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-1) Synthesis and Characterization of Modified Biodegradable Polyaspartate with Phosphonate and Sulphonate groups as Environmentally Friendly Oilfield Scale Inhibitors.

-2) Design and Synthesis of a Novel Series of Hydroxy Bisphosphonate as Environmentally Friendly Oilfield Scale Inhibitors.

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Abstract

Scale formation is one of the major problems faced during production in the oil industry. A common method to control scale is the utilization of chemicals known as scale inhibitors (SIs). Several SIs are available commercially but with one or more disadvantages. Poor biodegradation of PVS, ATMP and DTPMP limited their use in environmental restricted regions. Polyaspartate (PASP) is an eco-friendly SI but is not stable thermally. Moreover, SIs containing a greater number of phosphonate groups has less calcium tolerance. None of them is good enough to overcome inhibition efficiency, thermal stability, calcium compatibility and biodegradability issues altogether. So, in this study, we focused on the synthesis of green and thermally stable SIs to increase squeeze lifetime and their versatility.

In project 1 poly aspartate was modified with phosphonate and sulphonate functional groups due to known biodegradability of PASP and good thermal stability of phosphonate and sulphonate groups. Inhibition performance of the final products was evaluated against carbonate and sulfate scales using a high-pressure dynamic tube blocking rig at 80 bar and 100oC. The calcium compatibility and thermal stability of synthesized SIs were also examined in this study. Results indicate that the performance of all modified scale inhibitors was improved after modification for both carbonate and sulphate scales. Phosphonated-PASP SIs showed good thermal stability against carbonates and sulphates while other was not thermally stable against both carbonate and sulphate scales. Moreover, phosphonated inhibitors showed limited calcium compatibility after modification than others.

In project 2 a novel series of hydroxy bisphosphonate SIs was synthesized by the substitution of carboxylic acid using different amino and dicarboxylic acids. The inhibition performance, thermal stability and calcium compatibility of final products were tested the same as above. The results exhibited that the products containing one hydroxy bisphosphonate functional group showed excellent inhibition efficiency against carbonate than sulphate scales before and after thermal ageing. Products that contain two hydroxy bisphosphonate functional groups exhibit a reasonable performance against both carbonate and sulphate scale before and after thermal ageing. The results represent that the compatibility of all inhibitors with calcium was limited except SI-10 that was compatible in all given concentrations of calcium ions.

1 Introduction

Scale formation is a deposition and growth of least soluble inorganic salts from aqueous solutions. Scales occur in the reservoirs that produce water during production. They cause resistance in material-flow by reducing the rock porosity of reservoir and by blocking the tubing and valves of a wellbore, leads to the production loss and sometimes cause complete closure of operations. Like corrosion and gas hydrates, scale deposition is also a most challenging problem occurred during oil extraction and must be predicted in advance to avoid any severe loss.

Calcium carbonate, calcium sulfate, strontium sulfate and barium sulfate are the scales that are commonly faced in the oil industry. Carbonate scale formation depends on the equilibrium between bicarbonate, carbonate, and carbon dioxide relative to the change in temperature and pressure. Sulfate scale formed when the metal ions from group II, that are mostly present in formation water react with sulfate ions from injected seawater. In sulfates $BaSO_4$ are the hardest scale to control [1]. Several commercially available SIs for carbonate and sulfate scales are generally polymers, such as, polysulfonates etc. [2].

SIs having phosphonate functional groups are more efficient and applied especially for squeeze treatment to give long squeeze lifetimes as they have strong adsorptive properties with the formation rock. However, commercial phosphonic acid SIs, for example diethylenetriaminepentakis (methylenephosphonic acid) (DTPMP), and aminotris (methylenephosphonic acid) (ATMP) are not eco-friendly due to poor biodegradations. So, this type of SIs are not allowed anymore in the regions with strict environmental regulations such North Sea [3].

Since the year 2000, many environmentally friendly chemicals have been synthesized but normally with more or fewer disadvantages such as PASP [2] PASP is very efficient for both calcium carbonate and barium sulfate at a lower temperature its bad performance at higher temperature limited its application range. Currently, PASP showed better performance at even high temperature when it was modified with various functional groups [4].

1-Hydroxyethylidene diphosphonic acid (HEDP) and its tetrasodium or potassium salts are well-known SIs and corrosion inhibitors. The binding affinities of SIs with group II scales can be increased by the introduction of the hydroxy group because crystal growth stopped due to simultaneous coordination of the cations and hydrogen bonding of the anions at the active growth spots on the crystal surface [1].

In this study two projects were accomplished, in project-1 we introduced specified phosphonate and sulphonate functional groups in polyaspartate side chain via amino group to improve thermal stabilities and squeeze lifetime of polyaspartate for squeeze treatment. In project-2 a novel series of scale inhibitors having hydroxy bisphosphonate as main functional group was synthesized from different amino, mono, and dicarboxylic acids and scale inhibition performance, thermal stabilities, calcium compatibilities and biodegradations were tested for both projects.

2 Background and State of the Art

2.1 Scale

2.1.1 What is Scale

Scales are termed as the crystalline solids (salts) comes from the precipitation of mineral or inorganic mixes present in water [5]. From various aspects, oil and gas operations rely on water greatly. During hydrocarbon's production water is always produced. It helps hydrocarbon to move through many different paths. To sustain pressure and enhance oil recovery water is also pumped into the reservoirs. Some severe issues, for instance, scaling can arise in the presence of water [6]. A thick scale lining is shown in figure 01.

Figure 01. Thick lining of scales in production tubing [7].

In addition to gas hydrate and corrosion, the scale is considered among the three biggest water-related production issue. The mixing of incompatible waters is the most crucial factor of oil field scale formation. If two waters start to interact chemically and cause mineral precipitation on mixing are referred to be incompatible to each other. Seawater with a high-level of SO_4^{-2} and low-level of Ca^{+2}, Ba^{+2}/Sr^{+2} and formation water with a very low-level of SO_4^{-2} and high level of Ca^{+2}, Ba^{+2}/Sr^{+2} are the classic examples of two incompatible waters. Therefore, contacting of seawater and formation water produces precipitation of $CaSO_4$, $BaSO_4$ and/or $SrSO_4$. Moreover, when seawater is mixed with disposal water for reinjection, scale formation is possible. Scale deposition also takes place when formation water becomes supersaturated with scale forming minerals due to change in the physical environment of the reservoir [8]. It can occur in places that comparatively less reachable for example in pipelines, topside production hardware, water introduction systems, and in production and injection wells. The ultimate result of scale deposition can be the blockage of material flow in the reservoir, valve, perforations, production pipes and underground hardware. During hydrocarbon extraction, layers of scale are starting to deposit in wellbore tubing which causes resistance in the material flow in tubing and becomes thick enough to block and clog the flow of materials. The pressure in well can be dropped remarkably by scale deposition which causes decline in efficiency of the well. The production yield of a well can fall to zero in a very short time and could waste a lot of time in recovery.

Scale can also increase the chances of corrosion and block the fluid flow pathways; results can endanger the economic safety of production processes. It deposited in pores of formation and injection wells and decrease injectivity, permeability and porosity over time. Temperature and rate of injection affect the change in rock`s porousness. The ionic chemistry of injected water has a significant role in raising the concentration of salt-forming ions. Reduction in heat transmission properties is another negative effect of scales [9-11].

Most common examples of inorganic scales include anhydrite ($CaCO_3$), gypsum ($CaSO_4.H_2O$), hemihydrates ($CaSO_4.1/2H_2O$), barite ($BaSO_4$), celestite ($SrSO_4$), magnesium sulphate ($MgSO_4$), formed by the reaction of seawater, brines, and formations. Another example of scales is iron scale like iron hydroxide gel ($Fe(OH)_3$) arise from the acid dissolution and other iron minerals such as pyrrhotite (FeS), pyrite (FeS_2), hematite (Fe_2O_3), magnetite (Fe_3O_4) and siderite ($FeCO_3$) [5]. Different kinds of scales can be seen in figure 02.

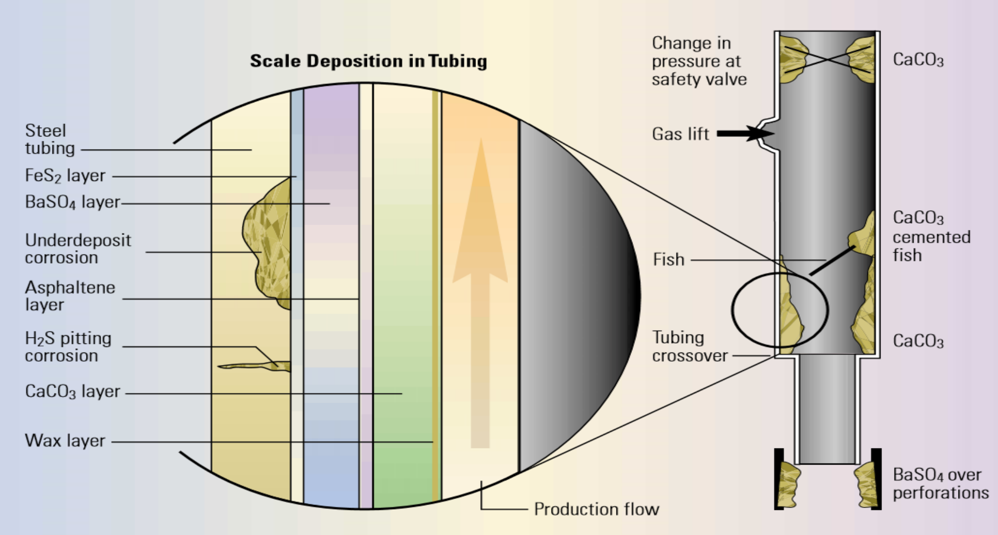


Figure 02. Scale deposition in a tubing [7].

To maintain pressure by injecting water in the wells is a cheaper way for hydrocarbon recovery. Scale formation classified into seven group formation damage mechanism that includes (i) fluid-fluid interaction (ii) rock-fluid incompatibilities (iii) solids invasion (iv) phase trapping/blocking, (v) chemical adsorption/wettability alteration (vi) fines migration, and (vii) biological activity.

The cost of scale associated issues around the world is being projected to be more than billions. The unproductive assumed costs with scale were evaluated at 0.8 billion, 3 billion and 9 billion US dollars in Great Britain, Japan, and USA, respectively. For that reason, it is very important to stop scale formation during production. Therefore, steps should be taken to anticipate the scales forming mechanisms and relevant treatments, for example, chemical scale inhibitors should be investigated to minimize scale formation [12,13].

2.1.2 Scale Formation Mechanism

The anticipation of scale is the primary step to inhibit scale formation [14]. Thermodynamically, precipitation or crystallization occurs when the activity of ions in a brine reaches above its saturation limit and the brine becomes supersaturated. Furthermore, kinetics of precipitation plays a key role in the extremity of scaling. When brines cross the critical value, crystal growth is induced by nucleation of scales on particles and nucleation sites that have low concentration decrease the crystallization kinetics [15]. High energy surface has higher nucleation rate than that on low energy surface [16]. Energetically homogeneous nucleation on surfaces is less welcoming compared to heterogeneous nucleation [17].

Scale deposition can occur by two crystallization routes possibly i.e. bulk crystallization and surface crystallization. Other physical conditions such as pressure, pH, flow velocity, temperature, permeation rate and co-existence of other ionizable particles also affect scale formation during operations. One main source of scaling is the incompatibility among the anions and cations in water. That is why adjusting the salinity of injection water before injection has a significant role in the prevention of scale formation in production operations [15].

Scaling in pipelines is the combinations of complicated processes comprising both transport mechanism and crystallization. The process conditions in the pipe systems highly influence these two severe mechanisms. Surface crystallization takes place because of heterogeneous crystallization of scale deposit on the pipe surfaces causing blockage of pipes. Bulk crystallization occurs when crystal seeds appear in bulk phase due to homogenous crystallization that forms a cake layer on the pipe surfaces by depositing on it as sediments [18]. An illustration of scale formation mechanism is shown in figure 03.

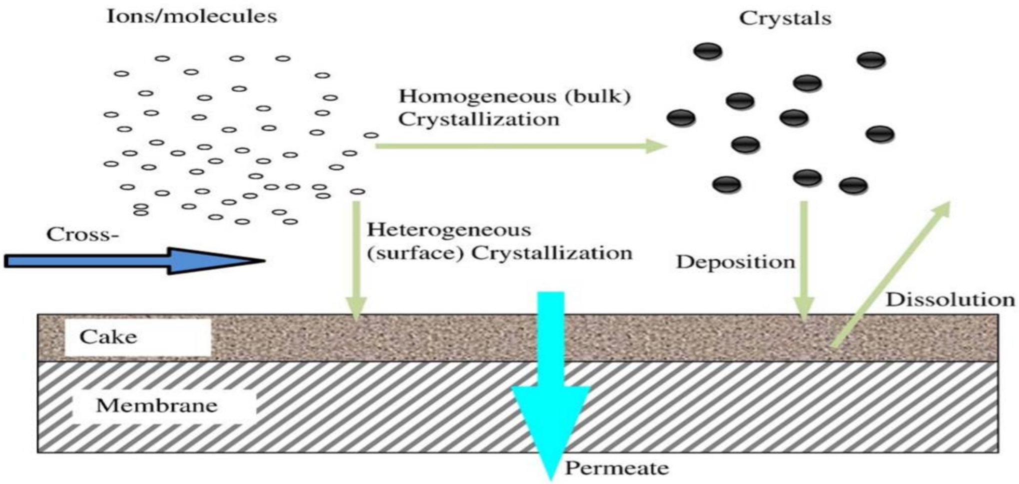


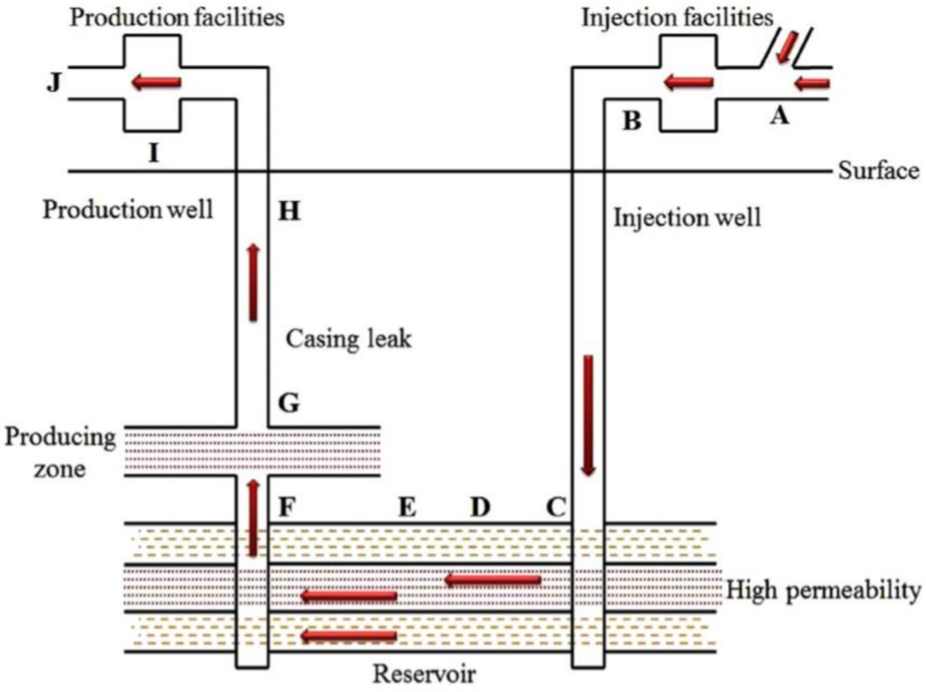
Figure 03. Schematic representation of inorganic scaling mechanism [18].

Surface crystallization and bulk crystallization are interconnected processes, but both have different kinetics. In petroleum operations, the composition of deposited scales would be different from one place to another i.e. the process of scale formation on the underground surface would not be similar to the components on the ground due to:

(A) the difference of saturation rate and water chemistry between two regions and

(B) the appearance and aggregation of particles and crystals in solution during the transportation to the ground level components [19]

The carbonate scale disposition depends on the partial pressure of carbon dioxide gas in contact with the solution [20] and sulphate scale formed principally due to mixing of two incompatible water brines where brine that has high concentration of sulphate ions mix with brine having high concentration of calcium or barium ions [21]. Figure-04 shows the different condition under which scales are formed.



Location	**Changes which could produce scale formation**
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 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 04. Conditions responsible for scale formation at different locations during water flooding [22].

Due to huge difference in pressure and temperature carbonate scale formed dominantly at the initial phase of hydrocarbon extraction while in the later phases of extraction sulphate scale formed dominantly. The factor behind sulphate scale formation is that seawater, which is economical and easily available, is injected in the reservoirs to enhance oil recovery during oil production operations. However, sometimes to minimize sulphate scale complexities de-sulphated seawater is also pumped in the reservoirs but this method is not productive economically [23]. The process of formation and progression of scales can be recapitulated in the following steps.

Aggregation

When the environment of a reservoir gets supersaturated, oppositely charged ions Ca^{+2}, Ba^{+2}, Sr^{+2} and CO_3^{-2}/SO_4^{-2} collide among each other and formed pairs in solution. Then these paired up particles assembled into micro aggregates which are tiny centres of embryos, micro-nuclei, and crystal.

Nucleation

A few of these micro aggregates act as nucleation sites for crystallization which prompt the formation of micro crystals. In the fluid bulk, nucleation arises at higher supersaturation ratio comparatively to the substrate.

Crystal growth

Adsorption of previously formed microcrystals takes place to the surfaces of each other by which growth of comparatively bigger microcrystals occurs. Then these bigger microcrystals fuse and made macro crystals.

Agglomeration

The growth of macro crystals continued by adsorption of further scaling ions from the brines. In this way, formation of scale layer/film on the surface is started. Finally, this scale film develops into scale deposition [24].

2.2 Types of Scales

From heavier like uranium to lighter like hydrogen, seawater is composed of approximately all elements and has 96.7 percent of water and 3.3 percent of dissolved salts in it. From this 3.3 percent, seven elements i.e. Na, Mg, K, Ca, Cl, S and Br made 93.5 percent of total dissolved salts and these alkaline earth metals are the main constituents of the scales [25]. Most abundant scales are $CaCO_3$, $BaSO_4$, $SrSO_4$, $CaSO_4$, CaC_2O_4, $Mg(OH)_2$ and can be categorized into two main groups according to their pH behaviour as “pH independent” and “pH sensitive” scales.

2.2.1 pH Independent Scales

Sulphate ions (SO_4^{-2}) usually present in seawater reacts simply with Ba^{+2}, Sr^{+2}, and or Ca^{+2} ions which already exists in formation water according to the geographical record of reservoirs. Therefore, the formation of sulphate scales like $BaSO_4$, $SrSO_4$ and $CaSO_4$ and NaCl (non-sulphate) is not strongly influenced by the pH of brine.

$$Ba^{+2}\ (Sr^{+2} or\ Ca^{+2}) + SO_4^{-2} \rightarrow BaSO_4 \downarrow (SrSO_4\ or\ CaSO_4)$$

Sulphate scales are less soluble in water and they are precipitated out and made suspension in solution which ultimately leads to permanent scale formation.

2.2.2 pH Dependent Scales

The carbonates ($CaCO_3$, $CaMg(CO_3)_2$, $FeCO_3$) and sulphide (FeS, PbS, ZnS) scales are categorized as acid-soluble scales therefore their scaling behavior is greatly affected by the pH of brine. The anticipation of scales for pH-sensitive scales is more difficult because other factors that control the pH of brine also influence their scaling behavior.

Their scale formation equations are shown below:

$$Ca^{+2}\ (Fe^{+2}) + CO_3^{-2} \rightarrow CaCO_3 \downarrow (FeCO_3)$$

$$Fe^{+2}\ (Zn^{+2} or\ Pb^{+2}) + S^{-2} \rightarrow FeS \downarrow (ZnS\ or\ PbS)$$

The deposition of ZnS and PbS scales become more considerable in several North Sea fields as higher concentration of both produce H_2S gas and forms metal ions. Other rare scales such as calcium naphthenate and iron oxides are also recorded from acidic crudes [26,27]. Table 01 shows some factors that directly influence to common scales.

Table 01. pH and other factors affecting some common oil field scales [28].

Name of scale	Chemical formulae	Primary factors affecting deposition
Calcium carbonate	$CaCO_3$	partial pressure of CO_2, temperature, total dissolved salts, pH
Calcium Sulfate:		temperature, total dissolved salts, pressure
a) Gypsum	$CaSO_4{\cdot}2H_2O$	
b) Hemihydrate	$CaSO_4{\cdot}\frac{1}{2}\ H_2O$	
c) Anhydrite	$CaSO_4$	
Barium Sulfate	$BaSO_4$	temperature, pressure
Strontium Sulfate	$SrSO_4$	temperature, pressure, total dissolved salts

$SrSO_4$ scales usually appeared along $BaSO_4$ so the concern in oilfield operations regarding $SrSO_4$ scales formation is growing nowadays as well. Silica and silicates scales also have been experienced in some oil field operations. Deposition of silicate scales in the presence of highly alkaline solutions has become more prominent. Lithium scales are also observed in many fields and their concentration in produced waters is different from a reservoir to another reservoir [29-32].

2.2.3 Calcium Carbonate Scales

Calcite or calcium carbonate scales are experienced largely in oil production wells. Calcite is the most stable form of calcium salts present in reservoirs; therefore, it is found frequently in oilfields. In general calcium carbonate crystals have large size but form very uniform scales when they co-found with impurities as finely divided crystals. Calcite scales are formed due to calcium carbonates precipitates according to the following equation:

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

$CaCO_3$ scales can also be formed by the dissociation of $Ca^{+2}(HCO_3^{-2})$ giving CO_2 gas and H_2O as by-products shown in equation below and this dissociation is the main factor of $CaCO_3$ scale formation in oilfield operations. Formation water having dissolved scale-forming active sites in it that becomes supersaturated with $CaCO_3$ precipitates due to pressure drop during hydrocarbon extraction. A thick layer of $CaCO_3$ scales is formed and later start to grow on production systems due to the constant flow of supersaturated solutions through it. Calcium carbonate scales usually formed in the wellbore region chiefly near the wellhead where dissolved CO_2 evolved from produced water due to drop in pressure and become the reason of pH increase in produced water and enhance the saturation index of carbonate scales.Carbonate scales formed, when formation water crosses the bubble point and CO_2 gas is escaped. As CO_2 gas is released solubility of carbonates in solution decreases quickly and cause precipitation, reacting with available divalent cations such as Fe^{+2} and Ca^{+2}.

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

Various mechanisms are involved in the formation of calcium carbonate scales. Because many waters do not have carbonate anions, the scaling rate is increased by the dissociation of calcium bicarbonates. This dissociation occurs due to the escape of CO_2 gas as pressure drops at separators or chokes and causes shifting of equilibrium by increasing pH of above reaction to the right by forming calcium carbonates. The precipitation takes places when the amount of produced $CaCO_3$ crosses its solubility limit in water [33].

$CaCO_3$ is a polymorphic mineral which is precipitated out from supersaturated solution in various forms for instance calcite, aragonite and vaterite are precipitated out in rhombohedral, orthorhombic, and hexagonal crystal systems, respectively. Thermodynamically every polymorph of $CaCO_3$ has its distinctive reactivity and stability and can be dissolved or converted or both as the composition of solution reaches the equilibrium with thermodynamically stable phase. Thermodynamically calcite is the most stable and vaterite is the least stable form of calcium carbonate at room temperature and pressure. It is almost 100 times more soluble in amorphous form compare to crystalline aragonite and calcite that is why crystals forms are easy to identify. As mentioned, early calcite is formed as a result of the transitory formation of more soluble forms of calcium carbonate. It is observed aragonite is the primary form that precipitated out from solution especially at high temperature. Calcite is the least and vaterite is the most soluble in water from 0 to $90^{O}C$ temperature. In some cases, aragonite is recrystallized to calcite with time. It is noticed vaterite is the very first solid phase that causes the formation of $CaCO_3$ scales. Chemical composition of water plays a key role in the determination of $CaCO_3$ precipitation phase [34].

The reservoir with a high concentration of scale-forming ions is crucial for precipitation. Various factors affect the scaling of $CaCO_3$ during production. The precipitation of $CaCO_3$ can be analyzed by the change in equilibrium between CO_2 gas and ions in the water. When the pressure goes down to the saturation pressure, CO_2 gas is evolved from brine in the reservoir [35]. The newly formed crystals grow at a high rate initially but after reaching an asymptotic value growth rate decreased exponentially as crystals become large. Thus, priorly formed crystals slow down the growth of the latterly formed crystals [36].

2.2.4 Barium Sulphate Scales

When injected water and formation water mixed in the reservoir during secondary oil recovery, a very hard scale of $BaSO_4$ occurred in offshore hydrocarbon extraction systems. Formation of $BaSO_4$ takes places frequently and known as the most unwelcome scales in oilfield operations.

$$Ba^{+2}\ SO_4^{-2} \xrightarrow{\qquad} BaSO_4$$

To maintain pressure in the reservoirs, seawater is being used for many years. Barite scale deposition is associated with the excessive use of seawater having high concentration sulphate ions during injection operation in the reservoirs having a high concentration of barium ions. $BaSO_4$ scales formed as a result of incompatibilities between injected seawater containing a high amount of sulphate ions and formation water containing a high amount of barium ions [37-42].

Due to very low aqueous solubility (about $2mgL^{-1}$) removal of $BaSO_4$ scale is extremely tough. Solubility is the minimum amount of solute that can be dissolved in a solvent under some specified physical conditions. Solutes are present in solutions as ions and some characteristics of these ions makes compounds less soluble. When solubility limit gets over dissolved substance precipitated out from the solution. That is why precipitated materials may cause scaling if:

(i) The water has ions that make the compounds less soluble.

(ii) Some variations in physical conditions that decrease the solubility.

With the increase of solvent concentration or temperature, solubility might be decreased, increased, or remained constant according to the nature of the system. For instance, solubility decreased with increase in temperature if the dissolution reaction is exothermic and for the endothermic reaction solubility increased with temperature. Barites are non-acid soluble scales and are resistant to traditional mechanical and chemical scale removal methods [43,37,44].

Therefore, the periodic change of wellbore tubes and mechanical descaling treatments of $BaSO_4$ scales increase average operational production cost. $BaSO_4$ is the prominent scale in North Sea offshore oil wells as well. Barite scale deposition cause surface facilities and downhole pipes blockage. It is one of the main financial loads on Petro industry that slowdown and sometimes cut-off total production and needs very expensive scale removal exercises [41,45,39]. Figure 05 shows the $CaCO_3$ and $BaSO_4$ scaling in the reservoir.

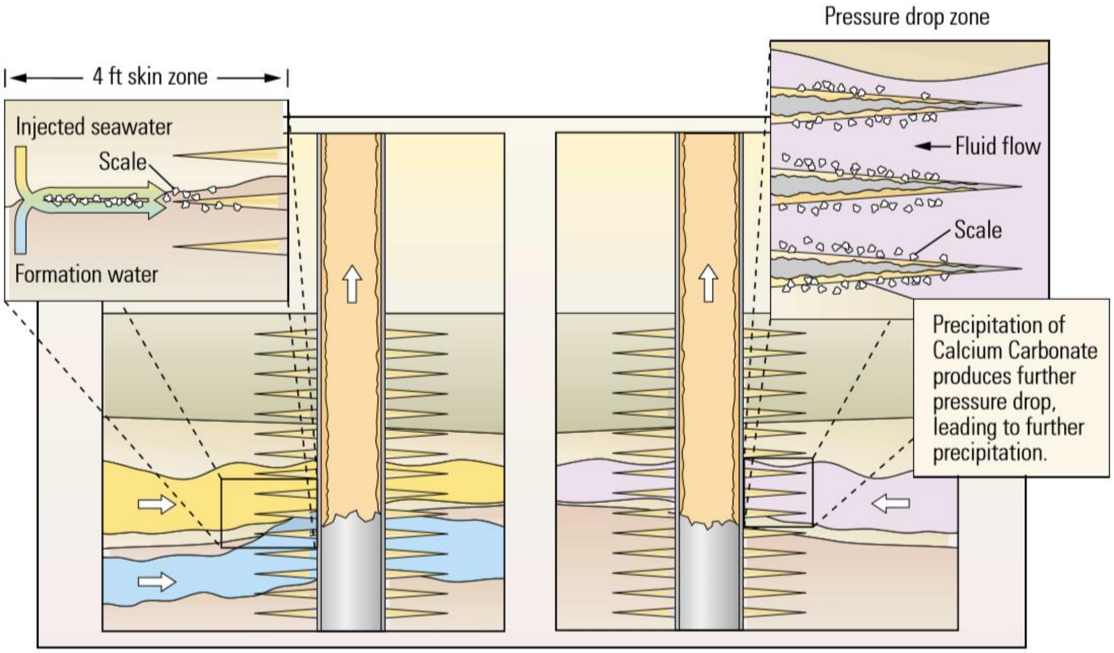


Figure-05. $CaCO_3$ scaling near the perforation throat by pressure drop (right) and $BaSO_4$ scaling near perforation throat by incompatible waters (left) [7].

2.3 Scale Inhibitors

Once scales are formed it is very difficult to handle them, so their prevention is the best available option [28]. The advance horizontal production well technologies to enhance the marginal oilfields productions has been applied to monitor the scaling both downhole and in flowlines [46]. The most familiar, efficient, and very economical method to control the scale is the practice of chemicals known as scale inhibitors. These inhibitors can either lessen or inhibit scale deposition by changing the nature of crystals in a way that they cannot adsorb or grow on the surfaces [47,48]. Scale inhibitors can either act as dispersing agent or stabilizing agents. Dispersing chemicals prevent small seed crystals of scales from adhering to tubing walls and other crystal particles and stabilizing chemicals modify the deposited crystal structures preventing additional crystal attachment [7]. Figure 06 shows the dispersion and stabilization of scale crystals by inhibitors.

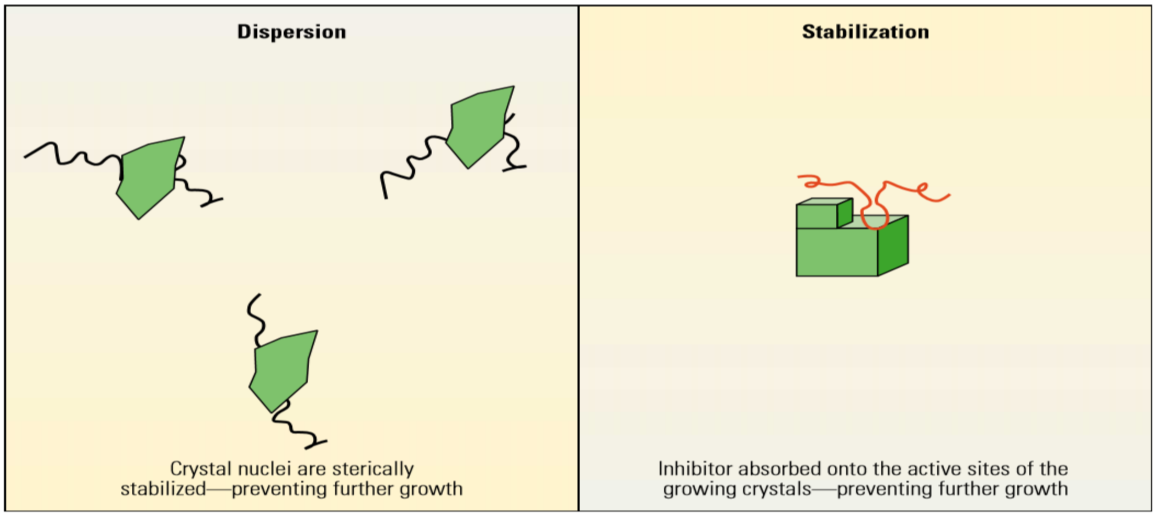


Figure 06**.** Dispersion and stabilization of crystals by scale inhibitors.

There are several factors such as type of scale, type of inhibitor, the chemical composition of brine and physical conditions of the reservoir that affects the efficiency of the inhibitors [49].

The ideal inhibitors could be applied in both, topside and squeeze treatments and should be:

- efficient at minimum inhibitor concentration
- compatible with formation and seawater
- balanced absorption and desorption properties
- thermally stable
- highly biodegradable and least toxic
- cheap [50]

Numerous scale inhibitors available commercially that have anionic groups linked to the organic backbone and have good interactions with group II metals. The most common are following:

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

The molecules have two or more, or a mix of these ions in their structures have been proved as efficient scale inhibitors for several oilfields. The inhibitors with these functional groups can be synthesized in acid form but they are more active in their anionic dissociated form normally as sodium, potassium, or ammonium salts. Besides polyphosphates, all other anionic groups are connected to the backbone of the molecule through carbon atoms. Most common classes of scale inhibitors having these ions or acids are given below:

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

Numerous copolymers and terpolymers having phosphonic, carboxylic and/or sulphonic acid groups are considered as good scale inhibitors as well. Due to the resemblance of functional groups, a variety of scale inhibitors can obstruct multiple scales. Few phosphonate scale inhibitors are available in the market as potassium salt, assuming better performance of this cation over others. Polyaminocarboxylate which is a scale dissolver also gives better results as a potassium salt. Tannic acid has been assessed for squeeze treatments and results showed it improves the core permeation marginally. Gambier extracts also shown good performance against carbonate scales [51].

Due to high instability, inorganic phosphates go through self-hydrolysis in water solutions and lose their scaling performance. The hydrolysis of organic phosphorus scales can also occur. Because of less thermal stabilities and less biological resistance polyphosphates are being replaced by other polymers such as polymaleic and polyacrylic acids [52].

The minimum amount of scale inhibitor that is required to inhibit the scale formation at a certain level is known as minimum inhibitor concentration (MIC). Any good scale inhibitor must have the capability of inhibition or prevention of crystal growth at threshold (sub-stoichiometric) level.

When scale inhibitors are applied properly, they can prevent scale deposition with concentration below than 10mgL^{-1} [28]. The especial mechanism behind threshold action is not completely known but commonly it is considered that threshold chemicals make stable complexes by reacting with multivalent cations. Scale inhibiting agents adsorb at active growth site of crystal which prevents the crystals to grow further. Threshold agents inhibit or retard the scale growth by altering the structure of the crystals and make them stable at nucleation time. The ultimate objective of scale inhibitor is to minimize scale formation at any level [53,54].

Instead of traditional chemical reactions, some complicated physical mechanisms such as adsorption, nucleation and crystal growth are involved in scale deposition. Due to their high chelating attractions with metallic ions and super dispersion properties macromolecules are giving extraordinary performances for some scales and gaining more significance nowadays [55].

The application of scale inhibitor is the most appropriate method to prevent scale formation. Scale inhibitors are only useful to avoid scale formation during production operations they are unsuitable for already existed scales. However, scale inhibitors play the main role in control mechanisms, but they may not overcome all scaling problems and other kinds of chemicals called scale dissolver may be needed for some cases. In some cases, inhibitors cannot control scales alone due to the following reasons:

i. When the scaling intensity of a reservoir has not been examined properly
ii. When the introduced inhibitor is not appropriate according to heterogenic composition and physical conditions of the well
iii. When squeeze treatment is not useful and other treatments are costly
iv. When scale dissolver treatment is far cheaper compare to scale inhibitor treatment

2.3.1 Theory of Thermodynamic Scale Prediction vs. Kinetics of Surface Deposition

By the kinetics and thermodynamics of the reaction, one can explain and find the probability of scale formation. Both theories describe particular aspects of a reaction. Thermodynamics tells about the feasibility of a reaction based on Gibbs free energy (ΔG) propositions. It shows the energy transformation relationship between products and reactants. Assume that Y is a reactant and Z is a product. If the Gibbs free energy of a product Z is lower than the reactant Y during the reaction the energy will be produced, and it will be a spontaneous exothermic reaction. This reaction will be favorable as the energy of the product is lower than the reactant. In this case, the value of Gibbs free energy will be negative. On the other hand, if the energy is absorbed during reaction it will be a non-spontaneous endothermic and unfavorable reaction as the product is less stable and will require an additional energy source to continue. Thermodynamics did not provide any information about the reaction rates; it only guides about the equilibrium conditions of products and reactants. However, the kinetics explains the reaction rates i.e. how fast or slow the reaction would occur. The kinetics depend on the idea of activation energy which is assumed as the energy barrier. The reactant must have to cross this barrier to form the product. Generally, scale inhibitor works by following two mechanisms i.e. thermodynamic and kinetic inhibition.

2.3.1.2 Kinetic Inhibition

During kinetic inhibition, inhibitor adsorbed on the surface of the crystal and inhibit its further growth. It is familiar as threshold inhibition and usually preferred over thermodynamic inhibition as a very small amount kinetic inhibitor is enough to stop the crystal to grow. It is divided into two major classes further as nucleation inhibition and crystal growth inhibition.

2.3.1.2.1 Nucleation Inhibition

Inhibitors disrupt the scale crystals and then re-dissolved them during nucleation inhibition. At the time of homogeneous crystal formation, growing nucleons are influenced by this disruption thermodynamically. Normally, small polymers like polyvinyl sulphonate show this mechanism. The scale inhibition performance of this kind of compounds gets better at lower pH and temperature than the inhibitors follows the crystal growth mechanism. Phosphinopolycarboxylic acid (PPCA) is the scale inhibitor that follows the nucleation inhibition mechanism commonly. Studies about nucleation mechanism show that inhibitor modifies the crystal morphology in such a way that crystals undergo thermodynamic redissolution instead to enter the crystal growth stage. Crystals must cross the critical ratio of surface area to volume to stabilize themself in the nucleation process. Nucleation inhibitors increased the ratio of surface area to volume of proto crystals by changing their structure and create an extra energy barrier for crystals to survive and grow.

2.3.1.2.2 Crystal Growth Inhibition

Crystal growth mechanism blocks the growth of scaling forming crystals. In this mechanism inhibitor adsorbed at the active site of already formed crystal and block them to grow further.

According to this mechanism, inhibitors did not inhibit precipitation completely but delayed the precipitation and scale formation by increasing induction time. Inhibitors having small phosphonates groups like DTPMP shows this kind of mechanism normally. This type of inhibitors can be applied at different temperature and pH. But their efficiency is better at high temperature and pH. They might become less effective when applied in supersaturated brine due to the high concentration of divalent cation.

2.3.1.3 Thermodynamic Inhibition

Thermodynamic inhibition can be achieved by lowering the supersaturation of brines. This can be acquired by decreasing ionic activities of ions present in brine by reducing pH (acidizing) of solution or by the addition of cation binding chelating agents that prevent cations and anions reactions in the solution [28].

Many classes of traditional scale inhibitors, such as acrylate-based polymers or aminophosphonates, have poor biodegradability. In addition, produced water discharges containing N- or P-containing inhibitors are involved in eutrophication process as nutrients. Such antiscaling treatments may lead to the massive development of biological species and to the death of aquatic organisms, due to deoxygenation of water. Nowadays, discharges of chemicals which modify biological cycles are strictly controlled by legislation. It is therefore of prime importance for industry to find alternative solutions, i.e. green inhibitors against scale formation. A chemical is defined as being “green” according to three criteria: nontoxicity, non-bioaccumulation, and biodegradation [51,56].

Several of these are now commercially available. d-Gluconamides have been proposed as green BaSO4 scale inhibitors; however, they only showed mediocre performance Ascorbic acid has been investigated as a green scale inhibitor. A laboratory study on pteroyl-l-glutamic acid as a green calcium carbonate scale inhibitor has been published [51].

2.4 Scale Inhibitor Treatments

The reservoirs are modified gradually to get the maximum commercial benefit therefore all available treatments are used to accelerate hydrocarbon extraction. The application of the most relevant method to control the scales is very important [57]. The aqueous solution of scale inhibitor is introduced in the reservoir during water flooding to control scale formation. Adsorption and desorption properties of inhibitors play a primary role in the success of scale treatment [58]. Following three methods are commonly used to control scale formation:

2.4.1 Batch Treatment

In batch treatment, a large amount of inhibitor is injected periodically and used for longer periods. Inhibitors are introduced in the reservoir from the top of the tubing. During this treatment, the operation is stopped temporarily. This method is not that much common and usually used under some specific circumstances.

2.4.2 Continuous Injection

In continuous injection method, an aqueous solution of chemical inhibitor is injected in the reservoir via an injection point of the well. To prevent scaling during production, this method is being exercised for many years. To get a homogeneous mixture, the scale inhibitor is introduced at turbulence point. During the introduction, a constant amount of chemical inhibitor is pumped at a controlled rate. A defined amount of inhibitor is required to control scale formation, so the injected amount of inhibitor is monitored continuously to get optimal performance of scale inhibitor. The inhibitor will be adsorbed on the rock surface until the rock reached to its maximum absorbency. The time consumed by the rock surface to gain its adsorption limit is called its retardation time. The retardation time depends on the porosity, composition of the rock, inhibitor concentration, chemistry of brine and physical conditions of the reservoir etc.

The porosity of formation rock, strong attraction between inhibitor and rock and less concentration of inhibitor may cause an increase in retardation time. Continuous scale injection is recommended for those inhibitors which do not have good adsorption affinity with formation rock. This is an efficient method to control many types of scale but the expenses of required operational facilities limit its utilization.

2.4.3 Squeeze Treatment

The technique frequently utilized for injecting inhibitors to the scaling solution is the "squeeze treatment" which is typically the best choice for the reservoir that needed to secure the wellbore. The expression "squeeze treatment" normally used for any treatment of an unfractured well achieved by introducing an inhibitor (i.e., erosion or scale inhibitor) into the wellbore to pump the inhibitor into the reservoir. In a "squeeze treatment," the solution of a scale inhibitor having concentration somewhere in the range of 2.5% and 20% by weight is forced (henceforth the "squeeze" name) in the reservoir through the wellbore. This treatment is being applied continuously in North Sea oilfields to prevent mineral scale information [59,60]. SI squeeze treatment comprises of following five phases:

(i) a pre-flush chemical is introduced in the reservoir to replace unwanted fluids from the surface of formation rock and make it ready for scale inhibitor injection.
(ii) main scale inhibitor injection
(iii) an over flush to drive the scale inhibitor further away from the wellbore
(iv) the shutting off wellbore to let inhibitor to adsorb on the rock surface
(v) resume the well operations and observe the scale inhibitor flow back profile

The performance of scale inhibitor for squeeze treatment depends on the time scale inhibitor takes to flow back with production fluids to reach minimum inhibition concentration. The affinities between scale inhibitor and formation rock affect the adsorption time and backflow of inhibitor. Porous surface bodies adsorb more inhibitor and enhance the efficiency of scale inhibitor in squeeze treatment [61,60].

Squeezed inhibitors are supposed to be leach slowly to the rock surface. But in reality, due to bad adsorption to the rock one-third of scale inhibitor washed back quickly after a few days and one-third did not return during production as it is lost in the reservoir when forced to move away from the main well region to increase extraction rate. Figure 07 is the representation of the field scale inhibitor squeeze treatment.

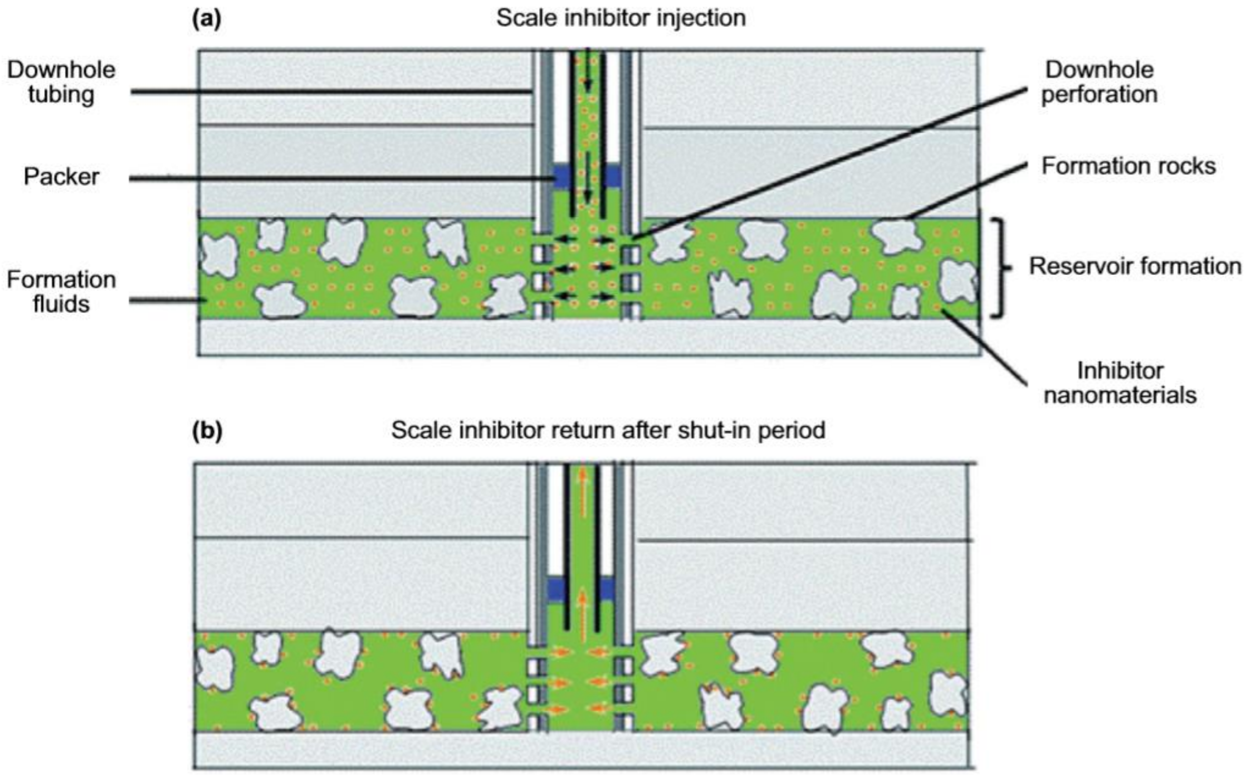


Figure 07. (a) The process of injecting chemical inhibitor into the formation. (b) The process of returning inhibitor after the shut-in period [59].

The impact of this treatment may remain from one month to around two years. Due to financial factors, long term prevention from scale formation is preferred. Adsorption squeeze treatment and precipitation squeeze treatment are the two main categories of squeeze treatments.

2.4.4 Adsorption Squeezes

In adsorption squeeze treatment scale inhibitor is expected to adsorb on the rock surface by a physicochemical mechanism. Inhibitor adsorbed on the rock by electrostatic and van der Waals forces. These interactions can be explained by adsorption isotherms, which are related to the interactions between the chemical inhibitor and formation rock materials. These isotherms describe the maintained equilibrium between the quantity of inhibitor that adsorbed on the formation rock surface and the concentration of scale inhibitor present in the solution.

The adsorption isotherms are the function of many factors, such as the pH, temperature, rock surface, chemical composition of brine, and the kind of inhibitor also. The adsorption isotherms for squeeze treatment are normally described with respect to Langmuir and Freundlich isotherms. The well is closed down for 12 to 24 hours to enhance the adsorption of scale inhibitor on the rock surface because during injection the temperature of reservoir is increased normally, that cause more adsorption of scale inhibitor on the rock [59,62]. Sandstone rocks are supposed to the best substrate to retain inhibitor longer through adsorption mechanism. This treatment can stay active from 3-6 months.

2.4.5 Precipitation (phase separation) Squeezes

In this method, the inhibitors interact and formed unsolvable salts which settle down in the rock pores. For example, scale inhibitor-containing phosphonate groups can be settled down as calcium salts. Inhibitors like phosphate esters are not reasonable as they formed dissolvable calcium salts or salt composites. A phosphonate squeezing solution having low pH is squeezed through well hole in the reservoir containing a higher concentration of calcium and carbonate ions. The squeezed acidic solution interacts with carbonate ions from reservoir and neutralized them. Then the remaining calcium cations are discharged into the brine that reacts with scale inhibitor and make unsolvable calcium salts. Phosphonated scale inhibitor precipitate as a calcium salt as follows.

$$\text{2H-(Phos.)} + CaCO_3 \xrightarrow{\qquad} \text{Ca(Phos.)} + H_2CO_3$$

(scale inhibitor) *(from rock formation)* *(insoluble inhibitor salt*)

Scale inhibitors form precipitate with multivalent ions usually with calcium cations. With the increase in pH and calcium ion concentration, scale inhibitor precipitated out inside the pores of the formation rock. Calcium salts of phosphonic acid, polymaleic acid, polyacrylic acid and copolymeric acid are also efficient scale inhibitor. The precipitation inhibitor required more amount of an inhibitor per squeeze, to increase the lifetime of treatment. Under normal conditions, the lifetime of this treatment is more than a year. So, the precipitation squeeze treatment is normally preferred compare to adsorption squeeze treatment. Figure 08 shows the adsorption and precipitation squeeze treatments.

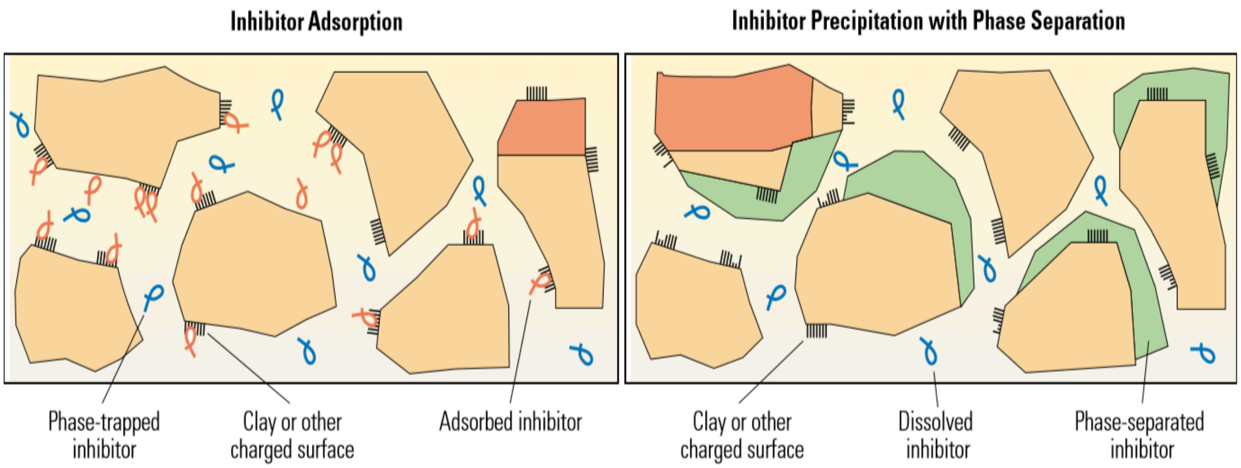


Figure 08. Scale inhibitors give the optimum lifetime when they stay on the rock surface by adsorption treatment (left) or precipitated in the rock pores by precipitation treatment (right) [7].

The main disadvantage of precipitation squeeze is that the inhibitor cannot move away from the main well region therefore only limited surface area is exposed to the scale inhibitor. hence, inhibitors have lower solubility are preferred for precipitation squeeze. The desorption property of inhibitor must be good to keep the inhibitor concentration above the minimum inhibition concentration (MIC) in produced water during production. Despite numerous uncertainties with squeeze treatments, it is among the best and efficient techniques used in various oilfield operations.

2.4.6 Squeeze Lifetimes

The efficiency of squeeze treatment is measured by squeeze lifetime, which can be defined as the total time duration by which a scale inhibitor reaches below the value of minimum inhibition concentration (MIC). The squeeze lifetime depends on many factors like adsorption and desorption abilities of rocks, over-flushed volume, inhibitor concentration etc. Rocks with high porosity hold more amount of scale inhibitor thus increase the lifetime of treatment. A huge amount of over-flush is favorable to optimize squeeze lifetime. With the utilization of more volume of over-flush, dilution of scale inhibitor occurs that allows the inhibitor to penetrate deeper and cause more retention of scale inhibitor in the rock pores.

2.4.7 Challenges for Squeeze Treatment

One main problem of squeeze treatment is the desorption of scale inhibitor. When pressure is increased downhole almost 30% of scale inhibitor is washed back because of poor retention with the rock surface. The remaining scale inhibitor that retained on the rock surface assists to inhibit scale deposition. During production, retained inhibitor also flows back slowly until further anti-scaling is needed. Another challenge that is faced in squeezing is the variation in permeability and wettability of formation rock. When an aqueous solution of chemical inhibitor is injected in a reservoir it changes the rock wettability that causes a change in rock permeability and ultimately come up water coning effect. In this effect, water starts to flow in the oil pockets. It is irreversible damage, after this a well cannot reach at its optimal production again.

One another problem of squeeze treatment is that this method is not productive in wells where formation rocks have lower fluid permeability and the wells which are horizontal or need horizontal extraction. The inhibitors that act as Newtonian fluids are not suitable for squeeze treatment as they can be deposited on nearby formation rocks and block the pores which result in the production loss. Moreover, precipitation squeezing is not that much productive for the non-carbonated reservoir as it is for carbonated reservoir because carbonated reservoirs have enough amount of calcium ions to precipitate scale inhibitor. Also, squeeze treatments do not show optimal return profile of inhibitor as at the initial stage a remarkable amount of scale inhibitor desorbed in produced water, much higher than that needed for scale prevention. Thus, the wells need to be retreated again and again which is uneconomical to get maximum production [60,59].

2.5 Environmental Regulations

The constant utilization of chemical agents is not just an economic burden but also unavoidably contaminate the oil well, environment and decrease oil production. Moreover, other traditional strategies for EOR, for example, CO_2, steam, and water injection, also have drawback of not to be eco-friendly [63]. Replacing the tubes contain $BaSO_4$ scale is not recommended as $BaSO_4$ contaminated tubes are considered as radioactive waste by environmental protection agencies**.** A large number of new chemicals have been synthesized and utilized every year but the complete profile about their ecological, chemical and physical properties is still not available, not even for commercial High Production Volume (HPV) chemicals [64-66].

The general concern of people over the adverse effects of resistant substances started in the 1960s. Since then remarkable advancement in science has boosted our knowledge about persistent, bio-accumulative and toxic substances and their characteristics and the mechanisms that harm our ecological system. Along with scientific development, many laws have been approved to identify and control the PBT substances around the world. The first proposal to categorize persistent toxic chemicals based on their half-lives was made in 1980 [67].

Since many years, Canada, United States and many other countries are taking actions to limit or stop the production, utilization and import of various PBTs according to Stockholm convention whose goal is to lessen and/or prohibit the use and discharge of persistent organic pollutants. European Union has REACH (registration, evaluation, authorization, and restriction of chemicals) regulation which needs evaluation of substances concerning to their persistence, bioaccumulation potential, and toxicity before discharge. Assessment criteria is described in Annex XIII of the REACH regulation. Also, approval will be needed for the utilization and commercialization of special classes of chemicals that have genuine negative impacts on ecological system [68,69,66].

The OSPAR (Oslo-Paris) Convention signed in Paris in 1992 is the cooperation between 15 governments and the EU for the protection of the marine environment in the North-East Atlantic [70,71]. The OSPAR Convention has some fundamental rules and regulations which are categorized into five Annexes and three accompanying appendices. The first four Annexes deal with as follows:

Annex I: land-based pollution sources
Annex II: incineration and dumping pollution
Annex III: offshore pollution sources
Annex IV: quality evaluation of the marine environment

Annex V, the Protection and Conservation of Ecosystems and Biological Diversity of the Maritime Area was practiced in 1998 along with Appendix 3 contains criteria to identify human involvement for Annex V and implemented in 2000. According to new OSPAR rules, the concentration of dispersed oil must be lower than $30 mgL^{-1}$ [72,73].

The conditions for ecotoxicological testing for all compounds utilized for offshore drilling in the North Sea are described in the OSPAR rules for the North-East Atlantic. These guidelines were executed in 2001 and required the following three tests by OSPAR:

- Acute toxicity
- Bioaccumulation
- Seawater biodegradation (persistence)

Acute toxicity is the antagonistic impact that occurred for a short period (almost for 14 days) after introduction or exposure of a small amount of toxic substance [74,75].

Bioaccumulation is the continuous accumulation of chemicals inside the body of organisms and can be associated with relative solubility of substances in lipids and water. The bioaccumulation chances of a substance can be anticipated based on relative solubility in octanol (as fatty tissue) and water. It is represented as the logarithm of octanol-water partition coefficient log P_{ow}. The chemical supposed to be a bioaccumulation risk if the coefficient is greater than or equal to 3 [66].

Biodegradation is calculated as the ratio of the amount of oxygen consumed during the degradation period to the calculated theoretical oxygen demand (ThOD). Biodegradation test is described in OECD 306 protocol and the normal lab test is usually completed after four weeks. Any harmful substance having half-life more than eight weeks in water is categorized as persistent [74,67].

Chemical additives that are under some special obligations for discharge are listed into four main classes (green, yellow, red, and black) according to their ecological effects.

1) **GREEN** Chemicals having no or very less environmental impact and can be discharged without any additional treatment.

2) **YELLOW** Chemicals that are being utilized and cannot be replaced by any other chemical. Discharge is possible without any special treatment.

3) **RED** Chemicals need to be replaced preferably but dischargeable with government permission.

4) **BLACK** The government can allow the discharging of these chemicals [76].

2.5.1 Technological Solutions

Technological advancements are very significant to meet the zero-emission goal. Technological solutions to reduce or eliminate the discharge of hazardous chemicals in produced water are:

- full or partial topside separation before downhole injection
- physicochemical blockage of water pocket near or in the reservoir
- underground or on ground separation before injecting back to the reservoir
- produced water treatment prior to discharge in the sea

2.5.2 Drilling Material Discharge Management

- reusing
- underground injection
- disposal on land

2.5.3 Zero Discharge Targets

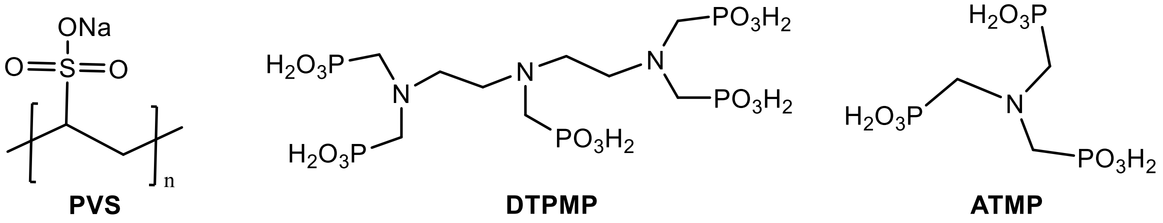
- no discharge or limited discharge of harmful chemicals in the environment listed in prohibition priority i.e. black and red.
- synthesis and commercialization of eco-friendly chemicals.
- substitution of less hazardous chemicals with more hazardous ones [77].

Increase in ecological and discharge restrictions, former traditional chemical treatments are facing many challenges. Thus, the discovery, synthesis, and commercial applications of green (eco-friendly) chemicals are getting much more attention of the researcher nowadays [78].

2.6 Earlier Studies

At present, the most common practice to control calcite and barite scales is the use of organic phosphorus scale inhibitor along with other additives to prevent bacterial fouling and corrosion. But their discharge is not allowed in eco-sensitive regions anymore. According to new environmental needs, the traditional phosphorus-containing inhibitors have been substituted with less toxic phosphorus scale inhibitors such as carboxyl hydroxyl methyl phosphonic acid, maleic and sulfonic acid homo, and copolymers. Some naturally occurring compounds such as plant polysaccharides also have been derivatized and being used for scale inhibition [79].

Phosphonation of amino acids has been carried in a study to make environmentally friendly scale inhibitors. Recently it is reported that the presence of a few sulfonate groups in the backbone of polymers resists the hydrolyzation of scale inhibitors under severe conditions in the reservoirs. Hence the efficiencies of polymers can be improved by derivatization [80-82].

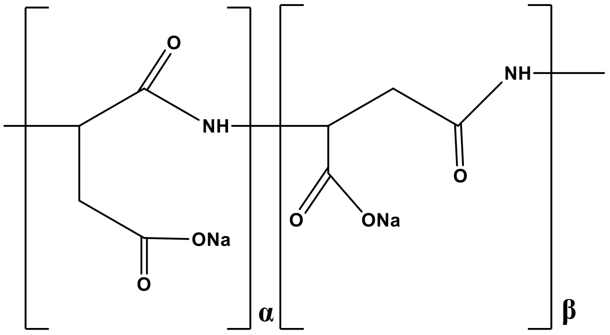


PVS **DTPMP** **ATMP**

Figure 09. Structural illustration of different commercial scale inhibitors.

However, commercial sulfonate and phosphonic acid SIs, such as polyvinyl sulfonate (PVS), diethylenetriaminepentakis (methylenephosphonicacid) (DTPMP), and aminotris (methylenephosphonic acid)(ATMP), show poor biodegradation properties and are to be phased out for offshore deployment in Norway. Polymers such polyacrylic acids are used as oilfield scale inhibitors very often but their nonbiodegradable nature limited their applications. Phosphonated amino acid inhibitors have been synthesized through Moedritzer-Irani reaction. Results have shown they have lower calcium compatibilities and are not thermally stable as well [83,84].

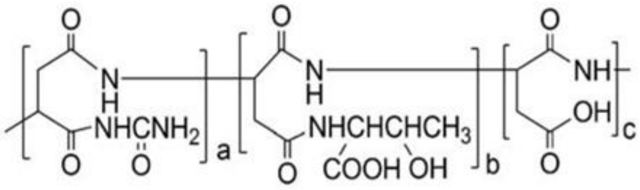
Since the last two decades, numerous environmentally friendly chemical additives have been synthesized and tested for scale inhibition but with one or more disadvantages. Polyaspartic acid (PASP) is one eco-friendly, multirole, and biodegradable polymeric scale inhibitor having good chelating and dispersing properties. The sodium salts of PASP are also easily biodegradable and fulfilled the requirements to be used in the North Sea. PASP can be synthesized by the hydrolyzation of poly succinimide (PSI). PASP is efficient at a lower temperature but its poor efficiency at the higher temperature limited its versatility [83,85,86,4].



PASP

Figure 10. Structural illustration of polyaspartate, a commercial eco-friendly scale inhibitor.

Several copolymers of imide/amide are soluble in water. These copolymers can be derivatized by nucleophilic addition of amine groups to produce sulfated, sulfonated, phosphated and phosphonated polyaspartate in water. PASP has been derivatized to PASPTU by introducing threonine and urea on its side chain. The biodegradable derivates of aspartate are the greenest scale inhibitors. Currently, PASP functionalization improved its scale inhibition performance. For instance, carboxylate and sulfonate functional groups enhance coordination and dispersion properties of a polymer accordingly [81,87,79,4].



PASPTU

Figure 11. Structural illustration of PASPTU, a modified polyaspartate scale inhibitor.

Even though many improvements have been made to increase the scale inhibition performance of PASP, problems like low biodegradation and toxicity of functionalized groups still cannot be overcome, which is contrary to the idea of green scale inhibitors [4].

2.7 New Idea for Project-1

Properties of a polymer can be improved by functionalization. Two main methods that are commonly used to functionalize the polymers are follows:

(i) the functional group is introduced to the monomer in the protected form prior to polymerization and deprotected after polymerization

(ii) functional groups are introduced to the chain of the prepared polymers

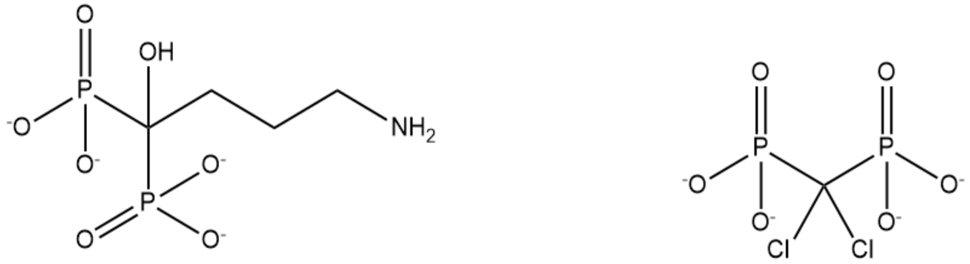
Polyaspartic acid is a biodegradable polymer which can be functionalized easily. Potassium and sodium salts of poly aspartic acid are considered to be good inhibitors for $CaCO_3$ and $BaSO_4$ scales. Polyaspartic acid can be synthesized by the hydrolyzation of Polysuccinimide. Hydrolysis or the type of reacting nucleophiles defines the properties and application Polysuccinimide [88-92].

Side chain functionalization is the most common method used to introduce scale inhibiting functional groups in the poly aspartic acid structure. In previous studies, PHMAA (poly(hydroxyethyl-co-methacryloxyethyl aspartamide) was synthesized by a sequential reaction of 2-aminoethyl methacrylate (2-AEMA) and ethanolamine with polysuccinimide. The introduction of different hydroxyl groups, sulfonic, phosphonic, carboxylic acid groups in the molecular structure of PASP also have been reported. To get a biodegradable inhibitor with remarkable properties it is important to introduce the new functional groups into the side chain of polyaspartic acid [93-95].

So, in project-1 we functionalize polyaspartate by introducing specified amino phosphonic and amino sulfonic acids as they are not reported in literature before and compared performance with commercially available polyaspartate. As polyaspartate is one of the greenest scale inhibitors but is not thermally stable so the main objective to introduce these groups was to increase the thermal stability of polyaspartate for squeeze treatment.This study would also have potential advantages in the improvement of SIs with respect to their proficiency for giving long squeeze lifetimes which save the time and money.

2.8 New Idea for Project-2

Phosphonic acid is a functional group consisting of two hydroxyl moieties, one P=O double bond and one P–C bond. This functional group is introduced in a variety of smaller and polymeric molecules to induce special characteristics such as water solubility, coordination etc. [87]. The salts of phosphonic acids (phosphonates) are being used extensively in pharmaceutical, agriculture, oilfields, and many other chemical industries [1,83]. Compounds contain bisphosphonate (BP) functional groups are considered as biologically active compounds. BPs are being used for many years in bone therapies. [96].



(4-amino-1-hydroxybutane-1,1-diyl)bis(phosphonate) (Dichloromethylene)-bis-phosphonate

(1-Hydroxyethylidene)-bis-phosphonate [1-Hydroxy-2-(1H-imidazole-1-yl)ethylidene]bis-phosphonate

Figure 12. Some well-known BP medicines available in the market.

Currently, BPs have been inspected for scale control in water boilers and to remove harmful heavy metals during wastewater treatment but have not been applied as scale growth inhibitors in oilfields.

Etidronic acid and its Na or K salts are well-recognised scales and corrosion inhibitor. The addition of the hydroxy group enhances the binding properties of the compound because crystal growth stopped due to simultaneous coordination of the cations and hydrogen bonding of the anions at the active growth spots on the crystal surface [97,1].

The low toxicity of BPs and high binding behavior of Hydroxyl group motivate us to design and synthesize a series of hydroxy bisphosphonate derivatives and test their scale inhibition performance, thermal stabilities, calcium compatibilities and biodegradations.The objective of this project was to synthesize such a kind eco-friendly scale inhibitor for oil fields that could maintain performance at high temperature and pressure and have good calcium compatibilities with very low MIC (Minimum inhibition concentration) compared to commercially available SIs.

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3 Experimental Procedure for Project-1

3.1 Chemicals

The chemicals used in this project were purchased by VWR, Sigma-Aldrich, TCI, Merck Scuchardt oHG and Nanochem solution Inc. The solvents were used without further purification.

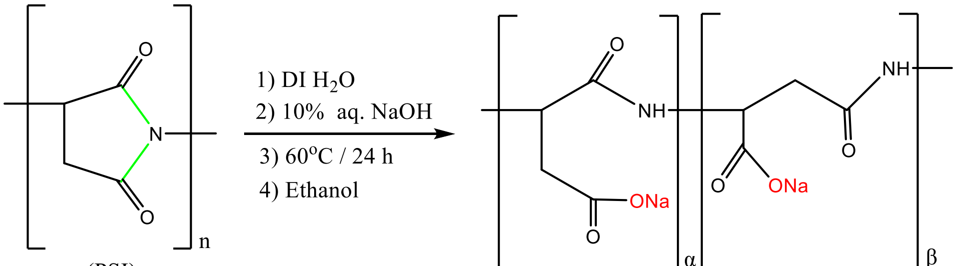
3.2 Synthesis and Characterization of Scale Inhibitors (SIs)

PASP was synthesized by the hydrolyzation of PSI according to literature [1] and functionalized by amino bisphosphonate and amino sulphonate groups. As for polymers like polyaspartate NMR analysis is quite challenging so in this project the structures of synthesized chemicals were analysed by Agilent Carry 630 FTIR-ATR. The wavenumber (cm^{-1}) values against reflectance was noted for different functional groups. FTIR spectra of all sample has been shown in appendix-A.

3.2.1 SI-1: Synthesis of PASP

Herein, 2.0g of polysuccinimide and 20mL of deionized water was mixed in a round bottom flask by magnetic stirrer. An aqueous solution of 10% NaOH was added dropwise in this suspension until it becomes a homogeneous solution by changing colour from brown to dark brown and then this material was refluxed at 80^{o}C for 1hr. The solvent was evaporated by rota vapours and brown solid of sodium polyaspartate was collected as a product and dried at 80^{o}C for 12 hrs. The product has 1.8g yield. Its synthesis route is shown in the figure 13.

FTIR-ATR: 3413cm^{-1} *N-H*, 1597cm^{-1} *C=O*, 1400cm^{-1} *-CONH*.



(PSI)

PASP

Figure 13. Synthesis route of Polyaspartate (PASP).

3.2.2 SI-2: Synthesis of Modified PASP as PASA/IBMPA

In a round bottom flask 0.473g/4.876mmole of polysuccinimide (PSI), 1.00g/4.877mmole of iminobis(methylphosphonic acid) (IBMPA) and 8mL of deionized water were mixed by magnetic stirrer at room temperature. In this suspension, 10% aqueous NaOH was added dropwise until it becomes a homogenous solution, the colour of material changed from brown to dark brown and then refluxed overnight at 60°C. The solution was transferred in a separating funnel and 50mL of ethanol was added in it. The product in the form of a brown oily layer was separated at the bottom of separating funnel that was collected and extracted completely by using 25mL of ethanol again. The collected product was dried at 80°C for 12 hrs to yield PASP/IBMPA as brown solid. The product has 2.1g yield. Its synthesis route is shown in the figure 14.

FTIR-ATR: 3300cm^{-1} *N-H*, 1588cm^{-1} *C=O*, 1403cm^{-1} *-CONH*, 1078cm^{-1} *PO_3*.

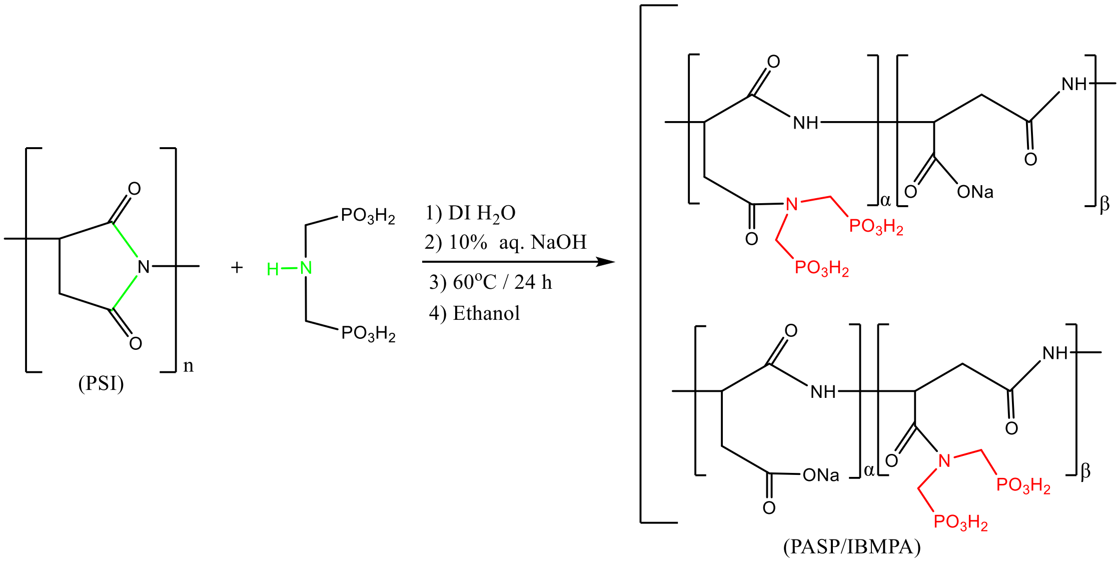


Figure 14. Synthesis route of modified PASP as PASP/IBMPA.

3.2.3 Synthesis of AEDPA

A two-neck Erlenmeyer flask fitted was charged with 10g/243.6mmole acetonitrile and 59.92g/730.7mmole of phosphorous acid under vigorous stirring at room temperature. Under the nitrogen environment, 66.9g/487.1mmol of phosphorus trichloride was added dropwise to the reaction material for 1 hr and the mixture was refluxed at 50°C overnight. Then the reaction mixture was quenched carefully with 50mL of H_2O under vigorous stirring that causes raise in temperature to 90°C and mixture was refluxed at 90°C overnight. Light yellow precipitates were formed during hydrolysis that was filtered under reduced pressure and washed with several portions of dry methanol to get 1-aminoethylidenediphosphonic acid as a product. The product was dried in an oven at 80°C for 4 hrs**.** The product has 22.8g yield. Its synthesis route is shown in figure 15.

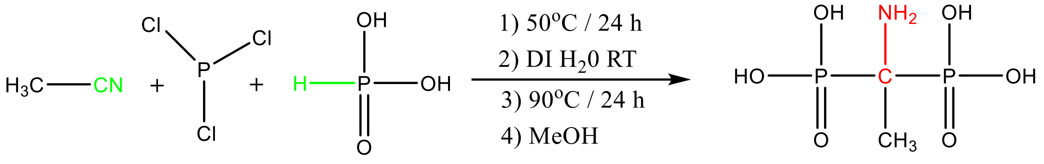


Figure 15**.** Synthesis route of AEDPA.

3.2.4 SI-3: Synthesis of Modified PASP as PASA/AEDPA

In a round bottom flask 0.473g/4.876mmole of polysuccinimide (PSI), 1.00g/4.877mmole of **1-** aminoethylidenediphosphonic acid (AEDPA) and 8mL of deionized water were mixed by magnetic stirrer at room temperature. In this suspension, 10% aqueous NaOH was added dropwise until it becomes homogenous solution, the colour of material changed from brown to dark brown and then refluxed overnight at 60°C. The solution was transferred in a separating funnel and 50mL of ethanol was added in it. The product in the form of a brown oily layer was separated at the bottom of separating funnel that was collected and extracted completely by using 25mL of ethanol again. The collected product was dried at 80°C for 12 hrs to yield PASP/AEDPA as brown solid. The product has 1.77g yield. Its synthesis route is shown in the figure 16.

FTIR-ATR: 3200cm^{-1} *N-H*, 1576cm^{-1} *C=O*, 1393cm^{-1} *-CONH*, 1055cm^{-1} *PO$_3$*.

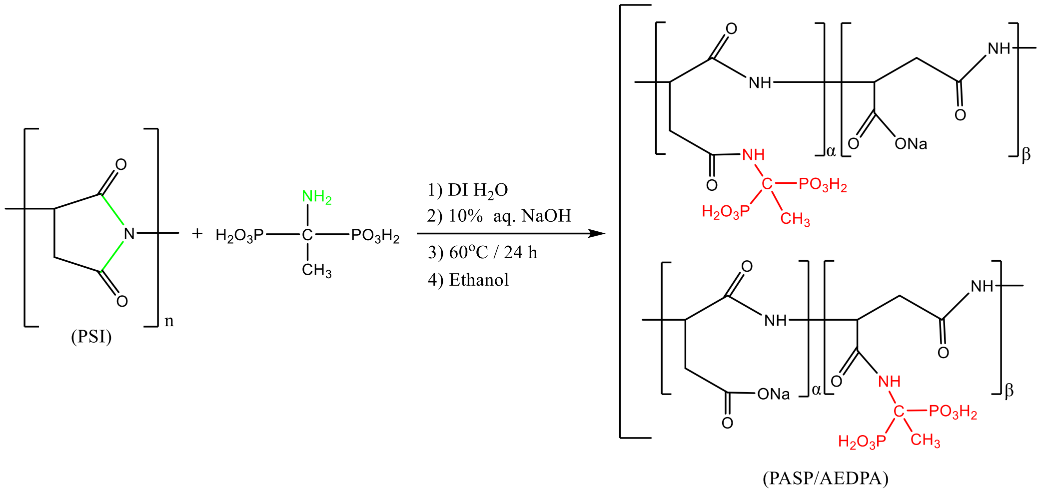


Figure 16**.** Synthesis route of modified PASP as a PASP/AEDPA.

3.2.5 SI-4: Synthesis of Modified PASP as PASA/2-AMSA

In a round bottom flask 0.775g/7.98 mmole of polysuccinimide (PSI), 1.997g/15.96 mmole of 2-aminomethanesulphonic acid (Taurine) and 8mL of deionized water were mixed by magnetic stirrer at room temperature. In this suspension, 10% aqueous NaOH was added dropwise until it becomes a homogenous solution, the colour of material changed from brown to dark brown and then refluxed overnight at 60°C. The solution was transferred in a separating funnel and 50mL of ethanol was added in it. The product in the form of a brown oily layer was separated at the bottom of separating funnel that was collected and extracted completely by using 25mL of ethanol again. The collected product was dried at 80°C for 12 hrs to yield PASP/2-AMSA as brown solid. The product has 2.69g yield. Its synthesis route is shown in the figure 17.

FTIR-ATR: 3280cm^{-1} *N-H*, 1575cm^{-1} *C=O*, 1389cm^{-1} *-CONH*, 1176cm^{-1} *SO$_3$*.

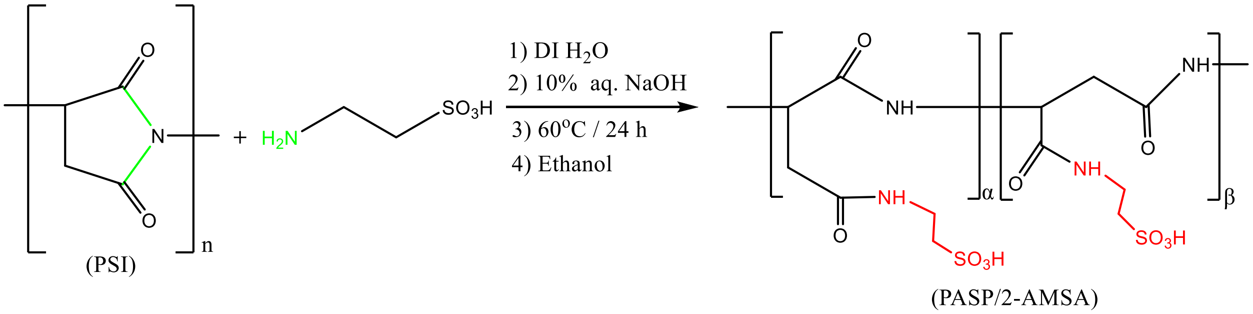


Figure 17. Synthesis route of modified PASP as a PASP/2-AMSA.

3.2.6 SI-5: Synthesis of Modified PASP as PASA/AMSA

In a round bottom flask 0.873g/9.00mmole of polysuccinimide (PSI), 2.00g/17.99mmole of aminomethanesulphonic acid (AMSA) and 8mL of deionized water were mixed by magnetic stirrer at room temperature. In this suspension, 10% aqueous NaOH was added dropwise until it becomes a homogenous solution, the colour of material changed from brown to dark brown and then refluxed overnight at 60°C. The solution was transferred in a separating funnel and 50mL of ethanol was added in it. The product in the form of a brown oily layer was separated at the bottom of separating funnel that was collected and extracted completely by using 25mL of ethanol again. The collected product was dried at 80°C for 12 hrs to yield PASP/AMSA as brown solid. The product has 2.52g yield. Its synthesis route is shown in the figure 18.

FTIR-ATR: 3300cm^{-1} *N-H*, 1588cm^{-1} *C=O* 1395cm^{-1} *-CONH*, 1172cm^{-1} *SO$_3$*.

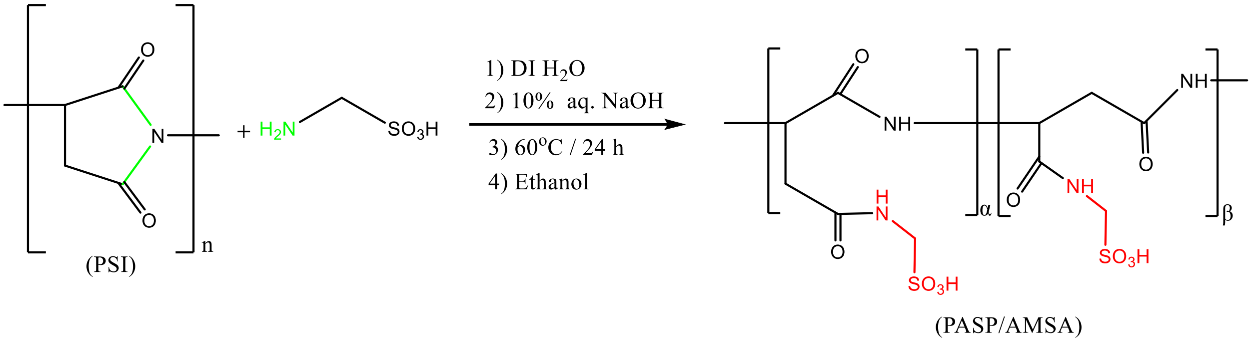


Figure 18. Synthesis route of modified PASP as a PASP/AMSA.

3.2.7 References

1. Shi, S., Wu, Y., Wang, Y., Yu, J., & Xu, Y. (2017). Synthesis and characterization of a biodegradable polyaspartic acid/2-amino-2-methyl-1-propanol graft copolymer and evaluation of its scale and corrosion inhibition performance. *RSC advances*, *7*(58), 36714-36721.

4 Experimental Procedure for Project-2

4.1 Chemicals

The chemicals used in project were purchased by VWR, Sigma-Aldrich, ACROS, Alfa Aesar, TCI and Merck Schuchardt oHG. The solvents were used without further purification.

4.2 Synthesis and Characterization of Scale Inhibitors (SIs)

The hydroxy bisphosphonates as disodium salt were synthesized by the reaction of different amino and carboxylic acids with phosphorus trichloride in methane sulfonic acid. The work-up included hydrolysis and pH adjustment followed by purification for all products [1]. The structures of synthesized chemicals were analysed by using 400MHz Bruker NMR spectrometer. The chemical shifts of samples for ^{1}H and ^{31}P NMR were recorded in Deuterium oxide (D_2O). NMR spectra of all samples have been shown in appendix-B.

4.2.1 SI-6: Synthesis of (3-amino-1-hydroxypropane-1,1-diyl)bis(phosphonic acid)

In a two-neck round bottom flask, 14.56mL / 151.51mmole of methane sulfonic acid was weighed and 3g / 33.67mmole of beta-alanine was added during stirring at room temperature. With the help of syringe 14.80g /107.76mmole of phosphorous trichloride was added dropwise in reaction material for 30 mins at room temperature. The contents of the flask were refluxed for 48 hrs. at 75^{o}C and then quenched carefully with 32.6mL of deionized H_2O at room temperature. The reaction mixture was refluxed again at 105^{o}C for 16 hrs. After this, the pH of the material was adjusted to 1.8 by adding 50% aqueous solution of NaOH, 127mL of methanol was added and stirred the material for 45 mins at room temperature. The crude product was collected by filtration and redissolved in 10mL of hot water. Again, 50mL of methanol was added in the flask and light-yellow fine precipitates appeared that was collected as a pure product and dried at 80^{o}C for 4 hrs. The product has 5.75 g yield. Its synthesis route is shown in figure 19.

^{1}H NMR (D_2O, 400 MHz) δ ppm: 2.19-2.28 (m, 2H, CH_2), 3.27-3.30 (q, 2H, CH_2).
^{31}P NMR (D_2O, 162.00 MHz) δ ppm: 17.01.

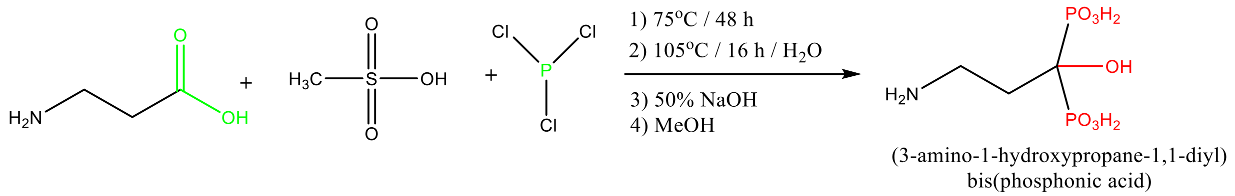


Figure 19. Synthesis route of SI-6.

4.2.2 SI-7: Synthesis of (5-amino-1-hydroxypentane-1,1-diyl)bis(phosphonic acid)

In a two-neck round bottom flask, 11.07mL / 115.23mmole of methane sulfonic acid was weighed and 3g / 25.61mmole of 5-aminovaleric acid was added during stirring at room temperature. With the help of syringe 11.25g / 81.95mmole of phosphorous trichloride was added dropwise in reaction material for 30 mins at room temperature. The contents of the flask were refluxed for 48 hrs. at 75°C and then quenched carefully with 24.82mL of deionized H_2O at room temperature. The reaction mixture was refluxed again at 105°C for 16 hrs. After this, the pH of the material was adjusted to 1.8 by adding 50% aqueous solution of NaOH, 127mL of methanol was added and stirred the material for 45 mins at room temperature. The crude product was collected by filtration and redissolved in 10mL of hot water. Again, 50mL of methanol was added in the flask and light-yellow fine precipitates appeared that was collected as a pure product and dried at 80°C for 4 hrs. The product has 7.35g yield. Its synthesis route is sown in figure 20.

^{1}H NMR (D_2O, 400 MHz) δ ppm: 1.59,1.60 (d, 4H, 2 × CH_2), 1.81-1.92 (m, 2H), 2.93,2.94 (d, 2H, CH_2).

^{31}P NMR (D_2O, 162.00 MHz) δ ppm: 18.24.

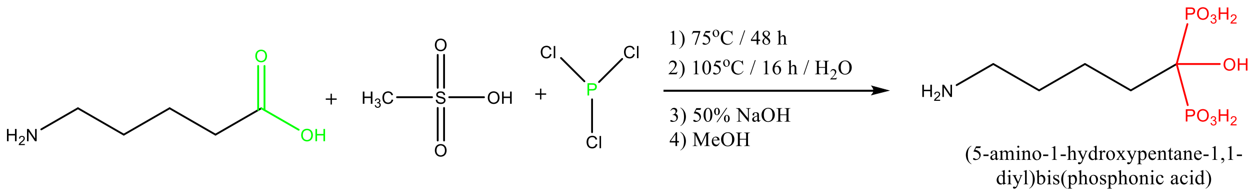


Figure 20. Synthesis route of SI-7.

4.2.3 SI-8: Synthesis of (1,4-dihydroxybutane-1,1,4,4-tetrayl)tetrakis(phosphonic acid)

In a two-neck round bottom flask, 21.97mL / 228.62mmole of methane sulfonic acid was weighed and 3g / 25.40mmole of succinic acid was added during stirring at room temperature. With the help of syringe 22.32g / 162.53mmole of phosphorous trichloride was added dropwise in reaction material for 30 mins at room temperature. The contents of the flask were refluxed for 48 hrs. at 75°C and then quenched carefully with 48.5mL of deionized H_2O at room temperature. The reaction mixture was refluxed again at 105°C for 16 hrs. After this, the pH of the material was adjusted to 1.8 by adding 50% aqueous solution of NaOH, 127mL of methanol was added and stirred the material for 45 mins at room temperature. The crude product was collected by filtration and re-dissolved in 10mL of hot water. Again, 50mL of methanol was added in the flask and light-yellow fine precipitates appeared that was collected as a pure product and dried at 80°C for 4 hrs. The product has 2.91 g yield. Its synthesis route is shown in figure 21.

^1H NMR (D_2O, 400 MHz) δ ppm: 1.65 (s, 4H, 2 × CH2).

^{31}P NMR (D_2O, 162.00 MHz) δ ppm: 17.68.

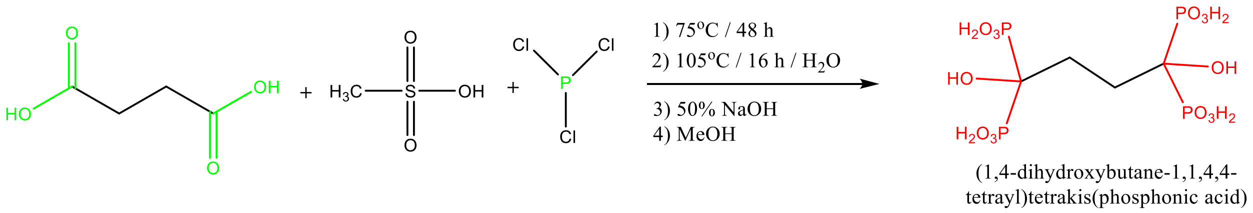


Figure 21. Synthesis route of SI-8.

4.2.4 SI-9: Synthesis of (1,6-dihydroxyhexane-1,1,6,6-tetrayl)tetrakis(phosphonic acid)

In a two-neck round bottom flask, 17.76mL / 184.81mmole of methane sulfonic acid was weighed and 3g / 20.53mmole of adipic acid was added during stirring at room temperature. With the help of syringe 18.04g /131.36mmole of phosphorous trichloride was added dropwise in reaction material for 30 mins at room temperature. The contents of the flask were refluxed for 48 hrs. at 75°C and then quenched carefully with 39.12mL of deionized H_2O at room temperature. The reaction mixture was refluxed again at 105°C for 16 hrs. After this, the pH of the material was adjusted to 1.8 by adding 50% aqueous solution of NaOH, 127mL of methanol was added and stirred the material for 45 mins at room temperature. The crude product was collected by filtration and redissolved in 10mL of hot water. Again, 50mL of methanol was added in the flask and black fine precipitates appeared that was collected as a pure product and dried at 80°C for 4 hrs. The product has 4.81g yield. Its synthesis route is shown in figure 22.

^1H NMR (D_2O, 400 MHz) δ ppm: 1.51 (s, 4H, 2 × CH_2), 1.87-1.90 (t, 4H, 2 × CH_2).

^{31}P NMR (D_2O, 162.00 MHz) δ ppm: 18.66.

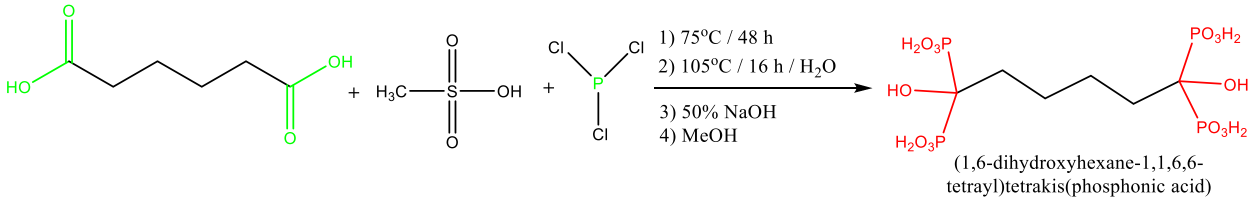


Figure 22. Synthesis route of SI-9.

4.2.5 SI-10: Synthesis of (hydroxy(phenyl)methylene)bis(phosphonic acid)

In a two-neck round bottom flask, 10.62mL / 110.51mmole of methane sulfonic acid was weighed and 3g / 24.57mmole of benzoic acid was added during stirring at room temperature. With the help of syringe 10.80g / 78.64mmole of phosphorous trichloride was added dropwise in reaction material for 30 mins at room temperature. The contents of the flask were refluxed for 48 hrs. at 75°C and then quenched carefully with 23.81mL of deionized H_20 at room temperature. The reaction mixture was refluxed again at 105°C for 16 hrs. After this, the pH of the material was adjusted to 1.8 by adding 50% aqueous solution of NaOH, 127mL of methanol was added and stirred the material for 45 mins at room temperature. The crude product was collected by filtration and redissolved in 10mL of hot water. Again, 50mL of methanol was added in the flask and white fine precipitates appeared that was collected as a pure product and dried at 80°C for 4 hrs. The product has 3.76g yield. Its synthesis route is shown in figure 23.

^{1}H NMR (D_2O, 400 MHz) δ ppm: 7.23-7.71 (m, 5H, 5 × CH)

^{31}P NMR (D_2O, 162.00 MHz) δ ppm: 15.59.

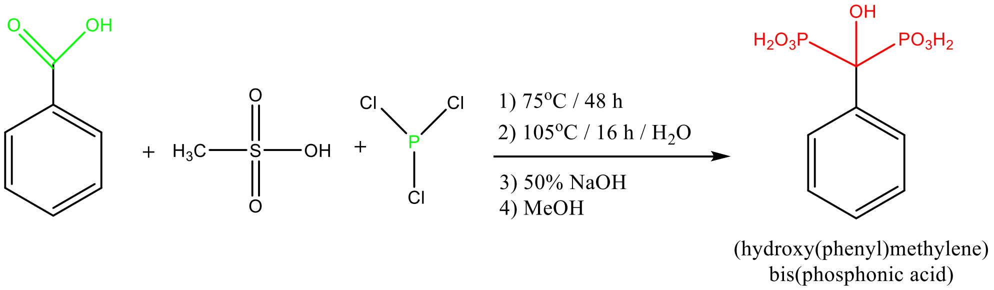


Figure 23. Synthesis route of SI-10.

4.2.6 SI-11: Synthesis of ((4-aminophenyl)(hydroxy)methylene)bis(phosphonic acid)

In a two-neck round bottom flask, 9.46mL / 98.44mmole of methane sulfonic acid was weighed and 3g / 21.88mmole of para benzoic acid was added during stirring at room temperature. With the help of syringe 9.61g / 69.98mmole of phosphorous trichloride was added dropwise in reaction material for 30 mins at room temperature. The contents of the flask were refluxed for 48 hrs. at 75°C and then quenched carefully with 21.20mL of deionized H_20 at room temperature. The reaction mixture was refluxed again at 105°C for 16 hrs. After this, the pH of the material was adjusted to 1.8 by adding 50% aqueous solution of NaOH, 127mL of methanol was added and stirred the material for 45 mins at room temperature. The crude product was collected by filtration and redissolved in 10mL of hot water. Again, 50mL of methanol was added in the flask and light-yellow fine precipitates appeared that was collected as a pure product and dried at 80°C for 4 hrs. The product has 3.68g yield. Its synthesis route is sown in figure 24.

^{1}H NMR (D_2O, 400 MHz) δ ppm: 7.27-7.31 (t, 2H, 2 × CH), 7.52-7.54 (d, 1H, CH), 7.82-7.84 (d, 1H, CH).

^{31}P NMR (D_2O, 162.00 MHz) δ ppm: 14.86.

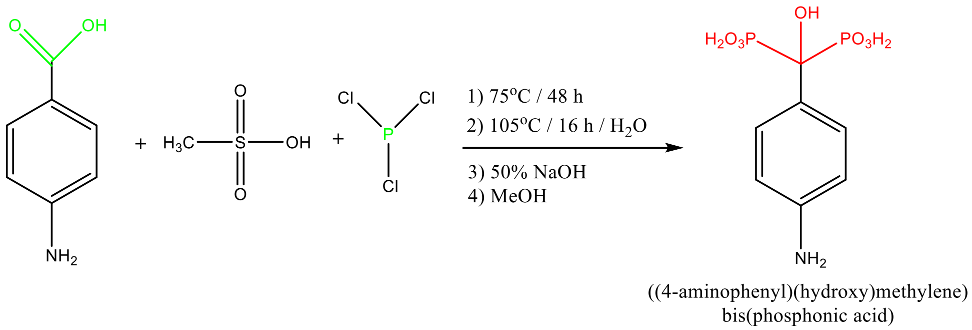


Figure 24. Synthesis route of SI-11.

4.2.7 References

1. Grun, A., Kovacs, R., Illes Nagy, D., Garadnay, S., Greiner, I., & Keglevich, G. (2014). The rational synthesis of Fenidronate. *Letters in Organic Chemistry*, *11*(5), 368-373.

5 Methods

5.1 High-Pressure Dynamic Tube Blocking Test

The performance of commercial and self-synthesize scale inhibitors was determined by high-pressure dynamic tube blocking scale rig manufactured by Scaled Solutions Ltd. Aberdeen, U.K shown in figure 25. It is a well-known and preferred laboratory method to check the efficiency of different oilfield scale inhibitors as it provides artificial conditions that occurred in the tubing during production. The test results from scale rig give a good assessment of minimum inhibitor concentration (MIC) of scale inhibitors. An acceptable MIC value is from 1-100 ppm, but the objective is between 1-5 ppm. The self-synthesized inhibitors were tested against calcite and barite scales.

There are three pumps in the rig that supply the specified fluids up to 10.00mL/min through a 3.00-meter long microbore coil under 80bar pressure. The coil is made up of 316 graded steel with an internal diameter of 1mm and fixed in an oven having 100°C temperature. Pump 1 is to supply brine 1(cationic solution, Table 2) pump 2 is to supply brine 2 (anionic solution, Table 3), and pump 3 is to supply specified scale inhibitor solution. Here pump 2 is also for the injection of cleaning solution (aqueous solution of Na_2EDTA and NaOH having pH 12-13 shown in Table-4) and for flushing deionized water according to programmed valve instructions.

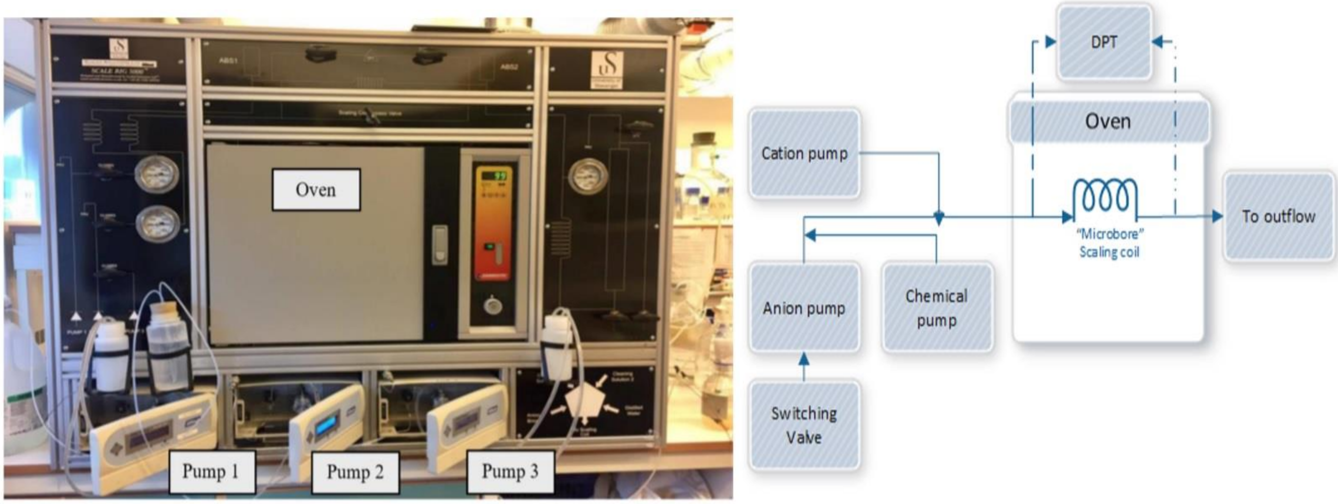


Figure 25. The high-pressure tube blocking scale rig used for testing of SIs.

The scale rig is programmed to complete four stages in each experiment as follows:

1. 1st blank: Just cationic and anionic solutions pumped until the scale is formed.
2. 1st scale: A series of programmed concentrations of scale inhibitor is pumped for one hour each or until the scale is formed along with cationic and anionic solution.
3. 2nd scale: Step two is repeated to reconfirm and to avoid any misleading results.
4. 2nd blank: Same as 1st bank.

In each step after the scale formation in the coil, the cleaning agents were pumped into the coil for 10min with the rate of 10mL/min to remove the scale from it

The concentration of scale inhibitors was set from 1-100 ppm for 1 hr or until the scale is formed. The lower limit for the SI concentration, fail concentration (FIC), is set to the SI concentration where the differential pressure increases more than 0.5 bar (7 psi). (FIC should not be confused with MIC, which is the minimum inhibitor concentration that prevents scale formation). The inputs of scale rig were programmed and controlled by its software from a nearby computer [1,2]. Different steps of data analysis have shown in figure 26.

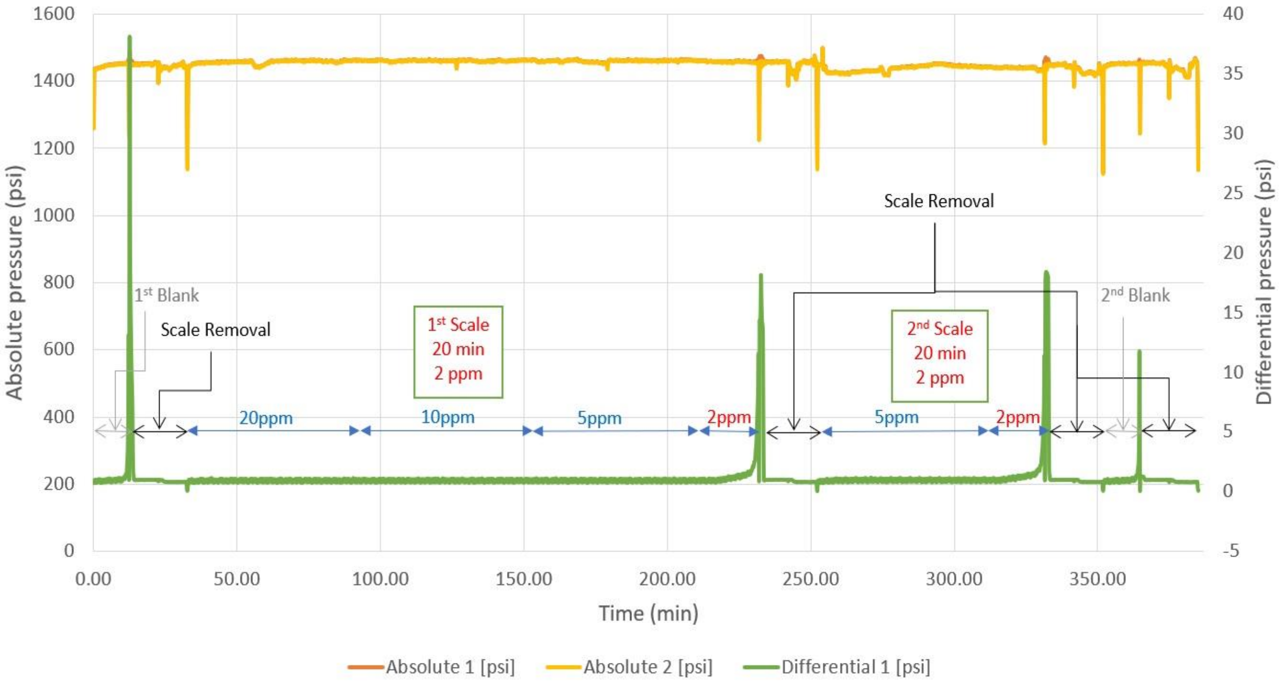


Figure 26. Graphical illustration of scale inhibitor`s test results.

Table 02. The composition of carbonate scale forming brines used in this study.

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

Brine 2					
Ions	Ppm	ion source	g/l	g/3L	g/5L
Na^+	19510	NaCl	35.04	105.12	175.20
SO_4^{-2}	2960	Na_2SO_4 Anhydrous	4.380	13.149	21.900
		Actual Cl^- ppm	30086.47		

Table 03. The composition of sulphate scale forming brines used in this study.

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

Brine 2					
Ions	Ppm	ion source	g/l	g/3L	g/5L

Na^+	19510	NaCl	35.04	105.12	175.20
SO_4^{-2}	2960	Na_2SO_4 Anhydrous	4.380	13.149	21.900
		Actual Cl^- ppm	30086.47		

Table 04. The composition of coil cleansing agent.

Scale removing agent	
$Na_2EDTA.H_2O$	120g
NaOH	40g
Deionized H_20	2 L

The concentration of brines used in this project was based on the concentration of produced water from the Heidrun oilfield Norway has shown in table 1 and 2. These brines were degassed by a vacuum pump for 15 min before using to avoid any bubble formation in flow-tubes [1].

5.2 Hydrothermal Stability Test

The thermal ageing test is needed to check either scale inhibitors are stable (maintain performance) or unstable (lose performance) at high temperature and it also helps to predict the squeeze lifetime. A 5% W/V solution of scale inhibitor in deionized water was made and its pH was adjusted to 4.5 either adding aqueous NaOH or aqueous HCl according to its prior pH. This solution was transferred into a pressure tube and attached to an air-free setup where the solution was stirred under the nitrogen environment. Gradually, the residual oxygen was sucked by a vacuum pump until no more bubbles formed and then the scale inhibitor solution was aged at 130^{o}C for 7 days in acquired conditions. The carbonate and sulphate scale inhibition performance of aged inhibitors was tested and compared with non-aged inhibitors lately. This method was adopted to age all synthesized and commercial-scale inhibitors.

5.3 Calcium Compatibility Test

The brines in the reservoir contains a high concentration of divalent ions such as calcium that can cause formation damage on mixing with scale inhibitors. The incompatibility of scale inhibitor with brines results in the precipitation which blocks the pores of formation rocks and cause poor placement of scale inhibitors etc. So, to check the compatibilities of synthesized and commercial-scale inhibitor compatibility test was conducted. The scale inhibitors that influence the pH of produced water also change the carbonate scaling potentials. The inhibitors have phosphonate functional groups in it leads to precipitation of Ca^{+2}-SI complex from brines that have a high concentration of calcium ions. These complexes are different from ordinary mineral scale formations.

Different concentrations of calcium salt and scale inhibitors were mixed in water to check either Ca^{+2}-SI complexation occurred or not. For this, 3% of NaCl was added in each glass bottle and four different concentrations of scale inhibitors of 100ppm, 1000ppm, 10000ppm and 50000ppm were added to assigned bottles. The calcium salt with the concentration of 100ppm, 1000ppm and 10000ppm was added to respective bottles then 10mL of deionized water was added to each bottle and shaken well at room temperature until the solution became clear. These bottles were kept in an oven at 80^{o}C and precipitation/ haze was observed after mixing, 30 mins,1hrs, 4hrs and 24hrs. This procedure was repeated for all inhibitors to check their calcium compatibilities. Figure 27 shows an image of different test bottles during the compatibility test.

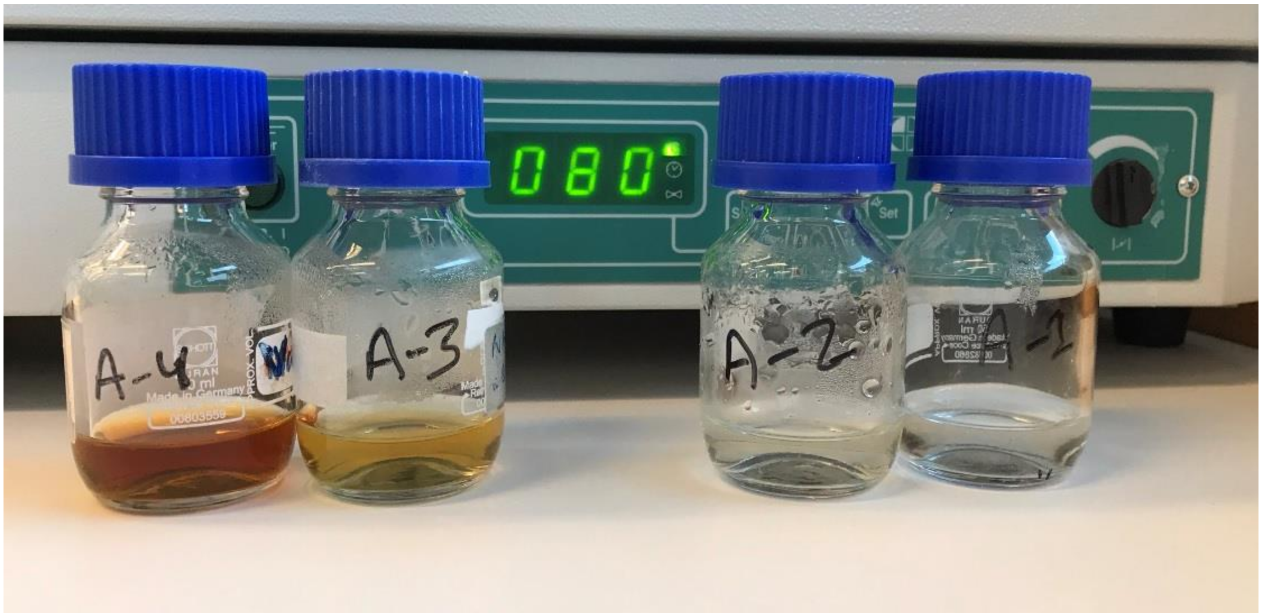


Figure 27. Calcium tolerance of SI-1 (PASP) in 100 ppm of calcium solution after 1 day.

5.4 SI Seawater Biodegradability Test

Due to Covid-19 pandemic, the campus gets close so this test could not be conducted during the semester. After reopening of the campus, scale inhibitors will be tested for biodegradations.

5.5 References

1. Mady, M. F., Charoensumran, P., Ajiro, H., & Kelland, M. A. (2018). Synthesis and characterization of modified aliphatic polycarbonates as environmentally friendly oilfield scale inhibitors. *Energy & Fuels*, *32*(6), 6746-6755.
2. Mady, M. F., Fevang, S., & Kelland, M. A. (2018). Study of novel aromatic aminomethylenephosphonates as oilfield scale inhibitors. *Energy & fuels*, *33*(1), 228-237.

6 Results and Discussion for Project-1

6.1 Synthesis

In project 1, the PASP was synthesized by the hydrolyzation of low molecular weight (97 g/mole) PSI with aq. NaOH. On hydrolysis, the rings of PSI open that forms monomers of sodium PASP and each monomer has alpha and beta units. For functionalization, the sodium PASP acted as a substrate for different bis phosphonic and sulphonic amino acids. The chances to be attached at either at the alpha unit or beta unit were the equal [1].

SI-1 was prepared by aq.NaOH hydrolyzation of PSI that gave sodium Na-PASP. To synthesized SI-2 and SI-3 bis phosphonic acids were used as raw material with PSI. SI-2 was synthesized by the mixing of PSI and IBPMA and hydrolysed by adding aq.NaOH. For SI-3 AEDPA was synthesized according to literature and functionalized as prior. For the synthesis of SI-4 and SI-5 the amino sulphonic acids 2-AMSA and AMSA were used respectively as raw material with PSI and remaining procure followed the same as above. All the above-mentioned reactions were succeeded and required products gained in a good yield.

6.2 High-Pressure Dynamic Tube Blocking Test

The scale inhibition efficiencies of various in-house synthesized inhibitors were tested against calcite and barite scales at 100^{o}C and 80 bars by High-Pressure Dynamic Tube Blocking scale rig. The results were gained by following the below-mentioned scale ring setup in all tests.

1st Blank + 1st Scale + 2nd Scale + 2nd Blank

Different concentrations of inhibitor of 100, 50, 20,10, 5, 2 and 1 ppm were injected by pump for 1 hr. or until the scale is formed at failed inhibition concentrations (FIC).

Different reservoirs have different pH according to their formation composition, usually from 4-9 and numerous scale inhibitors performed better at higher pH, but these inhibitors lose their efficiencies when applied to the reservoir having low pH. So, in this study, we adjusted the pH of all scale inhibitors to 4.5 in 1000ppm aqueous solution by adding HCL before to run in scale rig to check their performances at a reasonable lower pH. The FIC values of all inhibitors are placed in appendix-C.

Table 05 shows the failed inhibitor concentration (FIC) of SI-1 (PASP) and different modified PASP scale inhibitors against calcite scales. In that table, it can be seen that SI-1 is failed at 5 ppm for first and the same concentration for the second scale after 6 and 3 mins, respectively. The failure of SI-1 soon after 6 and 3 mins represents it hardly reach even at 5ppm. Its performance could be lost under a slight variation in reservoir conditions. All other modified PASP inhibitors showed better inhibition performance than PASP especially SI-2 and SI-3. The FIC values of SI-2 have shown in figure 28.

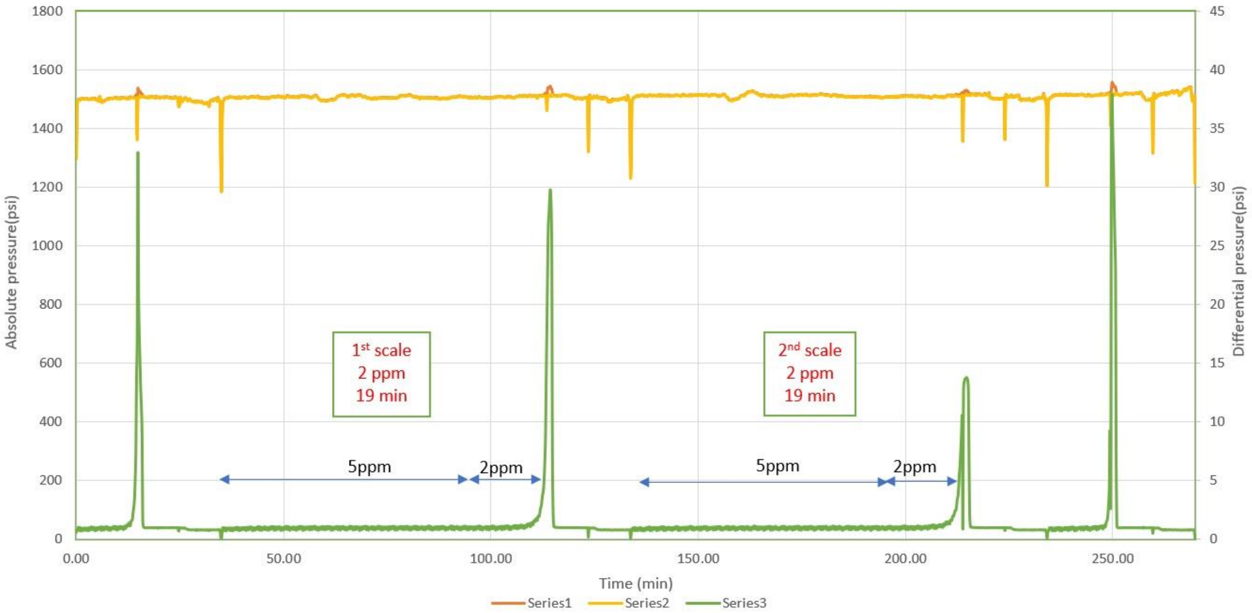


Figure 28. Failed inhibition concentrations of SI-2 for calcite scale.

SI-2 failed at 2 ppm for both first and second scale after 19 and 20 mins respectively and SI-3 failed at 2ppm for both scale after 32min, even more latter than SI-2. This is because SI-2 and SI-3 both have bisphosphonate functional groups and it is reported in literature also that phosphonate groups provide strong binding with metals and inhibits the scale formation at the lower concentration for a longer time [2].

SI-4 and SI-5 both showed better performance than PASP comparatively with respect to inhibition time. Both failed at the same concentration of 5 ppm like PASP, but the inhibition time of SI-4 has increased to 32 min and 40 min for first and second scale accordingly and 12 min for each scale of SI-5 after functionalization. In SI-4 and SI-5 the PASP was functionalized by amino sulphonic acids that showed less adsorption potential compare to phosphonated ones. SI-1 and sulphonated scale inhibitors (SI-4 and SI-5) failed at 5 ppm we speculate that carbonyl functional groups from SI-1 and sulphonate functional groups from SI-4 and SI-5 has somehow similar metal-binding properties or sulphonate has slightly better than carbonyls [3].

Table 05. FIC values of SI-1(PASP) and modified-PASP against carbonate scales.

Inhibitors	first blank	first scale		second scale		second blank
	time (min)	conc. (ppm)	time (min)	conc. (ppm)	time (min)	Time (min)
SI-1	15	5	6	5	3	14
SI-2	12	2	19	2	20	15
SI-3	28	2	32	2	32	22
SI-4	23	5	32	5	40	13
SI-5	27	5	12	5	12	13

In table 06 the FICs of PASP and modified PASP scale inhibitors have shown against barite. Here it can be seen all synthesized scale inhibitors are failed at 20 ppm after different time durations except for SI-1 that failed at 50ppm after 47 min for each first and second scale. Figure 29 shows the FIC value of SI-2 against barite scales.

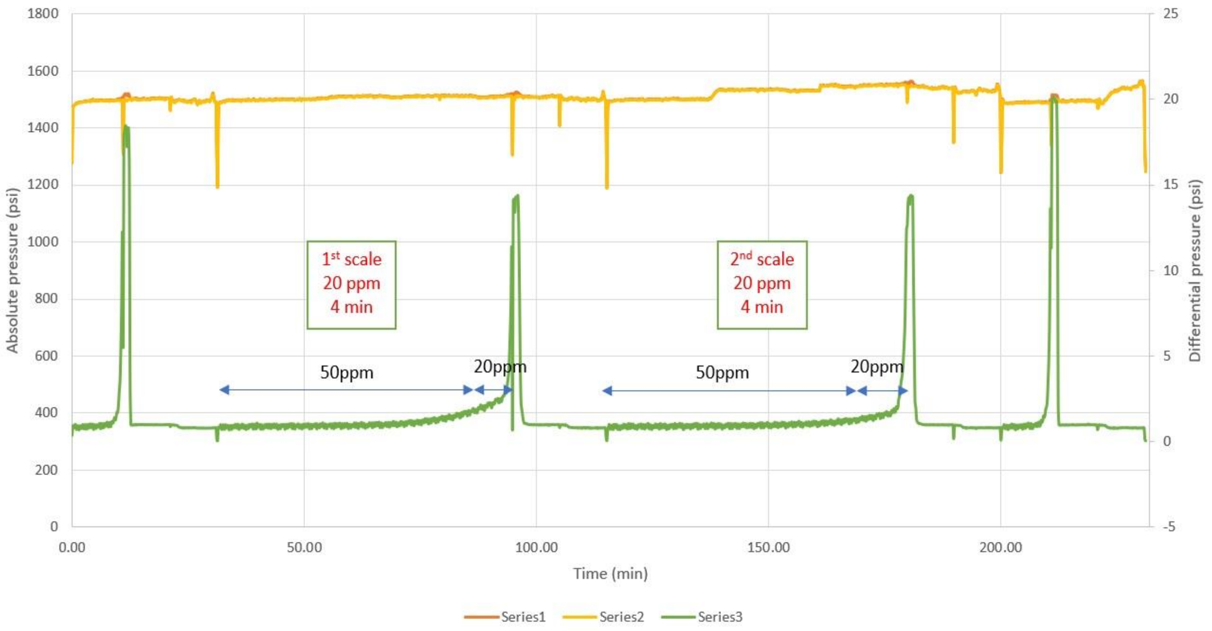


Figure 29. Failed inhibition concentrations of SI-2 for barite scale.

This high FIC for barite scale shows carbonyl functional groups of SI-1 are not that much good in inhibiting barite scales as they are good for calcite. On the other hand, modified scale inhibitors showed good performance than SI-1(PASP) against barite scale as well because of having bisphosphonate and sulphonate functional groups in it [3,2] Their inhibition potential is less against barite than calcite as barites are most stable and least soluble scale that makes them hard to control.

Table-06. FIC values of SI-1(PASP) and modified-PASP against sulphate scales.

Inhibitors	first blank	first scale		second scale		second blank
	time (min)	conc. (ppm)	time (min)	conc. (ppm)	time (min)	Time (min)
SI-1	11	50	47	50	47	10
SI-2	11	20	4	20	4	11
SI-3	11	20	11	20	13	11
SI-4	11	20	16	20	18	10
SI-5	10	20	4	20	10	10

In general, the inhibition performance of all modified inhibitors was improved significantly against calcite and barite scales as follows:

For carbonate:

SI-3 (2ppm) > SI-2 (2ppm) > SI-4 (5ppm) > SI-5 (5ppm) > SI-1 (5ppm)

For sulphate:

SI-4 (20ppm) > SI-3 (20ppm) > SI-5 (20ppm) > SI-2 (20ppm) > SI-1 (50ppm)

6.3 Hydrothermal Stability Test

Thermal stability is a key factor in the SI squeezing method. Thermal stabilities enhancement of SI-1 (PASP) by functionalization was the one main objective of this project. Because this can increase the range of wells which could be squeezed by PASP as it is thermally not stable and can be squeezed just at around 70^{o}C.

Therefore, all inhibitors were aged thermally at 130 °C for 7 days in anaerobic conditions and then tested against calcite and barite scales. The FIC values of inhibitors after thermal ageing are also shown in appendix-C.

Table 07 shows the performance of inhibitor after thermal ageing against carbonate scales and can be seen that SI-1 lost inhibition efficiency from 5 pm to 20 ppm after thermal ageing. Meanwhile, the SI-2 maintained its performance after thermal ageing same as prior (2ppm). Figure 30 shows the FIC values of SI-2 against calcite after thermal ageing.

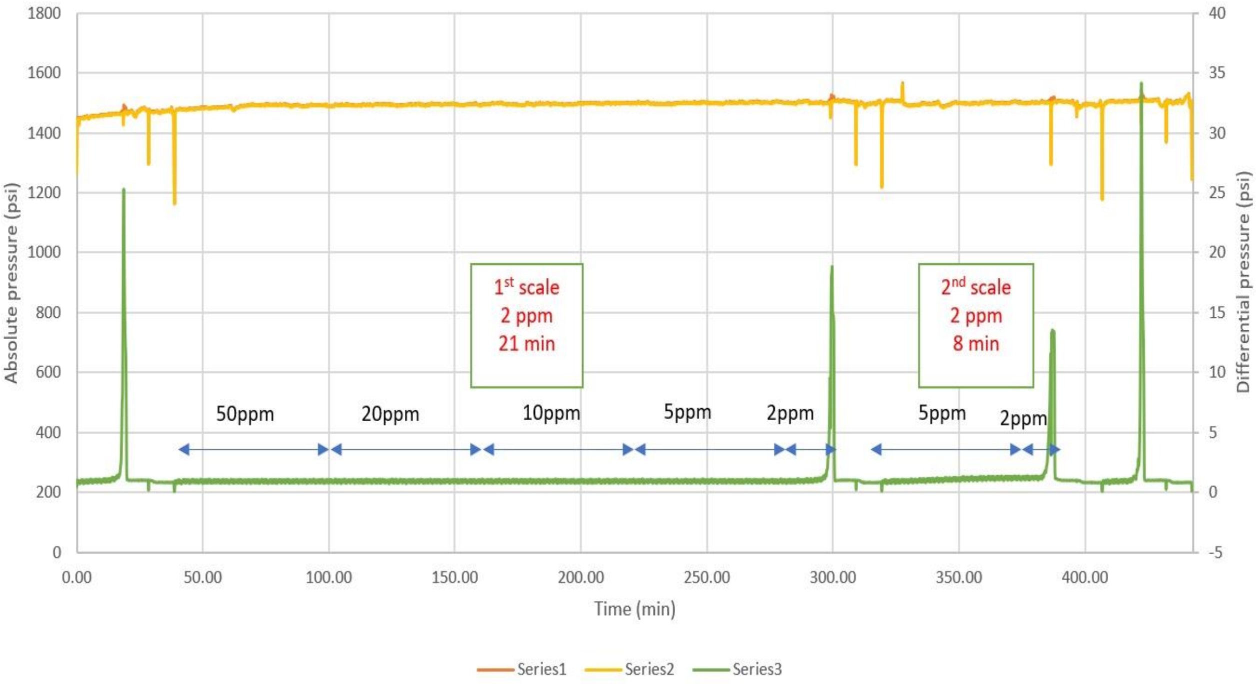


Figure 30. Failed inhibition concentrations of SI-2 for calcite scale after thermal ageing.

The performance of SI-3 was lost slightly from 2 ppm to 5 ppm, but it still has a reasonable inhibition potential at elevated temperatures. The thermal stability of SI-2 and SI-3 is probably due to the presence of phosphonate groups that have strong adsorption properties with group II metals as a similar finding in the literature have been reported as well [2].

SI-4 and SI-5 degraded completely at high temperature and lost inhibition performance from 5 ppm to 100ppm against calcite scales.

Table 07. FIC values of SI-1(PASP) and modified-PASP against carbonate scales after thermal ageing.

Inhibitors	first blank	first scale	second scale	second blank

	time (min)	conc. (ppm)	time (min)	conc. (ppm)	time (min)	Time (min)
SI-1	15	20	23	20	21	16
SI-2	18	2	21	2	8	16
SI-3	17	5	31	5	28	17
SI-4	10	100	22	100	21	11
SI-5	8	100	21	100	18	8

The failed inhibition concentrations (FICs) of synthesized inhibitors after thermal ageing have shown in table 08 against sulphate scales. Here we can see that none of them maintained its performance against sulphate scale after thermal ageing. SI-4 and SI-5 were not tested against sulphate scale due to poor performance against calcite scale after thermal ageing. In figure 31, FIC value of SI-2 against barite scales is represented.

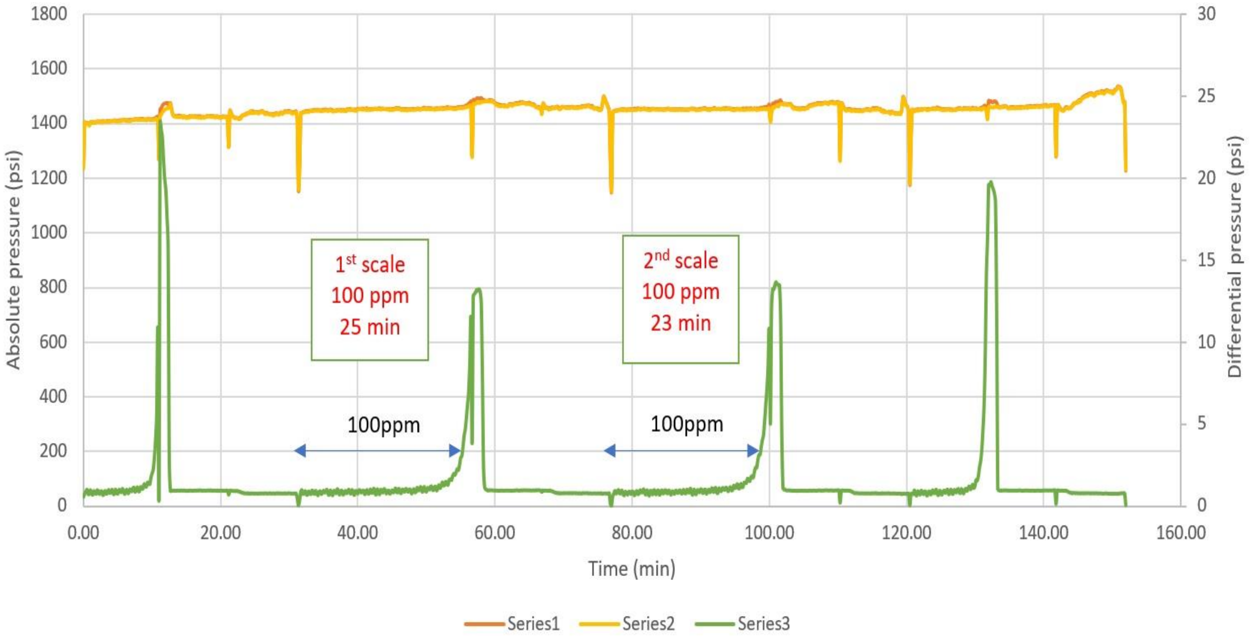


Figure 31. Failed inhibition concentrations of SI-2 for barite scale after thermal aging.

Table 08. FIC values of SI-1(PASP) and modified-PASP against sulphate scales after thermal ageing.

Inhibitors	first blank	first scale		second scale		second blank
	time (min)	conc. (ppm)	time (min)	conc. (ppm)	time (min)	Time (min)
SI-1	11	100	29	100	23	11
SI-2	10	100	25	100	23	11
SI-3	11	100	35	100	29	11
SI-4	-	-	-	-	-	-
SI-5	-	-	-	-	-	-

6.4 Calcium Compatibility Test

The compatibility of scale inhibitors with calcium ion is very important for squeeze treatment. Numerous types of scale inhibitors form complexes with Ca^{+2} on interacting with brine in the reservoirs. Results from earlier studies showed scale inhibitors having phosphonate functional groups are less compatible with calcium than polysulphonate and polycarboxylate based scale inhibitors [3]. So, compatibility tests were carried according to protocols (mentioned above) to test the calcium tolerance of all synthesized scale inhibitors. The compatibility results of SI-2 are presented in table 09 to table 11 in which 100, 1000, 10000 and 50000 ppm scale inhibitor solution is tested in the 100, 1000 and 10000 ppm of Ca^{+2} solution. It can be noted that SI-2 remain compatible after 24 hr. when 1000ppm of inhibitor solution is applied in 10000ppm of calcium solution. While it forms some clouds when its 10000ppm and 50000ppm solution is applied in 1000ppm calcium solution, but these clouds do not cause severe formation damage SI-2 precipitated by making complexes when 10000ppm and 50000 ppm solution is applied in 10000ppm of calcium solution. This kind of precipitation causes serious formation damages. According to given results, it can be suggested that SI-2 is applicable in the reservoirs which have 1000ppm of the calcium concentration approximately. The incompatibility of SI at higher concentration is due to phosphonate-Ca^{+2} complexes as phosphonate base scales are reported as less compatible in higher concentrations of calcium [2].

Table 09. Calcium tolerance of SI-2 (PASP/IBMPA) in 100ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Clear
10,000	Clear	Clear	Clear	Clear	Clear
50,000	Clear	Clear	Clear	Clear	Clear

Table 10. Calcium tolerance of SI-2 (PASP/IBMPA) in 1000ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Clear
10,000	Clear	Clear	Cloudy	Cloudy	Cloudy
50,000	Clear	Cloudy	Cloudy	Cloudy	Cloudy

Table 11. Calcium tolerance of SI-2 (PASP/IBMPA) in 10,000ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours

100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Clear
10,000	Precipitated	Precipitated	Precipitated	Precipitated	Precipitated
50,000	Precipitated	Precipitated	Precipitated	Precipitated	Precipitated

In Appendix-D the compatibilities of all inhibitors are reported where it can be seen that PASP is showing compatibility at higher (10000) concentration of calcium whereas SI-3 is compatible if 1000ppm solution is applied in 1000ppm of calcium solution. As sulphonate are reported as calcium compatible groups so to overcome the compatibility issue [4] of modified PASP, sulphonate containing inhibitors SI-4 and SI-5 were synthesized and tested for calcium compatibilities along with scale inhibition performance. In table 00 compatibility test results for SI-4 and SI-5 are presented that shows they are compatible with calcium same as SI-1(PASP).

6.5 References

1. Shi, S., Wu, Y., Wang, Y., Yu, J., & Xu, Y. (2017). Synthesis and characterization of a biodegradable polyaspartic acid/2-amino-2-methyl-1-propanol graft copolymer and evaluation of its scale and corrosion inhibition performance. *RSC advances*, *7*(58), 36714-36721.
2. Mady, M. F., Fevang, S., & Kelland, M. A. (2018). Study of novel aromatic aminomethylenephosphonates as oilfield scale inhibitors. *Energy & fuels*, *33*(1), 228-237.
3. Mady, M. F., Malmin, H., & Kelland, M. A. (2019). Sulfonated Nonpolymeric Aminophosphonate Scale Inhibitors—Improving the Compatibility and Biodegradability. *Energy & Fuels*, *33*(7), 6197-6204.
4. Mady, M. F., Bayat, P., & Kelland, M. A. (2020). Environmentally-Friendly Phosphonated Polyetheramine Scale Inhibitors-Excellent Calcium Compatibility for Oilfield Applications. *Industrial & Engineering Chemistry Research*.

7 Result and Discussion for Project-2

7.1 Synthesis

In project 2, different amino and carboxylic acids were reacted with PCl_3 in methane sulphonic acid as a solvent at 75°C for 48 hrs. The reactions were followed by the hydrolysis at 105°C for 16 hrs. and then pH adjusted by 50% aq. NaOH to 1.8. The crude product hydroxy bisphosphonate as disodium salt was obtained by precipitation using MeOH. Further purification carried by two additional precipitations from water solution and final extraction of solid product with MeOH at boiling point to remove all impurities. The main impurity of crude product was the $MeSO_4Na$ formed in the reaction of MSA and NaOH [1].

For SI-6 and SI-7 two amino acids, beta-alanine and 5-aminovaleric acids were used as substrate accordingly. Both have a different number of carbons in the backbone and after derivatization, each molecule got one new terminal hydroxy bisphosphonate functional group. To synthesize SI-8 and SI-9 two dicarboxylic acids, succinic acid and adipic acid were used as substrate respectively and after the substitution, each molecule got two new terminal hydroxy bisphosphonate groups. In SI-10 and SI-11 aromatic molecules, i.e. benzoic acid and para-aminobenzoic acid were used as a carboxylic acid source where substitution occurred.

7.2 High-Pressure Dynamic Tube Blocking Test

In table 12 failed inhibition concentrations of different synthesized scale inhibitors against calcite scales have shown where we can see that SI-6, SI-7, SI-10, and SI-11 showed very good performance. They all failed at 2 ppm for both the first and second scales. The reason for the good performance of these scale inhibitors is possibly having one amino and one hydroxy bisphosphonate functional groups in each scale inhibitor. In previous studies suggestions that amino group enhance the metal binding abilities acting as Lewis base ligand along with hydroxy bisphosphonate group and make great metal-ligand complex to inhibit calcite scales have been reported [2].The FIC values of all scale inhibitors are given in appendix-E.

Table 12. FIC values of hydroxy bisphosphonate SIs against carbonate scales.

Inhibitors	first blank	first scale	second scale	second blank

	time (min)	conc. (ppm)	time (min)	conc. (ppm)	time (min)	Time (min)
SI-6	17	2	26	2	26	17
SI-7	12	2	19	2	19	12
SI-8	16	10	4	10	4	14
SI-9	16	10	48	10	22	14
SI-10	20	2	26	2	28	17
SI-11	15	2	18	2	19	14

On the other hand, both SI-8 and SI-9 also showed good inhibition potential against calcite by failing at 10ppm for each scale, but their inhibition efficiency is not as good as like others in this study. SI-8 and SI-9 both have two hydroxy bisphosphonate groups on each molecule. Their less inhibition efficiency against calcite might be due to calcium-phosphonate compatibility as it is reported that phosphonate groups are less compatible with calcium ions [3].The FIC value for SI-6 against calcite has shown in figure 32.

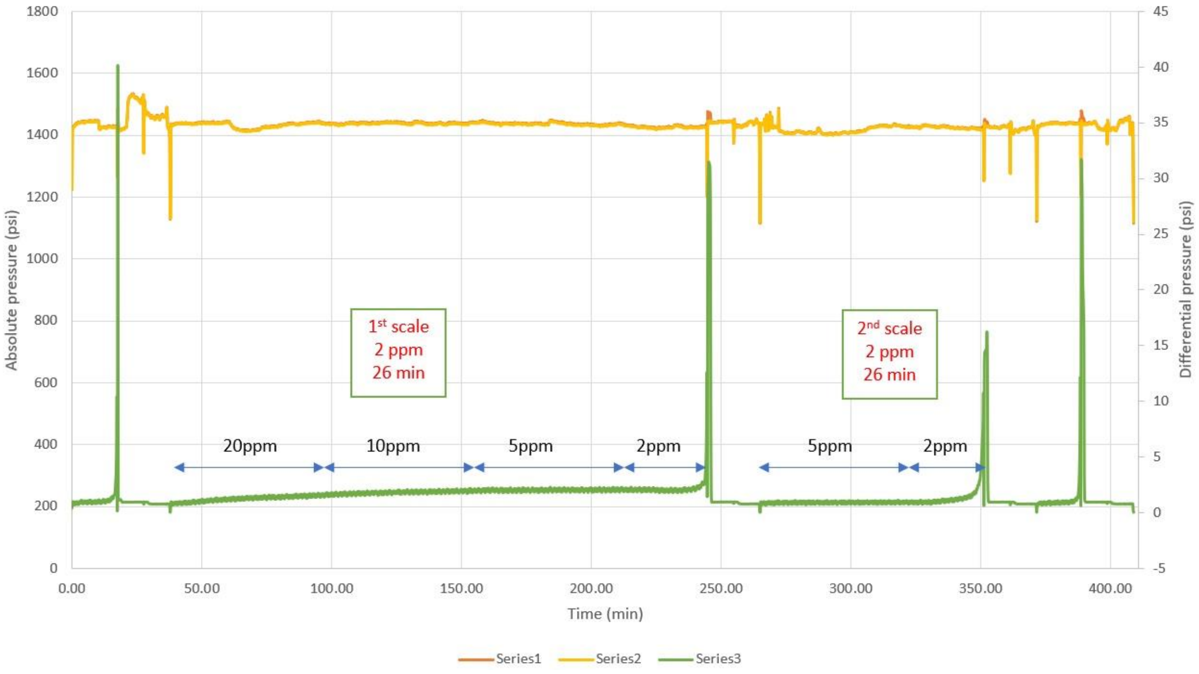


Figure 32. Failed inhibition concentrations SI-6 for calcite scale.

Table 13 showed the inhibition efficiencies of synthesized scales inhibitors against barite scale. For barite SI-8 and SI-9 showed good performance as both failed at 20 ppm for the first and second scale while SI-6, SI-7, SI-10 and SI-11 could not show good inhibition potential against barite scales as all latterly mentioned inhibitors failed at 100ppm.

Table 13. FIC values of hydroxy bisphosphonate SIs against sulphate Scales.

Inhibitors	first blank	first scale		second scale		second blank
	time (min)	conc. (ppm)	time (min)	conc. (ppm)	time (min)	Time (min)
SI-6	10	100	20	100	20	10
SI-7	10	100	25	100	21	11
SI-8	12	20	12	20	14	11
SI-9	10	20	28	20	23	11
SI-10	15	100	24	100	17	9
SI-11	10	100	15	100	14	10

The successful inhibition of SI-6 and SI-7 against barite is perhaps due to having a greater number of hydroxy bisphosphonate functional groups in these molecules than others tested in this study. In referred study it is justified that a greater number of phosphonate groups in a molecule can bind to more active sites of crystals that ultimately make inhibitor strong enough to inhibit tough scales like barites [4]. In figure 32 failed inhibition concentration with time for SI-9 against barite is shown.

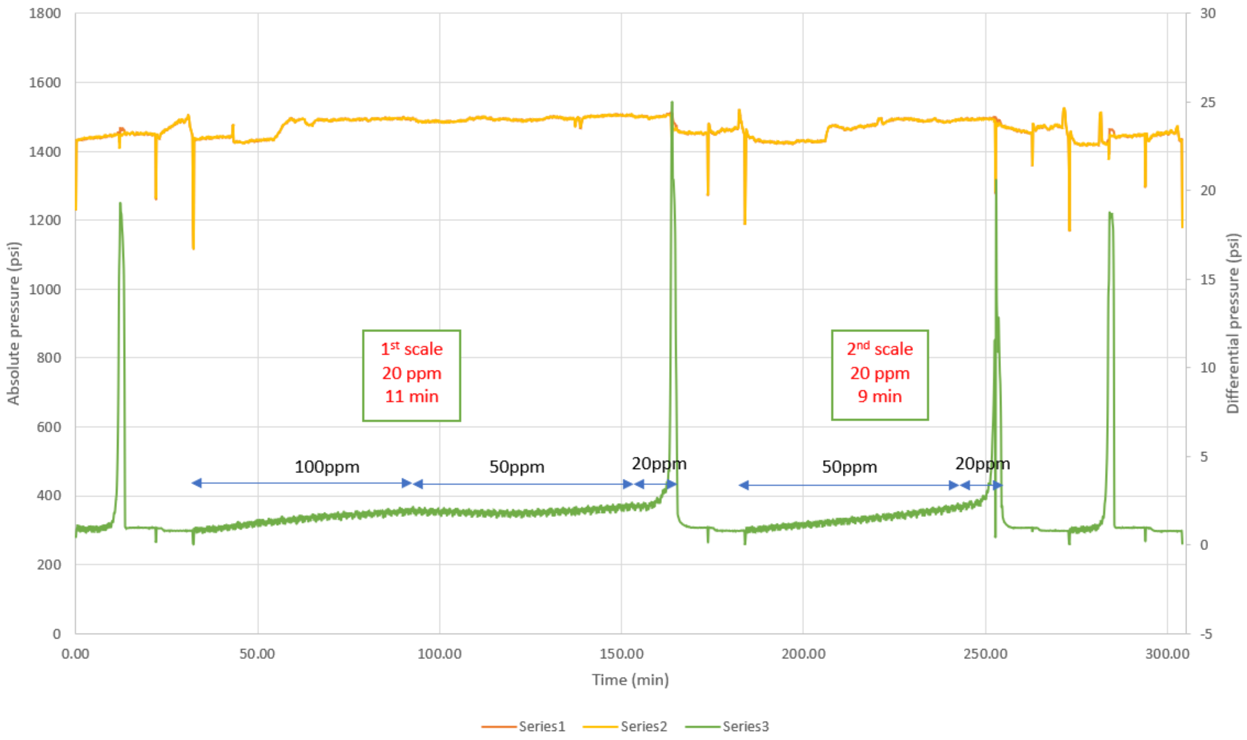


Figure 33. Failed inhibition concentrations of SI-9 for barite scale.

7.3 Thermal Stability Test

Thermal stabilities of synthesized scale inhibitors are tested at the same conditions as project 1. In table 14 performances of scale inhibitors have shown for calcite after thermal ageing where we can see that SI-6 and SI-7 and SI-8 maintained their performances against calcite after thermal treatment. SI-7 and SI-8 exhibited a unique behaviour as for SI-7 (shown in figure 34) the inhibition efficiency has been enhanced after thermal ageing from 2 ppm to 1 ppm and for SI-8 inhibition time was increased compared to pre-thermal SI-8 one.

Table 14. FIC values of hydroxy bisphosphonate SIs against calcite scales after thermal ageing.

Inhibitors	first blank	first scale		second scale		second blank
	time (min)	conc. (ppm)	time (min)	conc. (ppm)	time (min)	Time (min)
SI-6	15	2	31	2	32	19
SI-7	31	1	42	1	43	23

SI-8	23	10	56	10	56	15
SI-9	14	20	46	20	50	14
*SI-10	8	5	10	-	-	-
SI-11	15	5	20	5	39	16

**SI-10 tested just for first scale due to instrumental issue.*

The inhibition the concentration of SI-9 was increased from 10ppm to 20 ppm after thermal treatment, but it is still reasonable to inhibit scale formation at elevated temperatures. SI-10 and SI-11 lost their performance slightly as inhibition concentration has increased from 2ppm to 5ppm, but this performance is still excellent to inhibit calcite scaling.

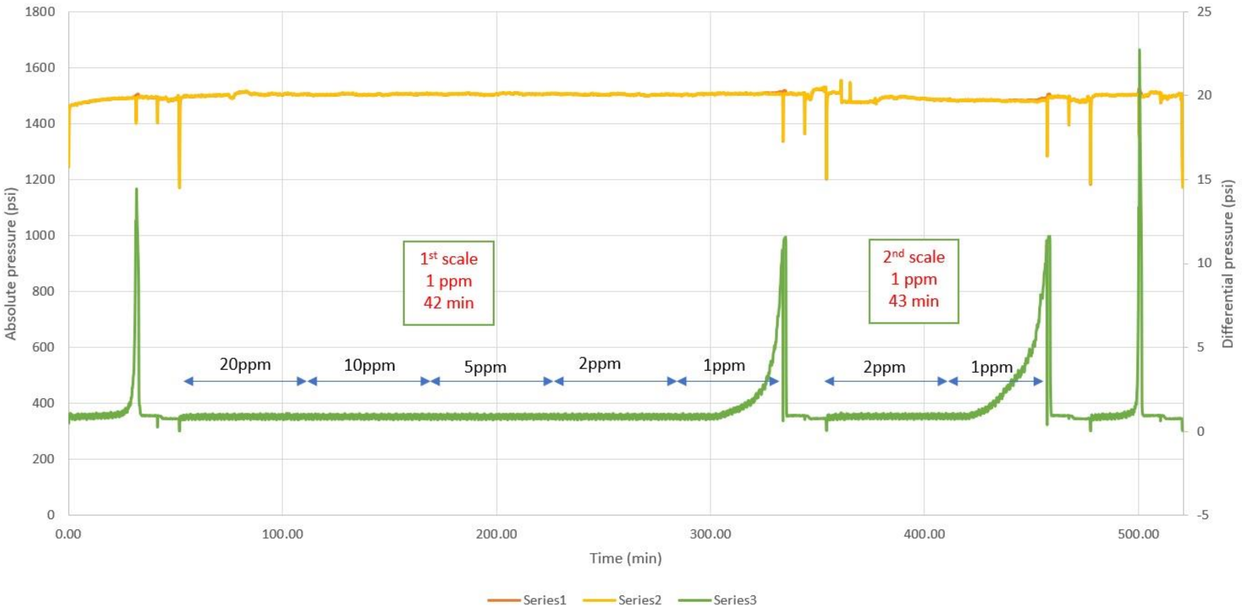


Figure 34. Failed inhibition concentrations of SI-7 for calcite scale after thermal ageing.

SI-6, SI-7, SI-10 and SI-11 were failed at 100ppm against barite scale before thermal treatment, so they were not tested for thermal ageing treatment due to poor performance for barite. SI-8 and SI-9 showed excellent inhibition potential against barite scale after thermal ageing as both failed at 20ppm for first and second scale shown in table 15. Figure 35 shows the SI-9 inhibition graph after thermal ageing against barite. The FIC values of thermally aged scale inhibitors are also given in appendix-E.

Table 15. FIC values of hydroxy bisphosphonate SIs against sulphate scales after thermal ageing.

Inhibitors	first blank	first scale		second scale		second blank
	time (min)	conc. (ppm)	time (min)	conc. (ppm)	time (min)	Time (min)
SI-6	-	-	-	-	-	-
SI-7	-	-	-	-	-	-
SI-8	11	20	7	20	10	10
SI-9	11	20	11	20	9	11
SI-10	-	-	-	-	-	-
SI-11	-	-	-	-	-	-

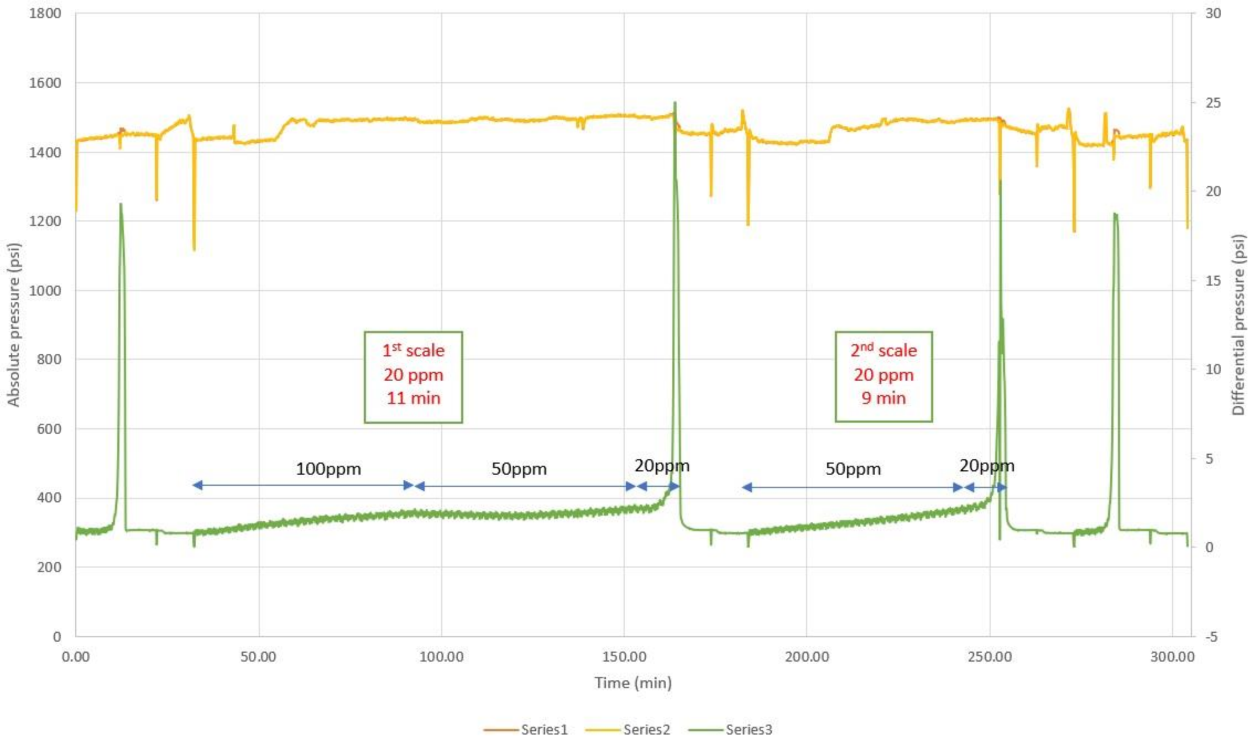


Figure 35. Failed inhibition concentrations of SI-9 for barite scale after thermal ageing.

7.4 Calcium Compatibility Test

The compatibility test for this project was also conducted the same as project 1 and in table 16 to 18 compatibility test results are shown for SI-10. It can be noticed that SI-10 showed excellent compatibility after the different durations of time, when its solution having 100ppm to 50000 ppm concentration is applied in 100ppm to 10000ppm of calcium solution. Among all synthesized inhibitors SI-7, SI-8 and SI-11 behaved to be least compatible with calcium ions while SI-6 and SI-9 showed a bit better compatibility than latterly mentioned look in appendix-F. SI-2 was compatible when its 100ppm solution applied in 10000ppm calcium solution and the compatibility of SI-8 was limited just to 100ppm of calcium concentration. SI-11 precipitated after 24 hrs in all concentration of calcium ions except 100ppm where it was compatible when its 1000ppm solution applied in 100ppm of calcium solution.

Table-16. Calcium tolerance of SI-10 in 100ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Clear
10,000	Clear	Clear	Clear	Clear	Clear
50,000	Clear	Clear	Clear	Clear	Clear

Table 17. Calcium tolerance of SI-10 in 1000ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear

1000	Clear	Clear	Clear	Clear	Clear
10,000	Clear	Clear	Clear	Clear	Clear
50,000	Clear	Clear	Clear	Clear	Clear

Table 18. Calcium tolerance of SI-10 in 10,000ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Clear
10,000	Clear	Clear	Clear	Clear	Clear
50,000	Clear	Clear	Clear	Clear	Clear

The results of calcium compatibility test for all scale inhibitor can be found in appendix-F. The least compatibility of all synthesized scale inhibitor was possibly due to bisphosphonate groups that usually forms complexes with metals when applied in highly concentrated calcium solution reason is mentioned above [3]. Here we find that SI-10 that is a derivative of benzoic acid showed excellent calcium compatibility. It can be applied in the wells that have a high concentration of calcium ions. We speculate that the reason behind good calcium compatibility of SI-10 is the mono substituted benzene ring that can enhanced the compatibility of hydroxy bisphosphonate.

7.5 References

1. Grun, A., Kovacs, R., Illes Nagy, D., Garadnay, S., Greiner, I., & Keglevich, G. (2014). The rational synthesis of Fenidronate. *Letters in Organic Chemistry*, *11*(5), 368-373.
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3. Mady, M. F., Bayat, P., & Kelland, M. A. (2020). Environmentally Friendly Phosphonated Polyetheramine Scale Inhibitors-Excellent Calcium Compatibility for Oilfield Applications. *Industrial & Engineering Chemistry Research*.
4. Mady, M. F., Fevang, S., & Kelland, M. A. (2018). Study of novel aromatic aminomethylenephosphonates as oilfield scale inhibitors. *Energy & fuels*, *33*(1), 228-237.

8 Conclusion and Recommendations

In project-1 poly aspartate was successfully modified by the functionalization of amino phosphonate and amino sulphonate functional groups. The structures of all synthesized scale inhibitors were confirmed by FTIR spectroscopy. All modified scale inhibitors showed better performance than SI-1 (PASP). SI-2, SI-3, SI-4 and SI-5 exhibit excellent performance against calcite scale but their inhibition potential against barite scale was not as better as against calcite. SI-2 and SI-3 failed at 2ppm and, SI-3 and SI-4 failed at 5ppm against calcite scales while all failed at 20ppm against barite. The high stability of $BaSO_4$ scales made them hard to remove comparatively. SI-2 and SI-3 maintained their performance against calcite scale while all remaining inhibitors lost inhibition performance for both calcite and barite after thermal ageing. We believe the strong adsorption properties of phosphonate groups from SI-2 and SI-3 made them thermally stable. SI-1, SI-4 and SI-5 were calcium compatible while SI-2 and SI-3 showed compatibility just at a lower concentration of calcium ions. We speculate that the -SO3 group from SI-4, SI-5 maintained calcium tolerance same as parent polymer SI-1 (PASP) while -PO3 groups from SI-2 and SI-3 became less compatible with calcium by forming -PO3-Ca^{+2} complexes. In general, the performance of all inhibitors was improved after modification.

In project-2 a novel series of novel hydroxy bisphosphonate scale inhibitors were synthesized successfully, and their structures were characterized by NMR spectroscopy. All these inhibitors showed excellent performance against calcite scales with FIC value of 2ppm except SI-8 and SI-9 as they failed at a moderate concentration of 10ppm for calcite. As the SI-8 and SI-9 contained one extra hydroxy bisphosphonate group than others. So, we believe that their comparatively less performance against calcite is due to incompatibility of phosphonate-calcium ions. On the other hand, SI-8 and SI-9 failed at a reasonable concentration of 20ppm while all remaining inhibitors showed very poor performance against barite scales and failed at 100ppm. We assumed that one extra hydroxy bisphosphonate group on each SI-8 and SI-9 helped them to inhibit tough barite scales by providing more binding sites. After thermal ageing SI-6, SI-7 and SI-8 maintained their inhibition efficiency while SI-9, SI-10, and SI-11 lost performance against calcite slightly. SI-8 and SI-9 maintained their inhibition potential against barite after thermal treatment as the phosphonate group helped the inhibitors in thermal stabilization. SI-10 exhibit excellent compatibility at every given concentration of calcium ions while SI-8 and SI-11 were least compatible with calcium. SI-6, SI-7 and SI-9 were compatible in a limited concentration of calcium ions as phosphonate groups are the main reason for less compatibilities. As SI-10 was derivatized from benzoic acid so we speculate that monosubstituted benzene enhanced its calcium compatibility.

All properties that could make an inhibitor ideal could not be gained in any synthesized inhibitor from both projects, everyone has one or more disadvantages. As the one monomer of PASP has two amino binding sites at alpha and beta subunits. So, for the modification of PASP 1 equivalent of an amino reactant or 2 equivalents of other similar amino reactant was treated with 1 equivalent of PSI in this study. The functionalization of one monomer of PASP with two dissimilar amino reactants (1 equivalent of each) can be helpful to overcome thermal stability and compatibility issues in future studies.

The FIC value of SI-7 was 2ppm before thermal ageing that went to 1ppm after thermal ageing. The evaluation of this unique behavior can be a part of future studies for further improvements. Moreover, calcium compatibility was the one main problem with most of the synthesized inhibitors. Here we found that the derivative of benzoic acid (SI-10) showed excellent compatibility and was thermally stable for calcite but lacks the barite inhibition potential. So, the functionalization of monosubstituted benzene with different other groups might be helpful to control the barite scale in future as well.

Appendix-A

FTIR Spectra for Project 1

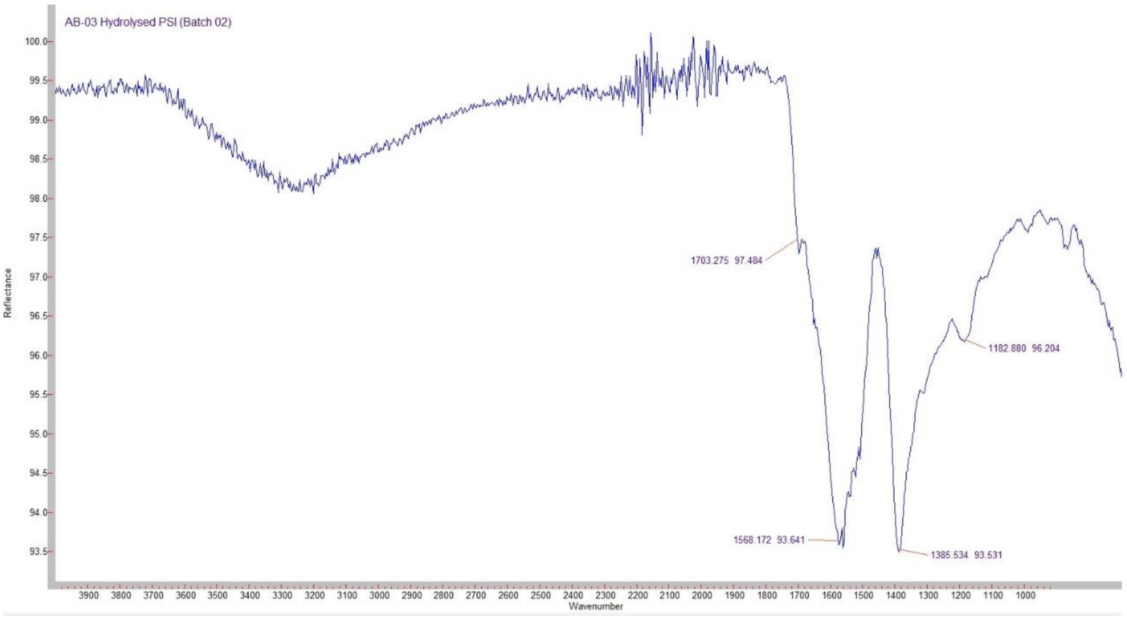

Figure01. FTIR spectra for SI-1.

Figure 02. FTIR spectra for SI-2.

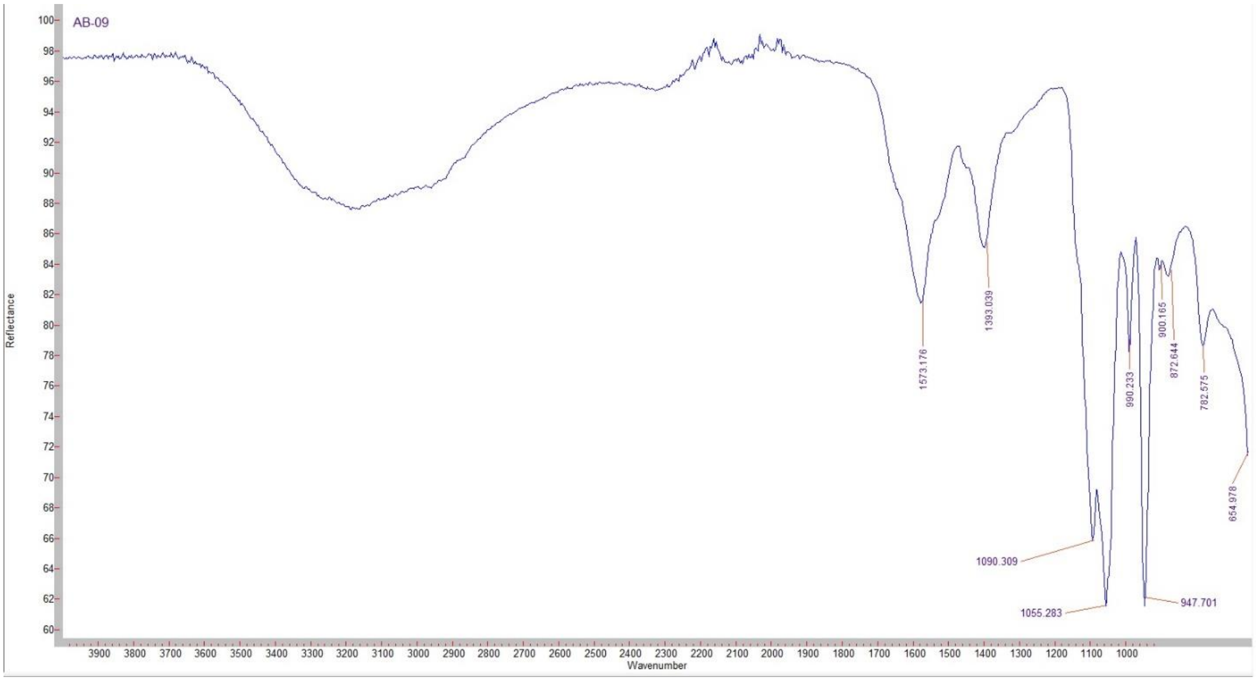

Figure 03. FTIR spectra for SI-3.

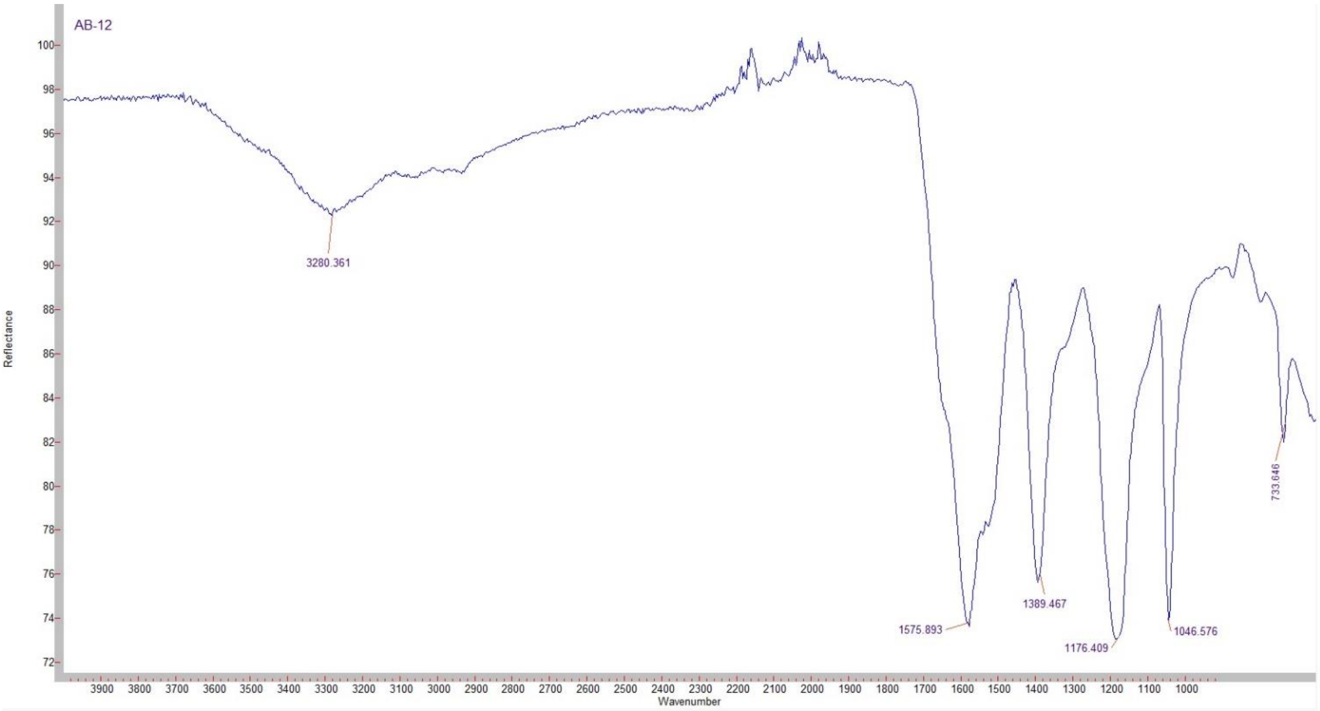

Figure 04. FTIR spectra for SI-4.

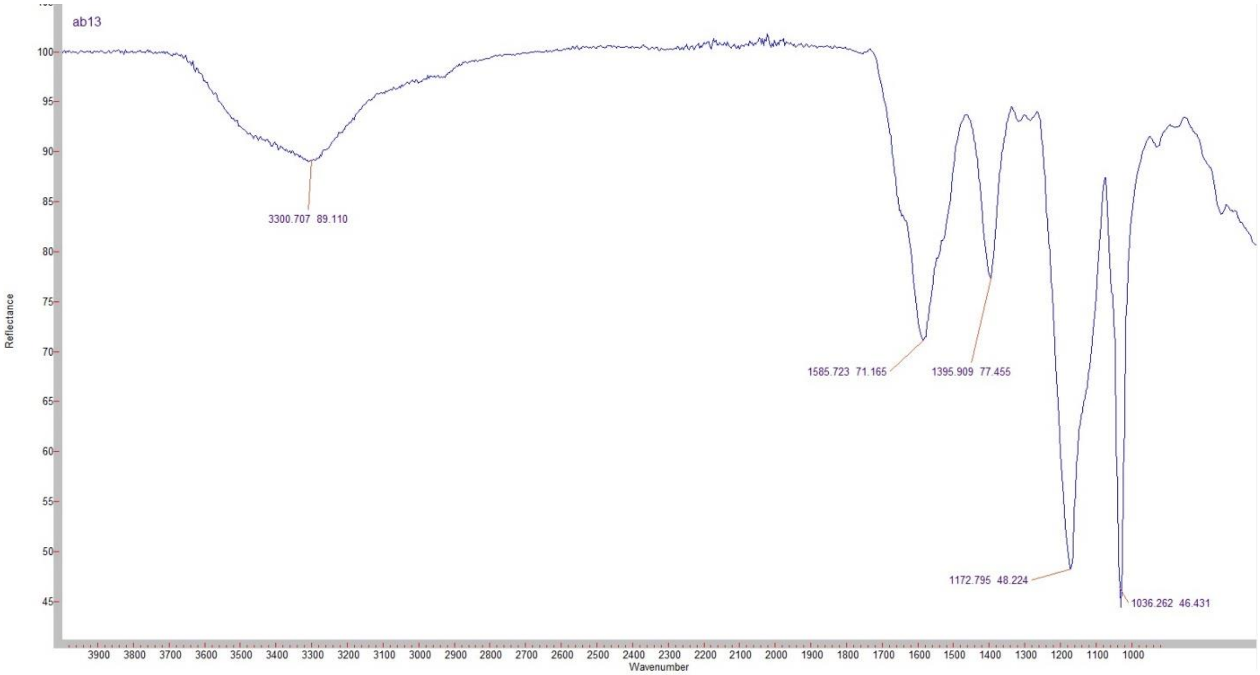

Figure 05. FTIR spectra for SI-5.

Appendix-B

NMR Spectra of Project 2

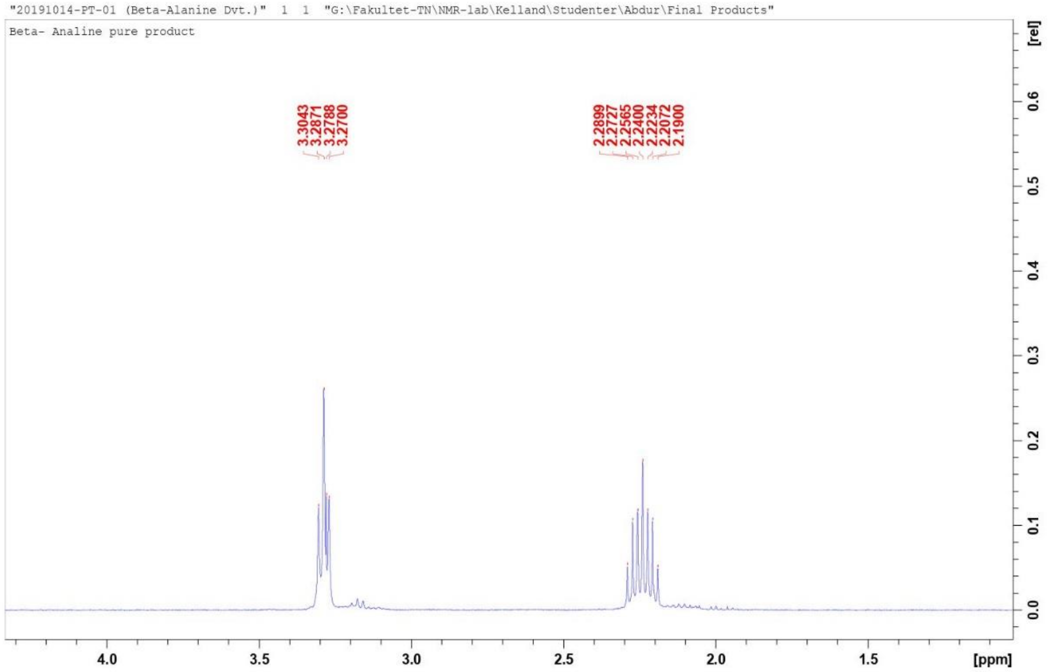

Figure 06. ^{1}H spectra for SI-6.

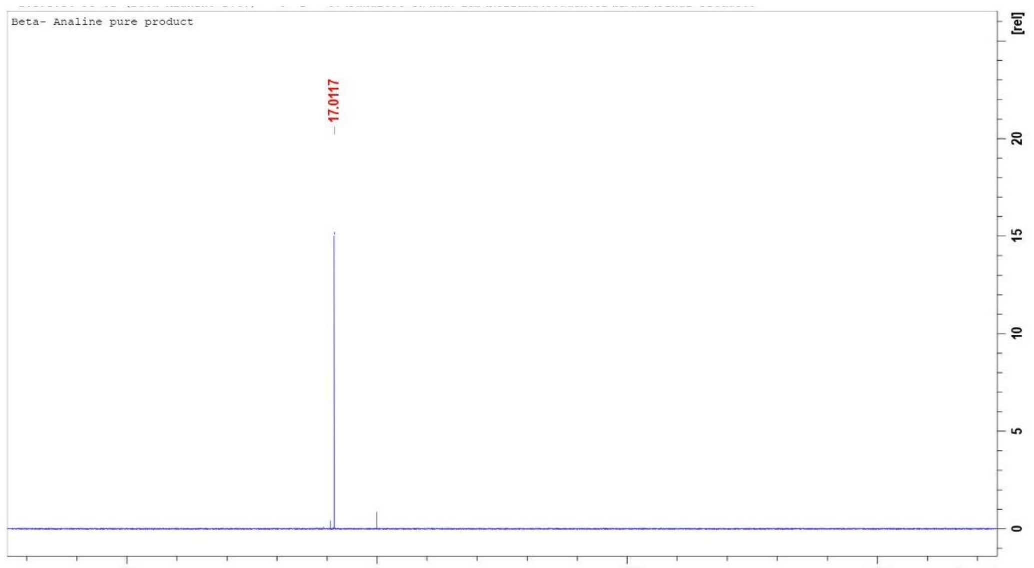

Figure 07. ^{31}P spectra for SI-6.

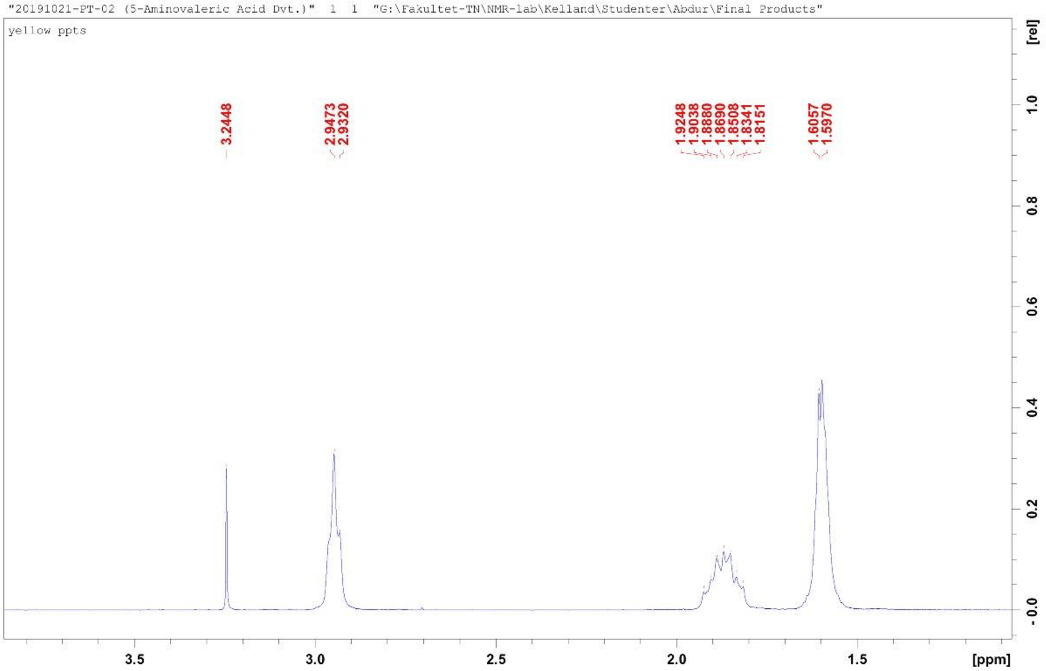

Figure 08. ^{1}H spectra for SI-7.

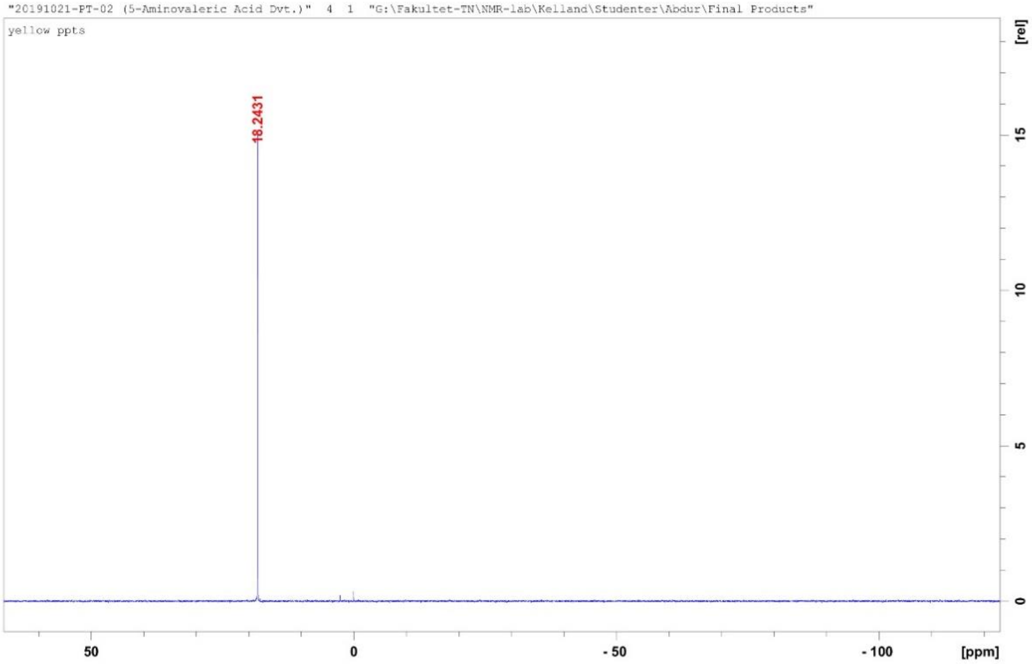

Figure 09. ^{31}P spectra for SI-7.

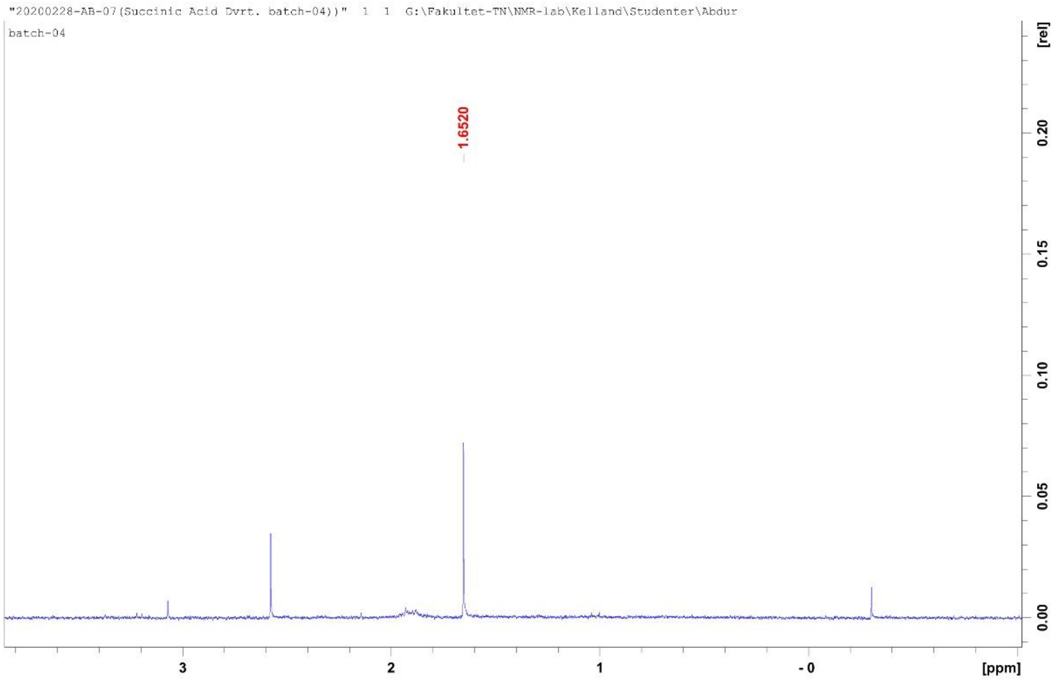

Figure 10. ^{1}H spectra for SI-8.

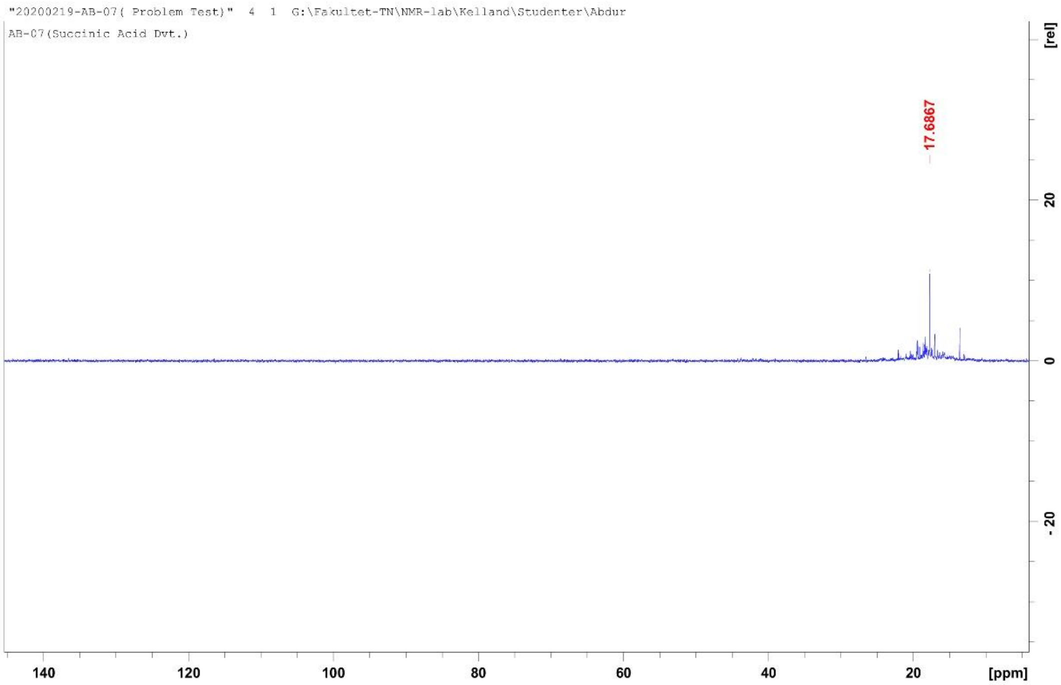

Figure 11. ^{31}P spectra for SI-8.

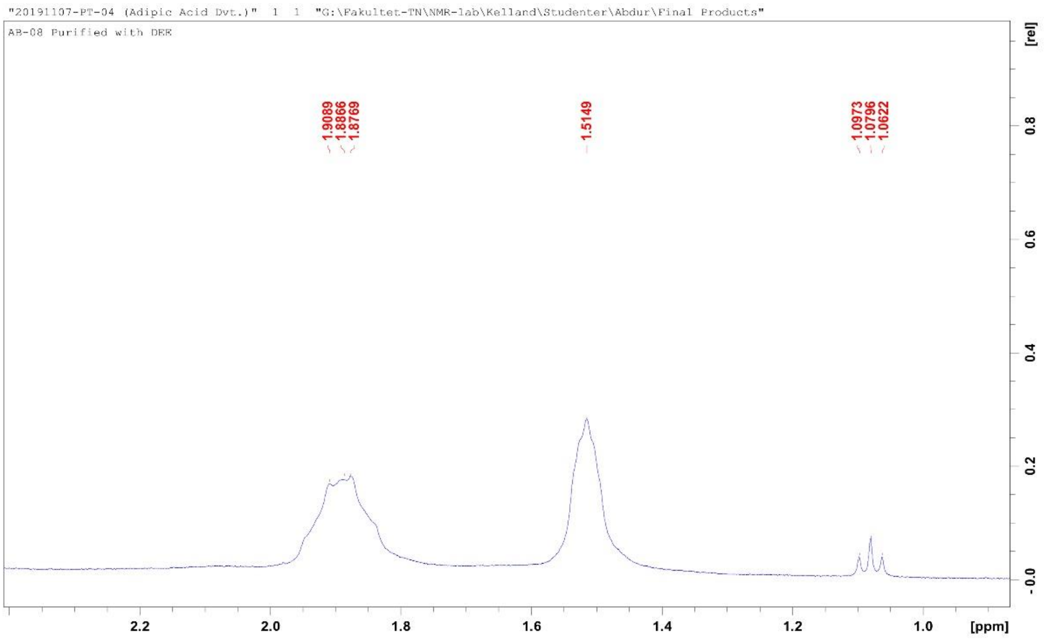

Figure 12. ^{1}H spectra for SI-9.

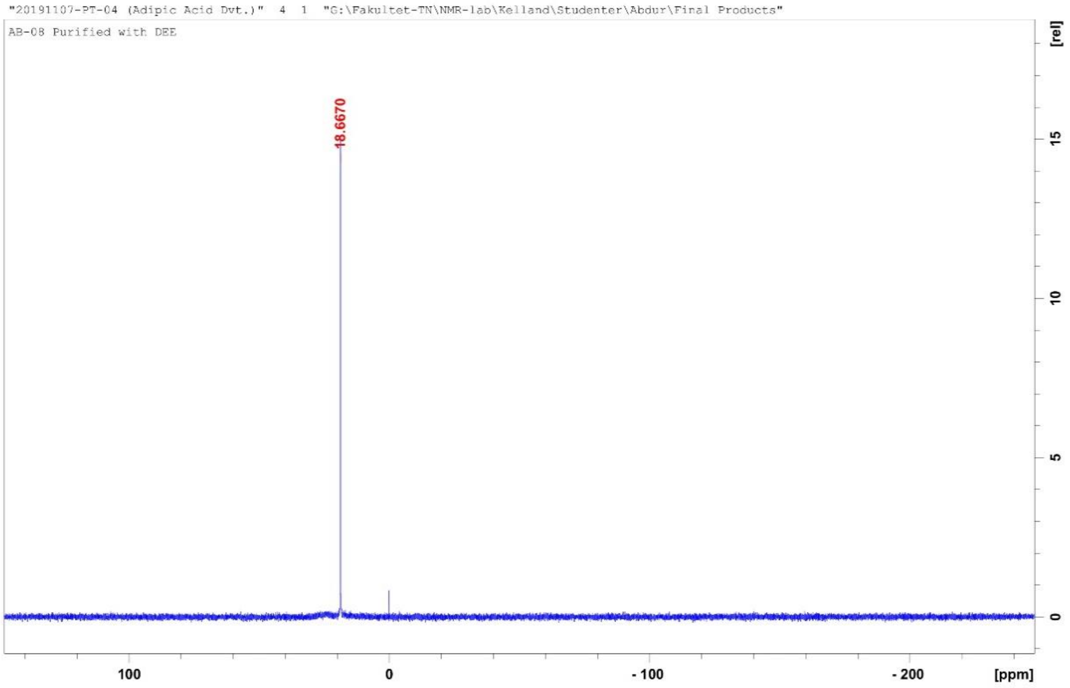

Figure 13. ^{31}P spectra for SI-9.

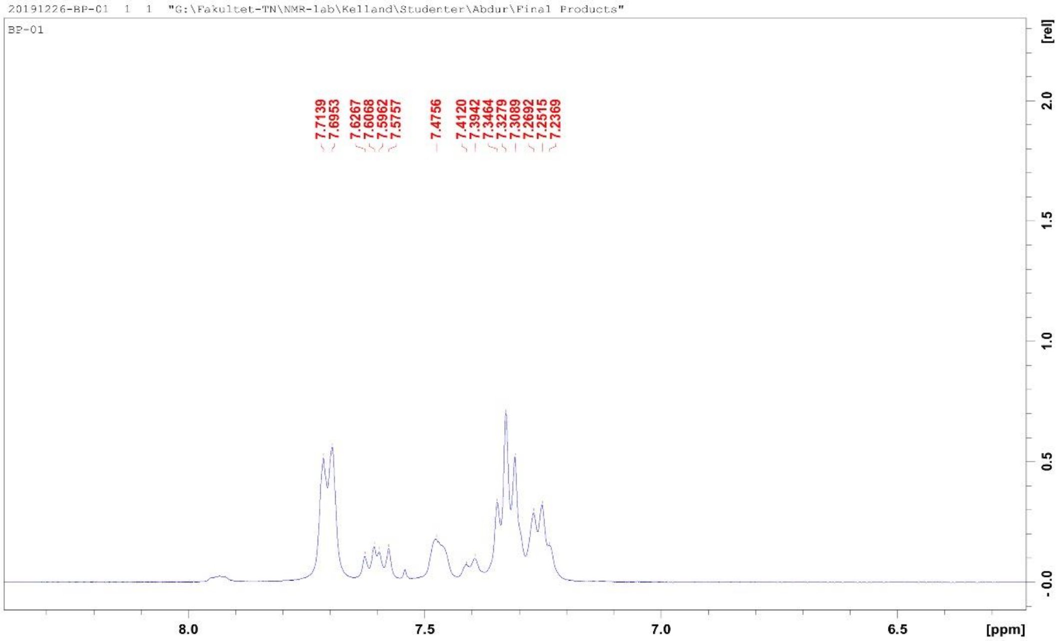

Figure 14. ^{1}H spectra for SI-10.

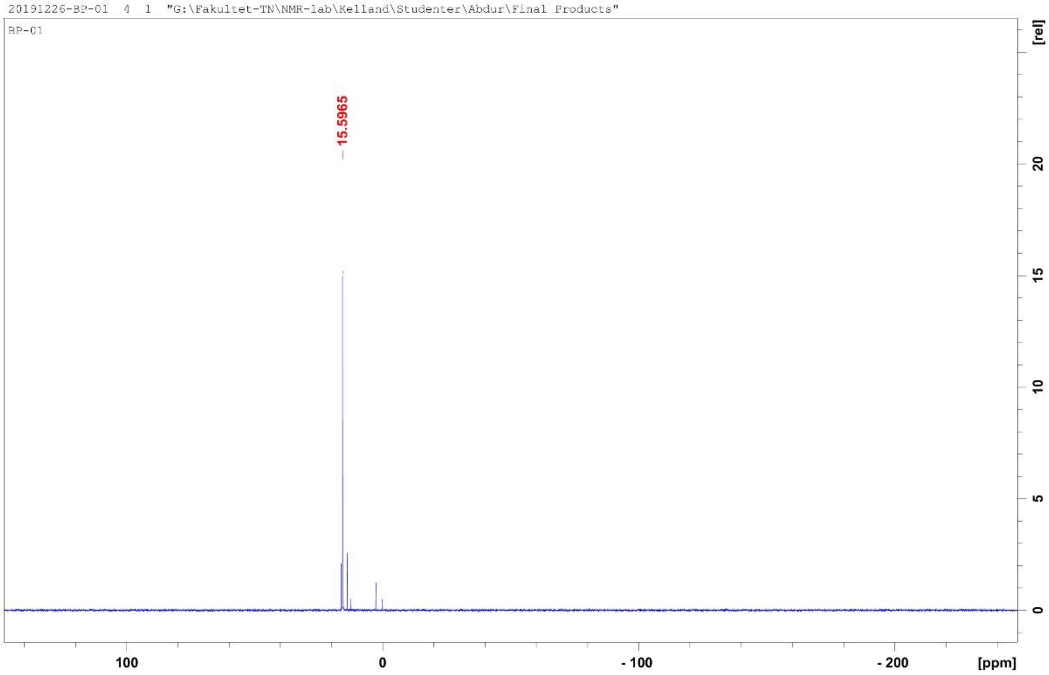

Figure 15. ^{31}P spectra for SI-10.

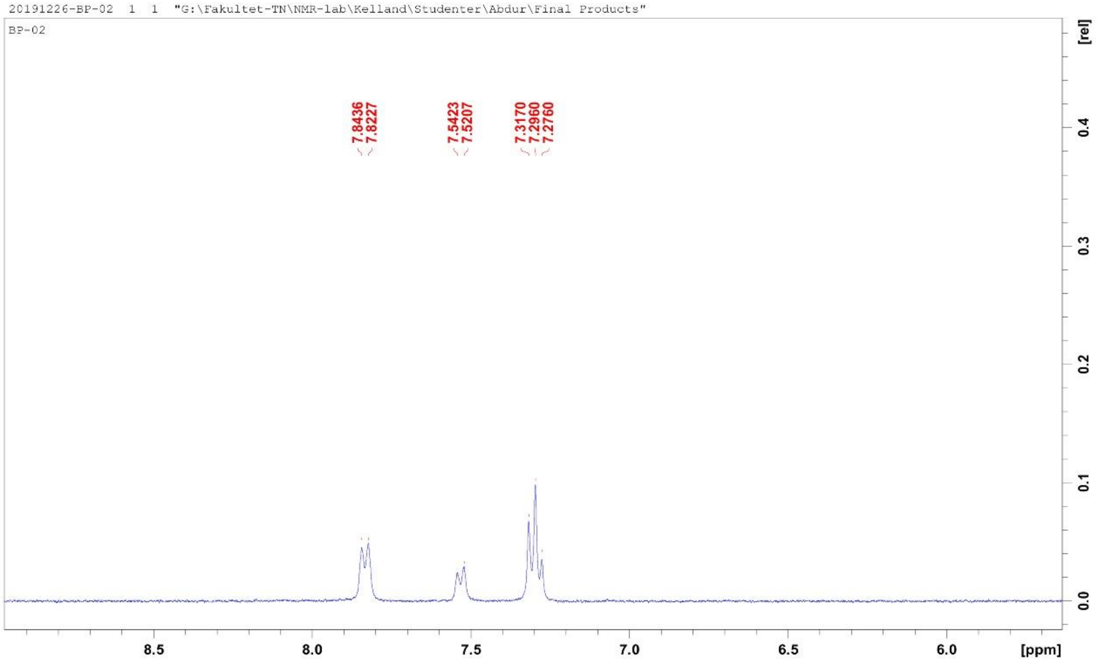

Figure 16. ^{1}H spectra for SI-11.

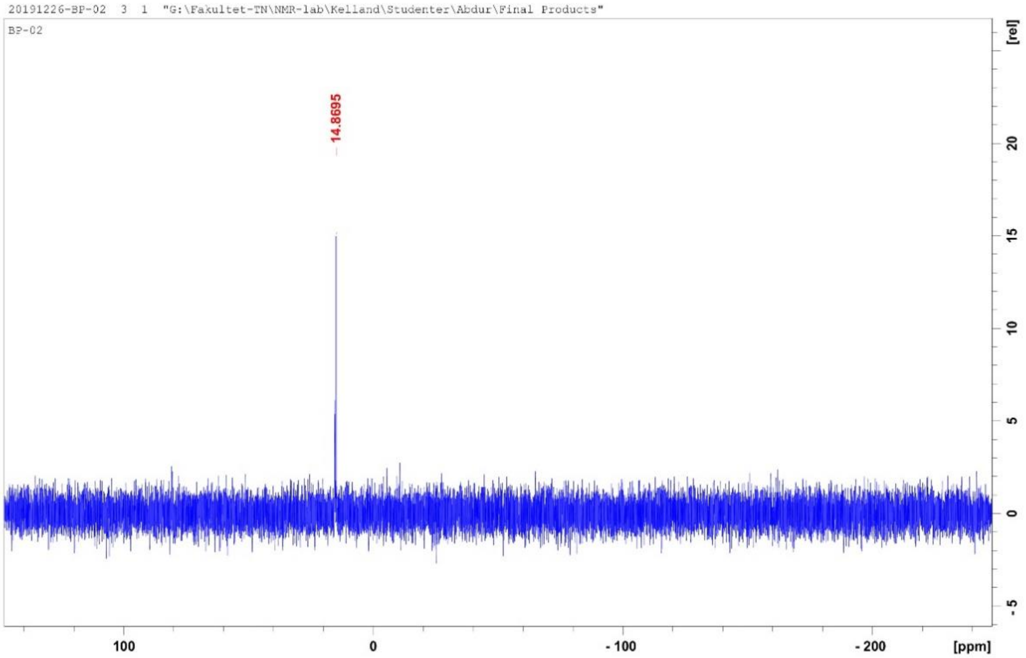

Figure 17. ^{31}P spectra for SI-11.

Appendix-C

FIC values for Project 1

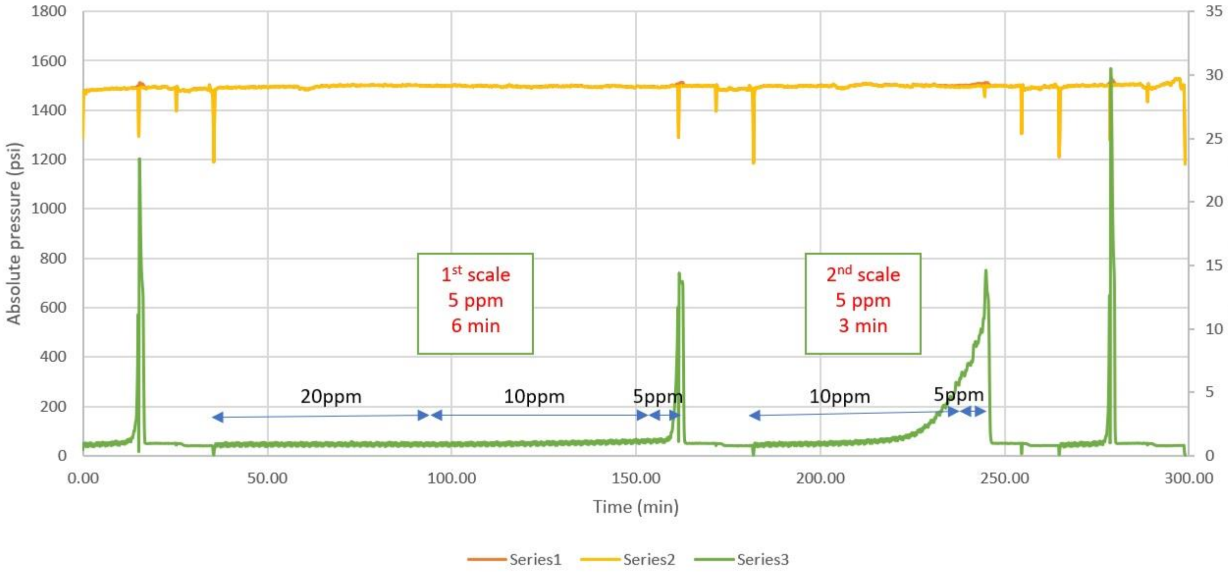

Figure 18. Failed inhibition concentrations of SI-1 for carbonate scale.

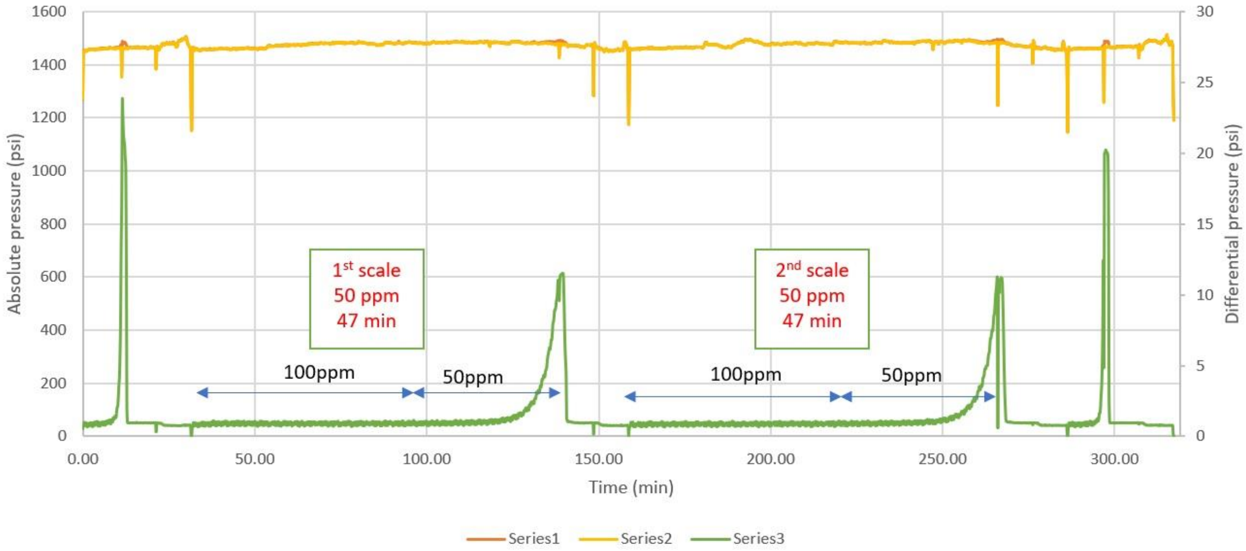

Figure 19. Failed inhibition concentrations of SI-1 for sulphate scale.

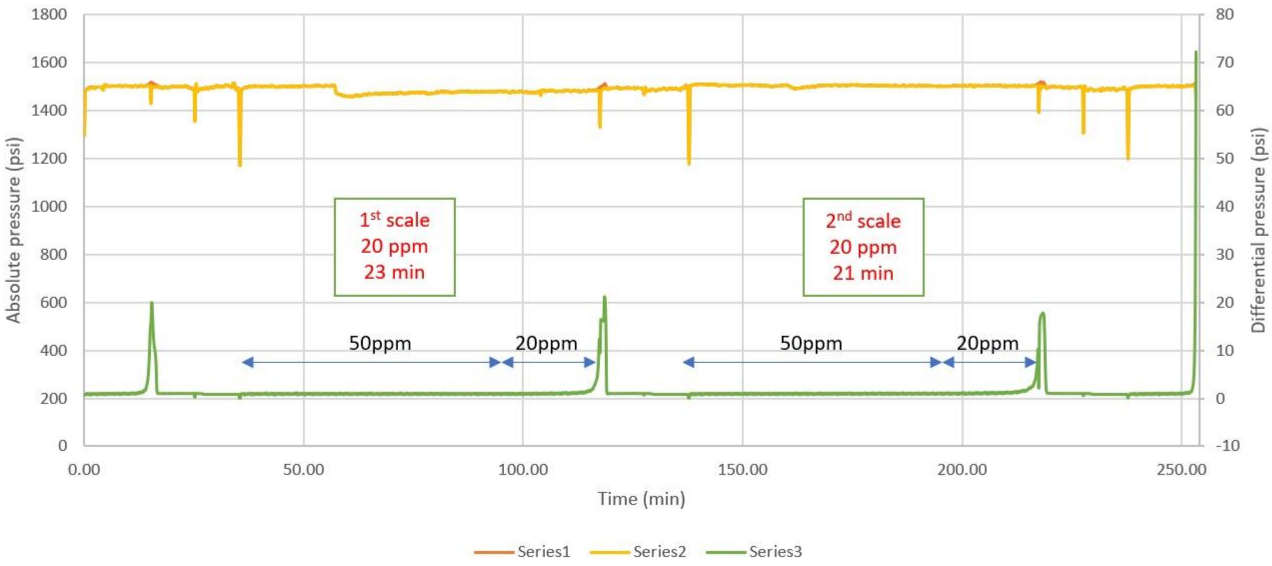

Figure 20. Failed inhibition concentrations of SI-1 for carbonate scale after thermal ageing.

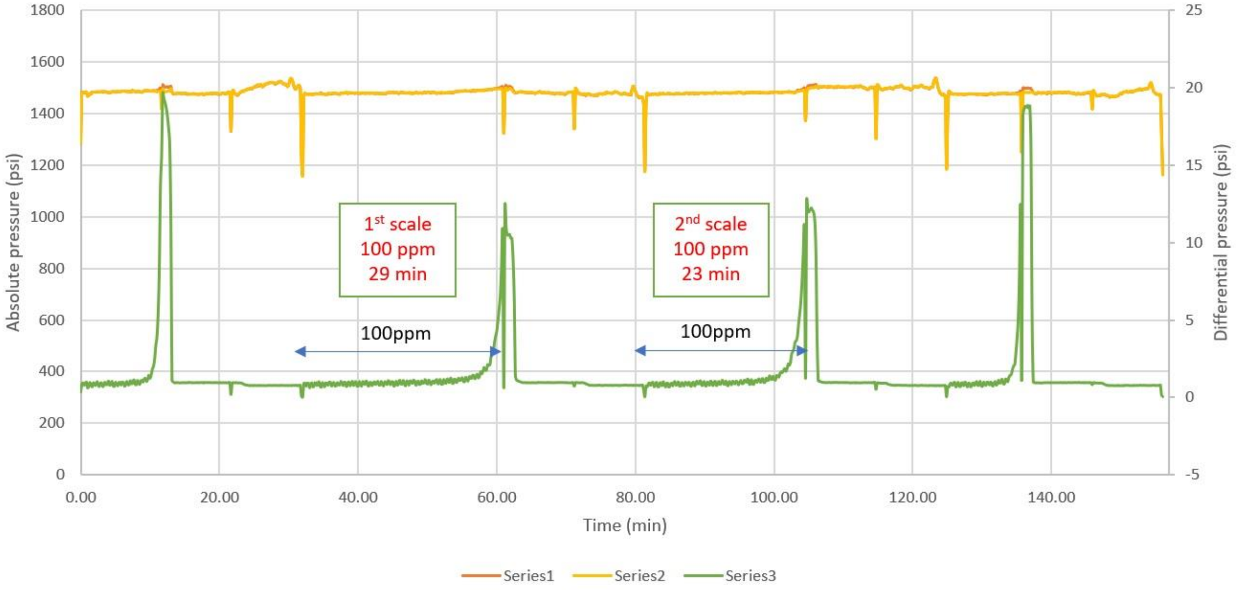

Figure 21. Failed inhibition concentrations of SI-1 for sulphate scale after thermal ageing.

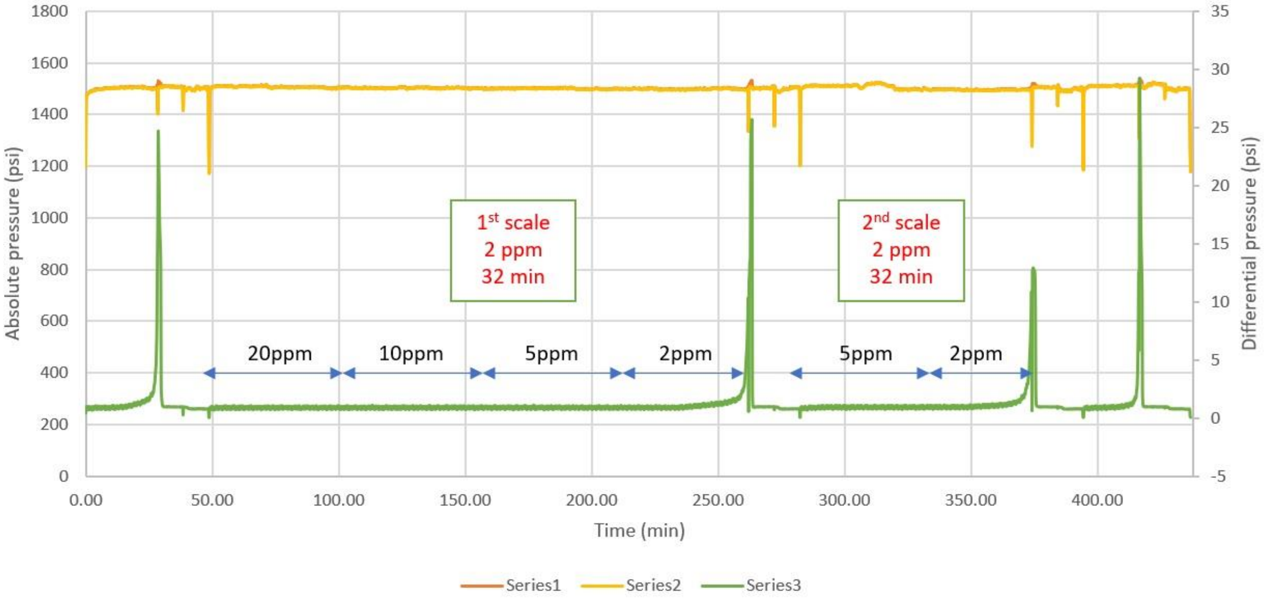

Figure 22. Failed inhibition concentrations of SI-3 for carbonate scale.

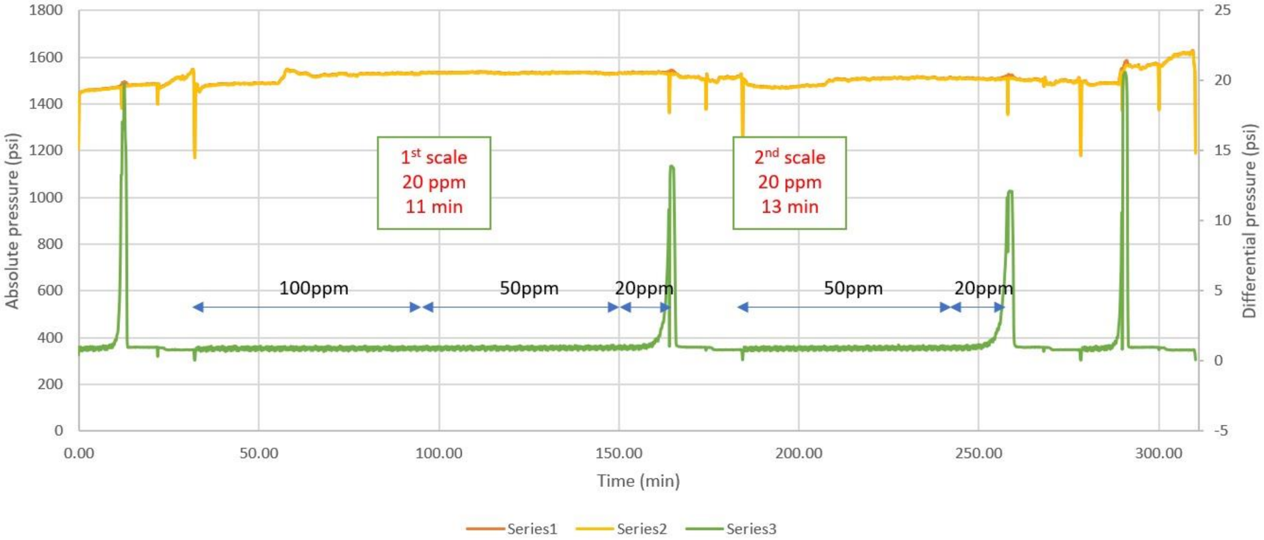

Figure 23. Failed inhibition concentrations of SI-3 for sulphate scale.

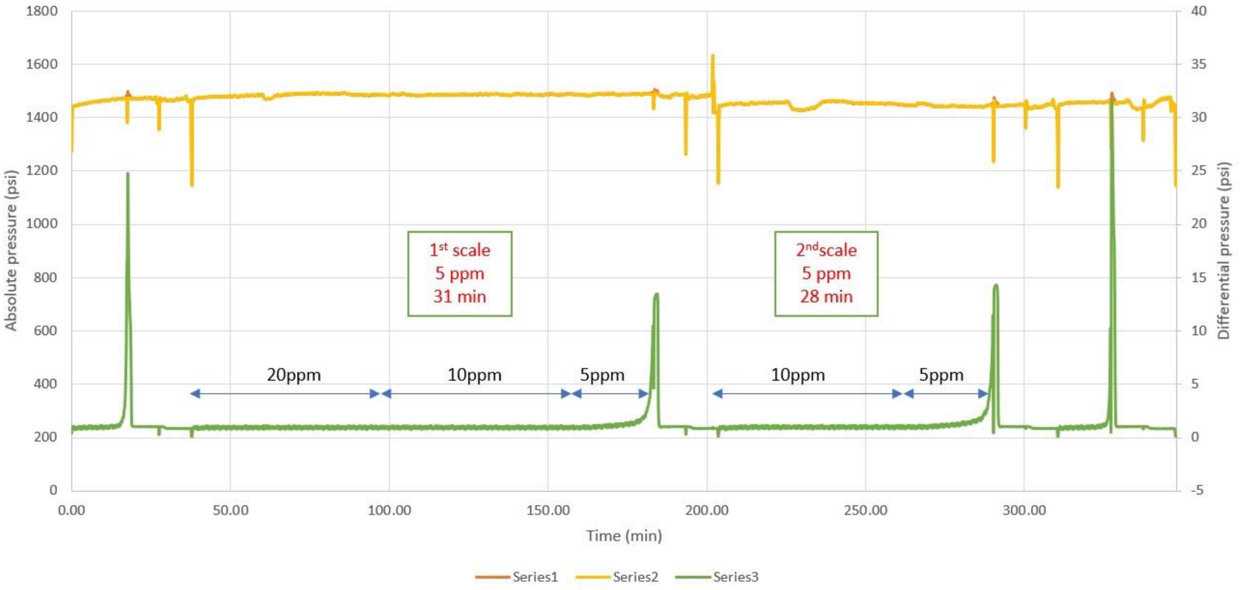

Figure 24. Failed inhibition concentrations of SI-3 for carbonate scale after thermal ageing.

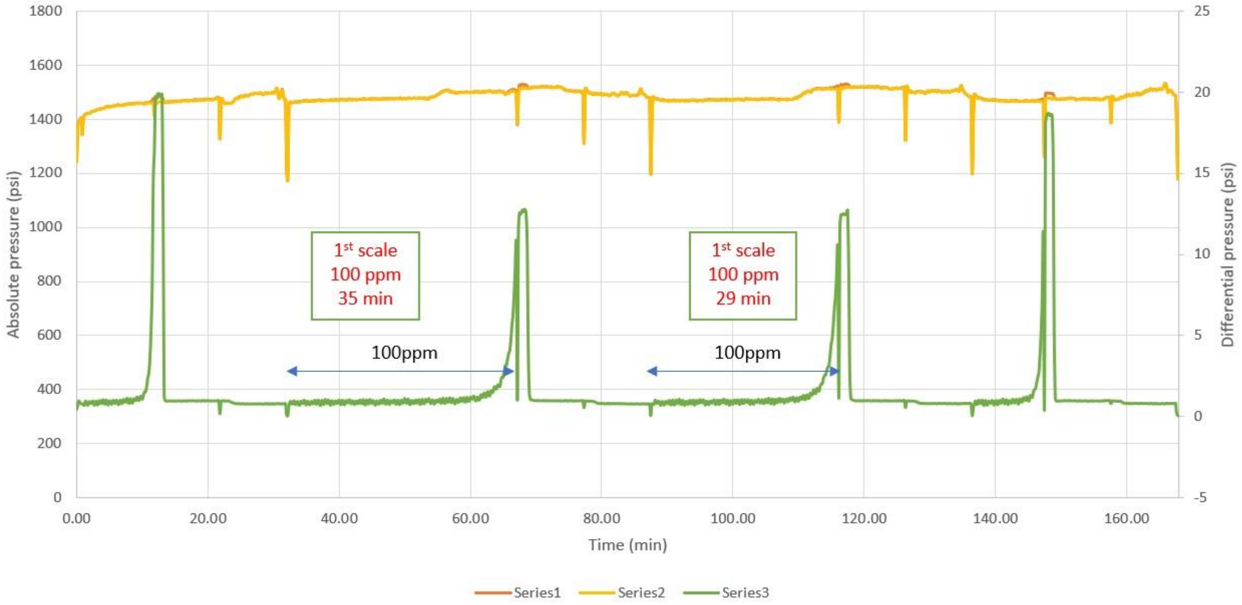

Figure 25. Failed inhibition concentrations of SI-3 for sulphate scale after thermal ageing.

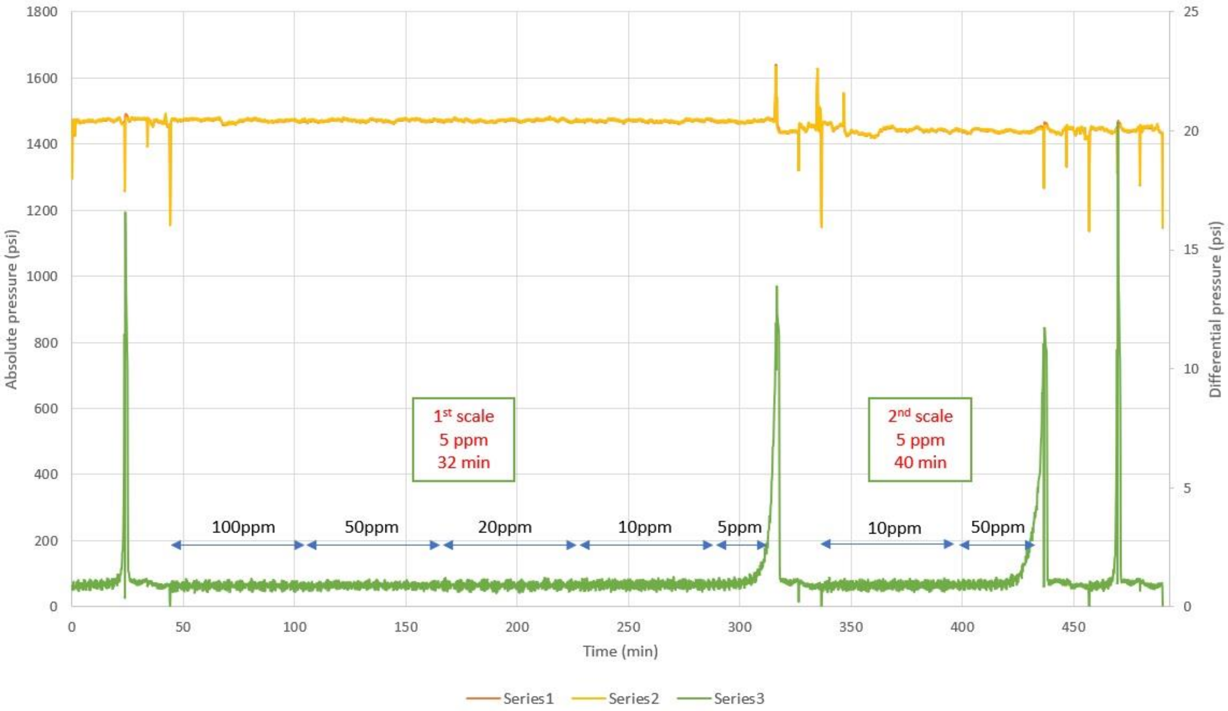

Figure 26. Failed inhibition concentrations of SI-4 for carbonate scale.

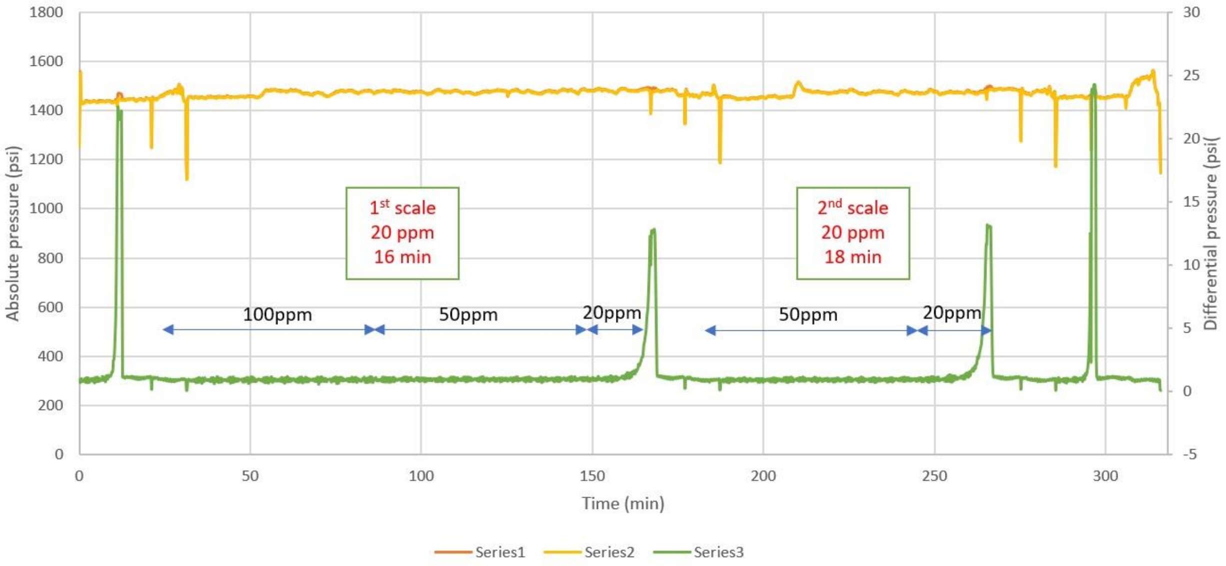

Figure 27. Failed inhibition concentrations of SI-4 for sulphate scale.

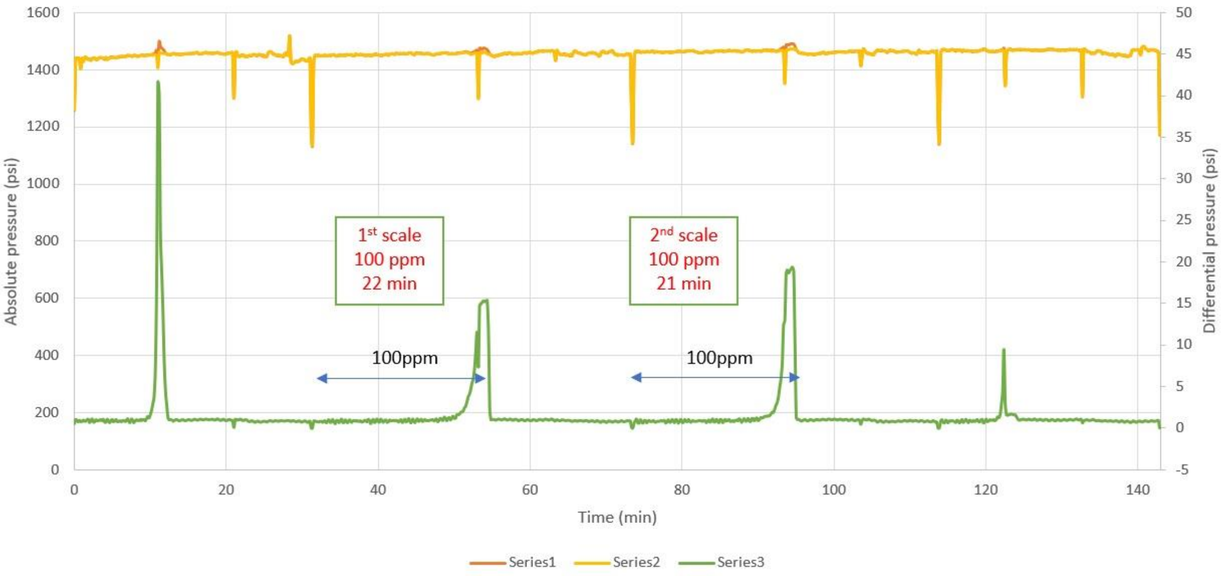

Figure 28. Failed inhibition concentrations of SI-4 for carbonate scale after thermal ageing.

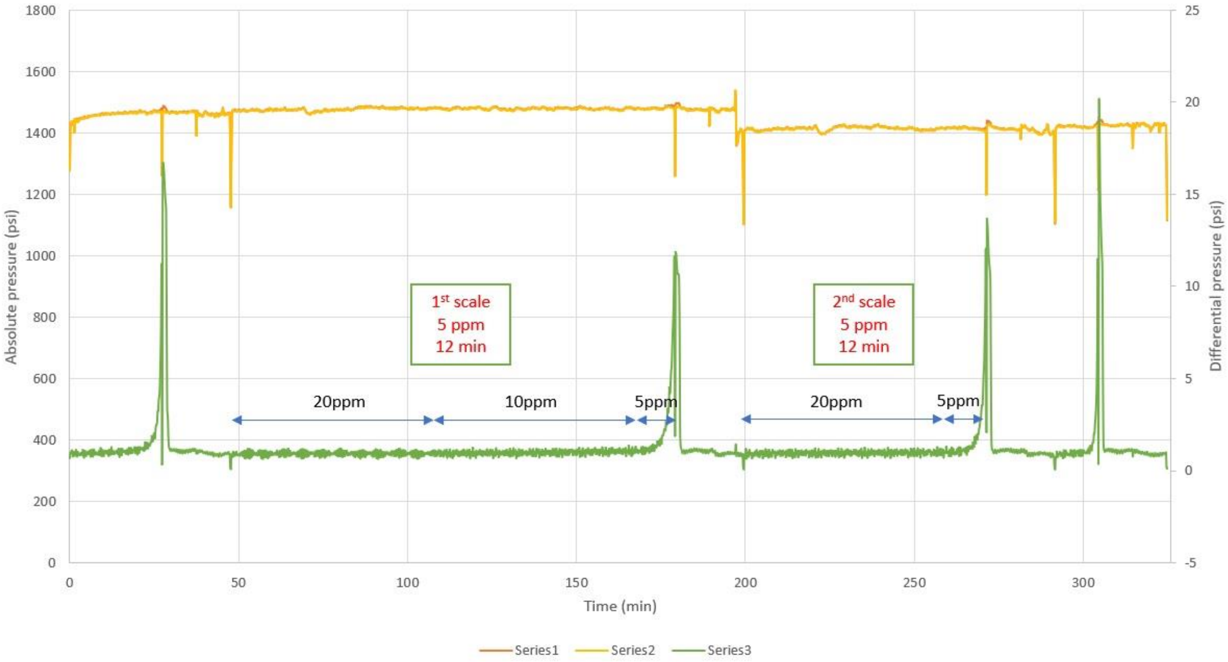

Figure 29. Failed inhibition concentrations of SI-5 for carbonate scale.

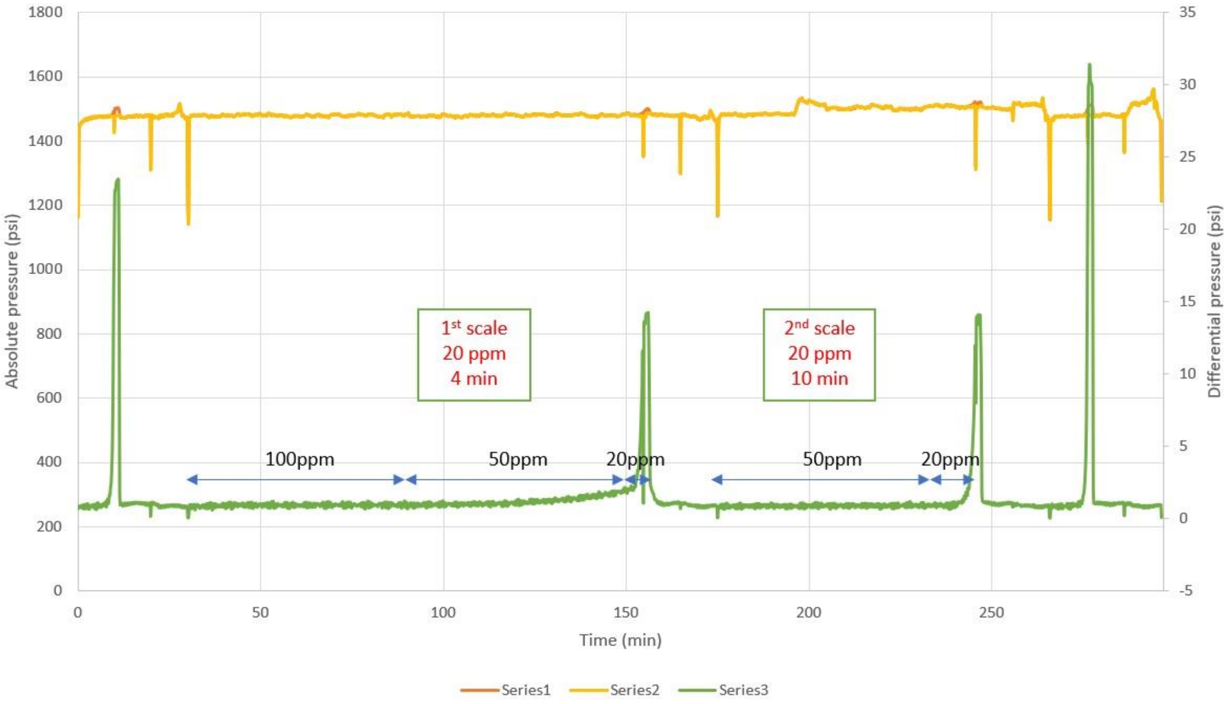

Figure 30. Failed inhibition concentrations SI-5 for sulphate scale.

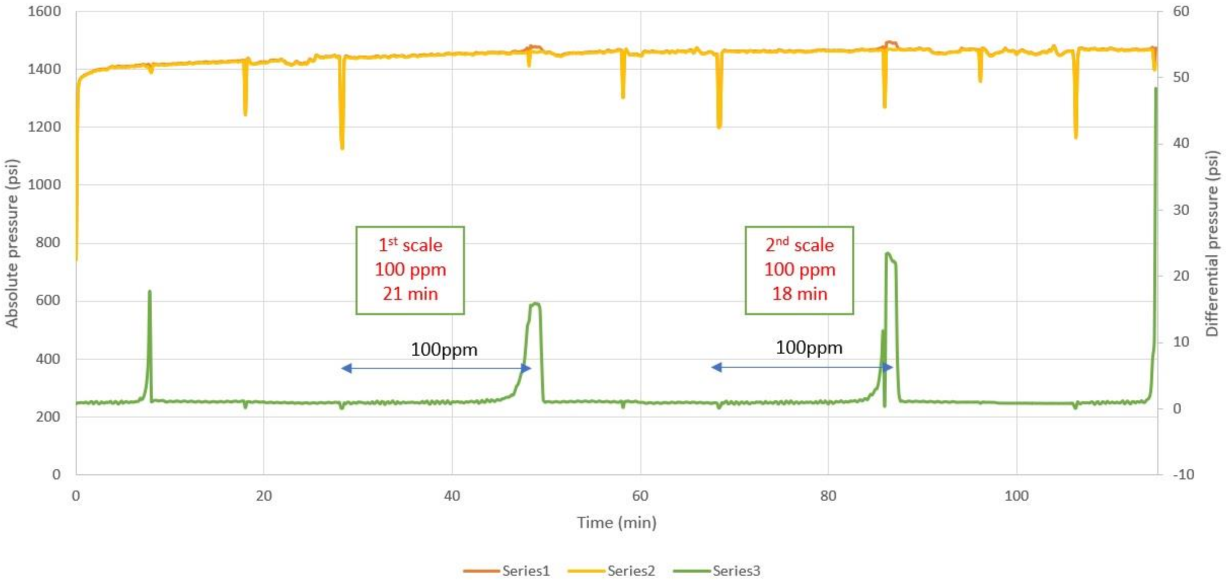

Figure 31. Failed inhibition concentrations of SI-5 for carbonate scale after thermal ageing.

Appendix-D

Calcium Compatibility Test Results of Project 1

Table 01. Calcium tolerance of SI-1(PASA) in 100ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Clear
10,000	Clear	Clear	Clear	Clear	Clear
50,000	Clear	Clear	Clear	Clear	Clear

Table 02. Calcium tolerance of SI-1(PASA) in 1000ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Clear
10,000	Clear	Clear	Clear	Clear	Clear
50,000	Clear	Clear	Clear	Clear	Clear

Table 03. Calcium tolerance of SI-1(PASA) in 10,000ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Clear
10,000	Clear	Clear	Clear	Clear	Clear
50,000	Clear	Clear	Clear	Clear	Clear

Table 04. Calcium tolerance of SI-3 in 100ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Clear
10,000	Clear	Cloudy	Cloudy	Cloudy	Cloudy
50,000	Clear	Cloudy	Cloudy	Cloudy	Precipitated

Table 05. Calcium tolerance of SI-3 in 1000ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear

1000	Clear	Clear	Clear	Cloudy	Cloudy
10,000	Clear	Cloudy	Cloudy	Cloudy	Cloudy
50,000	Clear	Cloudy	Cloudy	Cloudy	Precipitated

Table 06. Calcium tolerance of SI-3 in 10,000ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Clear
10,000	Clear	Clear	Clear	Clear	Clear
50,000	Clear	Clear	Clear	Clear	Clear

Table 07. Calcium tolerance of SI-4 in 100ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Clear
10,000	Clear	Clear	Clear	Clear	Clear
50,000	Clear	Clear	Clear	Clear	Clear

Table 08. Calcium tolerance of SI-4 in 1000ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Clear
10,000	Clear	Clear	Clear	Clear	Clear
50,000	Clear	Clear	Clear	Clear	Clear

Table 09. Calcium tolerance of SI-4 in 10,000ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Clear
10,000	Clear	Clear	Clear	Clear	Clear
50,000	Clear	Clear	Clear	Clear	Clear

Table 10. Calcium tolerance of SI-5 in 100ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear

1000	Clear	Clear	Clear	Clear	Clear
10,000	Clear	Clear	Clear	Clear	Clear
50,000	Clear	Clear	Clear	Clear	Clear

Table 11. Calcium tolerance of SI-5 in 1000ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Clear
10,000	Clear	Clear	Clear	Clear	Clear
50,000	Clear	Clear	Clear	Clear	Clear

Table 12. Calcium tolerance of SI-5 in 10,000ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Clear
10,000	Clear	Clear	Clear	Clear	Clear
50,000	Clear	Clear	Clear	Clear	Clear

Appendix-E

FIC Values for Project 2

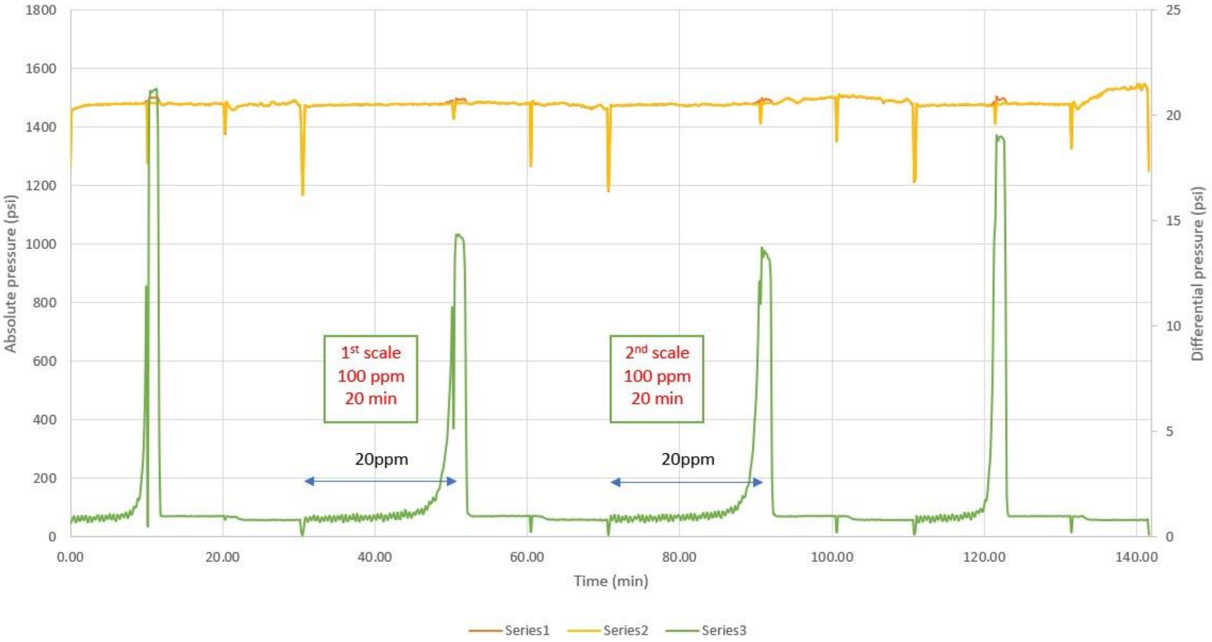

Figure 32. Failed inhibition concentrations of SI-6 for sulphate scale.

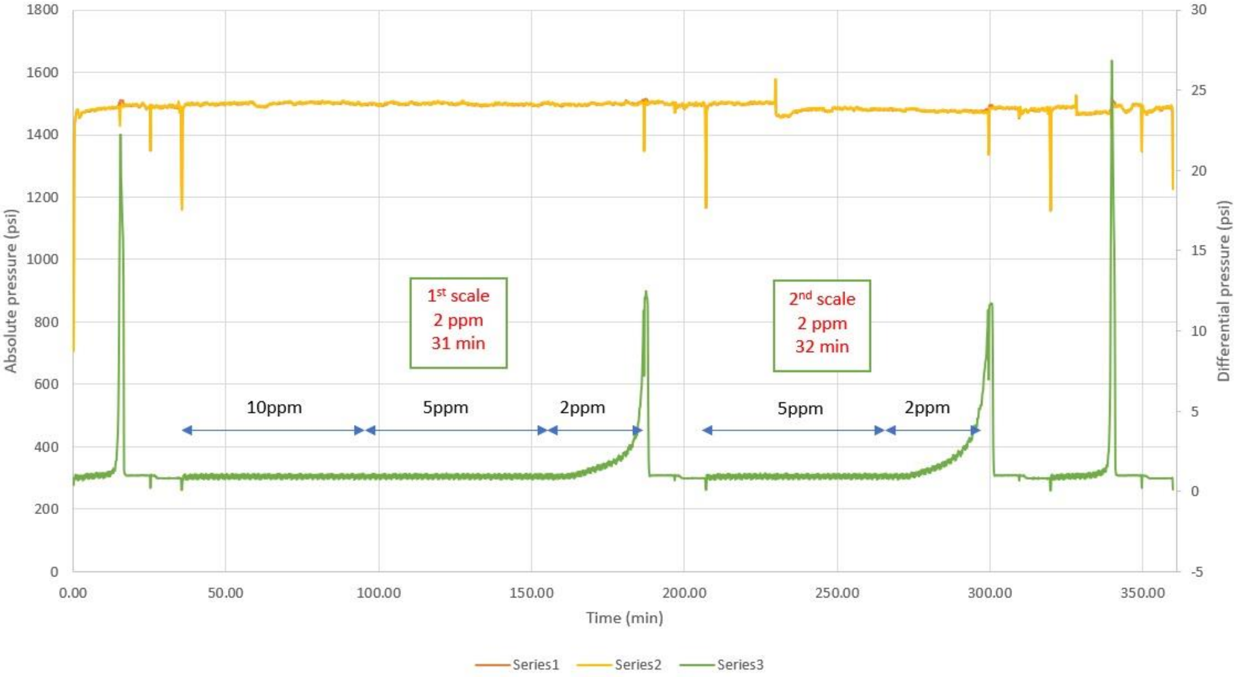

Figure 33. Failed inhibition concentrations of SI-6 for carbonate scale after thermal ageing.

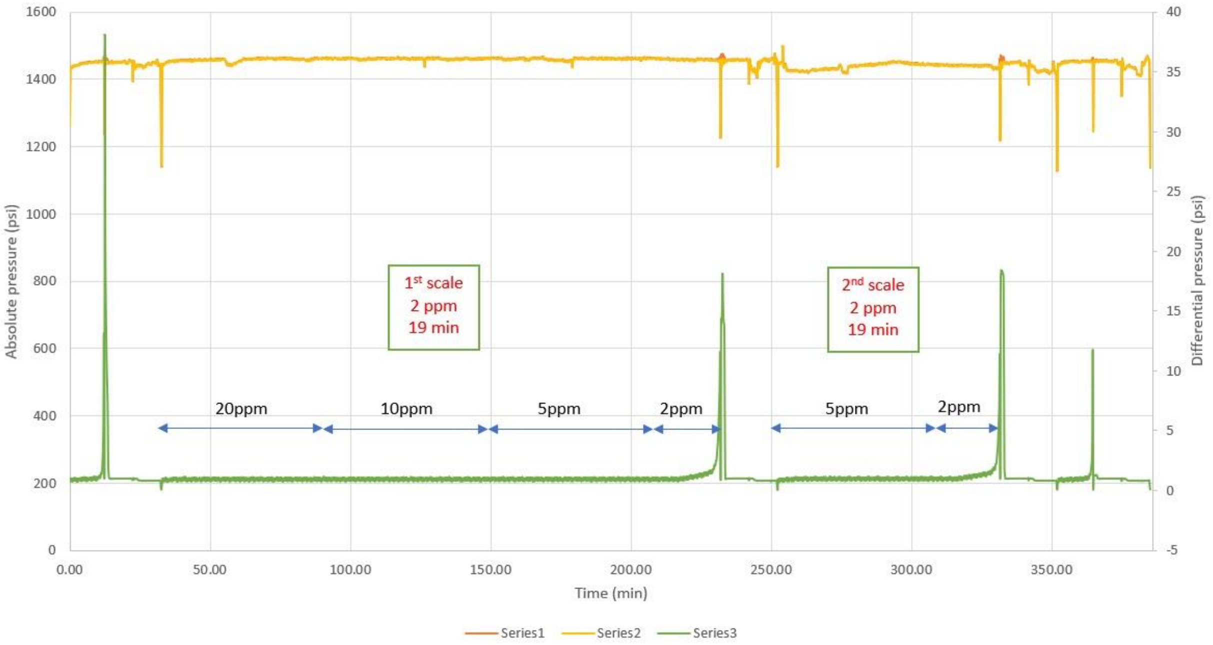

Figure 34. Failed inhibition concentrations of SI-7 for carbonate scale.

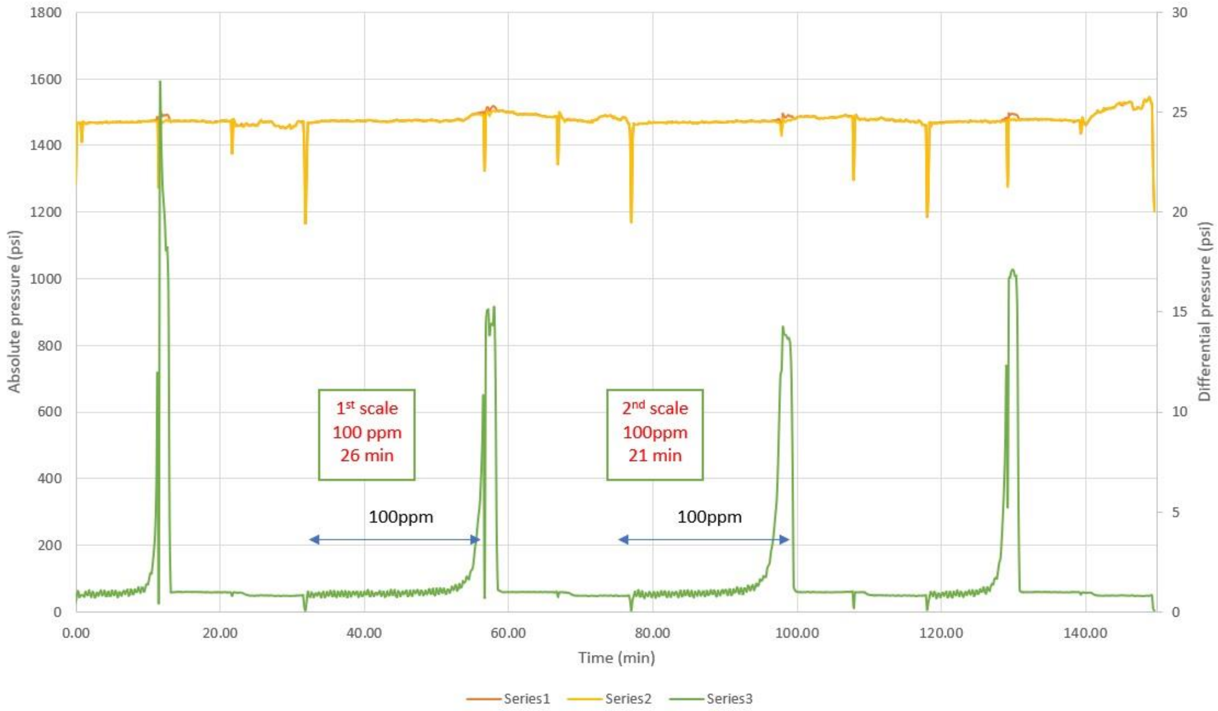

Figure 35. Failed inhibition concentrations of SI-7 for sulphate scale.

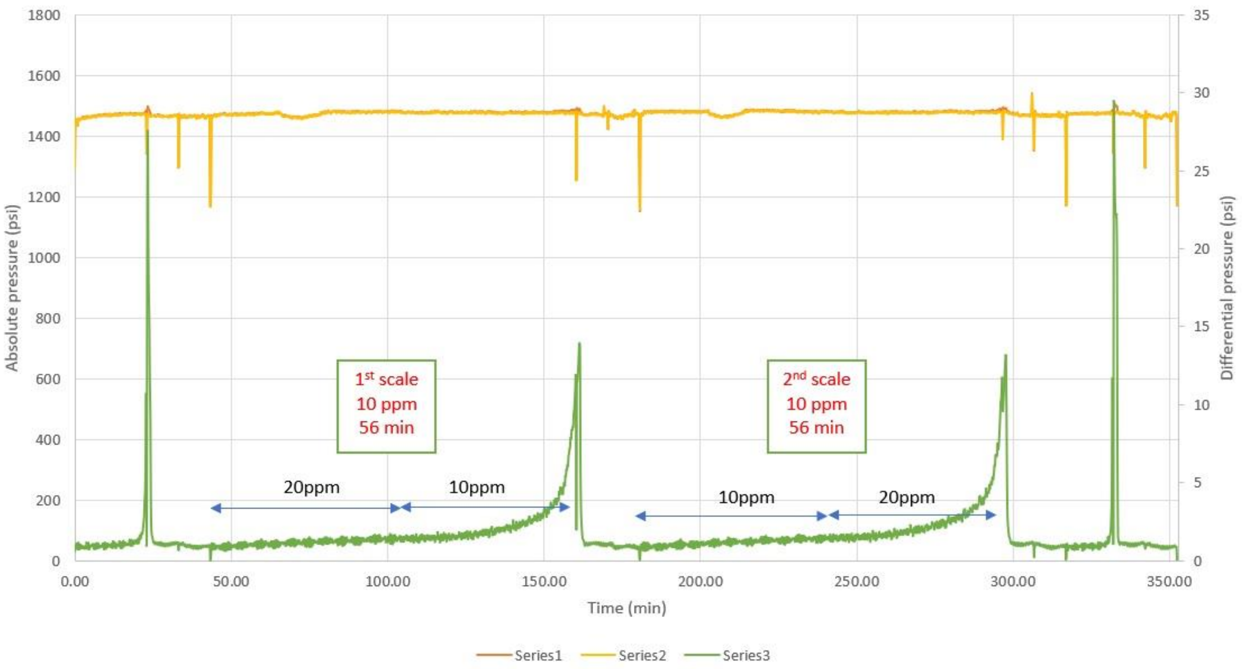

Figure 36. Failed inhibition concentrations of SI-8 for carbonate scale.

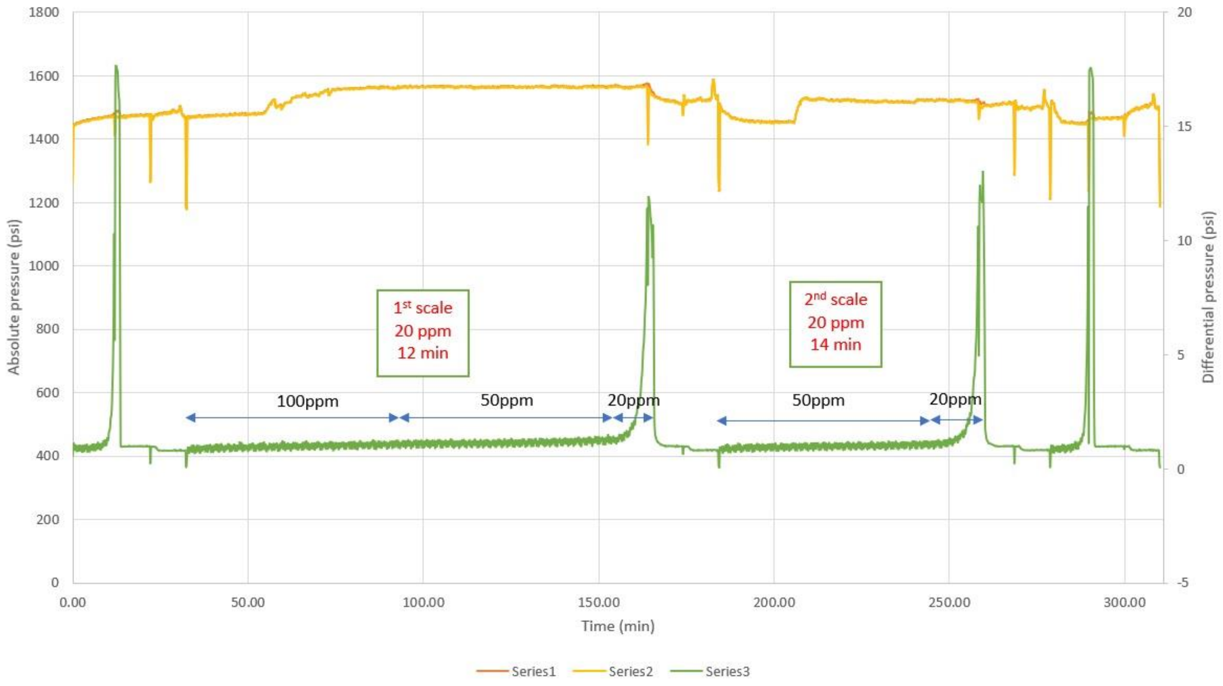

Figure 37. Failed inhibition concentrations of SI-8 for sulphate scale.

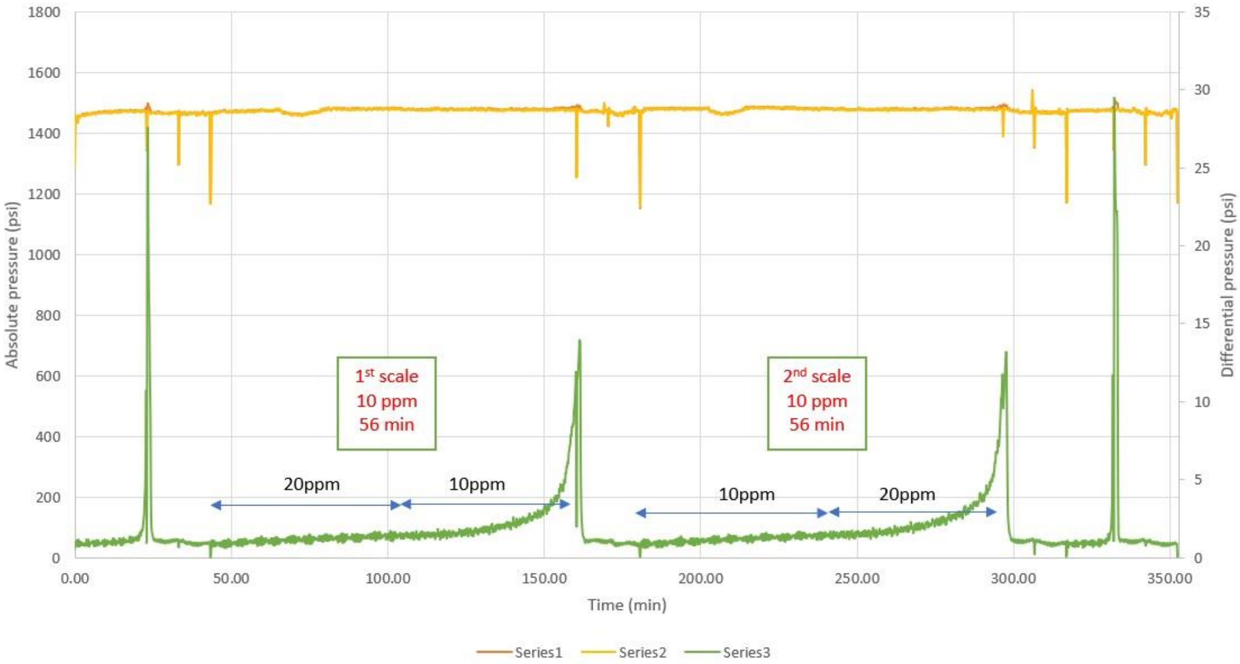

Figure 38. Failed inhibition concentrations of SI-8 for carbonate scale after thermal ageing.

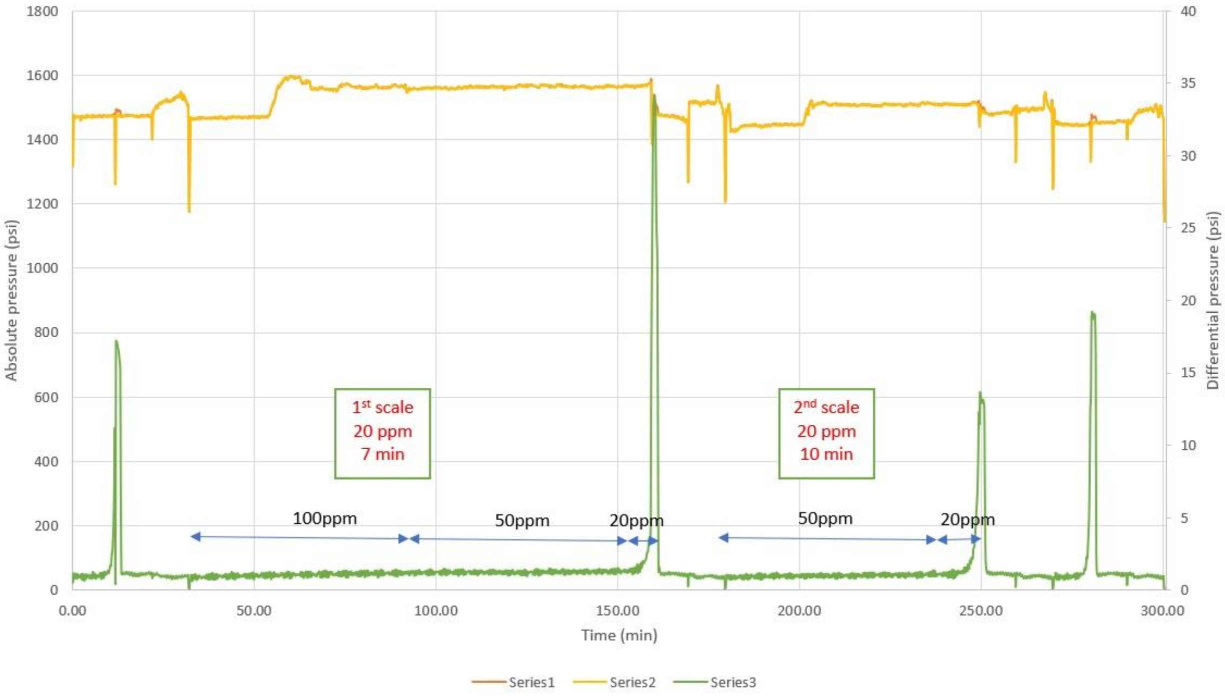

Figure 39. Failed inhibition concentrations of SI-8 for sulphate scale after thermal ageing.

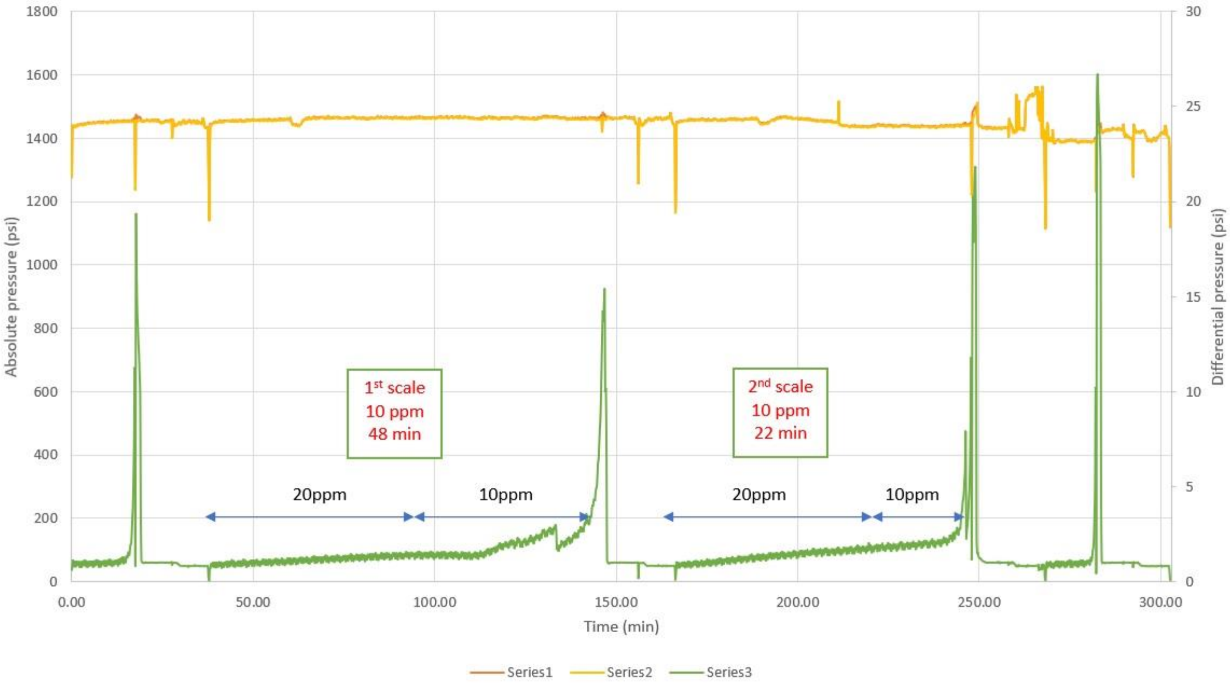

Figure 40. Failed inhibition concentrations of SI-9 for carbonate scale.

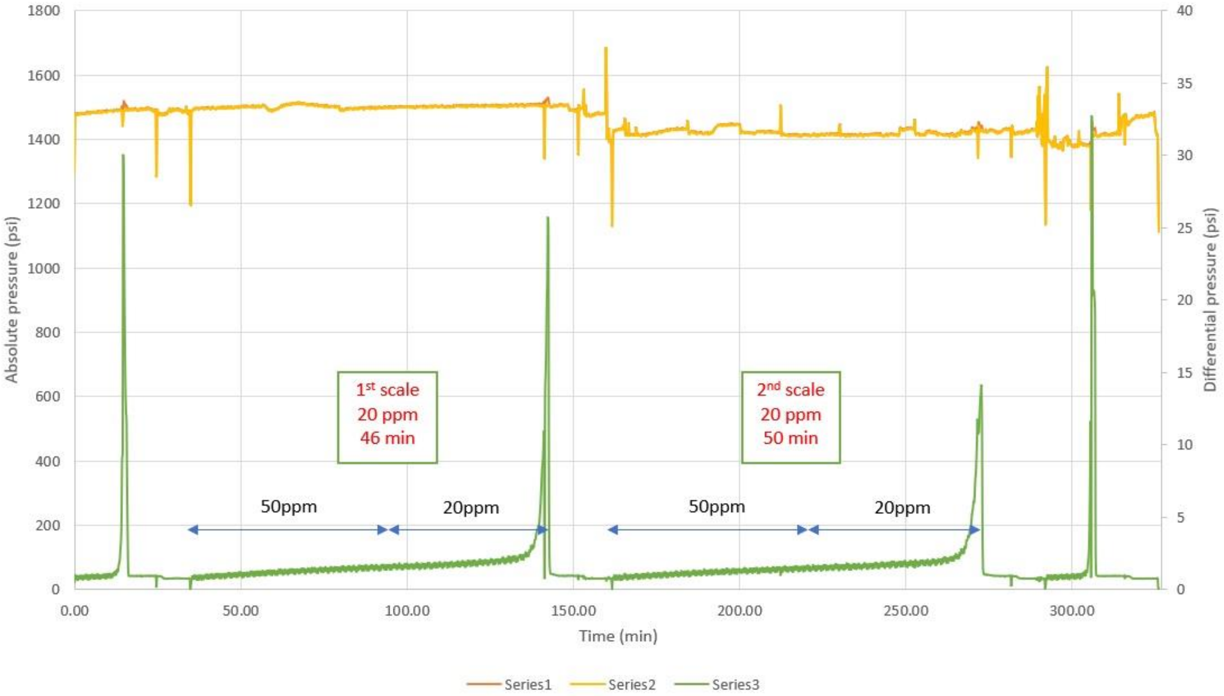

Figure 41. Failed inhibition concentrations of SI-9 for carbonate scale after thermal ageing.

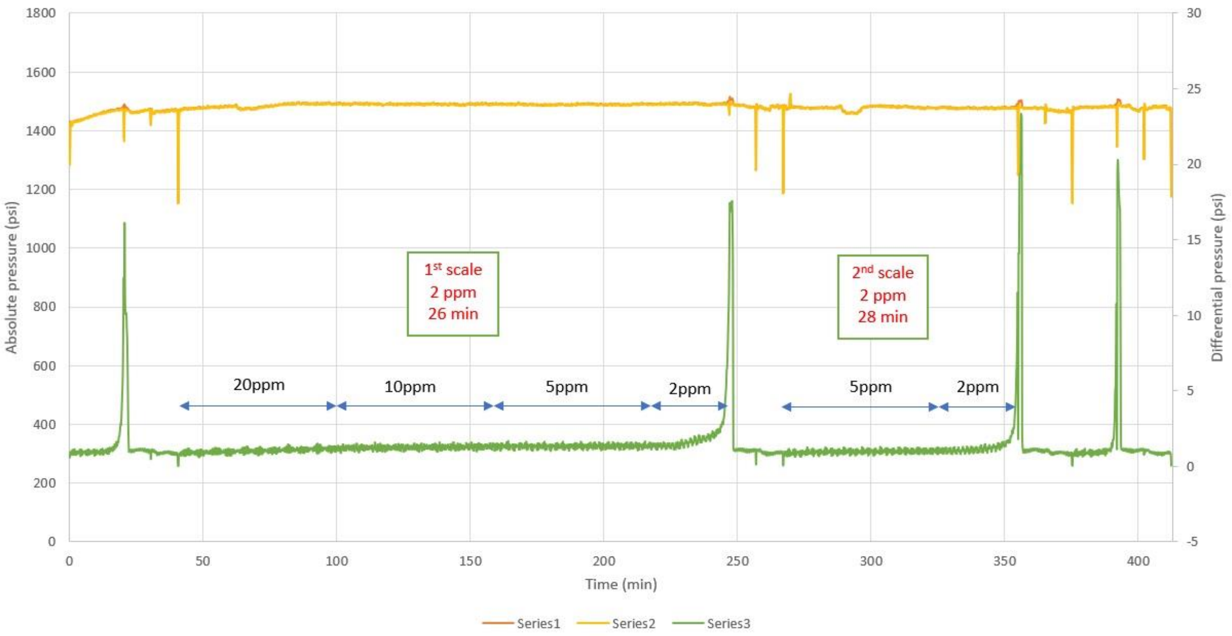

Figure 42. Failed inhibition concentrations of SI-10 for carbonate scale.

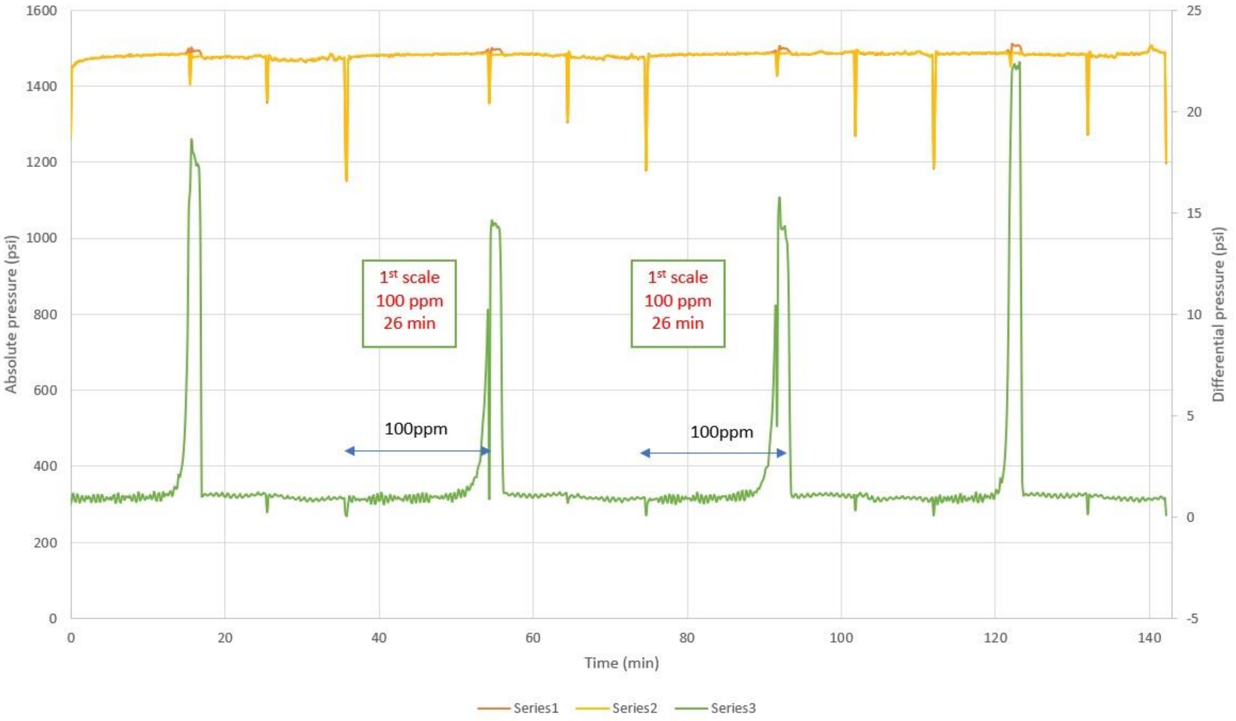

Figure 43. Failed inhibition concentrations of SI-10 for sulphate scale.

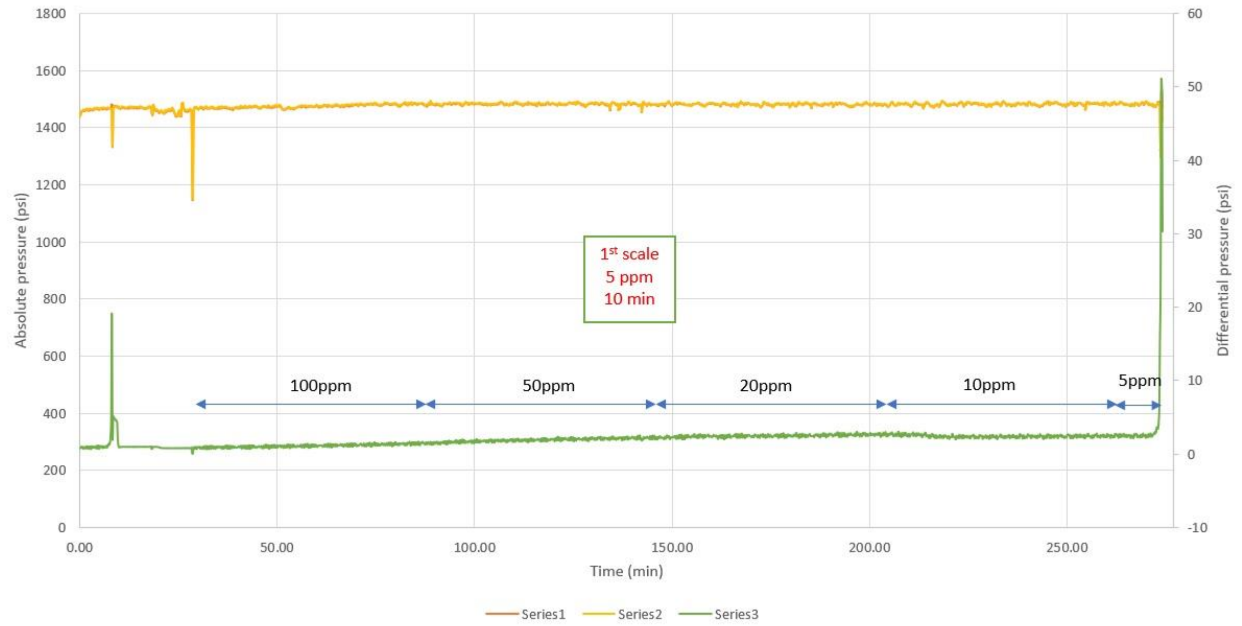

Figure 44. Failed inhibition concentrations of SI-10 for carbonate scale after thermal ageing.

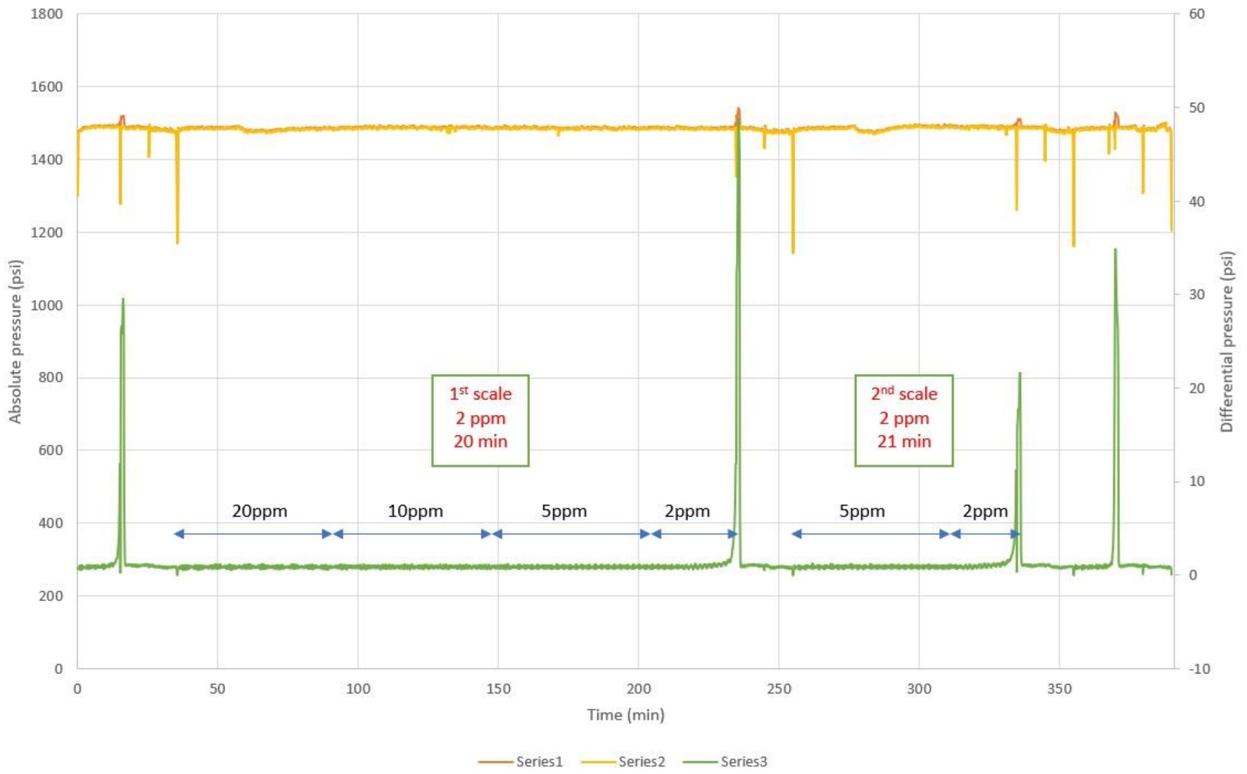

Figure 45. Failed inhibition concentrations of SI-11 for carbonate scale.

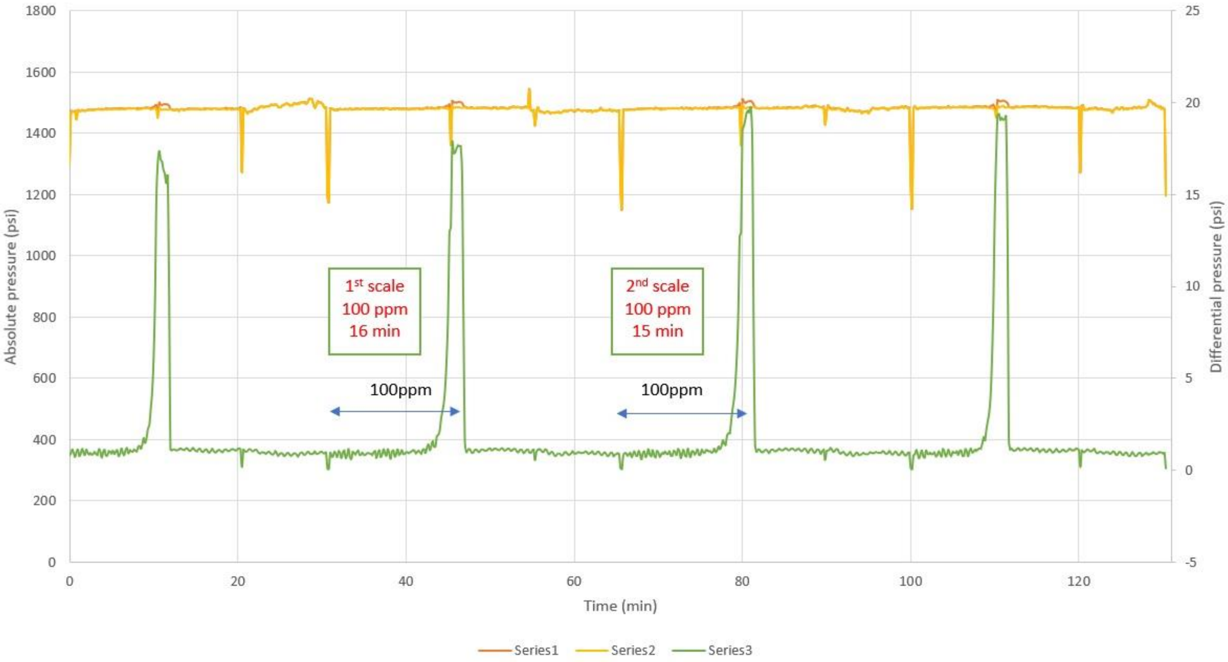

Figure 46. Failed inhibition concentrations of SI-11 for sulphate scale.

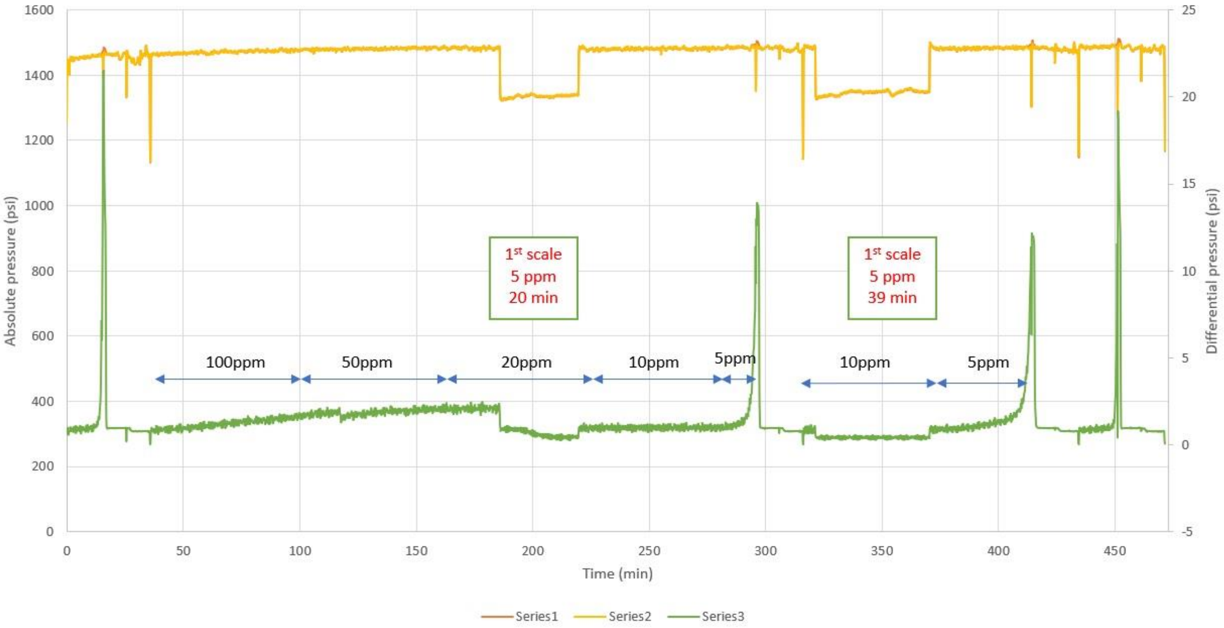

Figure 47. Failed inhibition concentrations of SI-11 for carbonate scale after thermal ageing.

Appendix-F

Compatibility Test for Project 2

Table 13. Calcium tolerance of SI-6 in 100ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Clear
10,000	Clear	Clear	Cloudy	Cloudy	Cloudy
50,000	Precipitated	Precipitated	Precipitated	Precipitated	Precipitated

Table 14. Calcium tolerance of SI-6 in 1000ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Clear
10,000	Precipitated	Precipitated	Precipitated	Precipitated	Precipitated
50,000	Precipitated	Precipitated	Precipitated	Precipitated	Precipitated

Table 15. Calcium tolerance of SI-6 in 10,000ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours

100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Clear
10,000	Precipitated	Precipitated	Precipitated	Precipitated	Precipitated
50,000	Precipitated	Precipitated	Precipitated	Precipitated	Precipitated

Table 16. Calcium tolerance of SI-7 in 100ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Precipitated
10,000	Clear	Cloudy	Cloudy	Precipitated	Precipitated
50,000	Precipitated	Precipitated	Precipitated	Precipitated	Precipitated

Table 17. Calcium tolerance of SI-7 in 1000ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Precipitated
10,000	Clear	Cloudy	Cloudy	Precipitated	Precipitated
50,000	Precipitated	Precipitated	Precipitated	Precipitated	Precipitated

Table 18. Calcium tolerance of SI-7 in 10,000ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Precipitated
10,000	Clear	Cloudy	Cloudy	Precipitated	Precipitated
50,000	Precipitated	Precipitated	Precipitated	Precipitated	Precipitated

Table 19. Calcium tolerance of SI-8 in 100ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Clear
10,000	Clear	Clear	Clear	Clear	Clear
50,000	Clear	Clear	Clear	Clear	Clear

Table 20. Calcium tolerance of SI-8 in 1000ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Precipitated	Precipitated	Precipitated	Precipitated	Precipitated

1000	Precipitated	Precipitated	Precipitated	Precipitated	Precipitated
10,000	Precipitated	Precipitated	Precipitated	Precipitated	Precipitated
50,000	Precipitated	Precipitated	Precipitated	Precipitated	Precipitated

Table 21. Calcium tolerance of SI-8 in 10,000ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Precipitated	Precipitated	Precipitated	Precipitated	Precipitated
1000	Precipitated	Precipitated	Precipitated	Precipitated	Precipitated
10,000	Precipitated	Precipitated	Precipitated	Precipitated	Precipitated
50,000	Precipitated	Precipitated	Precipitated	Precipitated	Precipitated

Table 22. Calcium tolerance of SI-9 in 100ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Clear
10,000	Clear	Clear	Clear	Clear	Clear
50,000	Clear	Clear	Clear	Clear	Clear

Table 23. Calcium tolerance of SI-9 in 1000ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear
1000	Clear	Clear	Clear	Clear	Clear
10,000	Clear	Cloudy	Cloudy	Precipitated	Precipitated
50,000	Clear	Cloudy	Cloudy	Precipitated	Precipitated

Table 24. Calcium tolerance of SI-9 in 10,000ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Precipitated	Precipitated	Precipitated	Precipitated	Precipitated
1000	Precipitated	Precipitated	Precipitated	Precipitated	Precipitated
10,000	Precipitated	Precipitated	Precipitated	Precipitated	Precipitated
50,000	Precipitated	Precipitated	Precipitated	Precipitated	Precipitated

Table 25. Calcium tolerance of SI-11 in 100ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Clear	Clear

1000	Clear	Clear	Clear	Clear	Clear
10,000	Clear	Cloudy	Cloudy	Precipitated	Precipitated
50,000	Clear	Cloudy	Cloudy	Precipitated	Precipitated

Table 26. Calcium tolerance of SI-11 in 1000ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Precipitated	Precipitated
1000	Clear	Clear	Clear	Precipitated	Precipitated
10,000	Clear	Precipitated	Precipitated	Precipitated	Precipitated
50,000	Clear	Precipitated	Precipitated	Precipitated	Precipitated

Table 27. Calcium tolerance of SI-11 in 10,000ppm calcium solution.

SI conc. (ppm)	Appearance				
	after mixing	30 mins	1 hour	4 hours	24 hours
100	Clear	Clear	Clear	Precipitated	Precipitated
1000	Clear	Precipitated	Precipitated	Precipitated	Precipitated
10,000	Clear	Precipitated	Precipitated	Precipitated	Precipitated
50,000	Clear	Precipitated	Precipitated	Precipitated	Precipitated