	Clear	Clear
SI-1	10000	Clear	Clear	Clear	Clear	Clear
SI-1	50000	Clear	Clear	Clear	Clear	Clear

Table 25. Compatibility test in 10000 ppm of Ca^{2+} and 30000 ppm (3.0 wt.%) NaCl for P.XTJ-568.

SI	Dose (ppm)	Appearance				
		At Mixing	30 mins	1 hour	4 hours	24 hours
SI-1	100	Clear	Clear	Clear	Clear	Clear
SI-1	1000	Clear	Clear	Clear	Clear	Clear
SI-1	10000	Clear	Clear	Clear	Clear	Clear
SI-1	50000	Clear	Clear	Clear	Clear	Clear

APPENDIX E- Composition of nutritional solutions

Solution A (pH = 8,2)

16,2g K_2HPO_4

0,8g KH_2PO_4

Solution B

25g $NaNO_3$

0,6g NH_4Cl

0,05g $FeCl_2$

Legg til 0,2g/l EDTA

Solution C

2,5g $CaCl_2$

1,5g $MgSO_4$

Solution D

0,5g EDTA

0,5g $MnSO_4 \cdot 2H_2O$

3g $MgSO_4 \cdot 7H_2O$

1g NaCl

0,1g $FeSO_4 \cdot 7H_2O$

0,1g $CoCl_2 \cdot 6H_2O$

0,1g $CaCl_2 \cdot 2H_2O$

0,1g $ZnCl_2$

0,01g $CuSO_4 \cdot 5H_2O$

0,02g NiCl2 · 6H2O

0,001g Na2SeO3

0,01g AlK(SO4)2

0,01g H3BO3

0,01g Na2MoO4

0,01g Na2WO4 · 2H2O

APPENDIX F - Vitamins and amino acids

Vitamins are supplied from a premixed stock solution containing 20 mg L-1 myoinositol, 0.1 mg L-1 thiamine hydrochloride, 0.1 mg L-1 pyridoxine hydrochloride, 0.1 mg L-1 nicotinic acid, 0.5 mg L-1 glycine, 0.01 mg L-1 biotin and 0.1 mg L-1 folic acid (Balch et al., 1979).

Amino acids are added from a commercially available solution called RPMI 1640 amino acid solutions (50x) ("RPMI 1640 Amino Acids Solution (50 ×) R7131," n.d.).