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1 Abstract

A common production problem for oilfield operation is the formation of inorganic scale in the wellbore, surface facilities and near wellbore formation. Scale formation causes loss in production in most of the production wells mainly after water breakthrough if nothing is done to prevent the formation of scale. The most common method for preventing scale is by use of scale inhibitors. Phosphonate-based scale inhibitors (SIs) have been used in the oil industry for a long time. They have shown excellent inhibition for mainly Group II sulphate scales, but also for other SIs that contain predominating carboxylate or sulphate groups. Phosphonate gives a long squeeze treatment, because it easily binds to reservoir rocks. Most non-polymeric oilfield SIs have generally poor biodegradability, which limits their use in regions with strict environmental regions, such as in the Norwegian continent shelf (NCS). Green (biodegradable) scale inhibitors is on the market today, but only scale inhibitors that is stable at low temperatures ($>100^{\circ}\text{C}$). In this study, the focus is on making a green scale inhibitor which is stable at high temperature and high pressure formations.

Seven scale inhibitors have been synthesized from mono- and bis-finitrile attached to aromatics. These SIs include one or two aminobismethylenephosphonate groups, $\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_2$. To investigate their performance as a SI, they have been tested for inhibition of calcium carbonate and sulphate scale, thermal stability, biodegradability in seawater, and their compatibility with calcium (Ca^{2+}) ions. Some of the self-synthesized scale inhibitors shows acceptable to good inhibition for carbonate and sulphate scale. However, none of them were thermal stable at high temperatures.

A part of this study was also to test commercial available scale inhibitors (SIs). Most of the commercial SIs showed good to excellent inhibition, and the one tested for thermal stability was stable.

The biggest challenge is that neither the self-synthesized or the commercial SIs seems to be biodegradable in seawater, according to OECD 306.

2 Acknowledgement

This thesis is the final step in completing my master degree in Environmental Technology at the University of Stavanger, Norway. As most of this master program consist of theoretical courses, I wanted to do some laboratory work, to combine practical and theoretical work. The work in this thesis was carried out from January 2017 to June 2017.

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5 Introduction

Oilfield scaling is a common problem in the oil and gas industry. Problems with scale cost the industry millions of dollars in damage and lost production. Seen worldwide, scale is one of the leading causes of production decline. It is considered together with corrosion and hydrates one of the biggest water-related operational challenges in the oil industry. Scale can deposit on almost any surface. If scale once formed, the layer will continue to get thicker unless it is treated. If scale forms in the near-well bore region or in the well, it can block the pore throats and cause damage and loss in production. Scale can occur anywhere along the production tubing narrowing the internal diameter and blocking flow, it can even reach the processing facilities. The four most common scale formations in the oil industry are calcium carbonate (calcite and aragonite) and sulphate salts of calcium (gypsum), strontium (celestite), and barium (barite).

Scale inhibitors (SIs) is the most common method for preventing scale formation in the oil industry[1]. SIs are used to prevent nucleation and/or crystal growth of the scale. The concentration of SIs is in the range 1-500 ppm. The most common SI in the oil industry is water-soluble organic SIs. The SI concentration must be above a certain threshold to fully prevent scale formation. The limit is referred to as the minimum inhibitor concentration (MIC).

The SIs are often used in a downhole squeeze treatment or by continuous injection at the well head. Squeeze treatment is a method where a SI solution is pumped directly into a formation, usually through the production well. An over flush of seawater is used to push the inhibitor further into the formation and into a region around the production well[1]. The SI is absorbed or deposited on the formation rock in the near-well area. When the well is put on production SI is dissolved into the produced water, preventing scale formation during production. Commercial SIs for carbonate and sulphate scaling are generally polymeric, polyphosphonates, polyacrylates, polymaleates, polysulphonates, and copolymers.

Phosphonic acids are organophosphorus compounds buildup of C-PO(OH)₂ moieties[2, 3]. These compounds and their salts, phosphonates, have a wide field of application in agriculture, chemical and pharmaceutical industries[4-8]. Organophosphonic acid and their salts are an essential class of SIs used for scale in the oil industry[9-15]. Some of the SIs in this class are small non-polymeric SI molecules with just a few phosphonate groups, while others are

polymeric molecules which have higher amounts of phosphonates groups attached[1]. The phosphonate is in most cases attached to an aminomethylenephosphonate group. The amine group in this molecule act like a Lewis base ligand, which helps the inhibition process. Phosphonate groups in the SI can be helpful to determine the concentration of the SI in the produced water. The number of phosphonate groups in the SI gives an indication of when it is needed to re-squeeze a well, for complete scale inhibition. The properties of phosphonates groups make phosphonates a good option for the inhibition of scale in the oilfield industry, especially if they show good biodegradability.

6 Theory

6.1 Scale

6.1.1 What is scale?

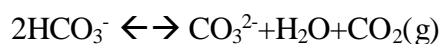
“Scale formation is the deposition of sparingly soluble inorganic salts from aqueous solutions” [1]. It is caused by a change in the saturation equilibrium when there is variation in temperature, pressure, or change in the solution chemistry [16]. Oilfield scale will only occur when free-water is produced. Water is a strong solvent for many materials and can carry scaling minerals. Scale can deposit on almost any surface. If a scale layer is formed it will get thicker over time. Figure 1 shows a thick scale layer of calcium carbonate in a production tubing. Most minerals are less soluble as the temperature decreases [1]. Similarly, with decreasing pressure the solubility of mineral decreases [17]. There are exceptions, the solubility of calcium carbonate increase with decreasing temperature.



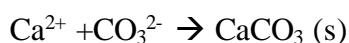
Figure 1 Calcium carbonate scales

6.1.2 The formation of scale

The driving force for scale formation is mainly temperature or pressure change, out-gassing, a pH-shift or mixing of incompatible water. Formation of calcium carbonate can deposit following the equation:



If the pressure drops, the above equilibrium will move to the right (by Le Chatelier's principle). The reaction is forming more CO_2 to increase the pressure. This leads to more carbonate ions and the pH rises. At a certain point, the concentration of carbonate ions will be high enough for calcium carbonate to precipitate.



The first stage in scale formation is nucleation, either in solution (homogeneous nucleation) or on a substrate (heterogeneous nucleation). The first development within a saturated fluid is a formation of unstable clusters of atoms, a process called homogenous nucleation showed in Figure 2. The atom clusters form small seed crystals triggered by local fluctuations in the equilibrium ion concentration in supersaturated solutions. The seed crystals grow by ions absorbing onto the rough surface on the crystal[17].

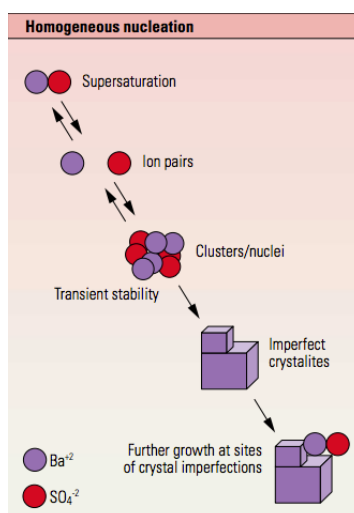


Figure 2 Scale growth starts in supersaturated solutions with ion pairs forming single crystals in solution [6]

Crystal growth also tend to initiate on a pre-existing fluid-boundary surface, a process illustrated in

Figure 3, called heterogeneous nucleation. This process includes surface defects such as a pipe surface roughness or perforations in production liners, or even joints and seams in tubing and pipeline. High degree of turbulence can catalyze scale deposition. This explains why scale deposits build rapidly on downhole completion equipment [17].

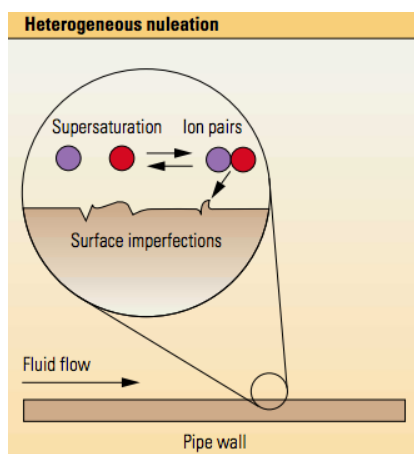


Figure 3 Shows that scale can also grow on pre-existing surface defects, such as rough spots on the liquid-tubing surface [17]

The effect of scale formation has on the production depends on the location. Scale in the near wellbore can cause severe formation damage. It can block the fluid flow by clogging the pores, leading to reduced production rates. If the scale is formed in the production tubing the flowing area is reduced as shown in Figure 4, resulting in a reduction in the production rate. Scale in the topside process may lead to accumulation of scale in the surface facilities, insufficient separation, and poor water quality. This can result in significant production losses.

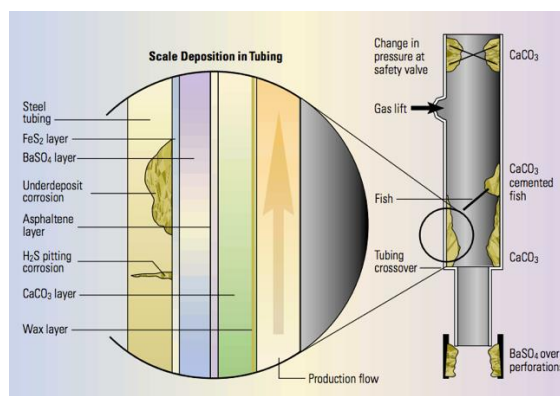


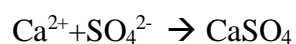
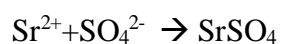
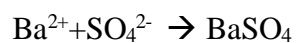
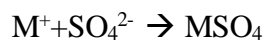
Figure 4 Scale in tubing, location of scaling can vary from downhole perforation to the surface [17]

6.1.3 Different types of scale

There are many different scale types that can be formed during the production of oil and gas. The most common in order to prevalence are [1]:

- Calcium carbonate (calcite and aragonite)
- Sulphate salts of calcium (gypsum), strontium (celesite), and barium (barite)
- Sulphide scales-iron(II), zinc, and lead(II), (these salts are the most common)
- Sodium chloride (halite)

Sulphate scaling is usually a problem in the seawater-flooded reservoirs. Sulphate scales forms by mixing of sulphate ions and group II metal ions, except magnesium. Reactions given:



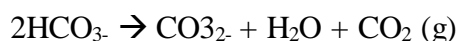
6.2 Types of scale

6.2.1 Carbonate scale

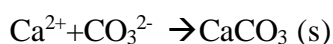
Carbonate scale can be formed when formation water being produced. This water contains carbon dioxide and scale ions like calcium and Magnesium, which can form scale. Calcium carbonate is the most common type of scale found in the oil field well environment, and it is one of the major problems in the North Sea oil production wells.

Calcite, aragonite, magnesite and vaterite, CaCO_3 , which are thermodynamically crystalline polymorphs, are some of the carbonate scales that occur in production wells. Calcite is the most common stable. Calcium ions, bicarbonate and/or carbonate ions, must be present in the formation water for scale to form. The saturation limit for dissolving ions in the produced water have to be reduced in order for calcium scale to occur. There are many factors that affect the water-solubility. A pressure drop, pH increase, increase of temperature and a decrease in ionic strength will increase the chance for carbonate scaling to occur.

Carbonic acid dissociates to form carbonate and bicarbonate, and by Le Chatelier's principle, the reaction will move to the right to try to increase the pressure by forming more CO_2 gas [2].



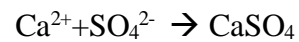
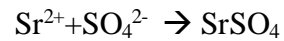
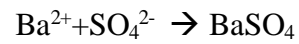
This result in more carbonate ions are formed and the pH rises. Calcium carbonate will precipitate when the concentration has reached a certain level [2].



The critical drop in pressure can occur anywhere in the production system. Calcium carbonate will not deposit in the well due to the high CO_2 content and low pH. Calcium carbonate scaling occurs after several years in the field, at this point the pressure drops in the production line to a level where carbonate scales will form. As the pressure drops, the scaling will escalate upstream further into the producing well.

6.2.2 Sulphate scale

Sulphate scaling is usually a problem in the seawater-flooded reservoirs. Sulphate scales form by mixing of sulphate ions and group II metal ions, except magnesium. This reaction gives:

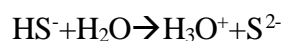
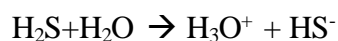


As you go down in group II the solubility of the sulphates decreases, consequently, Barium sulphate is the least soluble and the hardest to control. Sulphate scaling, is usually formed when formation water is mixed with injected seawater. This causes precipitation of sulphate scales. It is the high concentration of sulphate ions in the seawater mixing with group II metal ions in the formation water that lead to scale formation.

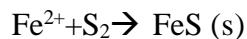
The hardness of the sulphate scale depends on the ratio of freshwater to seawater. Thus, in the early stages of a field, when the seawater is first injected, the severity of the sulphate scale can be dramatic. However, in the late stages of the field, there may be a little or no sulphate scale as the produced water is mainly seawater [2].

6.2.3 Sulfide scale

Sulfide scales are less common scale formation, but can still cause serious problems. This type of scale is formed mainly by the interaction between hydrogen sulfide and iron, zinc or lead, the most common among them is iron sulfide, mainly from corrosion of steel in producing wells. In oil wells, the bulk of hydrogen sulfide comes from activity of sulfate-reducing bacteria, SRBs, on the sulfate ions in the injected seawater. The SRBs reduce sulfate ions to hydrogen sulfide (H₂S), which is in equilibrium with hydrosulfide and sulfide ions [2]:



Iron(II) ions are formed mainly by corrosion of steel either in the injector or producing wells. They can react with the sulfide ions and form iron sulfide scale [2].



6.3 Scale inhibitors

6.3.1 What is a scale inhibitor?

Scale inhibitor is a chemical that is used for preventing the formation of scale. An inhibitor is defined as “Any chemical agent that reduces the rate of formation of a fouling scale” [16]. Scale inhibitors are water-soluble chemicals that prevent or retard the nucleation and/or crystal growth of inorganic scales, causing deformation of the normal crystal growth pattern and block the formation of larger crystals. Some polymers are good nucleation inhibitors and dispersants. [1]. A good scale inhibitor should be:

- Efficient: it must be able to inhibit the scale in question, irrespective of the mechanisms operating
- Stable: it must be stable under the high temperatures
- Compatible: it must not interfere with the action of other oilfield chemicals, nor be affected itself by them. It must be compatible with the chemical injection system under operating conditions.

For scale inhibitors to give full protection, a minimum inhibitor concentration (MIC) in the solution is needed. When the concentration falls below the MIC, scale can be formed.

There are different types of scales. In the oilfield, scales such as carbonates and sulphate consist of divalent anions, CO_3^{2-} and SO_4^{2-} , together with group II metal cations. The scale inhibitor must interact either with the anions or the cations, to successfully bind to the scale particle. These interactions are often necessary to hold the inhibitor tightly on the scale surface, to prevent the molecules with similar functional groups to interact with the lattice ions on the crystal surface [1].

There are different anionic groups attached to an organic molecule that interacts well with group II cations on the scale crystal surface. The most common are [1]:

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

Molecules with two or more of these ions, or a mixture of these ions, can be good inhibitors for oilfield scale. The molecules can be prepared in acid form, but it is in the anionic dissociation form that they are most effective as scale inhibitors. Carbon atoms bound all the anionic groups to the main part of the molecule except in polyphosphate.

A list of the most common classes of scale inhibitors[1]:

- Polyphosphates
- Phosphate
- Small, non-polymeric phosphonates and aminophosphonates
- Polyphosphonates
- Polycarboxylates
- Phosphino polymers and polyphosphinates
- Polysulphonates

Phosphate esters, Figure 5, are well known to be environment-friendly scale inhibitors. However, they are not the most efficient scale inhibitors. They are made by reacting phosphoric acid with alcohols. Varying the length of the alkyl tail in the alcohol make the phosphate esters either water-soluble or oil-soluble.

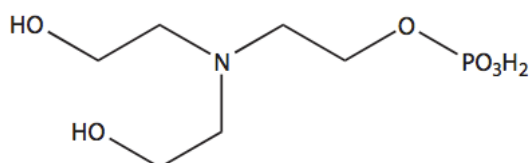


Figure 5 Triethanolamine phosphate ester

There are also some small non-polymeric scale inhibitors, with only a few phosphonate groups, see Figure 6. In these molecules, almost all the phosphate molecules contain aminomethylenephosphonate groups, where the nitrogen atom can also ligate to divalent cations, increasing the chelate effect. An increase of the chelate effect lead to a more stable chelate complex, the reaction gets a larger reaction entropy and is more favorable.

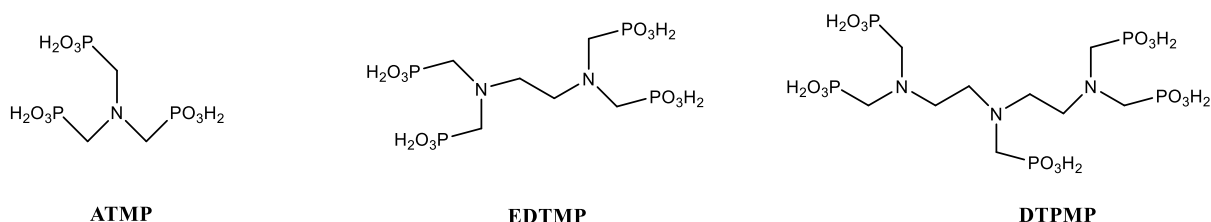


Figure 6 Common oilfield SIs containing phosphonate groups

An earlier study has shown that compounds containing one or more bisphosphonate (BP) groups which are an important class of biologically active compounds [18-20]. BP's have been used for decades in the therapy of bone related diseases, because of their bone-targeting agents[21, 22]. BP's are enzyme-resistant analogues of pyrophosphates, which will normally inhibit mineralization in the bone[23]. BP medicines are available in the market today, some of them are showed in Figure 7.

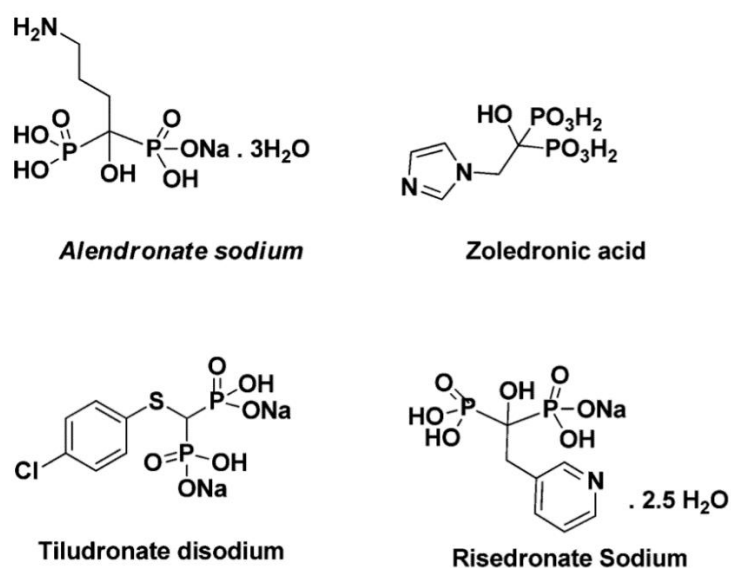


Figure 7 Examples of osteoporosis medications incorporating the BP group

Phosphonate-based SIs has proved several advantages in squeeze treatment. One disadvantage with these SIs is that they are poorly biodegradable. There have been several attempt to make environmentally friendly, biodegradable, SIs but rarely phosphonate-based[1, 24].

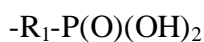
The most important property for a scale inhibitor with respect to the environment is biodegradability. Over the past decades, the water treatment industry and the oil companies have been increasingly concerned about the environmental impact of scale inhibitors. This has led to a development of an environmental friendly scale inhibitor. There are still many scale inhibitors which are poorly biodegradable.

Scale inhibitors are categorized based their biodegradability. The most biodegradable inhibitor is categorized as green or yellow, according to the Norwegian national environmental agency standards (Miljødepartementet). The limit to be categorized as green/yellow is minimum 20% biodegradable within 28 days [25]. Green category[26]. Chemicals in the red category are less than 20% biodegraded within 28 days.

Current environmental friendly scale inhibitors are not stable at high temperature (140°C) reservoir conditions over longer periods. Currently, there are no environmentally friendly and effective scale inhibitors which prevent scaling at these temperatures in the near well-bore area. To prevent scaling in the near well bore, a scale is injected into the formation (scale squeeze job) where the scale inhibitor absorbs on the reservoir rock and is released over time when the well is put on production. This requires that the scale inhibitors are thermally stable at reservoir conditions of a period of months to years.

6.3.2 Earlier studies

The chemicals used in the oil field to prevent often include phosphates, phosphate esters, phosphonates and polymeric agents. The term “phosphonate” means a group of molecules characterized by the presence of a covalent bond. Generally written:



Where R_1 represents an alkyl group, such as methyl, ethyl or butyl.

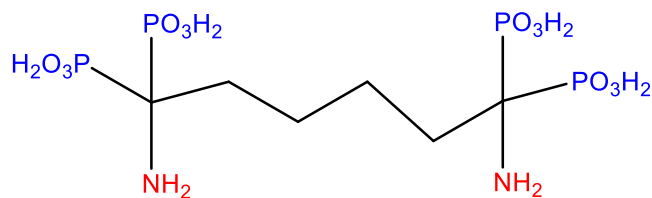
Amino phosphonates are another group of phosphonates, which refers to the group of molecules characterized by the fragments:



Where R_1 represents an alkyl group, and R_2 is selected from H, a second alkyl phosphonate group or another substituted such as $-R_1-OH$.

The processes used to manufacture amino phosphonates include starting with an amine containing one or more primary amino groups which react with other chemicals to bind onto each primary amine a (bis) phosphonoalkyl moiety. This process will lead to each primary amino group is substituted with two $(-R_1-P(O)(OH)_2)$ alkyl phosphate substituents. These substituted amines are proved to be effective as scale inhibitors[27].

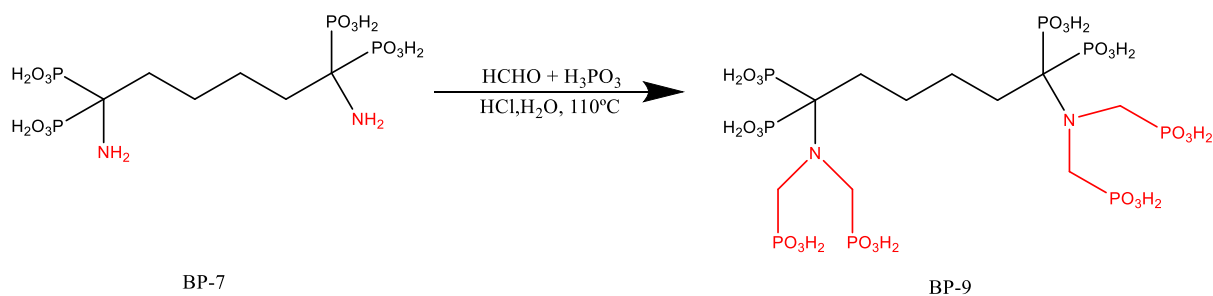
The low toxicity of bisphosphonates encouraged for a study to design and synthesize a series of bis-and tetra phosphonate derivatives that contain primary amino groups and check their biodegradability and scale inhibition performance [28]. In this study, it was found that the mono and diamino phosphonates were less effective to prevent calcium carbonate and barium sulfate scale compared with the commercial products. 1,6-Diaminohexane-1,1,6,6-tetrayl (BP-7), Figure 8, gave the best SI performance for this class of amino phosphonates. The FIC was 50 ppm after 6 min at the test conditions, which is only moderate inhibition. A favorable scale inhibitor gives good inhibition at 1-2 ppm.



BP-7

Figure 8 Diaminotetraphosphonic acid, BP-7 (unfunctionalized)

In addition, the amino phosphonates were functionalized with methylene phosphonate groups using Moedritzer-Irani reaction to give improvement as shown in previous studies [28]. The new methyl phosphonate compounds showed improved performance for both calcium and sulphate scale inhibition compared to the unfunctionalized starting materials. BP-9 (Figure 9), has a more optimal distance between the methylene phosphates which is shown to improve the SI performance. BP-9 showed the most potent SI performance, with FIC for carbonate scaling at 5 ppm for 59 min and at 20 ppm for 15 min for sulphate scaling.



BP-7

BP-9

Figure 9 synthesis of methylenephosphonate by the Moedritzer-Irani reaction.

The synthesized compounds were tested for biodegradability activities using the OECD 306 seawater test procedure. BP-7 gave 25 % seawater biodegradation, respectively, over 28 days. BP-9 gave 19 % biodegradation in seawater over 28 days.

In a study Bodnar, Fisher [29], Alkyl phosphonates were prepared from amino acids. The phosphonates were obtained as reaction mixtures where the level of alkyl phosphonation was deliberately controlled to provide only partial alkyl phosphonation of the amino acid. This study shows that alkyl phosphonates exhibit improved environmental properties compared to the fully substituted species, while still exhibiting acceptable efficacy in the control of scale. The

compositions possess advantages over existing phosphonates in that they exhibit higher biodegradation by method OECD 306. They also offer low toxicity to marine life [29].

These results encourage to design and synthesize further on amino phosphonates attached to methylenephosphonates, to improve the performance of the scale inhibitor, and at the same time increase the biodegradability.

6.4 New idea

As discussed above the amino phosphonates attached to methylenephosphonates, gives the SIs an improved performance. Biodegradation results for BP-7 and BP-7 from Figure 9, showed quite low biodegradability. The idea for this thesis consists of two main points. The first idea is to make phenolic amino acids, with phenol as starting material, by following Narcisos method for the preparation [30]. Then attach methylenephosphonates groups on the amines, as illustrated in Figure 10. Hoping the methylene phosphonate groups will improve the performance and help to increase the biodegradability activities, as discussed earlier.

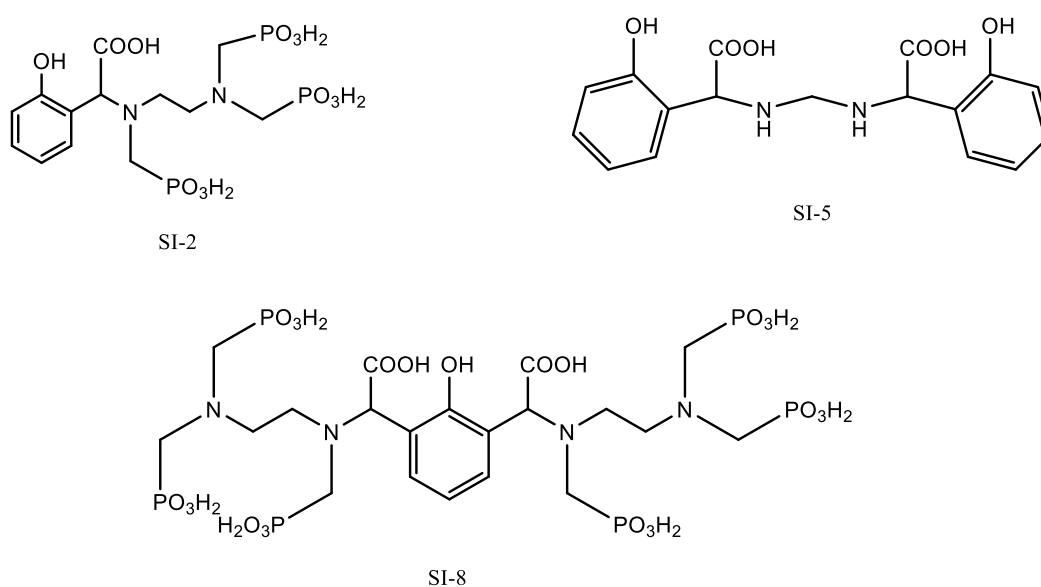


Figure 10 Self synthesized scale inhibitors, made with phenol as starting material.

The second idea was to investigate benzene attached with different functional groups, to compare the effect of each group. The functional groups that were studied was hydroxide, carbocyclic acid and sulfonic acid, as illustrated in Figure 11.

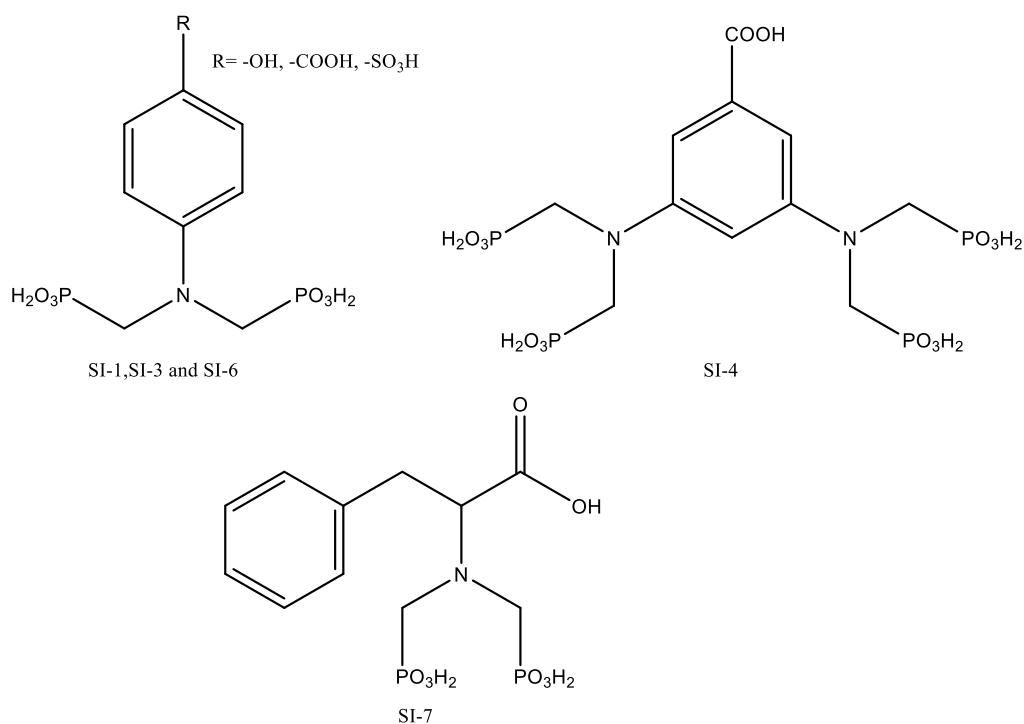


Figure 11 Self synthesized scale inhibitors, based on benzene, with different functional groups attached.

Phenol, Figure 12, is a toxic crystalline solid. It is commonly used as an antiseptic and disinfectant. It is also used in the preparation of cosmetics, such as sunscreen, and in the production of drugs, it is the starting material for the industrial production of aspirin, Figure 13 [31]. Phenol (hydroxybenzene) is both synthetically and naturally produced the aromatic compound. The microorganisms are capable of degrading phenol, and the process includes both aerobic and anaerobic degrading [32].

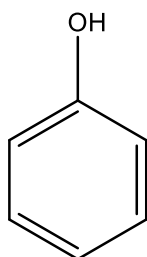


Figure 12 Structure of Phenol

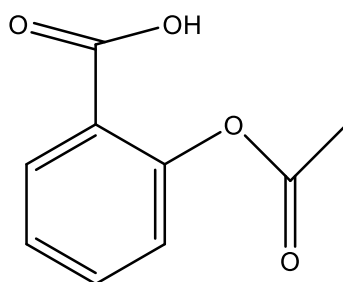


Figure 13 Structure of Aspirin

Alvarez-Cuevas Figuerola present a method consisting of three steps to synthesize phenolic amino acids [30]. The N-substituted phenolic acids are compounds widely used in agriculture as chelating agents in various metals. The three-step synthesis is presented in Figure 14, First step is a reaction of a phenol $R-C_6H_4OH$ with glyoxylic acid. The second step is hydrolysis of $Ac-NH-CH_2-CH_2-NH_2$ in aq. NaOH, hydrolysis with 15% HCl. The third step is a reaction with additional phenol and glyoxylic acid[33].

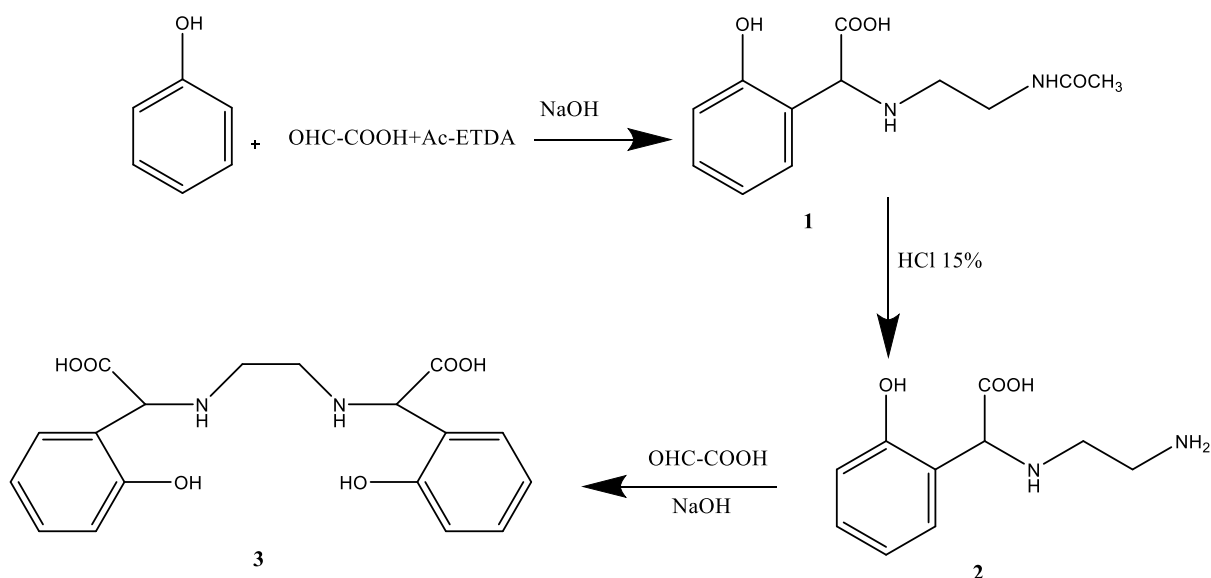


Figure 14 The three-step synthesis of phenolic amino acids

To improve the SI performance, methylenephosphonate groups are attached to the amines on molecule 2 and 3 from Figure 14. This is done through the Moedritzer-Irani Reaction.

To synthesize a good scale inhibitor some guidelines where given. A good green scale inhibitor complements these requirements [34]:

1. Minimum inhibitor concentration between 1-100 ppm (Optimal 1-5 ppm)
2. Thermal stability/aging
 - a. Stable up to 100°C → Scale inhibitor can be used at top side facility
 - b. Stable between 130°C-170°C → Scale Inhibitor can be used in squeeze treatment
3. Biodegradation should be minimum 60% within 28 days
4. pH → 4 < pH > 9
5. Compatibility with calcium
6. Cost efficient

6.5 Synthesis of aminomethylenephosphonic acids

The Moedritzer-Irani reaction was discovered in 1966 by Kurt Moedritzer and Riyad R. Irani[35]. This reaction is used for synthesis of N,N-disubstituted aminomethylphosphonic acids or N-substituted iminobis methylphosphonic acids. Moeditzer-Irani reaction operates in highly acidic solution. Mechanism of the reaction is illustrated in Figure 15.

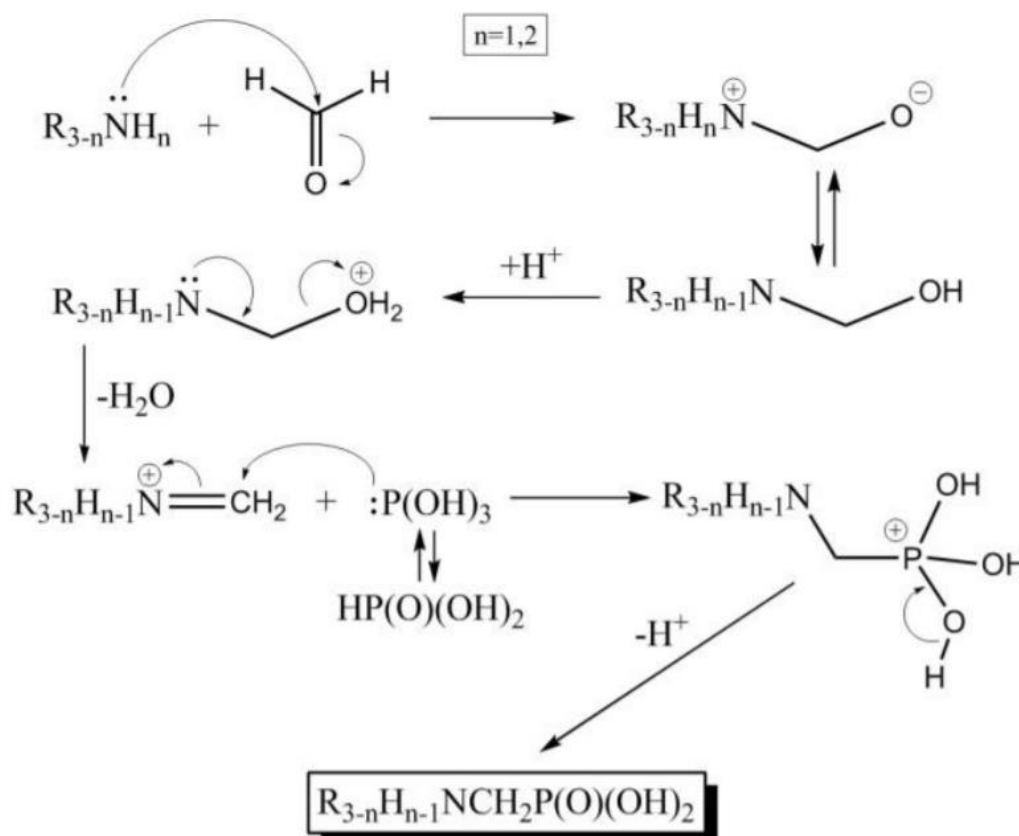


Figure 15 Mechanism for the Moeditzer-Irani reaction.

In the first step of the reaction it is a nucleophilic attack of N,N-dialkylamine nitrogen. Then the rearrangement gives N-hydroxymethylamine which undergoes elimination of water molecules yielding an imine salt, in strong acidic conditions. Phosphorous acid attacks the electrophilic imine salt, because it behaves like nucleophile in acidic conditions. The charged product is stabilized by loss of a proton to give N, N-distributed aminomethylenephosphonic acid. [36].

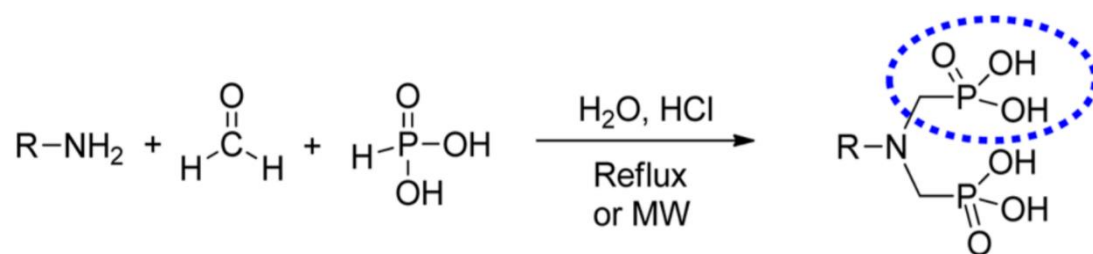


Figure 16 General equation for the synthesis of aminomethylenephosphonic acids by the Moedritzer-Irani reaction. A double substitution on a primary amine is illustrated here.

In Figure 16 a reaction of amine, formaldehyde and phosphorus acid forming aminomethylenephosphonic acid, in the presence of a catalytic amount of hydrochloric acid under reflux/microwave, using the Moedritzer-Irani reaction [28].

6.6 Scale squeeze

A scale inhibitor squeeze treatment is applied to prevent the scale formation in producing wells and in the near well-bore area. In a squeeze treatment, a solution of the scale inhibitor is injected into the well above the formation pressure whereby the inhibitor solution will be pushed into the near-well as illustrated in Figure 17 [1]. The well is then usually shut down for a period of hours to let the inhibitor absorb to the rock matrix. When the well is put back into production, produced water will pass the pores and dissolve some of the chemicals that is absorbed to the rock. The produced water should now contain enough scale inhibitor to prevent scale formation[1].

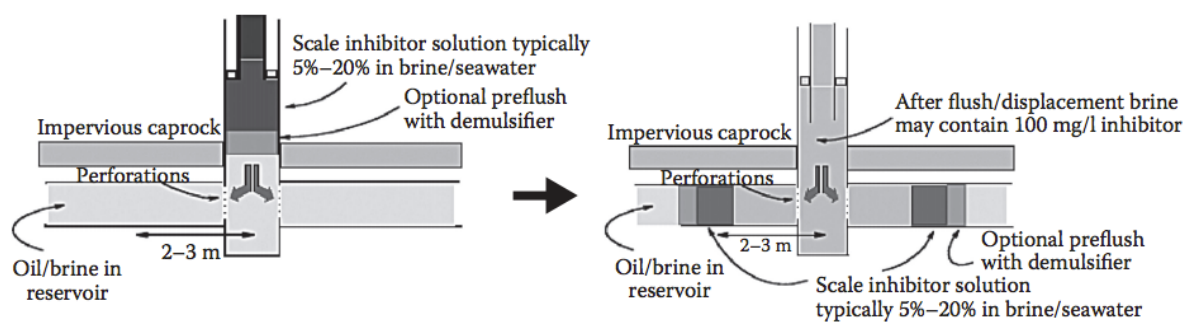


Figure 17 Illustration of scale inhibitor squeeze treatment

Squeeze treatments follow these five stages, which is illustrated in Figure 18[1]:

1. A preflush stage
2. The main treatment where the chemical scale inhibitor (usually aqueous) solution is injected into the formation with a concentration ranging from 2.5% -20%
3. An overflush, designed to push the main slug to a desired depth into the formation away from the wellbore
4. A shut-in, a period to allow the scale inhibitor to absorb on the rock surface
5. The well is put back on production

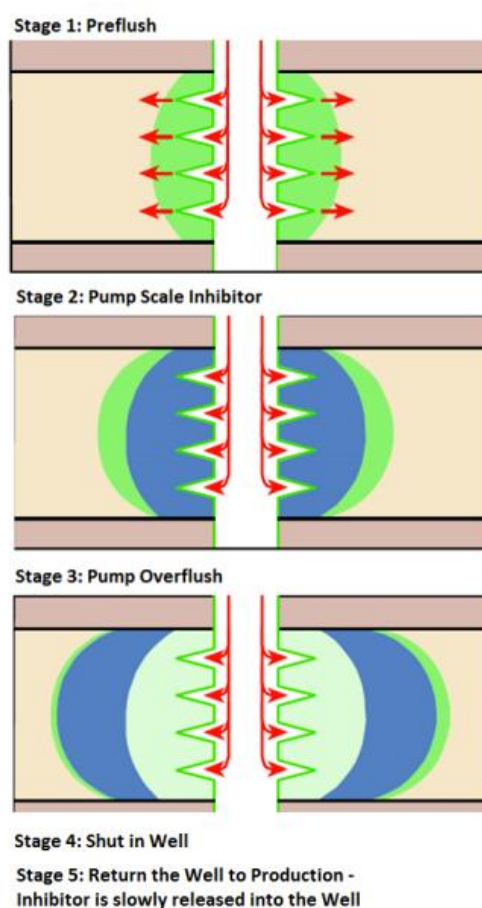


Figure 18 Showing the five different stages of scale inhibitor squeeze treatment

Scale inhibitor prevents the formation of scale above a certain concentration, known as minimum inhibitor concentration (MIC). The squeeze treatment lifetime is defined as the time from injection until the scale inhibitor concentrations drop below MIC[1]. The squeeze treatment lifetime is affected by factors such as production rate, water cut, and the reservoir geology/mineralogy of the reservoir. Figure 19 shows an example where the concentration of the inhibitor drops below the MIC, (~2ppm), after approximately 92 days.[1].

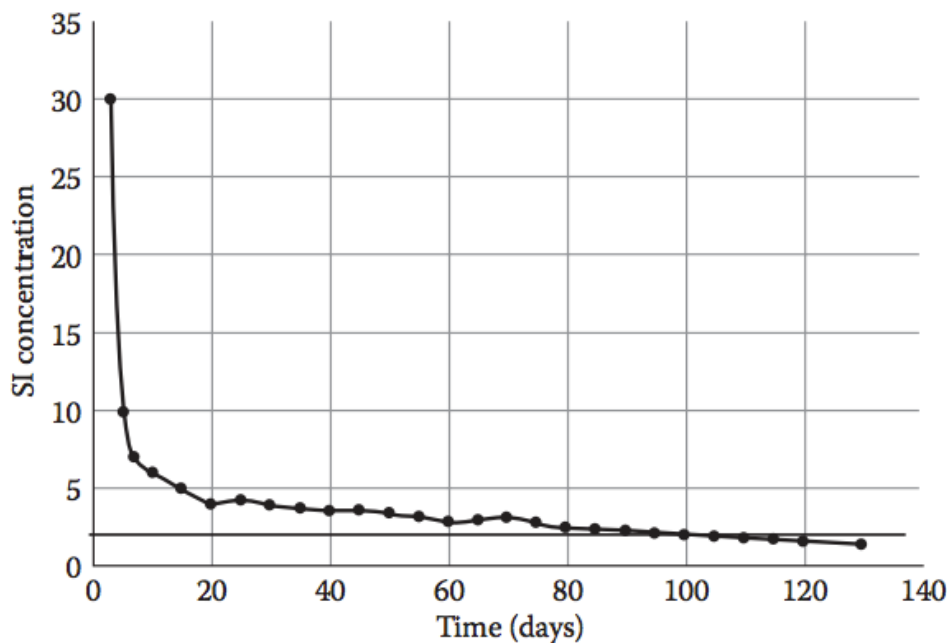


Figure 19 Post-squeeze scale inhibitor concentration (ppm) versus time showing the drop below MIC (2ppm) after about 92 days[1]

There are several techniques that have been developed to increase scale inhibitor retention on the rock formation and thus enhance the lifetime of a squeeze treatment [1]. They include:

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

To increase the retention of the scale inhibitor in the near-wellbore, a precipitation squeeze treatment can be used. A problem with many scale inhibitors is that they are incompatible with high calcium or magnesium concentration at reservoir temperatures and PH. Thus, by injecting these cations or Fe(II) ions with scale inhibitor, an inhibitor-cation complex will be precipitated in the near wellbore, this will give a better retention time than the inhibitor alone [1, 37-40].

The use of Zn^{2+} ions in squeeze formulation has also shown a significant increase of retention of the inhibitor[1, 41]. In laboratory studies Zn^{2+} also showed a synergistic effect on barite scale inhibition for certain scale inhibitors. Phosphonate and Zn^{2+} are showed to have e synergistic effect with corrosion inhibition[1].

Another method to increase scale inhibitor retention in a precipitation squeeze is to raise pH of the scale inhibitor. The pH of the inhibitor is increased *in situ* near the wellbore. This makes the acid groups in the inhibitor molecules become anions, then they can complex more easily with cations. This leads to precipitating of calcium/magnesium complexes[1].

Mutual solvent, small non-ionic amphiphile, is a method to increase the squeeze lifetime. This technique enhances inhibitor retention by making rocks more water wet[42, 43]. They also remove trapped water, water blocks, caused by an all-aqueous squeeze treatment. The mutual solvent is therefore used in the preflush, and in combination with the pH-modifying technique.

A fifth method claimed to increase the squeeze lifetime is to precondition rock surface with a cationic polymer such as polydiallyldimethylammoniumchloride, which is used as a clay stabilizing/sand control additive [1, 44]. This prevents permeability reduction that may occur with a conventional precipitation squeeze [45]. The positively charged surface is then better able to absorb negatively charged scale inhibitor ions. By adding cationic monomer into a scale inhibitor polymer has been showed to give a product, which is retained in the rock above the MIC for a longer period[1].

Cross-linked scale inhibitor has not been tried in the field yet[46]. According to laboratory study, cross-linked scale inhibitor has shown to double the squeeze lifetime of carboxylic polymeric scale inhibitors[11]. This technique is a combination of a scale squeeze treatment and a cross-linked polymer water shut-off treatment.

Another method that enhances scale inhibitor retention, and can be used for water shut-off, is the use of kaolinite clay[47]. Kaolinite is a clay type which is common in sandstone reservoirs. This clay type helps to increase the squeeze lifetime, by increasing the available surface for scale inhibitor adsorption. It has been demonstrated by core flooding that alteration of the near wellbore mineralogy by kaolinite injection can increase inhibitor adsorption. Therefore, it has an enhanced squeeze lifetime within clean, high-permeability reservoirs [1].

7 Experimental

7.1 Chemicals

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

7.2 Characterization of SIs

To characterize the chemicals, and to verify the reactions, nuclear magnetic resonance (NMR) were used. The NMR spectra recorded on a 400 MHz Varian NMR spectrometer in deuterium oxide (D_2O) and two drops of Sodium deuterioxide solution. 1H , ^{13}C and ^{31}P chemical shifts were obtained in D_2O . Thin-layer chromatography (TLC) was done after every reaction, to get an indication that the reactions were complete.

7.3 Syntheses of scale inhibitor

7.3.1 SI-1

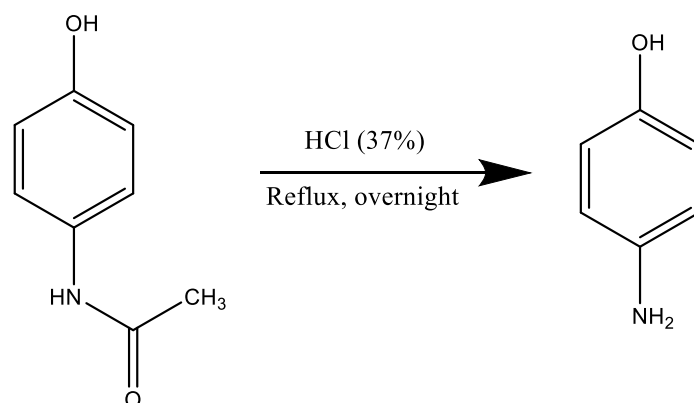


Figure 20 Step 1, Synthesis of phenol diamine from 4-acetamidophenol and HCl.

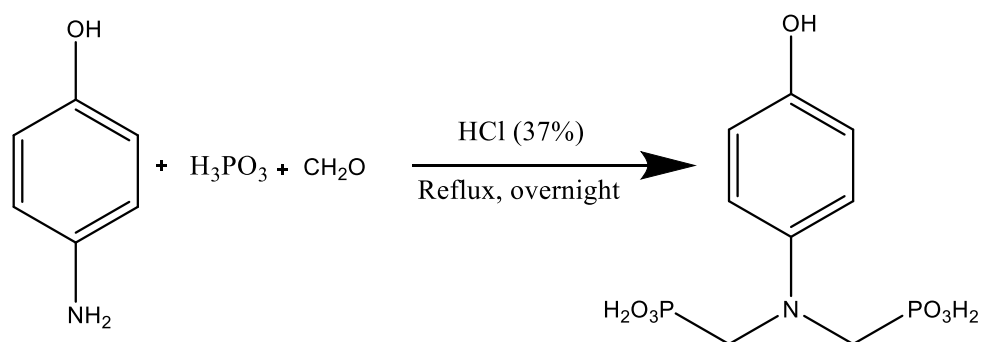


Figure 21 Step 2, Phosphonation of phenol diamine with phosphorous acid, formaldehyde and HCl.

Step 1 as illustrated in Figure 20. 4-acetamidophenol (10.0 g, 62.0 mmol) was weighed in a round flask. HCl (70 ml) was added to the flask. The mixture was added to the flask. The mixture was set to stirring and heating at 110°C, the reaction was held overnight. After removing the solvent under reduced pressure, the yield of the crystals was 9.44g

Step 2 as illustrated in Figure 21. Phenol diaminephosphors (3.0g, 27.49 mmol) was weighed in a two-neck round flask. Phosphorous acid (4.51g, 54.98 mmol) was added into the flask, while stirring. Then HCl (5.42g, 148.61 mmol) was added dropwise into the mixture, and heated in oil bath for 10 min at 100°C. Formaldehyde (4.90g, 163.47 mmol) was then added dropwise into the solution while stirring and heating at 100°C. The reaction was then left overnight at 110°C. Then the mixture was filtered, and the solvent of the liquid phase was removed under reduced pressure, the yield was 1.297g.

7.3.2 SI-2

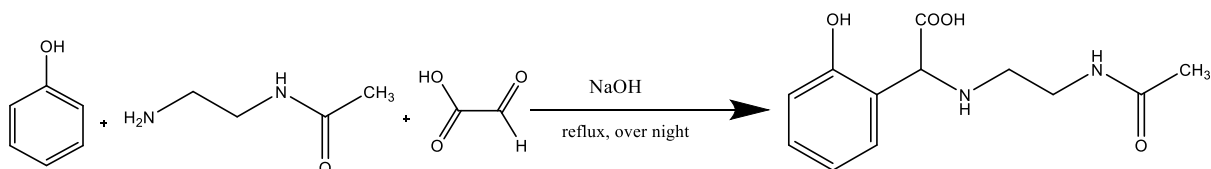


Figure 22 Step 1, synthesizing amide with phenol, monoacetyl ethylenediamine, glyoxylic acid and natrium hydroxide.

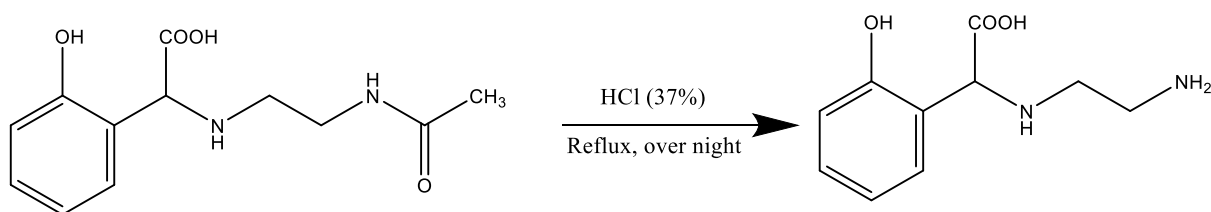


Figure 23 Step 2, Hydrolysis of acetamido group with HCl to get

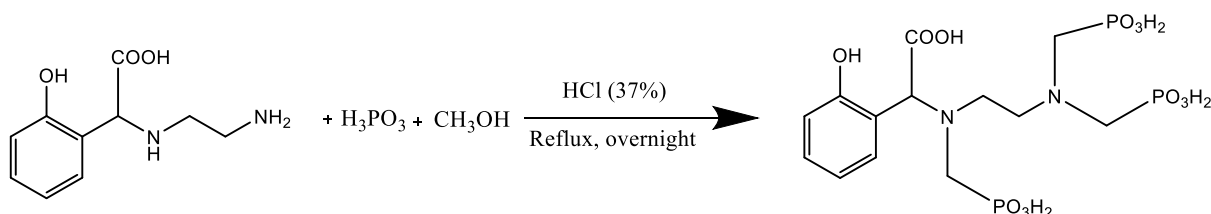


Figure 24 Step 3, Phosphonation of amine to get 2-(2-(bis(phosphonomethyl)amino)-ethyl)(phosphonomethyl)amino)-2-(2-hydroxyphenyl)acetic acid.

Step 1 as illustrated in Figure 22: Phenol (25.0g, 256.6mmol) was melted and stirred at 50°C in a two-neck flask. NaOH (50% w/w, 0.64 g, 7.97 mmol) was added dropwise into the mixture. The temperature was then decreased to 30-35 °C. Monoacetyl ethylenediamine (1.08 g, 10.62 mmol) was added to the mixture. Then Glyoxylic acid (50% 1.57 g, 10.62 mmol) was added dropwise into the solution while keeping the temperature below 40°C. The molar ratio of reactance used is phenol: NaOH: glyoxylic acid: Monoacetyl ethylenediamine (25:1:1:1). The mixture was kept at 75°C overnight and then kept at room temperature for 20 min. After addition of 60 ml water, the mixture was extracted with methyl tertiary buthyl ether (3x20 ml).

Then the water of the water phase was removed under reduced pressure to yield 3.729 g of amide.

Step 2 as illustrated in Figure 23: The hydrolysis of the acetamido group was carried out by reflux with HCl (37%, 60 mL) overnight. The solvent of the mixture was removed under reduced pressure to yield 3,03g of amine hydrochloride as a yellow/orange solid. (NMR)

Step 3 as illustrated in Figure 24. Phenol diaminephosphoures (3.0g, 27.49 mmol) was weighed in a two-neck round flask. Phosphorous acid (4.51g, 54.98 mmol) was added into the flask, while stirring. Then HCl (5.42g, 148.61 mmol) was added dropwise into the mixture, and heated in oil bath for 10 min at 100°C. Formaldehyde (4.90g, 163.47 mmol) was then added dropwise into the solution while stirring and heating at 100°C. The reaction was then left overnight at 110°C. Then the mixture was filtered, and the solvent of the liquid phase was removed under reduced pressure, the yield was 1.297g.

7.3.3 SI-3

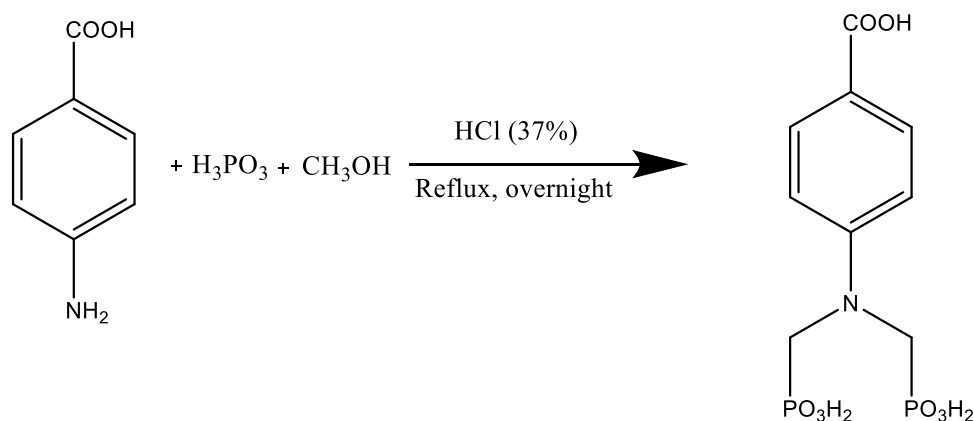


Figure 25 Phosphonation of 4-aminobenzoic acid

Phosphonation of 4-aminobenzoic acid is illustrated in Figure 25. 4-aminobenzoic acid (2.0g, 14.58 mmol) was weighed in a two-neck round flask. Phosphorous acid (2.3914g, 29.167 mmol) was added into the flask, while stirring. Then HCl (2.874g, 78.83 mmol) was added dropwise into the mixture, and heated in an oil bath for 10 min at 120°C. Formaldehyde (2.6014g, 86.713 mmol) was then added dropwise into the solution while stirring. The reaction was then left overnight at 120°C. Then the mixture was filtered, and the solvent of the liquid phase was removed under reduced pressure.

7.3.4 SI-4

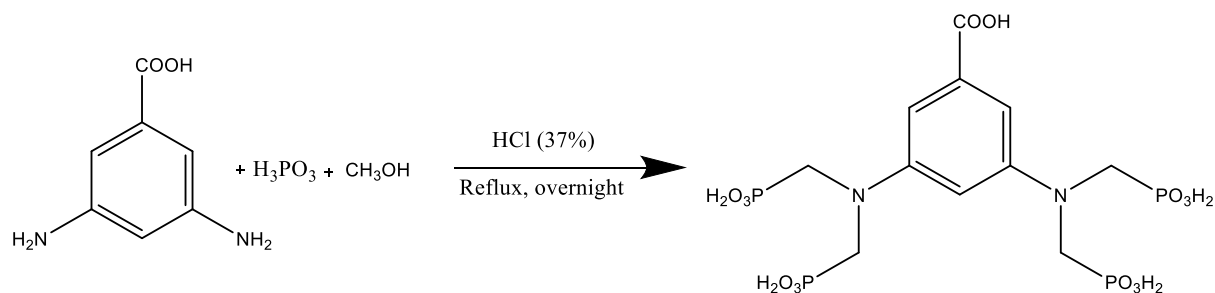


Figure 26 Phosphonation of 3,5-diaminobenzoic acid

Phosphonation of 3,5-diaminobenzoic acid is illustrated in Figure 26. 4-aminobenzoic acid (2.0g, 14.58 mmol) was weighed in a two-neck round flask. Phosphorous acid (2.3914g, 29.167 mmol) was added into the flask, while stirring. Then HCl (2.874g, 78.83 mmol) was added dropwise into the mixture, and heated in oil bath for 10 min at 120°C. Formaldehyde (2.6014g, 86.713 mmol) was then added dropwise into the solution while stirring. The reaction was then left over night at 120°C. Then the mixture was filtered, and the solvent of the liquid phase was removed under reduced pressure.

7.3.5 SI-5

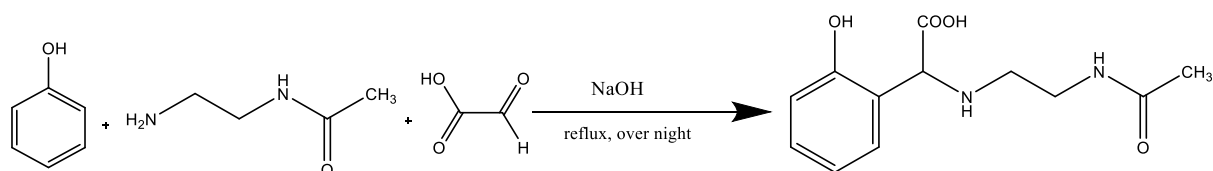


Figure 27 Step 1, synthesizing amide with phenol, monoacetyl ethylenediamine, glyoxylic acid and natrium hydroxide.

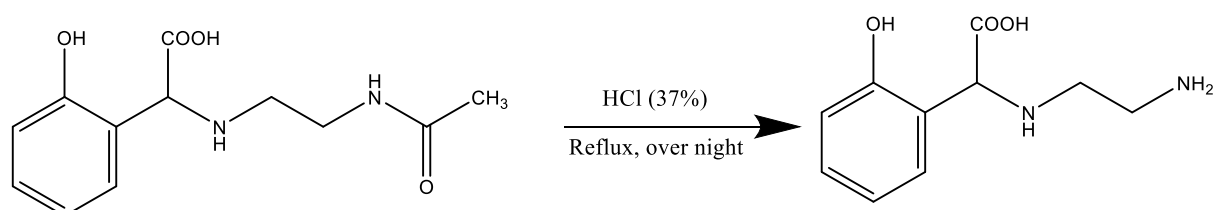


Figure 28 Step 2, Hydrolysis of acetamido group with HCl to get

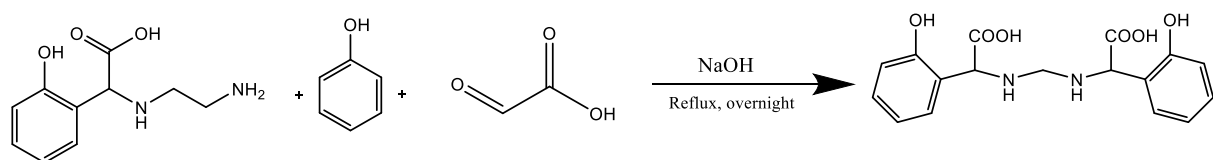


Figure 29 Step 3, Synthesis of ethylenediamine-bis(2-hydroxyphenylacetic acid) (EDDHA)

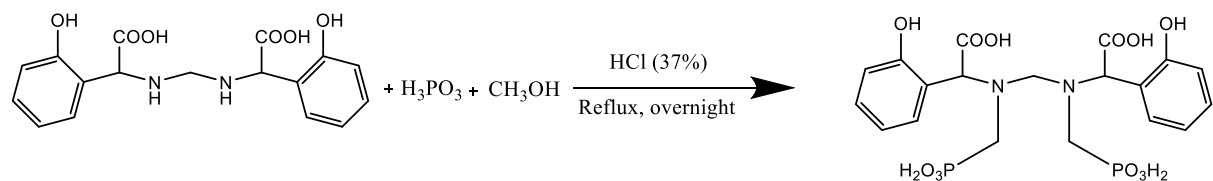


Figure 30 Step 4, Phosphonation of ethylenediamine-bis(2-hydroxyphenylacetic acid)

Step 1 as illustrated in Figure 27: Phenol (50.0g, 531.293mmol) was melted and stirred at 45-50°C in a two-neck round flask. NaOH (50% w/w, 1.28 g, 32.0 mmol) was added dropwise into the mixture. The temperature was then decreased to 30-35 °C. Monoacetyl ethylenediamine (2.16 g, 21.15 mmol) was added to the mixture. Then Glyoxylic acid (50% 3.14 g, 42.41 mmol) was added dropwise into the solution, while keeping the temperature below 40°C. The molar ratio of reactance used is phenol: NaOH: glyoxylic acid: Monoacetyl ethylenediamine (25:1:1:1).

The mixture was kept at 75°C overnight, and then kept at room temperature for 20 min. After addition of 60 ml deionized water, the mixture was extracted with methyl tertiary buthyl ether (3x20 ml). Then the water of the water phase was removed under reduced pressure.

Step 2 as illustrated in Figure 28: The hydrolysis of the acetamido group was carried out by reflux at 110 °C with HCl (37%, 120 mL) over night. The solvent of the mixture was removed under reduced pressure to get amine hydrochloride as a yellow/orange solid.

Step 3 as illustrated in Figure 29: The molar ratio of reactance used is phenol: NaOH: glyoxylic acid: Monoacetyl ethylenediamine (25:3:1:1). Phenol (42.20g, 448,411 mmol) was melted and stirred at 45-50°C in a two-neck round flask. Then 1 equiv. of NaOH (1.43 g, 35,83 mmol) is added to the mixture. The reaction is stirred until it reaches 30-35°C, then ethylenediamine-bis (2-hydroxyphenylacetic acid) (4.0g, 17.937 mmol), from step 3, and 2 equiv. of NaOH (2.86 g, 71.66mmol). After stirring, 37 % of Glyoxylic acid (3.589g, 48,473mmol) is added dropwise into the solution so the temperature does not exceed 40 °C. The mixture is then heated to 110 °C, and kept at this temperature and stirring overnight. The reaction is cooled down to room temperature, and 60 mL of deionized water is added. The solution was extracted with methyl tertiary buthyl ether (3x20 ml). Then the 70 % of the water in the water phase was removed under reduced pressure. Then 5% HCl (v/v) was added dropwise while stirring, until precipitation occurs. The precipitation was filtered and washed with acetone.

Step 4: Phosphonation of ethylenediamine-bis (2-hydroxyphenylacetic acid) is illustrated in Figure 30. Ethylenediamine-bis (2-hydroxyphenylacetic acid) (1.50 g, 4.020 mmol) was weighed in a two-neck round flask. Phosphorous acid (0.66g, 8.05 mmol) was added into the flask, while stirring. Then HCl (0.7923 g, 21.73 mmol) was added dropwise into the mixture, and heated in oil bath for 10 min at 120°C. Formaldehyde (0.7171g, 23.90 mmol) was then added dropwise into the solution while stirring. The reaction was then left overnight at 120°C. Then the mixture was filtered, and the solvent of the liquid phase was removed under reduced pressure. Washed with ethanol and filtrated.

7.3.6 SI-6

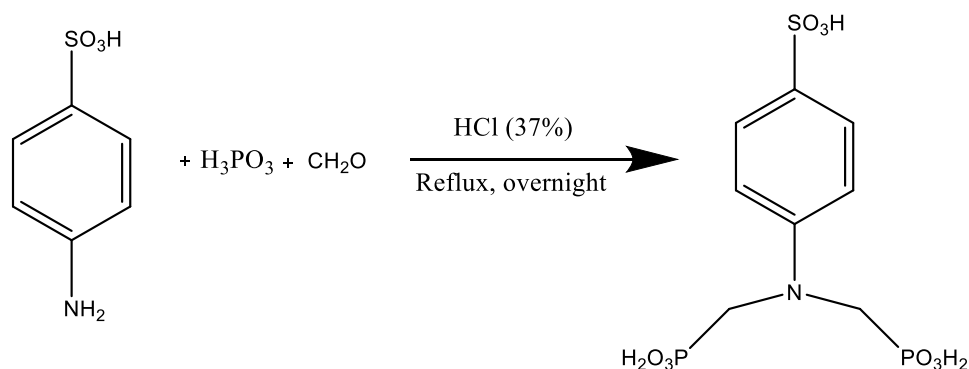


Figure 31 Phosphonation of sulfanilic acid

Phosphonation of sulfanilic acid is illustrated in Figure 31. Sulfanilic acid (3.0g, 17.323 mmol) was weighed in a two-neck round flask. Phosphorous acid (2.841g, 34.65 mmol) was added into the flask, while stirring. Then HCl (3.414g, 93.64 mmol) was added dropwise into the mixture, and heated in oil bath for 10 min at 120°C . Formaldehyde (3.09g, 103.0 mmol) was then added dropwise into the solution while stirring. The reaction was then left overnight at 120°C . Then the mixture was filtered, and the solvent of the liquid phase was removed under reduced pressure. Washed with ethanol and filtrated.

7.3.7 SI-7

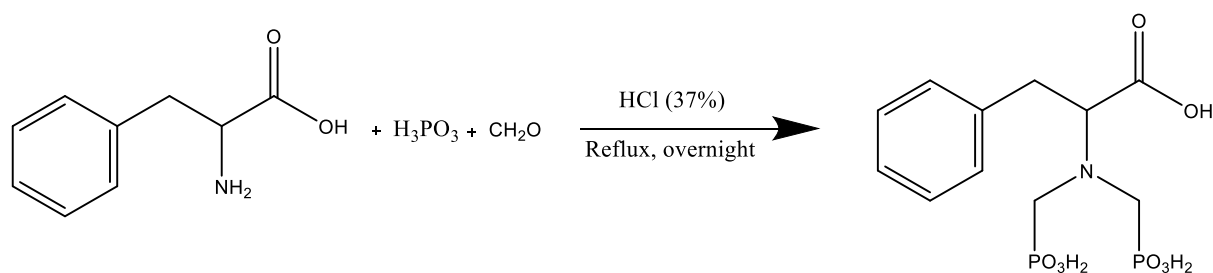


Figure 32 Phosphonation of L-phenyl-alanine

Phosphonation of L-phenyl-alanine is illustrated in Figure 32. L-phenyl-alanine (3.0g, 18.161 mmol) was weighed in a two-neck round flask. Phosphorous acid (2.978 g, 36.322 mmol) was added into the flask, while stirring. Then HCl (3.579 g, 98.16 mmol) was added dropwise into the mixture, and heated in oil bath for 10 min at 120°C. Formaldehyde (3.239 g, 107.984 mmol) was then added dropwise into the solution while stirring. The reaction was then left overnight at 120°C. Then the mixture was filtered, and the solvent of the liquid phase was removed under reduced pressure. Washed with ethanol and filtrated.

7.3.8 SI-8

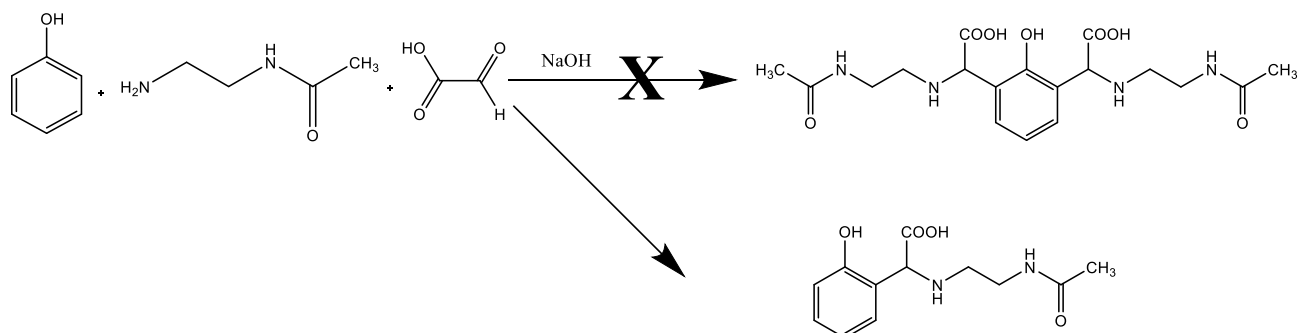


Figure 33 Synthesis of 2,2'-(2-hydroxy-1,3-phenylene)bis(2-((2-acetamidoethyl)amino)acetic acid), with phenol, monoacetyl ethylenediamine, glyoxylic acid and natrium hydroxide.

Step 1 as illustrated in Figure 33: Phenol (25.0g, 256.6mmol) was melted and stirred at 50°C in a two-neck flask. NaOH (50% w/w, 1.28 g, 32.0 mmol) was added dropwise into the mixture. The temperature was then decreased to 30-35 °C. Monoacetyl ethylenediamine (2.17 g, 21.24 mmol) was added to the mixture. Then Glyoxylic acid (50% 3.14 g, 42.41 mmol) was added dropwise into the solution while keeping the temperature below 40°C. The molar ratio of reactance used is phenol: NaOH: glyoxylic acid: Monoacetyl ethylenediamine (25:1:1:1). The mixture was kept at 75°C overnight, and then kept at room temperature for 20 min. After addition of 100 ml water, the mixture was extracted with methyl tertiary butyl ether (3x20 ml). Then the water of the water phase was removed under reduced pressure to yield 6.516 g of amide. Reaction did not work, according to NMR.

7.4 High-Pressure Dynamic Tube Blocking Test

The high-pressure dynamic tube blocking test is a common laboratory method to determine the relative performance of scale inhibitors used in oilfield applications. The main reason to use high-pressure dynamic tube blocking test, compared to static, is that it emulates the downhole conditions in a production tubing during production. The apparatus can a wide range of pressure and temperature [1]. The results from this test give a good estimate of the minimum inhibitor concentration (MIC) for the scale inhibitors. An acceptable value of MIC is from 1-100 ppm, but the target is between 1-5 ppm [34]. The test can be used to evaluate the performance of the SI in calcium carbonate – and sulphate brine.

The scale rig consists of three pumps that pump fluids up to 10.00 ml/min through a 3.00 meter microbore coil made of 316 steel with a diameter of 1 mm. The coil is placed in an oven, which in this experiment is set to 100°C. The pressure in the tube was 80.0 bar[28]. The three pumps are marked with the number 1, 2 and 3. Pump 1 is pumping brine 1 (scaling cations, Table 1), pump 2 is pumping brine 2 (scaling anions, Table 1) and pump 3 is pumping the scale inhibitor solution (SI) (Figure 34).



Figure 34 The scale Rig used for high-pressure tube blocking testing of SIs. (From the left: Pump 1, Pump 2, Pump 3)

The scale rig is set up to automatically test the inhibitors. It is programmed to complete four stages in each experiment[1]:

1. 1st blank test with no scale inhibitor.
2. A set of tests with different concentration of SIs is run for one hour each.
3. A repeated test is automatically conducted for the previous concentration of SI that led to scale formation.
4. 2nd blank test with no scale inhibitor.

The scale rig is connected to a computer with a software that automatically controls the minimum inhibition concentration of the SIs. For example, the concentrations of SI are set to 100, 50, 20, 10, 5, 2 and 1 ppm for one hour each or until scale is formed in the coil. 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 must not be confused with MIC, which is the minimum inhibitor concentration that prevents scale formation). Between each concentration added, the coil is cleaned with EDTA (pH= 12-13) for 10 min at 9.99 ml/min flow rate and for the next 10 min the coil is flushed with distilled water with the same flow rate, 9.99 ml/min. Then the coil is ready for the next test concentration[1].

Table 1 The composition of sulphate brine 1 and brine 2 used in the scale-rig

Brine 1					
ion	ppm		g/l	g/3L	g/5L
Na	19510	NaCl	38.640	115.93	193.2
Ca	2040	CaCl ₂ * 2H ₂ O	5.3100	15.930	26.55
Mg	530	MgCl ₂ * 6H ₂ O	13.660	40.980	68.30
K	1090	KCl	1.9200	5.7600	9.600
Ba	570	BaCl ₂ * 2H ₂ O	0.5100	1.5300	2.550
Sr	290	SrCl ₂ * 6H ₂ O	0.4400	1.3200	2.200
Cl		Actual Cl ppm	31166.40		
Brine 2					
ion	ppm		g/l	g/3L	g/5L
Na	19510	NaCl	35.04	105.12	175.20
SO ₄	2960	Na ₂ SO ₄ Anhydrous	4.380	13.149	21.900
		Actual Cl ppm	30086.47		

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

Brine 1					
ion	ppm		g/l	g/3L	g/5L
Na	19510	NaCl	49.59	148.77	247.97
Ca	2040	CaCl ₂ * 2H ₂ O	7.48	22.45	37.42
Mg	530	MgCl ₂ * 6H ₂ O	4.43	13.30	22.16
K	1090	KCl	2.0781	6.23	10.39
Ba	570	BaCl ₂ * 2H ₂ O	1.0138	3.04	5.07
Sr	290	SrCl ₂ * 6H ₂ O	0.8824	2.65	4.4122
Cl	0	Actual Cl ppm	35633.19		
Brine 2					
ion	ppm		g/l	g/3L	g/5L
Na	19510	NaCl	49.59	148.77	247.95
SO ₄	2000	Na ₂ SO ₄ Anhydrous	2.76	8.26	13.76
		Actual Cl ppm			

Table 3 The composition of EDTA used for flushing in the scale-rig

EDTA	
Na ₂ EDTA*2H ₂ O	120 g
NaOH	40 g
Dissolved in 2 L deionized water	

The brines in Table 1 and Table 2 is mixed and stirred until the salts are completely dissolved. Then the brines were degassed for 15 minutes using a vacuum pump to remove dissolved gas. Bubbles in the water might cause a pump stop as it prevents brines from flowing through the line. The same procedure was used for preparing EDTA following Table 3.

After a test of a SI in the dynamic tube blocking rig and the results are exported to Excel. Excel is used to plot the results. A typical graph is illustrated in Figure 35. The graph shows the four stages in one single run. From left a blank test with no inhibitor, a test to determine the FIC, a repeat for FIC and ends with a repeated blank test. In Figure 35, SI was injected at 20, 10, 5, 2, 1 ppm for 1 hour each. At 2 ppm, the scale is build up rapidly after 14 minutes.

After cleaning with water and EDTA, the repeated SI test is run, but starting from MIC, 5 ppm. After 9 minutes at 2 ppm, the scale build up rapidly again. The fourth stage is the repeated blank test.

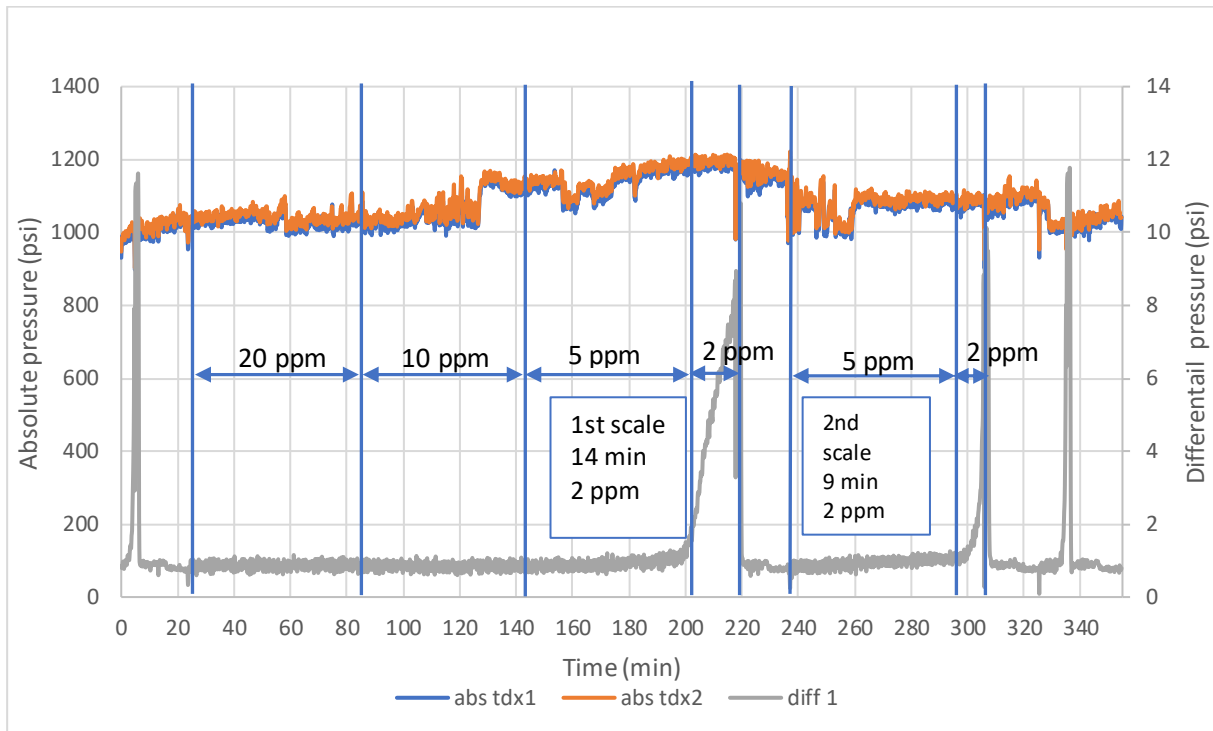


Figure 35 Graph showing the four stages of a SI test in the scale rig (pressure-time).

7.5 Compatibility with calcium test

Mixing of scale inhibitors and brine can cause issues when they react with each other. The reaction can cause a change in the physical and chemical structure of the scale inhibitor. Compatibility tests are needed to check that the inhibitor does not precipitate when mixing with formation brines causing formation damage [1]. Chemicals that affect the pH of the produced water will affect the carbonate scaling potentials [1, 48]. The use of some aminomethylene acid SI derivatives in the presence of high calcium ion concentrations can lead to precipitation. Too much calcium ions lead to incompatibility with the SI. This lead to precipitation and deposition, not of inorganic scale but a calcium – SI complex. This can cause poor placement of the SI and formation damage [49, 50]

The compatibility test follows a procedure. Solutions with different calcium content were mixed with various inhibitor concentrations, to evaluate if precipitation occurs. Scale inhibitors of 100 ppm, 1000 ppm, 10 000 ppm and 50 000 ppm was dissolved in 2 ml deionized water in 50 mL glass bottles. 30 000 ppm sodium chloride (3.0 wt %) and calcium dehydrate in doses from 10 to 10 000 ppm are added. The bottles are shaken until all is solved and the solution looks clear. The bottles are placed in the oven at 80°C, the test time is generally 24 hours. While checking the turbidity and/or precipitation of SIs with calcium ion in a synthetic brine solution after 30 min, 1 hour, 4 hours and 24 hours. Figure 36 shows a picture of the different test bottles after 24 hours in the oven.

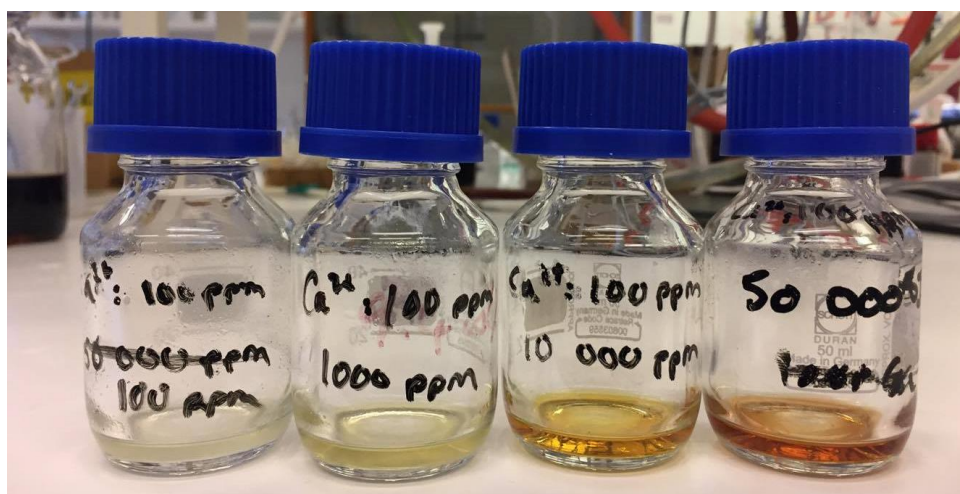


Figure 36 Compatibility test in 100 ppm Ca^{2+} and 3% NaCl in 2 ml. The bottles on the pictures shows the test after 24 hours, all bottles with clear solutions.

7.6 Thermal stability test

For high-temperature reservoirs thermal aging tests are needed. This is to make sure that the SIs are stable at the respective temperatures for the expected squeeze lifetime [1]. To accomplish this test, a 20 wt% additive solution in deionized water is nitrogen-sparged for 1 hour and placed in a pressure tube. It is then sparged again with nitrogen, to minimize head space of oxygen in the tube before heating at 100°C – 170°C for 1 week. The resultant solution is then checked for the SIs inhibition for sulphate and carbonate scaling.

7.7 SI Seawater Biodegradability test

Biodegradability test, is a laboratory test method which is used to determine biodegradability of a substance. This is an important parameter for the evaluation of the ecological behavior of the substances. Degradable substances will not be a long-term risk for the environment. There are internationally standardized methods (ISO, OECD) for the biodegradability test. The authorities have established quality criteria (GLP, EN 45000, ISO 9000) which is used to quantify the degree of biodegradation. These are used in this study to quantify the degree of biodegradation [1].

The biodegradability testing measures the biochemical process that develops when microorganisms consume a given type of material. The test gives an indication of the products ability to biodegrade, which depends on the amount of carbon available for microbial consumption. The regulations require that the biodegradability test is based on Aerobic Biodegradation, which normally measures oxygen consumption, carbon dioxide production and the condition of inorganic carbon intermediates [51].

To predict the biodegradation behavior of a SI in natural environments, the test should simulate such an environment as close as possible. This is the reason for having several standardized amounts of test methods, so the best test is chosen for the specific purpose. In this project, a method based on OECD 306 guidelines is used to determine the marine biodegradability of the SI's. For each SI, the biological oxygen demand (BOD) was measured, using the OxiTop Control manometric system (WTW, Germany) over a 28 days' period. By comparing the measured BOD and the calculated theoretical oxygen demand (ThOD) values, the percentage of biodegradability can be calculated. Seawater was used as the test medium, without added

inoculum. To ensure non-limiting conditions for microbial activity and growth, nutrients were added.[28]

To accomplish this test, test flasks containing seawater, nutrients, and the test chemical (SI) is needed. Three different types of control flasks are used. One blank with nutrient amended seawater only, to indicate contamination during the experiment. Number two, negative controls with autoclaved seawater, nutrients, and the test compounds at 69 mg/L final concentration. Number three, positive controls with nutrient amended seawater and an easily biodegradable substrate, sodium benzoate, at 100 mg/L final concentration. The positive and negative controls are used to minimize the influence of false positives and negatives. [28]

The seawater used in the test (20L) was collected at the International Research Institute of Stavanger (IRIS) in Mekjarvik (Stavanger, Norway). At the sampling day, the seawater had a temperature of 12 °C. The collected seawater was stored in a dark room at 20 °C overnight. The next day, seawater (297 mL) was distributed into 510 mL volume amber bottles and nutrient solution was added. The OxiTop control setup was prepared according to recommendations of the manufacturer, and bottles with measuring heads were incubated for 3 hours at 20°C prior to the start of the experiment. After the 3 hours incubation, 1.8 mL of a 1.0% (w/w) solution (in distilled water) of each test compound was added to the test and negative control flasks, while 1.0 mL of a 30 g/L sodium benzoate solution was added to the positive control flask. The bottles were capped with measuring heads and placed on magnetic stirrers in the incubator cabinet, and the measuring heads were started immediately. [28]

Oxygen consumption data were recorded over a 28 days' period, while all flasks were incubated in the dark at 20°C. After 28 days, data was and results were collected. ThOD of each scale inhibitor was calculated as described in the OECD 306 guidelines, taking in to account complete nitrification. Blank oxygen consumption values (BOD values representing background respiration in seawater) were deducted from the BOD of each test compound prior determining percent biodegradability according to the OECD 306 guidelines.

8 Results and discussion

In the following chapter the experimental results are presented and discussed. The main objective of the experiments is to test the effect of the scale inhibitors with aromatics and aminomethylenephosphonate groups attached. Green commercial inhibitors were also tested for comparison, nine SIs for sulphate scale and three for carbonate scale. Eight SIs were synthesized and tested by simulating the well conditions in a rig simulator for sulphate and carbonate scale. The SIs with best performance was further investigated for compatibility with calcium, thermal stability and the degree of biodegradation. Results are arranged according to the objective of each series of tests.

8.1 Synthesis

The synthesis of SI-2, SI-5 and SI-8 involved the reaction between Monoacety ethylenediamine, phenol glyoxylic acid and sodium hydroxide, under reflux overnight. Then further synthesized by the Moedritzer-Irani (6.5) reaction with phosphorus acid, formaldehyde and hydrochloride as a catalyst, under reflux overnight. The reaction for SI-8 was not successful. However, even after a long reflux period with an excess reagent, it was no sign of the desired products, according to the NMR, so this was not further investigated. SI-1, SI-3, SI-4, SI-6 and SI-7 were all synthesized by Moedritzer-Irani reaction. All synthesized compounds were characterized by spectroscopic techniques. ^1H , ^{13}C and ^{31}P NMR spectroscopies are efficient methods to identify the chemical composition of the SIs. The ^{31}P NMR spectra of SI-1 to SI-7 showed distinct signals in range δ 13-17 ppm as an indication of phosphonate groups. All the self-synthesized SIs was dissolved in water as a sodium salt, to get the SIs completely soluble.

8.2 High-Pressure Dynamic Tube Blocking Test

High pressure dynamic tube blocking test on sulphate and carbonate scales was used to test the performance of the SIs and find the fail inhibitor concentration, as described in 7.4. The results from the test apparatus at 100°C are consistent for the first and second test for all the tested scale inhibitors. At FIC, it is hard to evaluate the scaling rate as the time it takes for the apparatus to detect the scale, varies between the first and second test for many of the samples. Consequently, the apparatus can be used to detect FIC but not scaling rate.

The pH in this study were tried to be kept in the range 4-9, but some of the SIs needed a higher pH to get completely dissolved. The pH plays as significant role in scale inhibition by its effect on protonation of the SI were investigated [28, 52]. Results of this growth study show that an increase in the pH of the crystal growth medium over a pH of 4-9 shows an improvement in inhibitor performance and the poor inhibition performance is found at $\text{pH} < 4$.

Table 4 Results for sulphate scale in the scale rig

	First blank	First scale test		Second scale test		Second blank	pH
Inhibitor	Time	Concentration	Time	Concentration	Time	Time	
Commercial Scale Inhibitors							
CMI (ThermPhos [#])	7 min	2 ppm	7 min	2 ppm	12 min	8 min	7.76
LOT6C002	8 min	10 ppm	16 min	10 ppm	20 min	11 min	6.60
Tryptone N1	8 min	50 ppm	9 min	50 ppm	12 min	9 min	6.68
GF-175-45	8 min	2 ppm	2 min	2 ppm	10 min	9 min	8.27
Polyaspartate	9 min	1 ppm	12 min	1 ppm	13 min	9 min	8.35
HPPAA	9 min	20 ppm	9 min	20 ppm	22 min	9 min	6.96
CMI (Italmatch)	9 min	2 ppm	20 min	2ppm	17 min	-*	9.0
Polyaspartate (ThermPhos [#])	12 min	2 ppm	7 min	2 ppm	4 min	8 min	6.60
PESA	6 min	2 ppm	14 min	2 ppm	9 min	10 ppm	6.88
Self-synthesized Scale Inhibitors							
SI-1	10 min	20 ppm	36 min	20 ppm	44 min	11 min	9.23
SI-2	7 min	10 ppm	20 min	10 ppm	20 min	10 min	8.91
SI-3	7 min	100 ppm	13 min	100 ppm	12 min	11 min	11.80
SI-4	8 min	10 ppm	27 min	-*	-*	-*	10.90
SI-5	12 min	20 ppm	13 min	20 ppm	13 min	11 min	12.31
SI-6	9 min	100 ppm	27 min	100 ppm	33 min	11 min	6.61
SI-7	11 min	100 ppm	15 min	-*	-*	-*	6.44

*Test stopped (bubbles in line/errors), # Now a part of Italmatch

Table 5 Results for carbonate scale in the scale rig

	First blank	First scale test		Second scale test		Second blank	pH
Inhibitor	Time	Concentration	Time	Concentration	Time	Time	
Commercial Scale Inhibitors							
HPAA	7 min	0 ppm	1 min	0 ppm	11 min	14 min	6.96
PESA	16 min	1 ppm	6 min	1 ppm	1 min	18 min	6.88
CMI (Italmatch)	9 min	2 ppm	18 min	2 ppm	17 min	12 min	9.0
Self-synthesized Scale Inhibitors							
SI-1	8 min	50ppm	40 min	50 ppm	42 min	10 min	9.23
SI-2	7 min	2 ppm	22 min	2 ppm	41 min	14 min	8.91
SI-3	7 min	100 ppm	24 min	100 ppm	12 min	11 min	11.80
SI-4	6 min	20 ppm	46 min	20 ppm	51 min	8 min	10.90
SI-5	11 min	50 ppm	13 min	50 ppm	15 min	14 min	12.31
SI-6	8 min	10 ppm	13 min	10 ppm	11 min	8 min	6.61
SI-7	11 min	100 ppm	15 min	-*	-*	-*	6.44

*Test stopped (bubbles in line/errors)

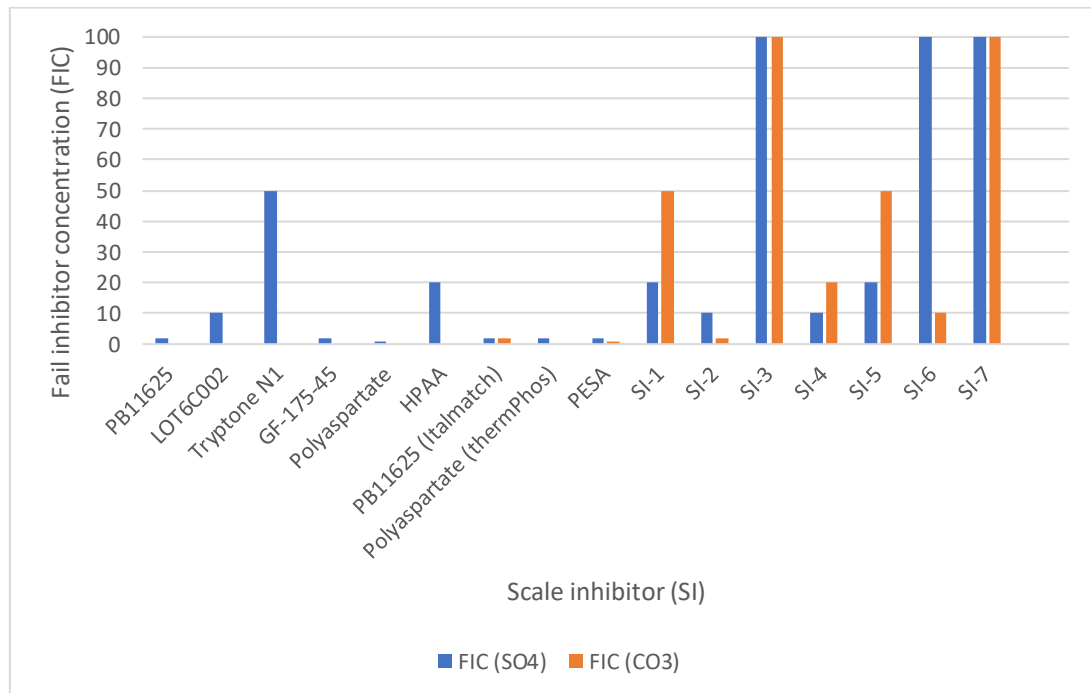


Figure 37 FIC results for self-synthesized and commercial SIs for sulphate and carbonate scales.

For the sulphate scales, the FIC value for the commercial SI, PESA, was 2 ppm. However, for carbonate scale the FIC was 1 ppm, as presented in Table 4, Table 5 and Figure 37, illustrated graphically in Figure 38 and Figure 39. For the commercial inhibitors, it was the HPAA and Tryptone N1 which gave the weakest inhibition effect for sulphate scale. HPAA gave rapid scale at 20 ppm and Tryptone N1 at 50 ppm, both after 9 min for sulphate scaling. For carbonate scaling HPAA showed very good inhibition compared to sulphate scaling, with no scale formation at 1 ppm. Generally, the tests for the commercial SIs showed no changes in pressure drop until FIC was reached, one example is shown in Figure 38.

Earlier studies has showed that the amino phosphonates gives poor to moderate performance for sulphate and carbonate scale inhibition [28]. In this study it was synthesized some SIs with amino bisphosphonate groups and some with aminomethylenephosphonate groups into the bisphosphonates (BPs) molecules via the Moedritzer-Irani reaction [35]. The $-\text{CH}_2\text{-PO}_3\text{H}_2$ group probably increase the metal binding abilities of the molecule via both the amine nitrogen and phosphonate interaction. The number of methylene linkages between the aminomethylenephosphonate groups in their backbone structure has a significant impact on scale inhibition [53].

For the self-synthesized inhibitors, SI-3, SI-6 and SI-7 showed a weak inhibition effect at 100 ppm for sulphate scale. The fail concentration of SI-3 gave rapid scaling after 13 min for the first run and 12 min for the second run. SI-7 gave rapid scaling after 18 min. For SI-6, the first and second tests gave a slightly longer time to scale than SI-3 and SI-7, with respectively 27 and 33 min. For carbonate scale SI-3 and SI-7 show poor inhibition with a FIC at 100 ppm. While SI-6 gave good carbonate scale inhibition, with a FIC at 10 ppm.

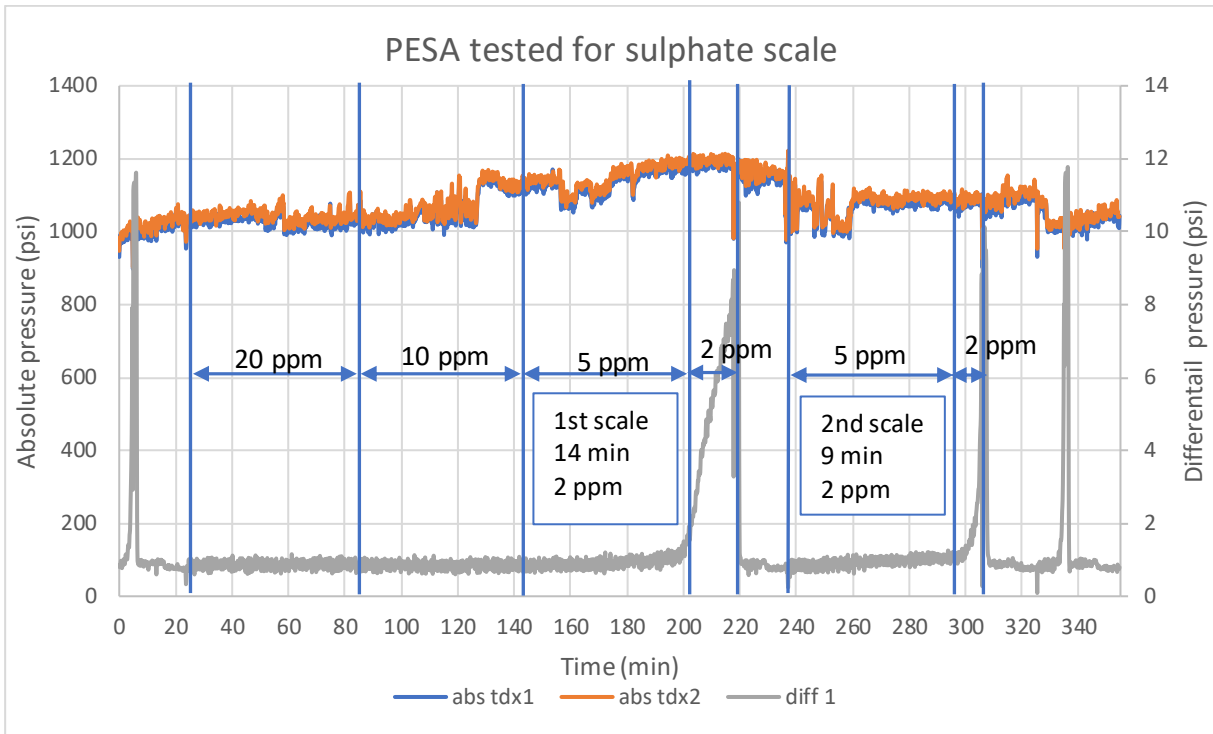


Figure 38 FIC and time values from high-pressure dynamic tube blocking experiments of PESA at pH 6.88 for sulphate scale

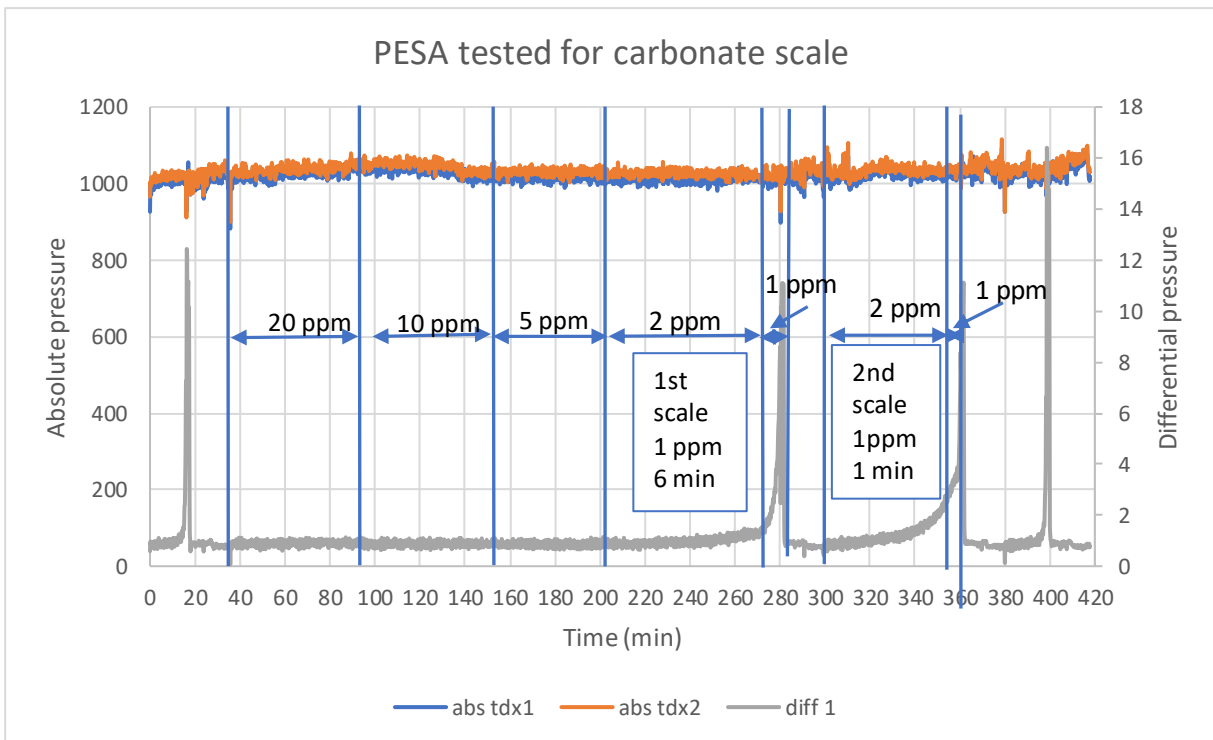


Figure 39 FIC and time values from high-pressure dynamic tube blocking experiments of PESA at pH 6.88 for carbonate scale

For SI-5 the FIC was 20 ppm for 13 min for both runs for sulphate scale, as presented in Figure 40. Figure 41 shows the test results for SI-5 for carbonate scale, the FIC was 50 ppm for 13 min in the first run and 15 min for the second run. The reason for the poor performance of SI-5 for carbonate scale may be related to the compatibility of the phosphonates with divalent metal ions. In this case, the Ca^{2+} ion concentration is higher in the carbonate scale test than in the sulfate test. In this case, the pressure drop increases slowly even at a higher concentration than FIC. However, as the test is limited to 60 minutes the threshold pressure differential is not reached. If the test period were longer FIC would probably be higher than 50 ppm.

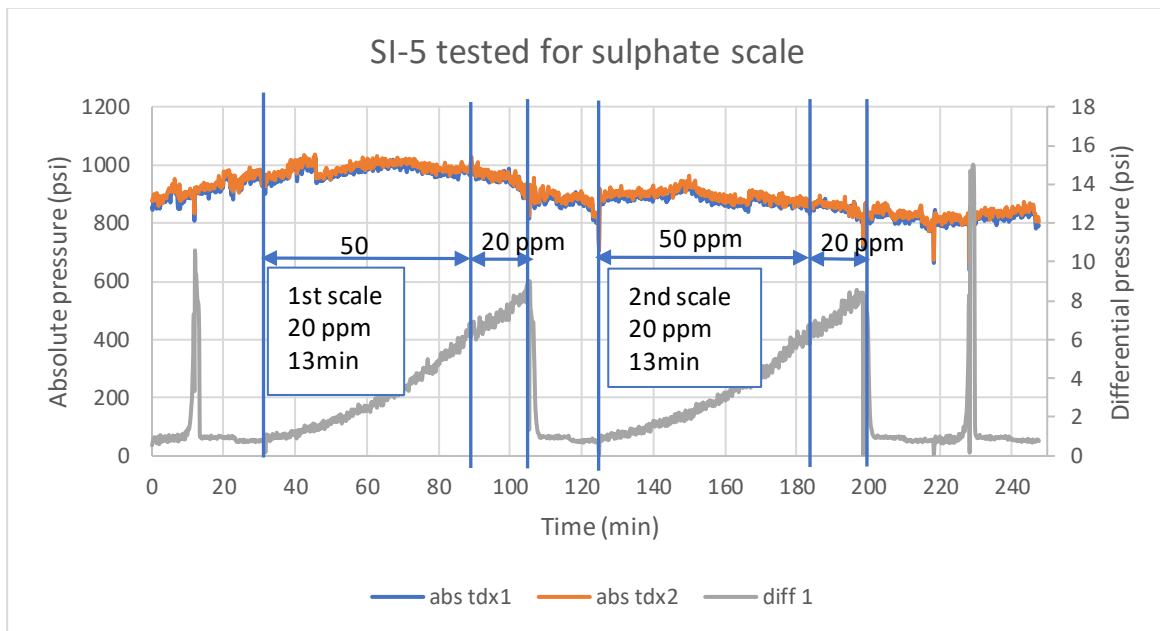


Figure 40 FIC and time values from high-pressure dynamic tube blocking experiments of SI-5 at pH=6.61 for sulphate scale

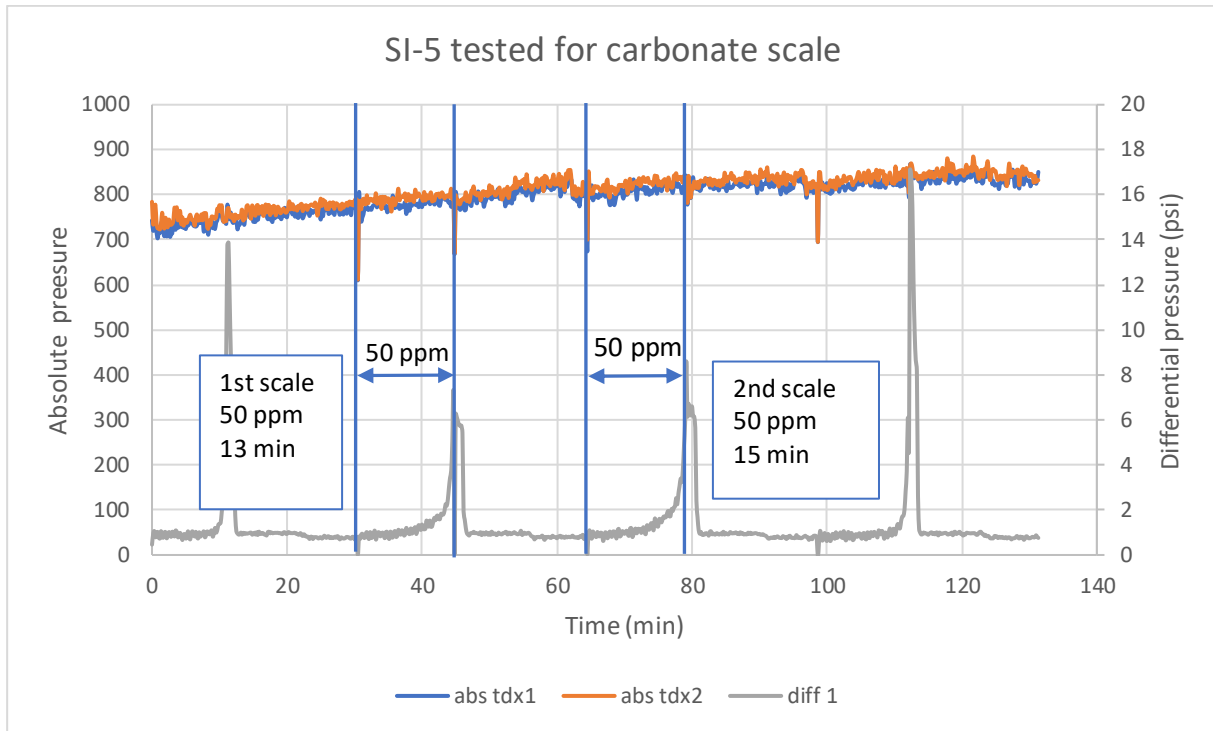


Figure 41 FIC and time values from high-pressure dynamic tube blocking experiments of SI-5 at pH=6.61 for carbonate scale

SI-2 showed good sulphate inhibition for both runs. The FIC was 10 ppm for 20 min for each run, as presented in Table 4 and Figure 42. For carbonate scale SI-2 gave good inhibition, which match the results for the commercial scale inhibitors. The FIC was 2 ppm for 22 min for the first run and 41 min for the second run, as presented in

Table 5 and Figure 43. The graphical slope in Figure 43 shows an indication of compatibility with calcium with SI-2, as discussed earlier.

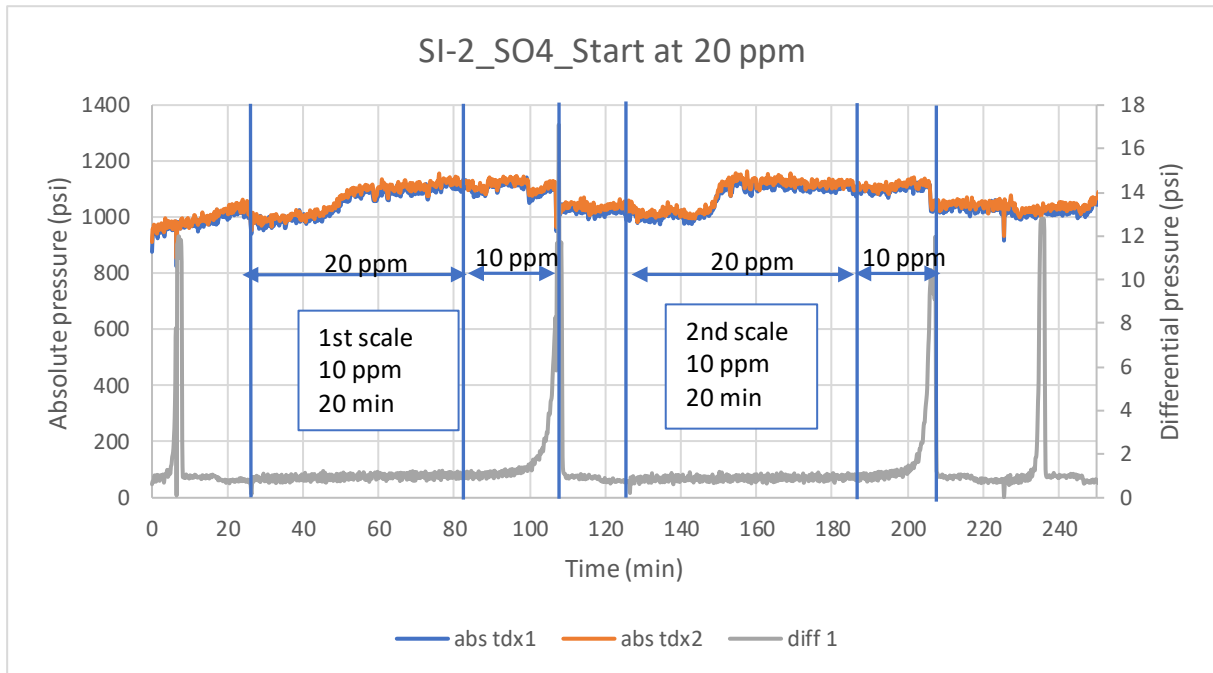


Figure 42 FIC and time values from high-pressure dynamic tube blocking experiments of SI-2 at pH 8.91 for sulphate scale

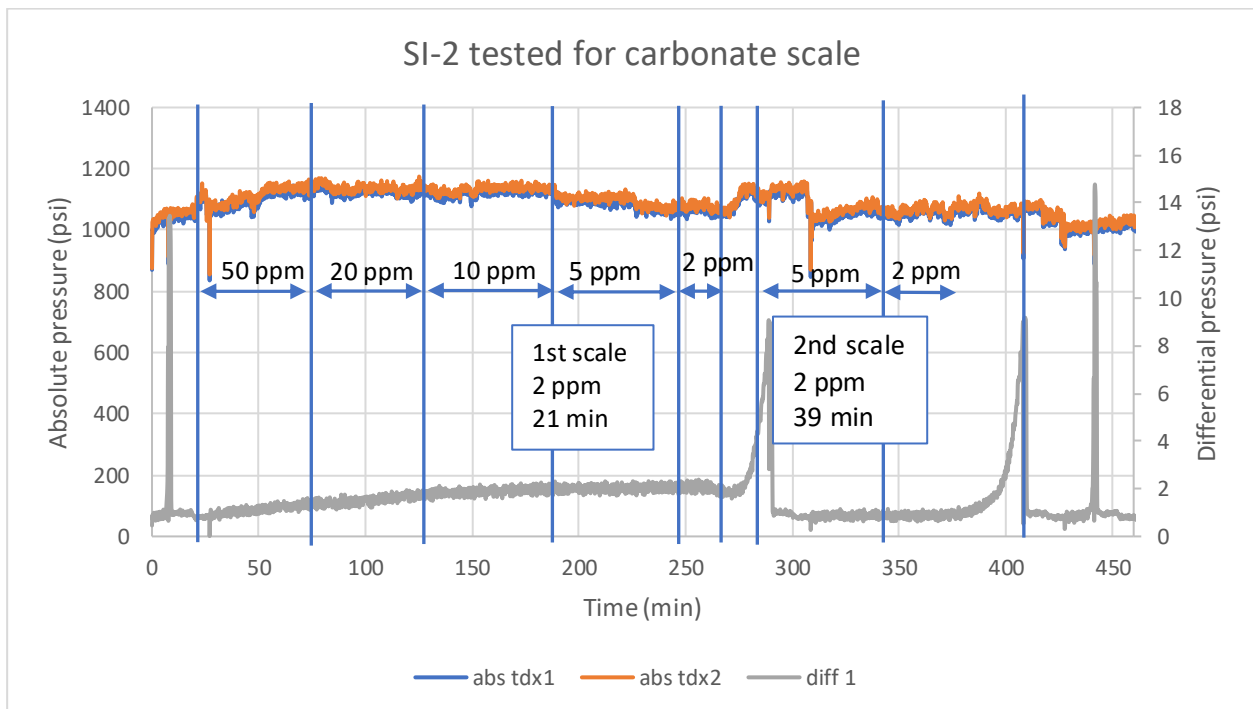


Figure 43 FIC and time values from high-pressure dynamic tube blocking experiments of SI-2 at pH 8.91 for carbonate scale

8.3 Compatibility with calcium test

In the industrial oilfield, calcium compatibility for the SIs is a well-known problem [1]. Sometimes the SIs precipitates with calcium ions, this can cause many problems in the oil production, as discussed in chapter 7.5. The High-Pressure Dynamic Tube test results gives an indication of calcium compatibility for the SIs. The gradual increase in pressure drop shown in Figure 40 and Figure 43 gives an indication of compatibility issues for SI-5 and SI-2 with Calcium (Ca^{2+}). SI-2 gave the best results from the High – Pressure Dynamic tube test, therefore this SI investigated further.

The compatibility test followed the procedure explained in 7.5. It was found that all the tested concentrations of SI-2 showed compatibility with Ca^{2+} at 100 ppm, presented in Table 6.

Table 7 shows that it was poor compatibility with Ca^{2+} (1000 ppm) at the SIs concentrations 100 and 1000 ppm. SI-2 was not compatible with Ca^{2+} at 10 000 ppm, as presented in Table 8.

Table 6 Compatibility Test in 100 ppm of Ca^{2+} and 30 000 ppm NaCl (3.0 wt%) for SI-2

SI	Dose (ppm)	Appearance				
		At mixing	30 min	1 h	4h	24h
SI-2	100	Clear	Clear	Clear	Clear	Clear
SI-2	1000	Clear	Clear	Clear	Clear	Clear
SI-2	10000	Clear	Clear	Clear	Clear	Clear
SI-2	50000	Clear	Clear	Clear	Clear	Clear

Table 7 Compatibility Test in 1000 ppm of Ca²⁺ and 30 000 ppm (3.0% wt%) of NaCl for SI-2

SI	Dose (ppm)	Appearance				
		At mixing	30 min	1 h	4h	24h
SI-2	100	Cloudy	Cloudy	Cloudy	Cloudy	Cloudy
SI-2	1000	Cloudy	Cloudy	Cloudy	Cloudy	Cloudy
SI-2	10000	Clear	Clear	Clear	Clear	Clear
SI-2	50000	Clear	Clear	Clear	Clear	Clear

Table 8 Compatibility Test in 10 000 ppm of Ca²⁺ and 30 000 ppm (3.0% wt%) of NaCl for SI-2

SI	Dose (ppm)	Appearance				
		At mixing	30 min	1 h	4h	24h
SI-2	100	Precipitation	Precipitation	Precipitation	Precipitation	Precipitation
SI-2	1000	Precipitation	Precipitation	Precipitation	Precipitation	Precipitation
SI-2	10000	Precipitation	Precipitation	Precipitation	Precipitation	Precipitation
SI-2	50000	Precipitation	Precipitation	Precipitation	Precipitation	Precipitation

8.4 Thermal stability test

To consider the possibility of using the SIs for squeeze treatments, in which good and long-term thermal stability is needed, a hydrothermal stability test is conducted. The objective of this test was to investigate the performance of the SIs at high temperature and high pressure.

A mixture of 5 wt% solution of SI was heated in a sealed tube at respectively 110 and 130 °C for 1 week, following the instructions in chapter 7.6. The results for thermal aging test is presented in Table 9, Table 10 and Figure 44. The FIC for SI-2 was found to be 20 ppm after 5 min after each run for sulphate scale, presented in Figure 45. For carbonate scale test, scale build up after 18 and 15 min at 10 ppm, as presented in Figure 46. After thermal aging the FIC went from 10 ppm to 20 ppm for sulphate scale, and from 2 ppm to 10 ppm for carbonate scale. This shows that the SI is not thermal stable, but it still has some inhibition effect. The commercial scale inhibitor, PESA, showed good thermal stability. The results showed no difference in FIC for sulphate scale and from 1 ppm to 2 ppm for carbonate scale, illustrated in Figure 47 and Figure 48 respectively.

Table 9 Thermal stability results for sulphate scale

	Thermal stability	First blank	First scale test		Second scale test		Second blank	pH
SI	Temperature	Time	Conc.	Time	Conc.	Time	Time	
Commercial Scale Inhibitors								
Polyaspartate	110	13 min	2 ppm	11 min	2 ppm	27 min	10 min	8.64
Polyaspartate	130	10 min	5 ppm	13 min	5 ppm	18 min	8 min	8.35
PESA	130	12 min	2 ppm	6 min	2 ppm	8 min	11 min	10.54
Self-synthesized Scale Inhibitors								
SI-2	130	5 min	20 ppm	5 min	20 ppm	4 min	11 min	10.54

Table 10 Thermal stability results for carbonate scale

SI	Thermal stability	First blank	First scale test		Second scale test		Second blank	pH
	Temperature	Time	Conc.	Time	Conc.	Time	Time	
Commercial Scale Inhibitors								
PESA	130	13 min	2 ppm	18 min	2 ppm	18 min	14 min	10.54
Self-synthesized Scale Inhibitors								
SI-2	130	8 min	10 ppm	18 min	10 ppm	15 min	7 min	10.54

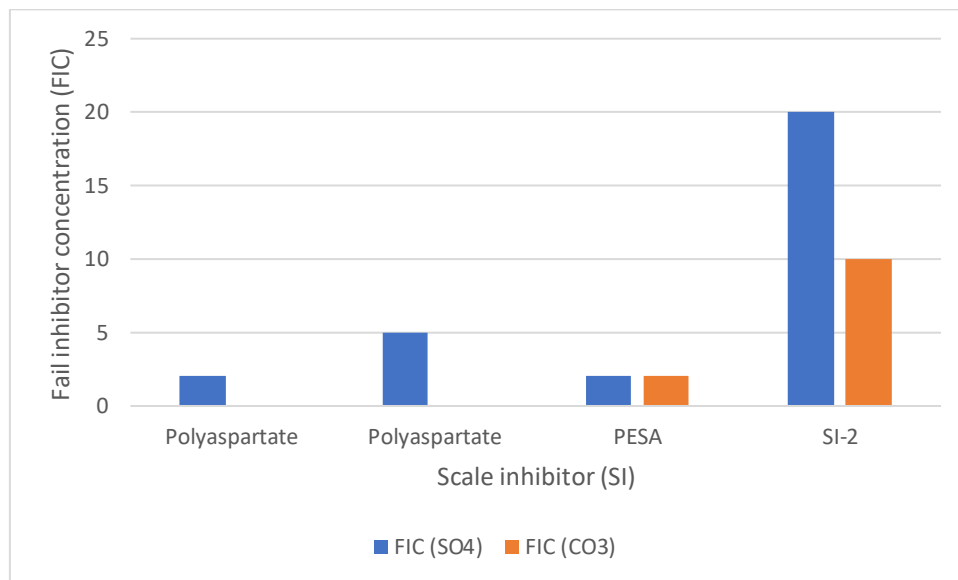


Figure 44 FIC results for self-synthesized and commercial SIs for sulphate and carbonate scales after Thermal aging.

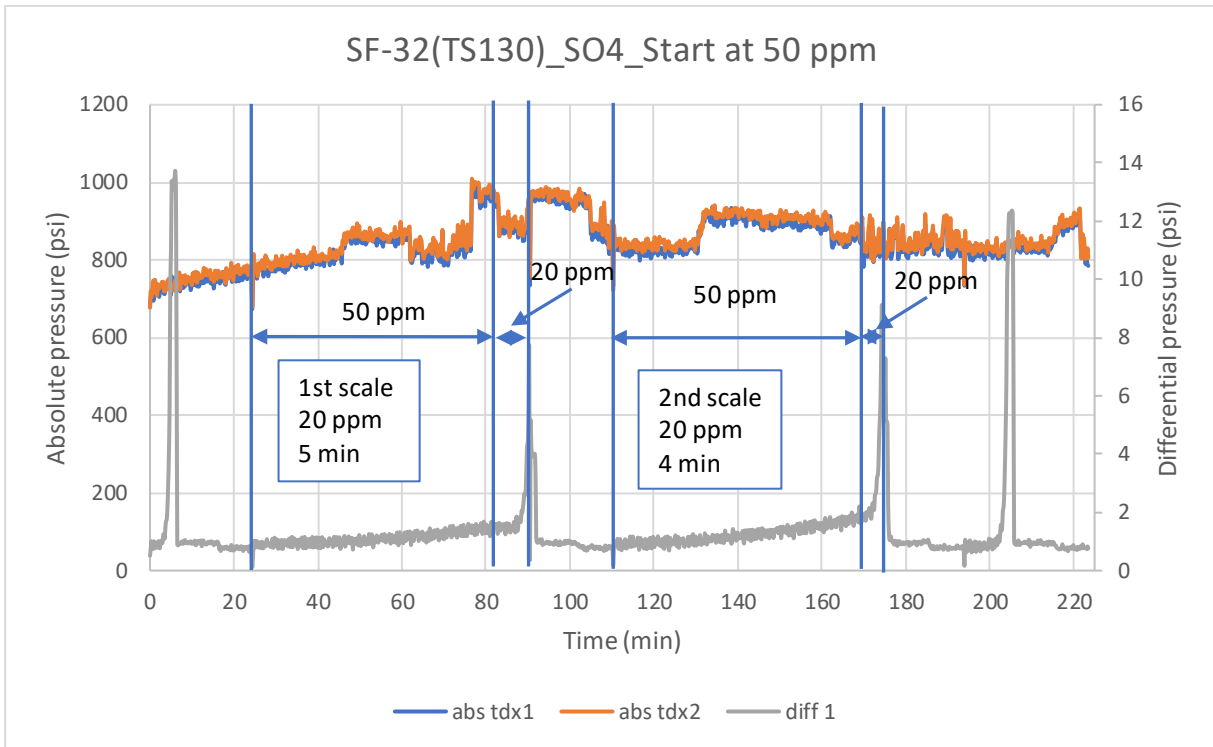


Figure 45 FIC and time values after 1 week thermal aging at 130 °C of SI-2 for sulphate scale

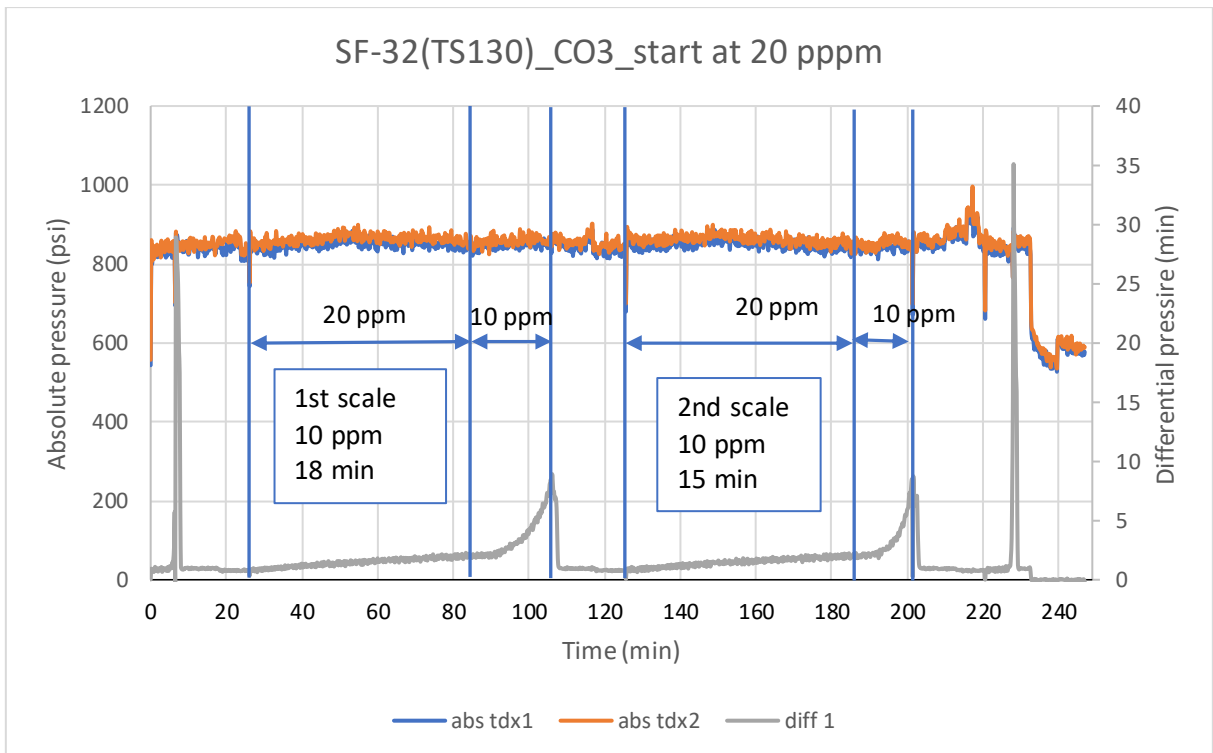


Figure 46 FIC and time values after 1 week thermal aging at 130 °C of SI-2 for carbonate scale

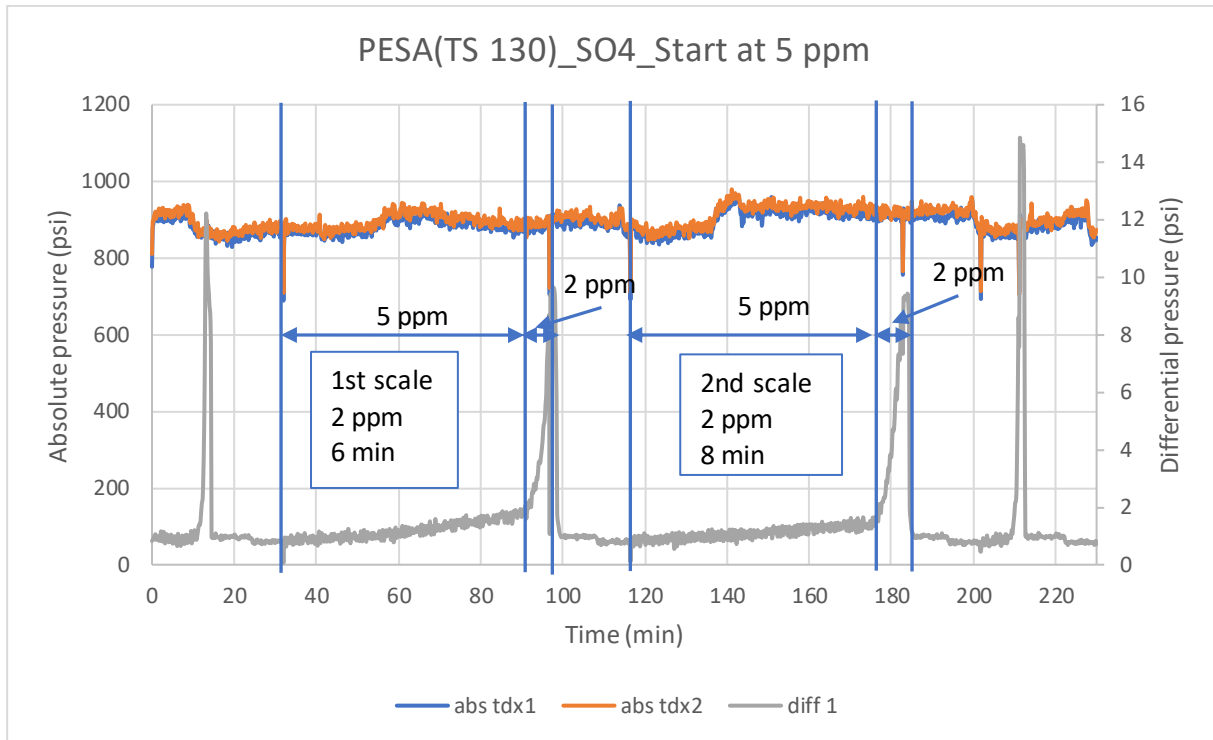


Figure 47 FIC and time values after 1 week thermal aging at 130 °C of PESA at pH=10.84 for sulphate scale

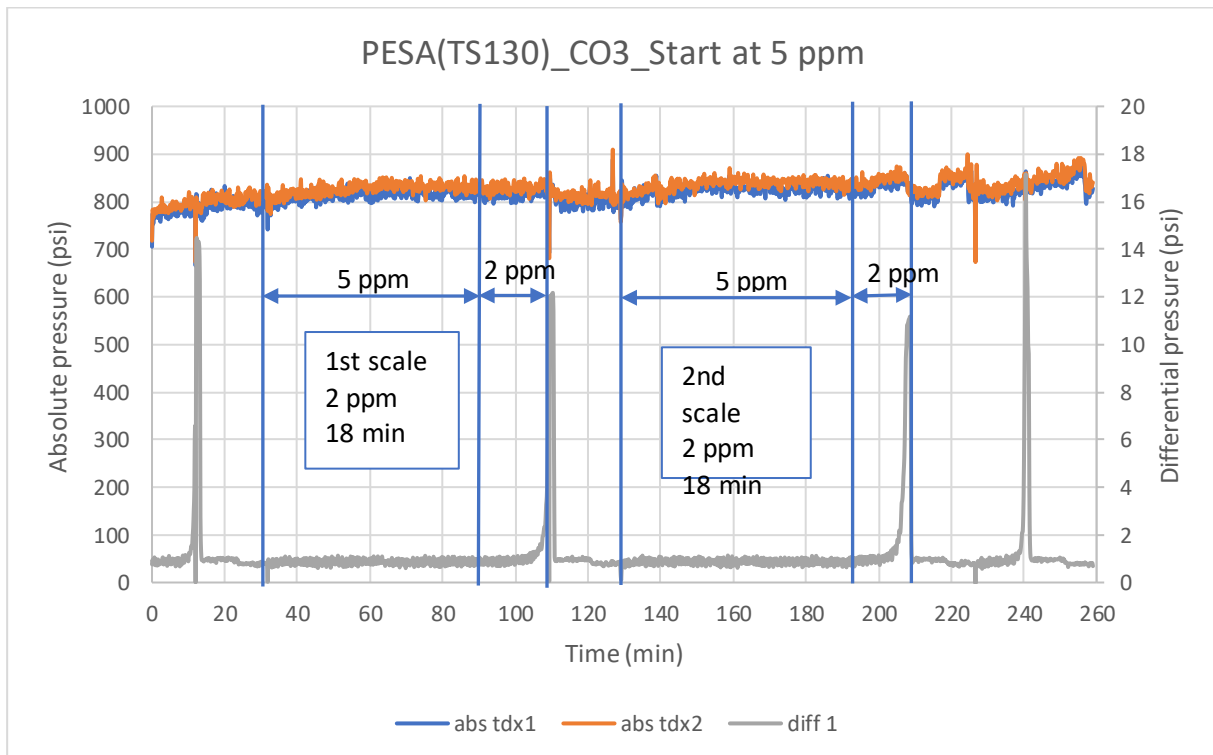


Figure 48 FIC and time values after 1 week thermal aging at 130 °C of PESA at pH=10.54 for carbonate scale

8.5 SI Seawater Biodegradability test

The biodegradation activities of the synthesized SIs were measured and evaluated in comparison to sodium benzoate as the biodegradable reference. Table 11 presents the BOD for the calibration standard, sodium benzoate, and SI with and without nutrients. It is well-known that sodium benzoate is degraded very well with no significant lag time, giving a 28 day biodegradation of about 84-94% without assimilation include in the calculation [28]. The results in Table 11 is test results from in-house (UIS), while Table 12 are test results from Baker Hughes Norway AS. The test results from Baker Hughes Norway are after 14 days, and is just an early indication of the biodegradability.

Table 11 Biodegradation Activity measured by the OECD 306 procedure over 28 days

Inhibitor	% BOD by OECD 306
Seawater	0
Sodium benzoate	85
SI-2 (before phosphonation)	56

The biodegradable test for SI-2 before phosphonation, Figure 49, was run to compare the degree of biodegradation before and after the aminomethylenephosphonate groups where added. The results showed fairly good degradation of 56 % before the phosphonation.

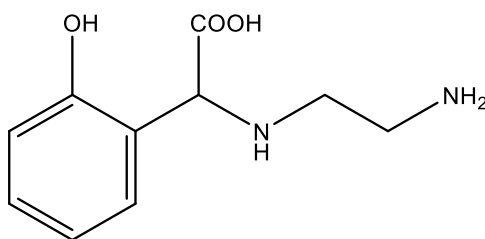


Figure 49 SI-2 before phosphonation, 2-((2-aminoethyl)amino)-2-(2-hydroxyphenyl)acetic acid.

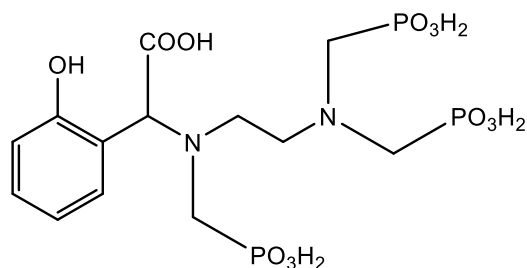


Figure 50 SI-2 after phosphonation, 2-((2-(bis(phosphonomethyl)amino)ethyl)(phosphonomethyl)amino)-2-(2-hydroxyphenyl)acetic acid

The BOD for the of the commercial SIs and one self-synthesized SI, is listed in Table 12. The Results after 14 days showed poor degradation of 9 % for HPAA and 17% for PESA. SI-2 showed low seawater biodegradation activity over 14 days in OECD 306, which indicates the phosphonation is the reason for poor biodegradation. This shows that SI-2 after the phosphonation, Figure 50, led to a lower biodegradability. However, the test is ongoing for 14 more days. This may result in a higher biodegradation activity after 28 days.

Table 12 Biodegradation Activity measured by the OECD 306 procedure over 14 days

Inhibitor	% BOD by OECD 306
Seawater	0
HPAA	9
PESA	17
SI-2 (before phosphonation)	11

9 Conclusion

In this study, seven self-synthesized SIs have been developed. The self-synthesized SIs have been compared and evaluated with commercial SIs through a series of tests. The tests include high-pressure dynamic tube blocking, thermal stability and seawater biodegradability.

1. The self-synthesized scale inhibitors were all functionalized with methylene phosphonates groups using the Moedritzer-Irani reaction. The difference between the SIs is that they have different functional groups (-OH, -SO₃H or -COOH) and consist of a various number of amines. Of all the seven self-synthesized SIs, only SI-2, SI-4 and SI-6 have promising results. It was found that SI-2 gave moderate inhibition for sulphate scaling and good inhibition for carbonate scale. SI-4 gave moderate inhibition for sulphate and carbonate scale. SI-6 gave poor inhibition for sulphate scale and moderate inhibition for carbonate scale. SI-2 has the following functional groups alcohol, carboxylic acid and aminomethylenephosphonates. SI-4 and SI-6 consist of benzene rings with attachment of two different functional groups. SI-4 has carboxylic acid as the functional group, in addition to the two methylene phosphonate groups attached to the amine. SI-6 has sulfonic acid as the functional group, in addition to the two methylene phosphonate groups attached to the amine. The structures are based on results from NMR.
2. The performance of the SIs was tested in a dynamic tube blocking equipment to determine the fail inhibitor concentration (FIC) at approximately 80 bar and 100°C. The self-synthesized SIs have been compared with the commercial SIs. CMI, GF-175-45, Polyaspartate (ThermPhos), Polyaspartate (Nanochem) and PESA gave good inhibition for sulphate and carbonate scale. Of the self-synthesized SIs, SI-2 gave good inhibition for carbonate scale (2 ppm) and moderate inhibition for sulphate scale (10 ppm). The performance of SI-4 was moderate for sulphate and carbonate scale inhibition, the FIC was respectively 10 ppm and 20 ppm. SI-6 gave good inhibition for carbonate scale and poor inhibition for sulphate scale, with a FIC respectively of 10 ppm and 100 ppm. The thermal stability test indicated that PESA is thermal stable after 1 week at 130°C. For SI-2 the thermal stability test indicates that the SI was not stable

at 130 °C. This means that SI-2 can only be used for continual injection (topside or downhole).

3. Unfortunately, the biodegradation test could not be completed before the end of this study. The conclusion in this study is based on the results after 14 days. The biodegradation test for SI-2 showed only 11 % seawater biodegradation after 14 days. It is likely that the phosphonate groups are the reason for the low biodegradation. As a separate biodegradable test for SI-2 before phosphonation result in a biodegradation of 56% after 28 days. The commercial scale inhibitors also show poor biodegradation after 14 days, HPAA with 9 % and PESA with 17 % biodegradation.

In summary, the commercial and some of the self- synthesized SIs, showed good to excellent inhibition. However, the self-synthesized SI does not seem to be thermal stable. The biggest challenge is probably that none of them is biodegradable in seawater.

The individual functional groups are all biodegradable. However, it seems like that when they are synthesized to one product they become much less biodegradable. It might be a good idea to study the process of biodegradation to understand why the combination gives poor biodegradation. With this knowledge, it might be possible to synthesize a biodegradable scale inhibitor.

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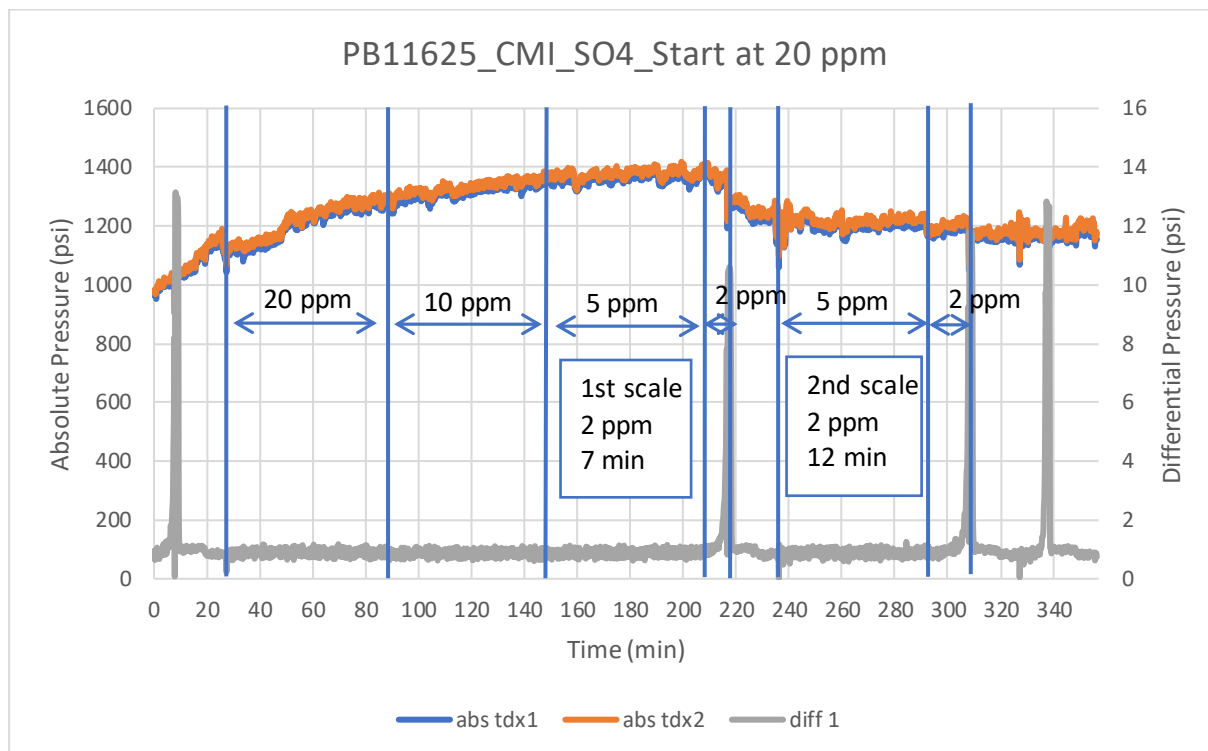
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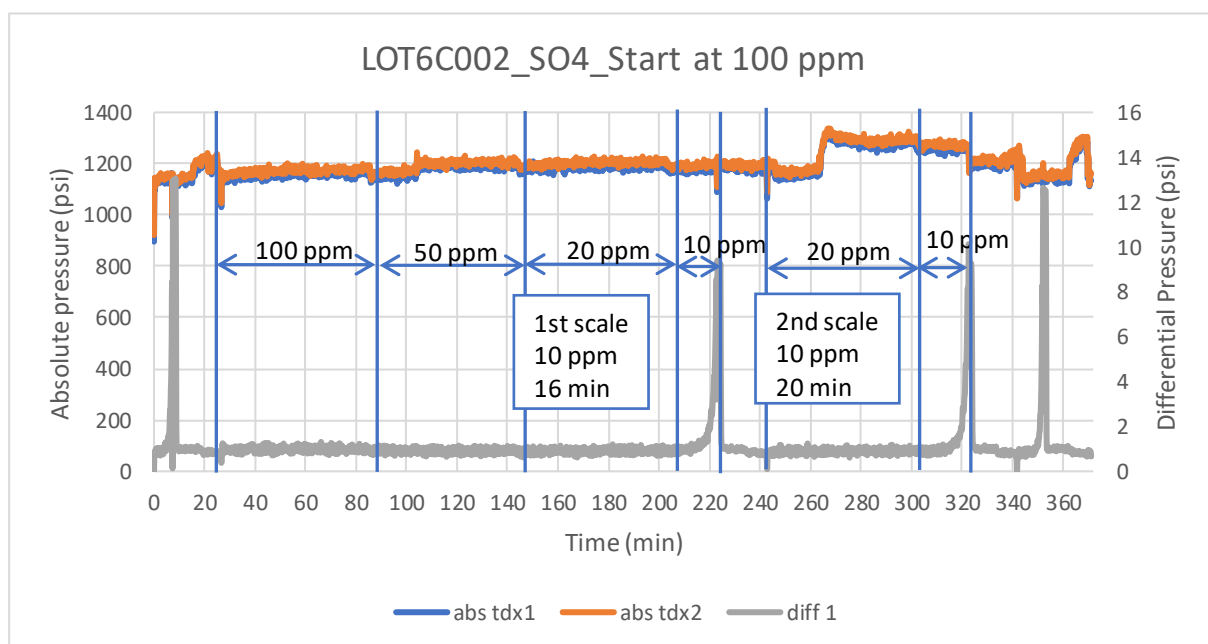
11 Appendix

11.1 High-pressure Dynamic Tube blocking graphic test results

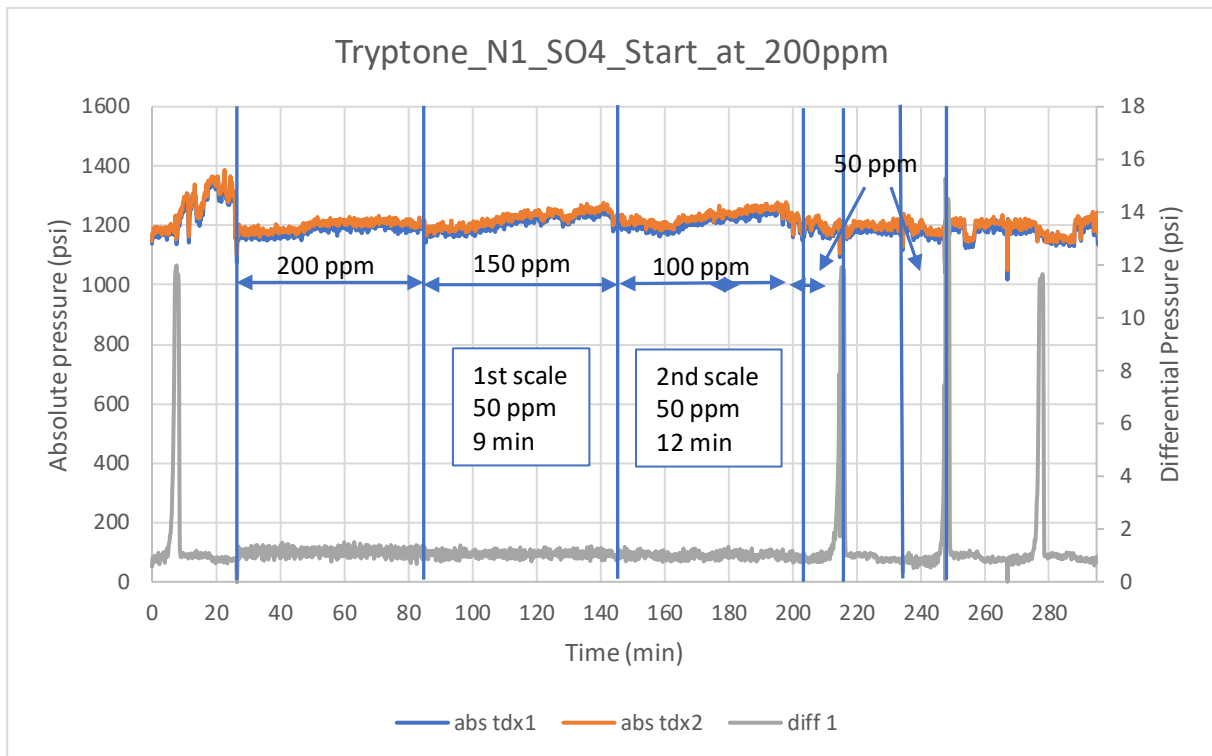
11.1.1 Commercial scale inhibitors



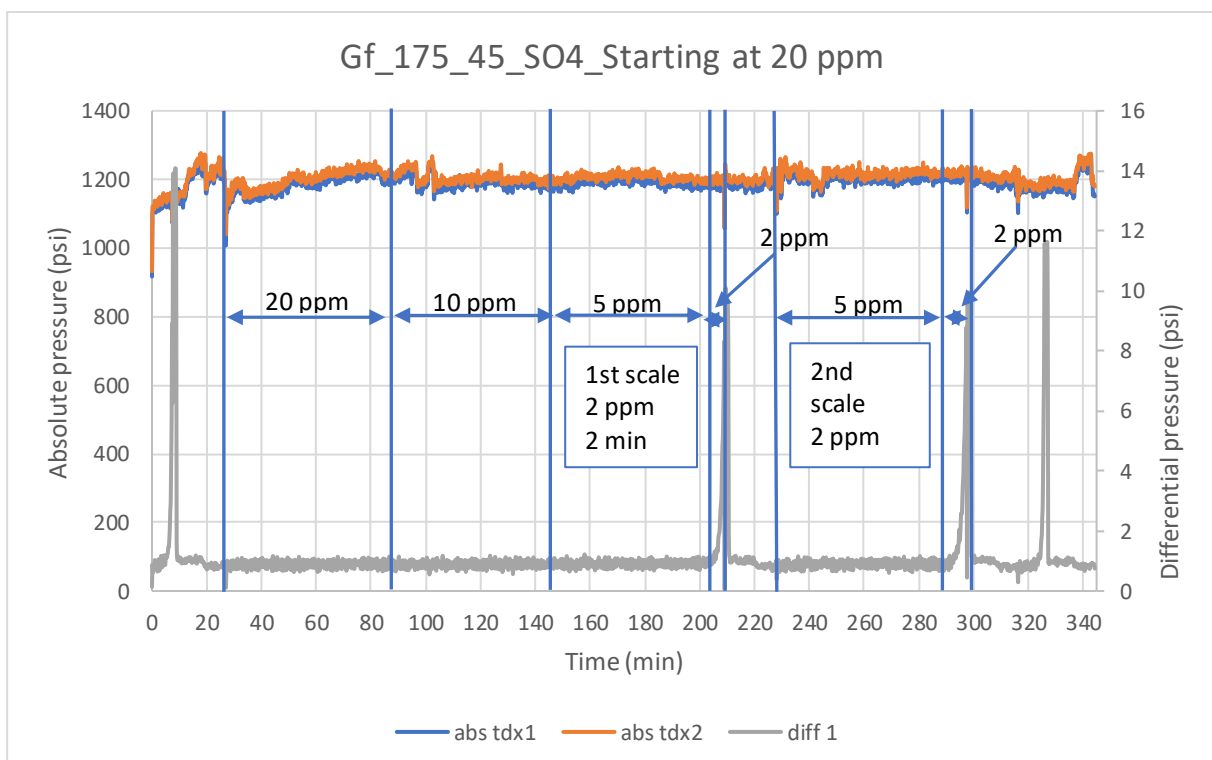
Graph 1 CMI (Thermphos) tested for sulphate scale, start at 20 ppm.



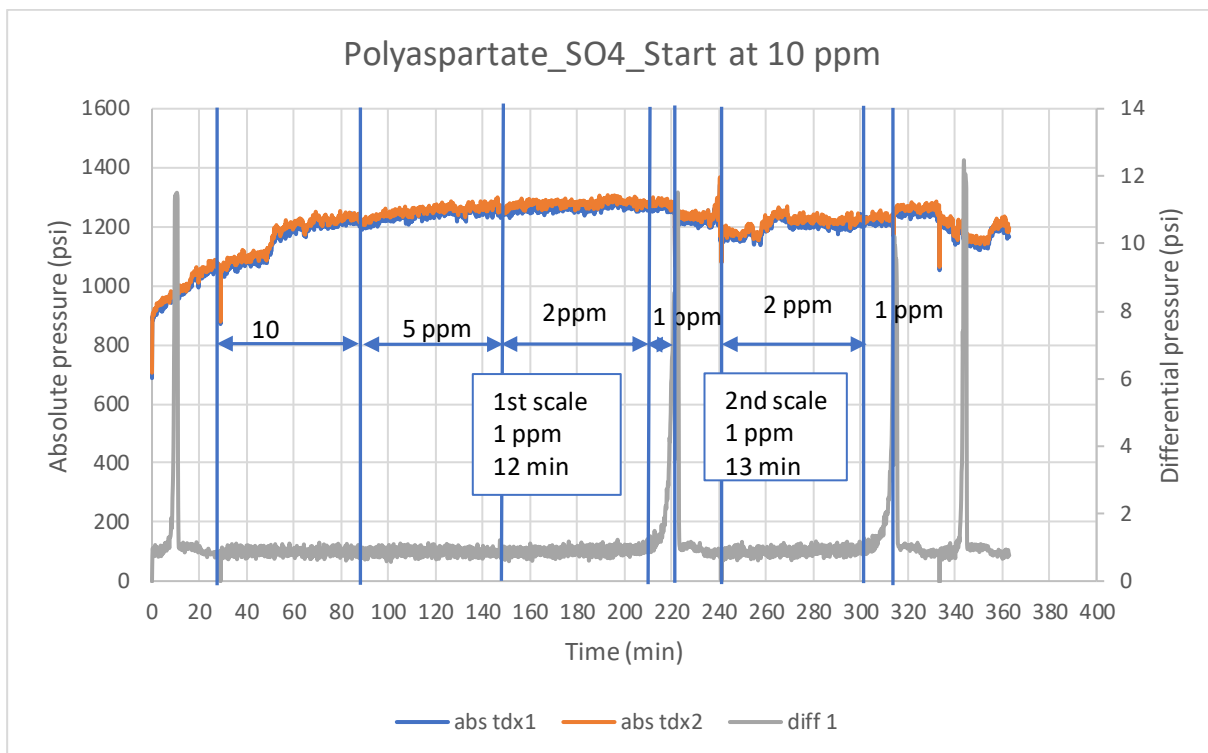
Graph 2 LOT6C002 tested for sulphate scale, start at 100 ppm.



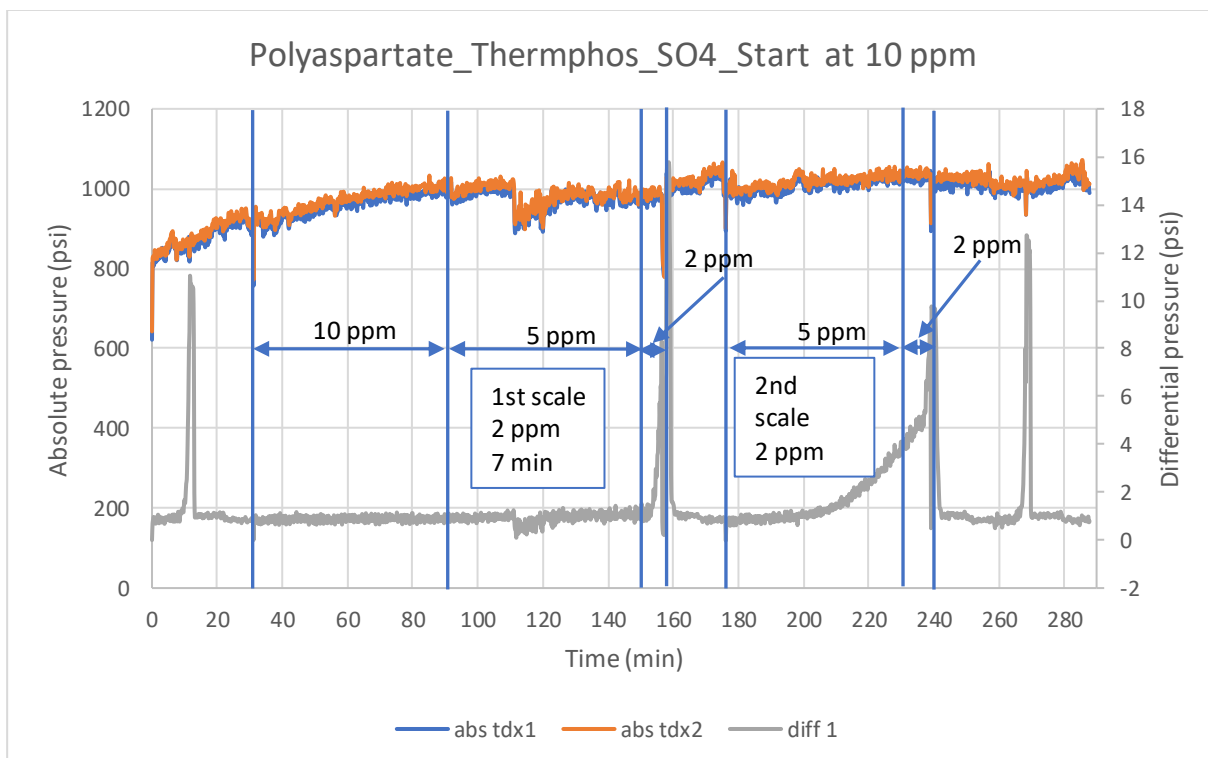
Graph 3 Tryptone N1 tested for sulphate scale, start at 200 ppm.



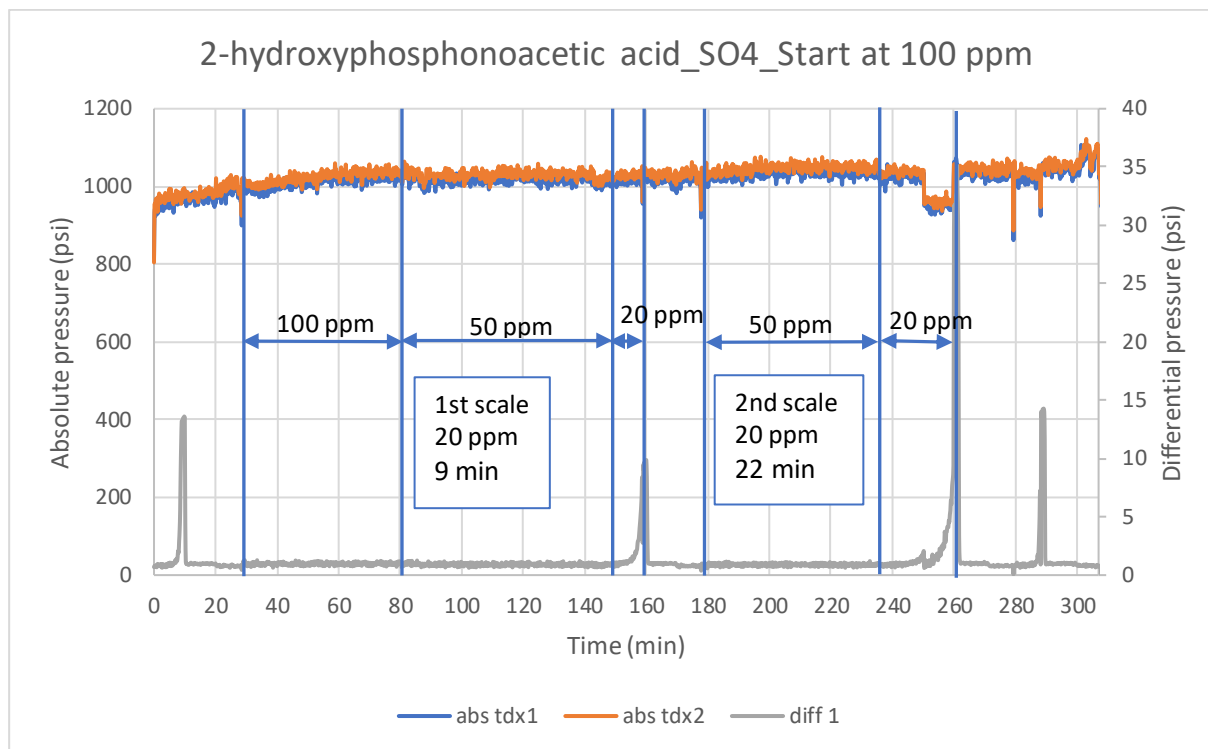
Graph 4 Gf 17545 tested for sulphate scale, start at 20 ppm.



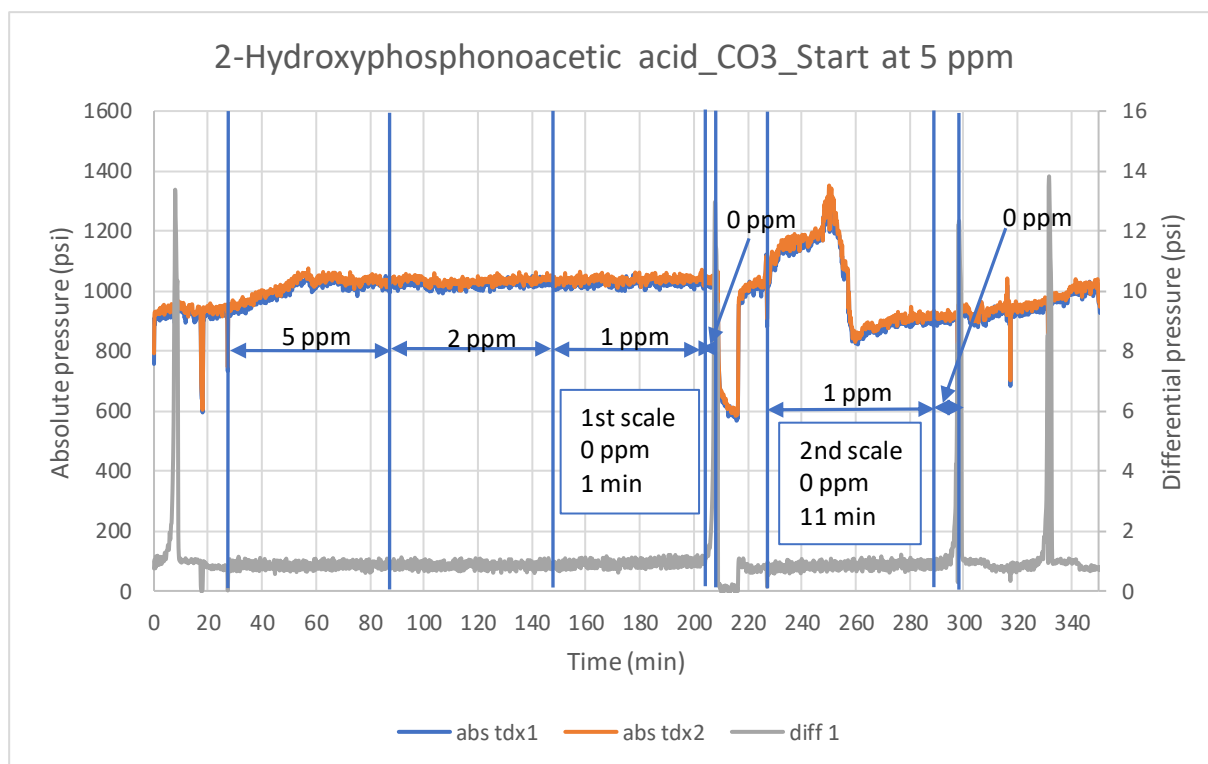
Graph 5 Polyaspartate tested for sulphate scale, start at 10 ppm.



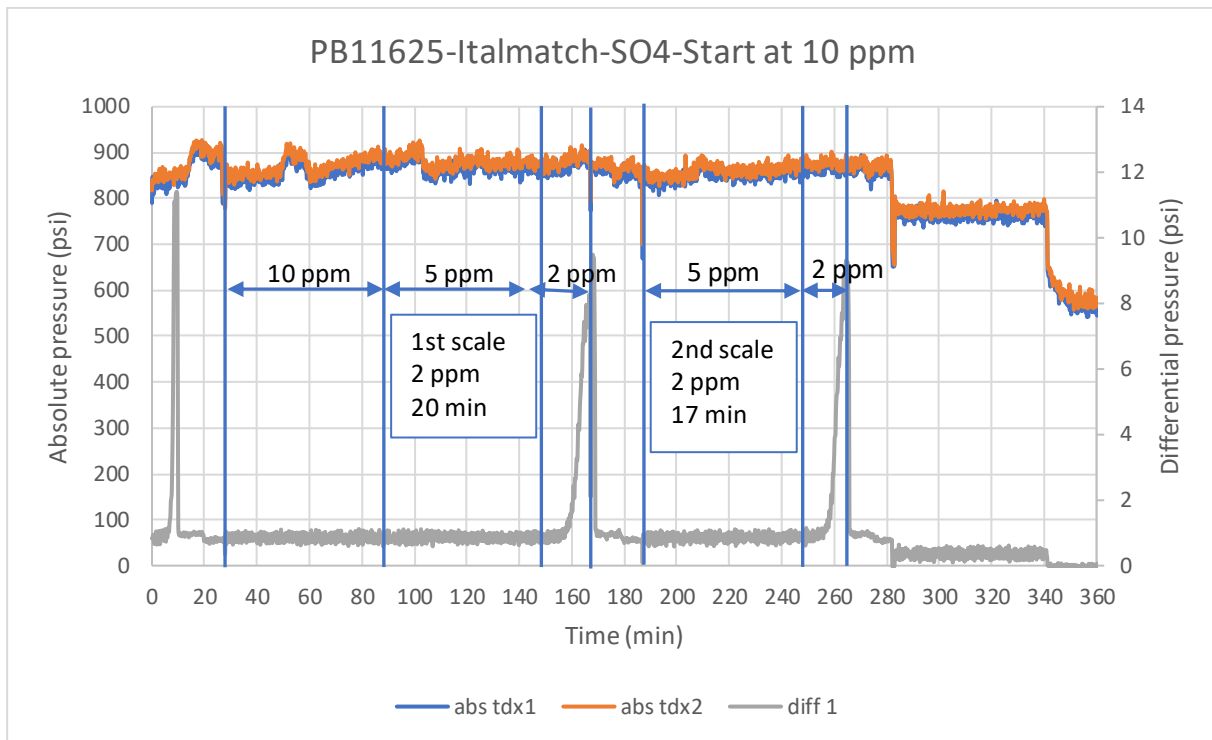
Graph 6 Polyaspartate (Thermphos) tested for sulphate scale, start at 10 ppm.



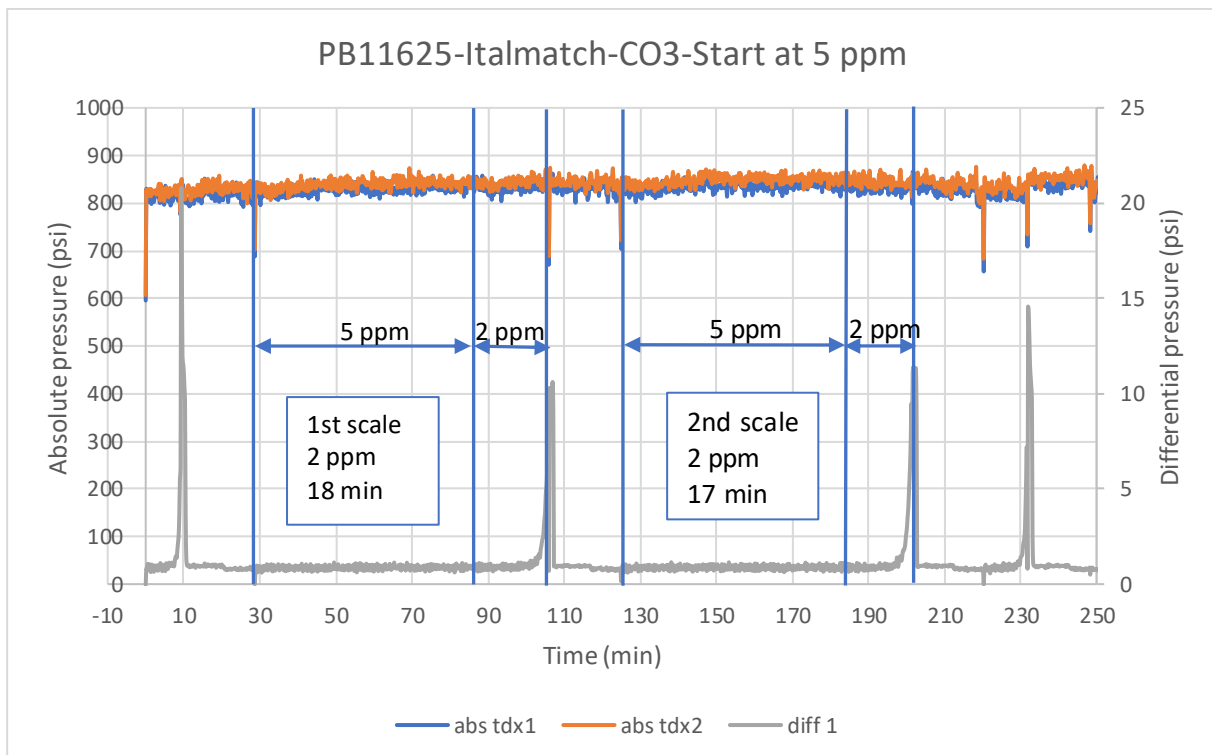
Graph 7 2-Hydroxyphosphonoacetic acid tested for sulphate scale, start at 100 ppm.



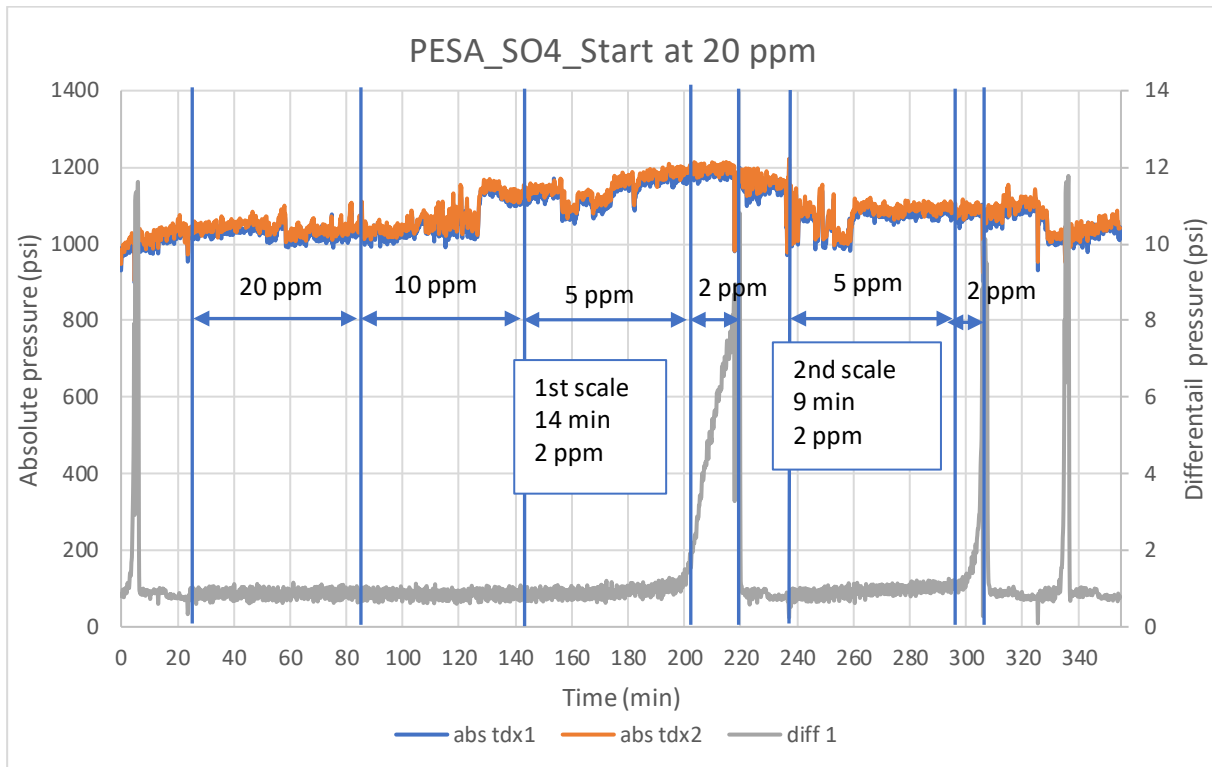
Graph 8 2-Hydroxyphosphonoacetic acid tested for carbonate scale, start at 5 ppm.



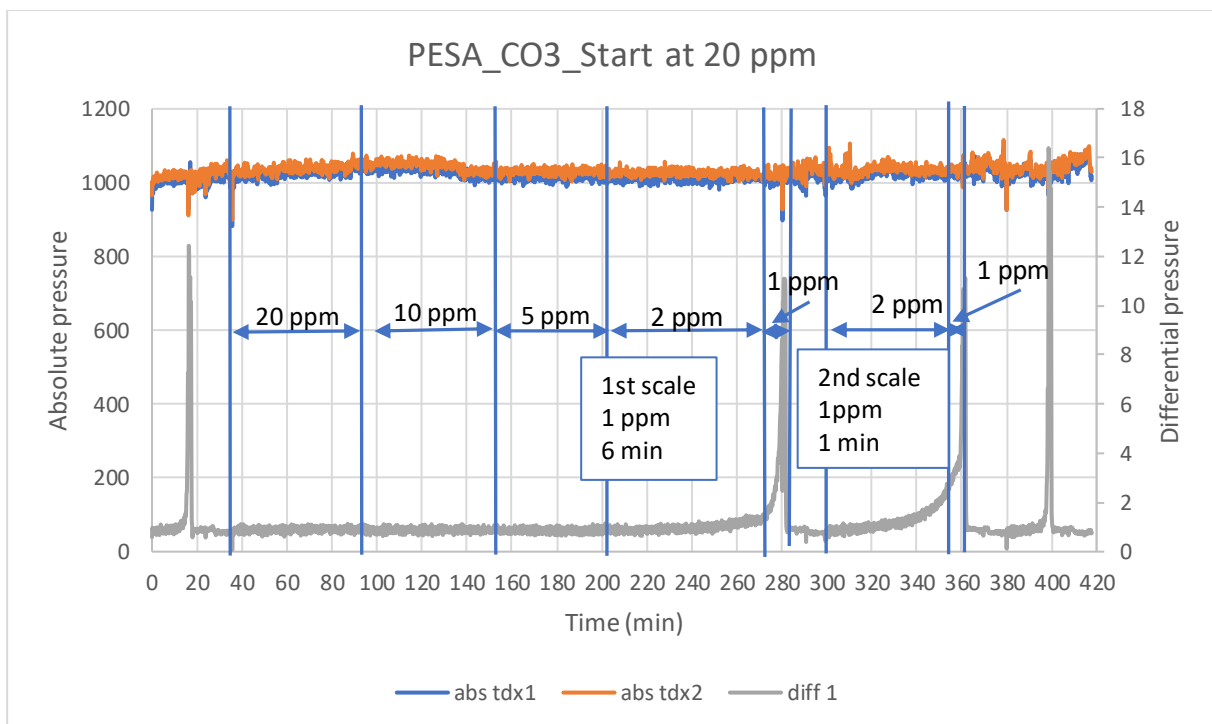
Graph 9 CMI (Italmatch) tested for sulphate scale, start at 10 ppm.



Graph 10 CMI (Italmatch) tested for carbonate scale, start at 5 ppm.

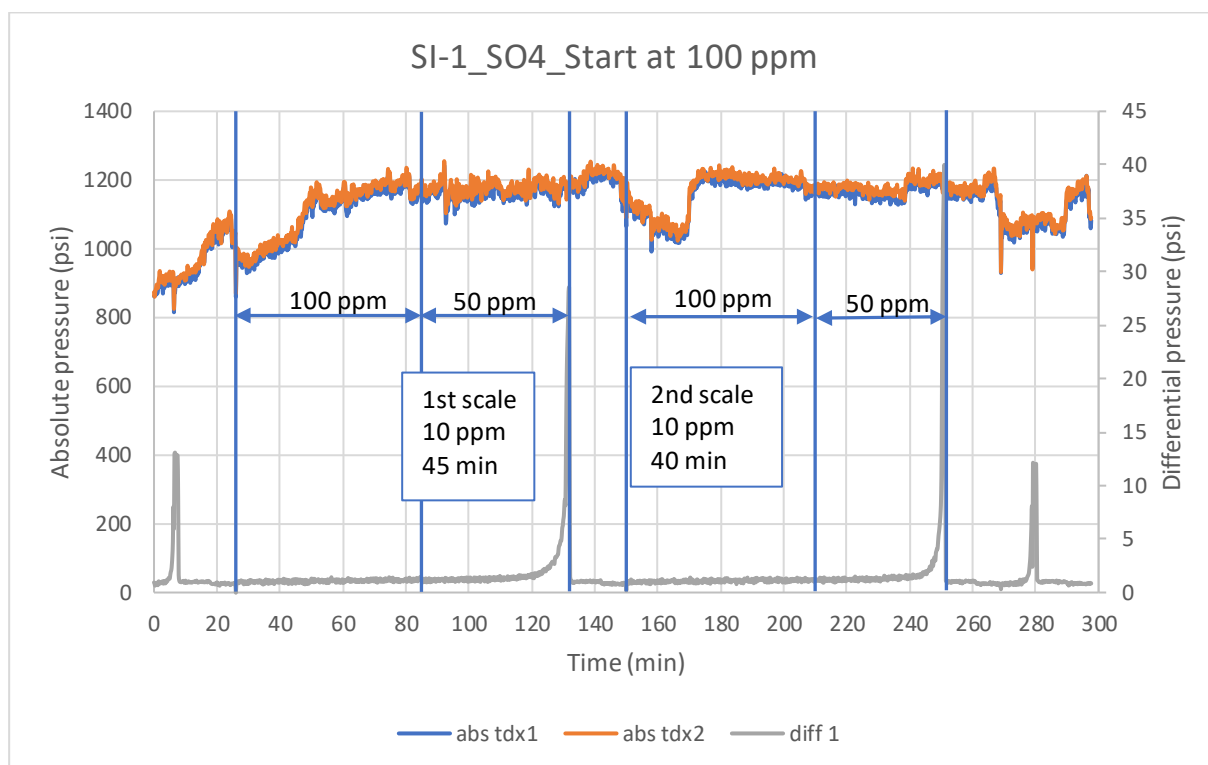


Graph 11 PESA tested for carbonate scale, start at 20 ppm.

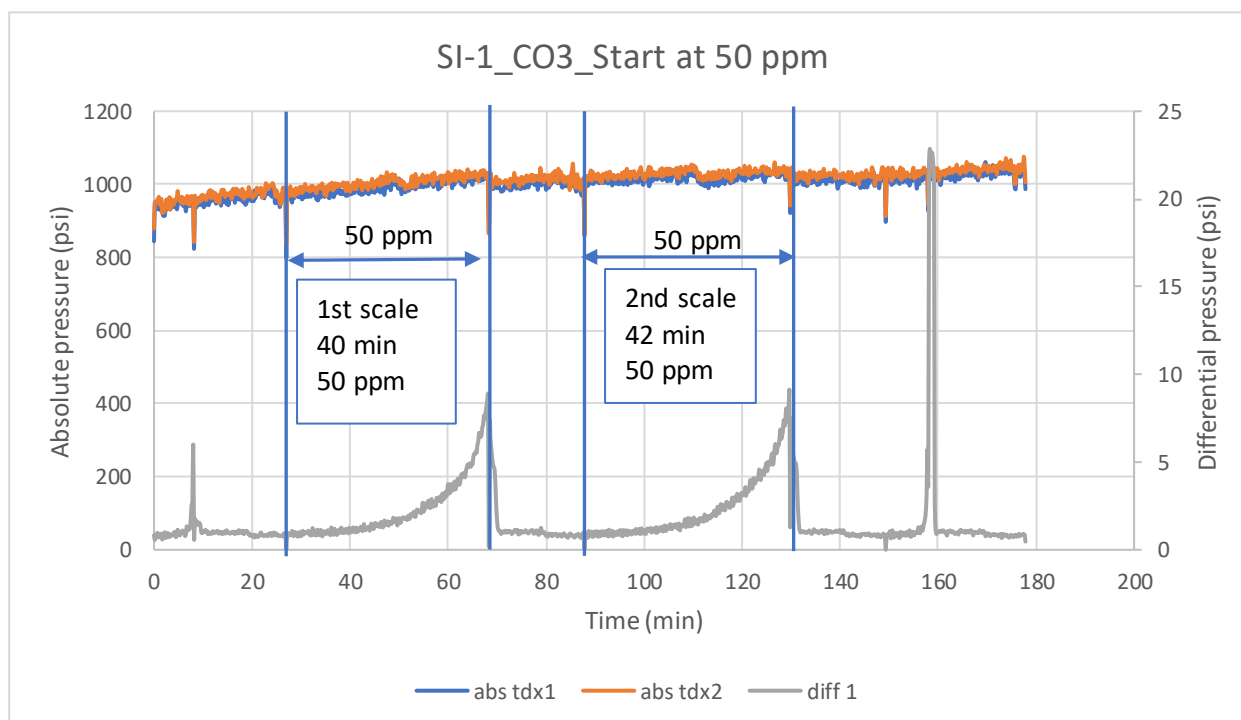


Graph 12 PESA tested for sulphate scale, start at 20 ppm.

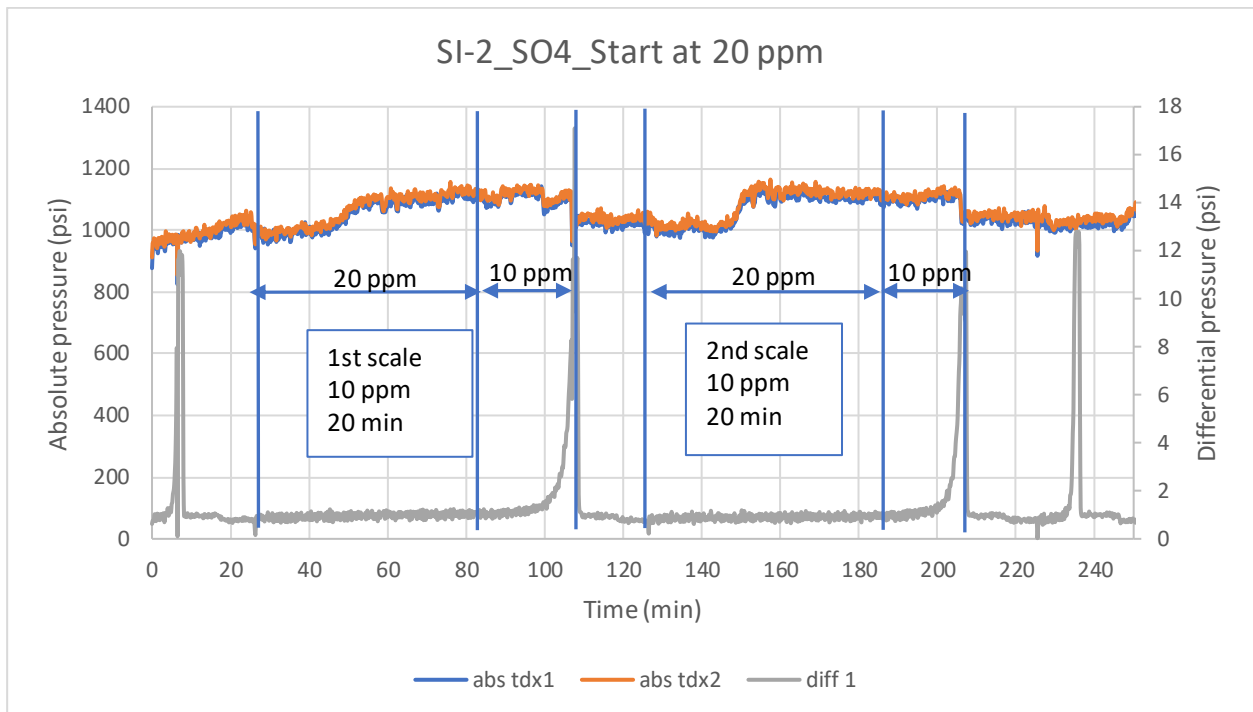
11.1.2 Self-synthesized scale inhibitors



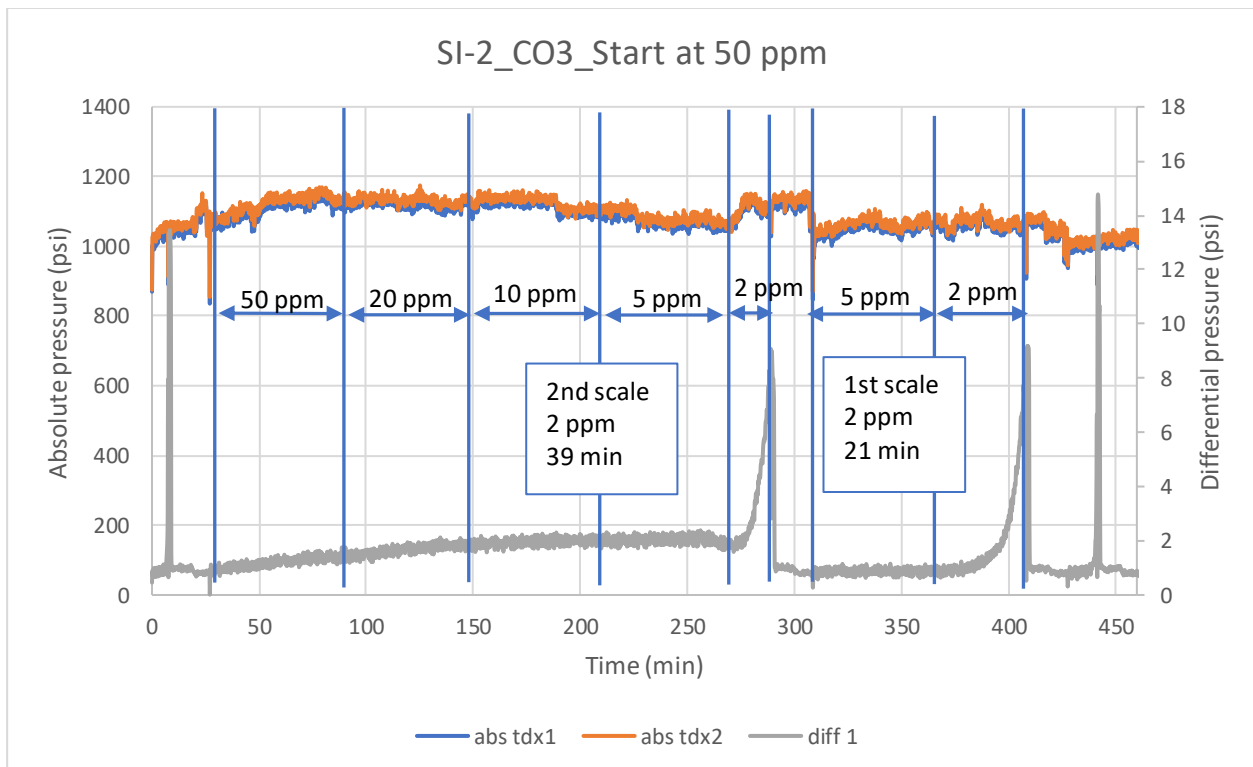
Graph 13 SI-1 tested for sulphate scale, start at 100 ppm.



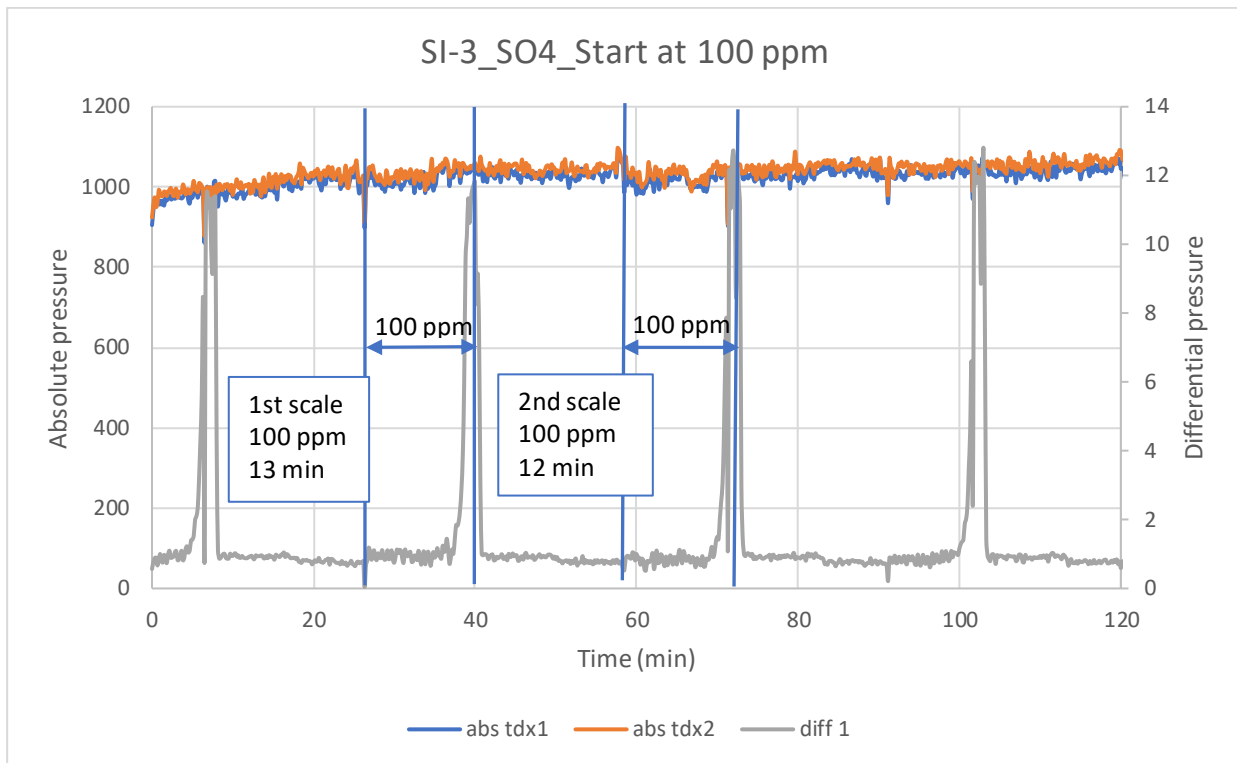
Graph 14 SI-1 tested for carbonate scale, start at 50 ppm.



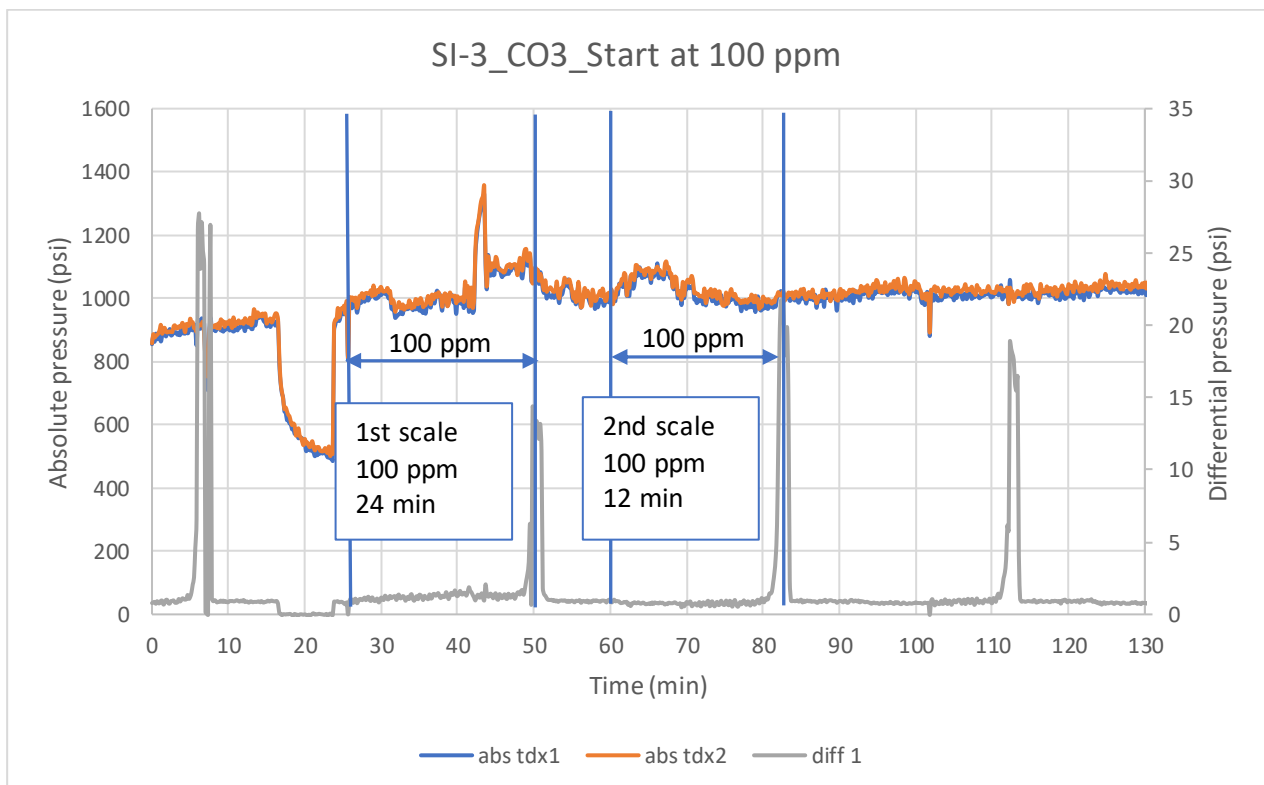
Graph 15 SI-2 tested for sulphate scale, started at 20 ppm.



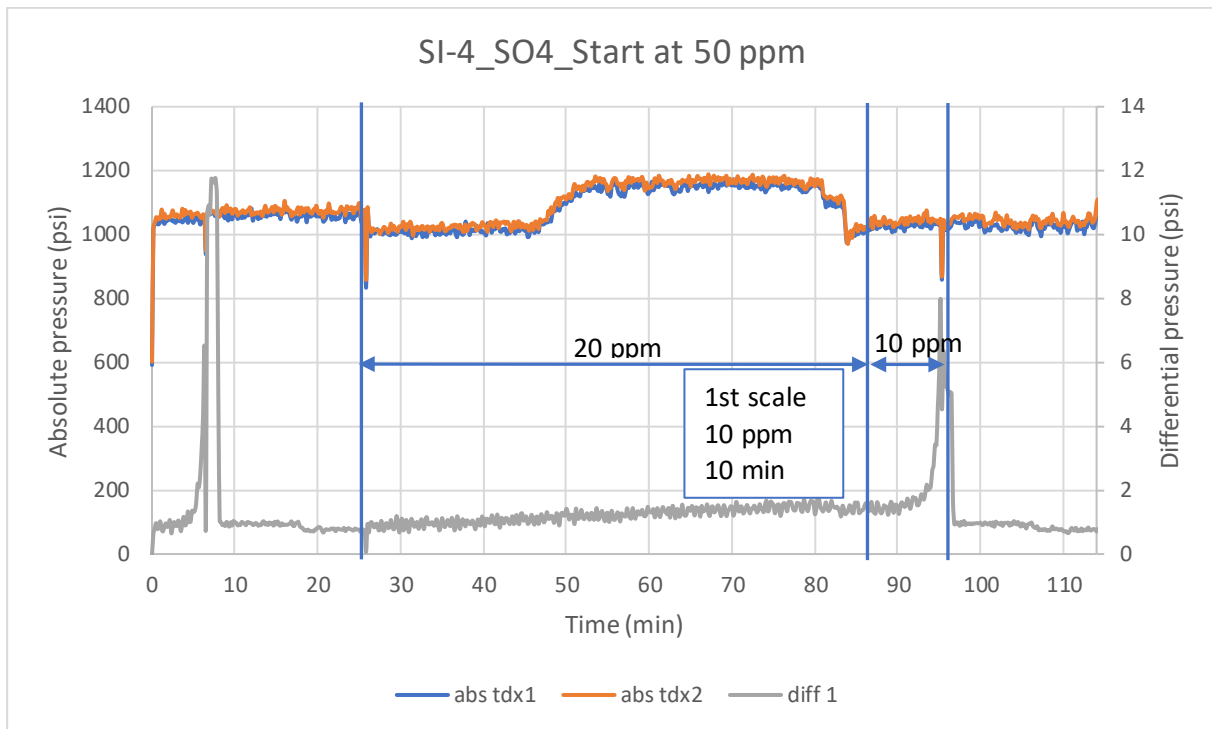
Graph 16 SI-2 tested for carbonate scale, started at 50 ppm.



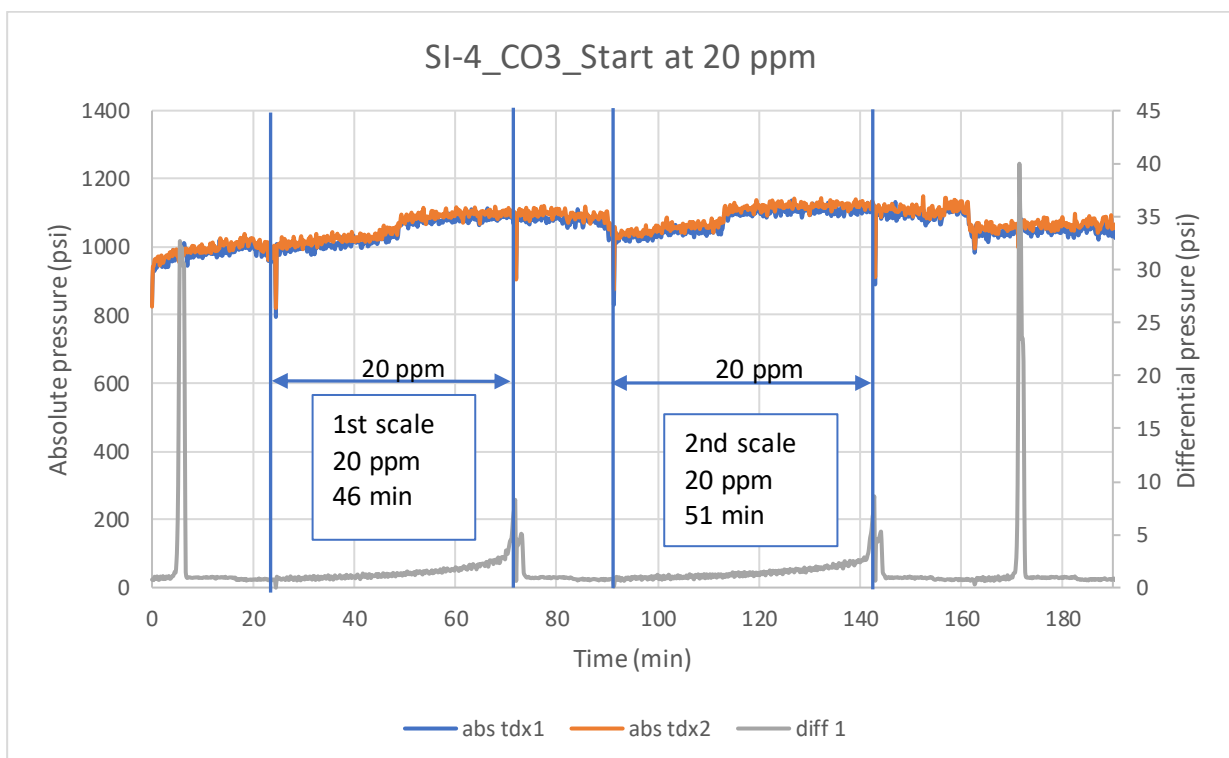
Graph 17 SI-3 tested for sulphate scale, start at 100 ppm



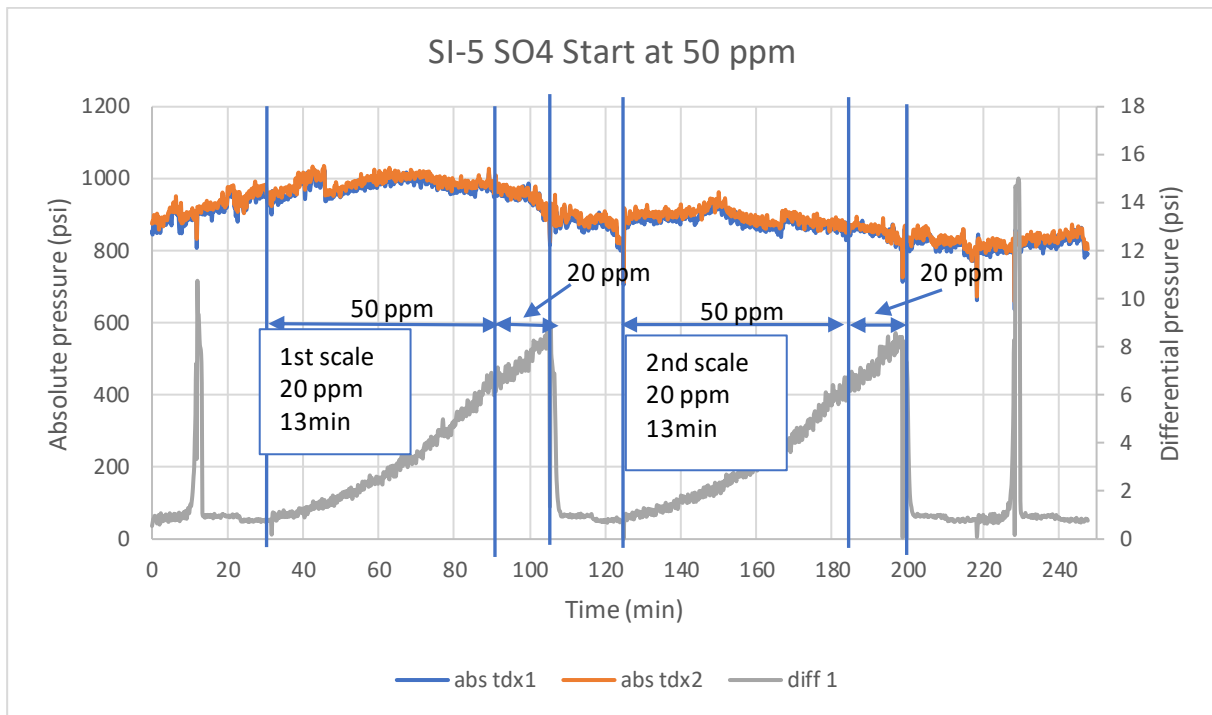
Graph 18 SI-3 tested for carbonate scale, start at 100 ppm.



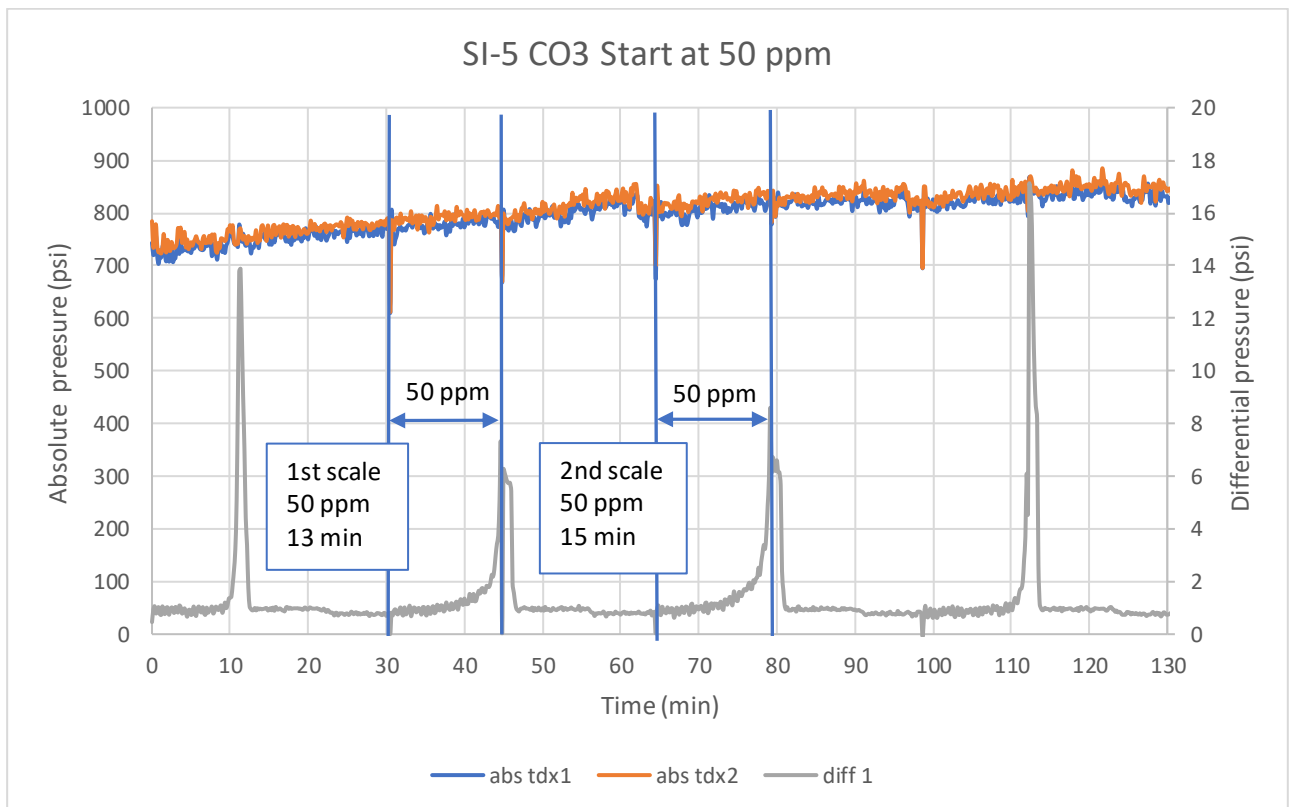
Graph 19 SI-4 tested for sulphate scale, start at 50 ppm.



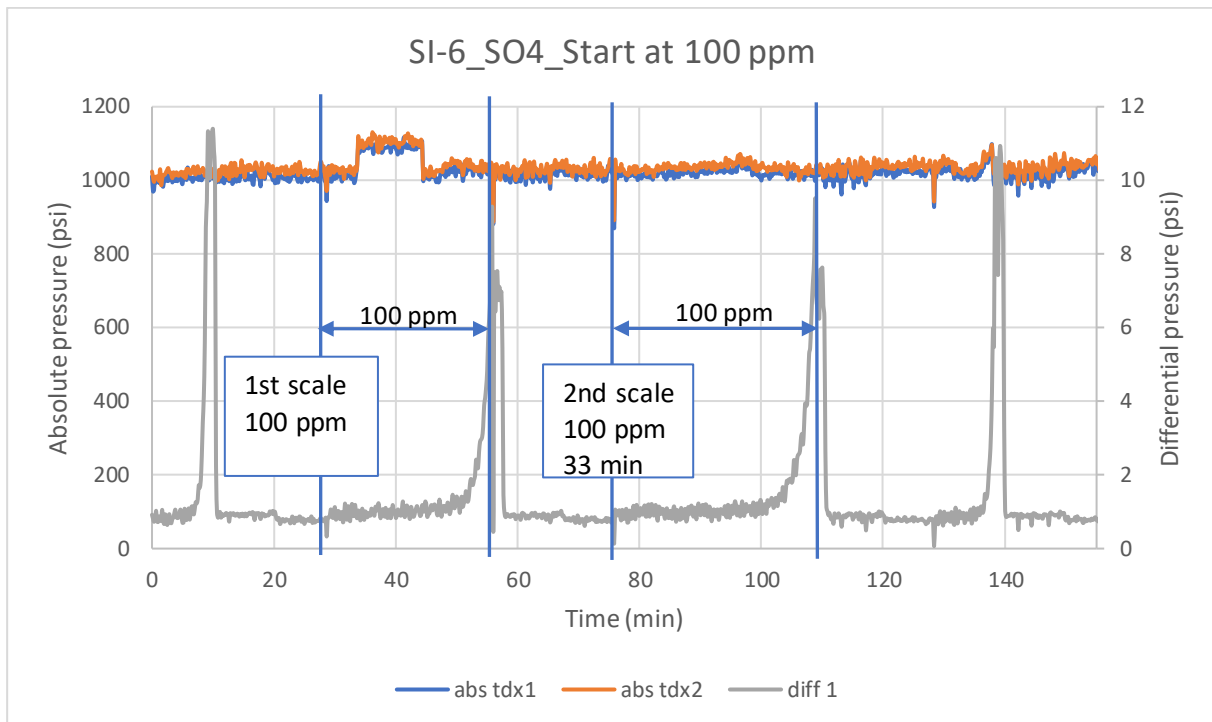
Graph 20 SI-4 tested for carbonate scale, start at 20 ppm.



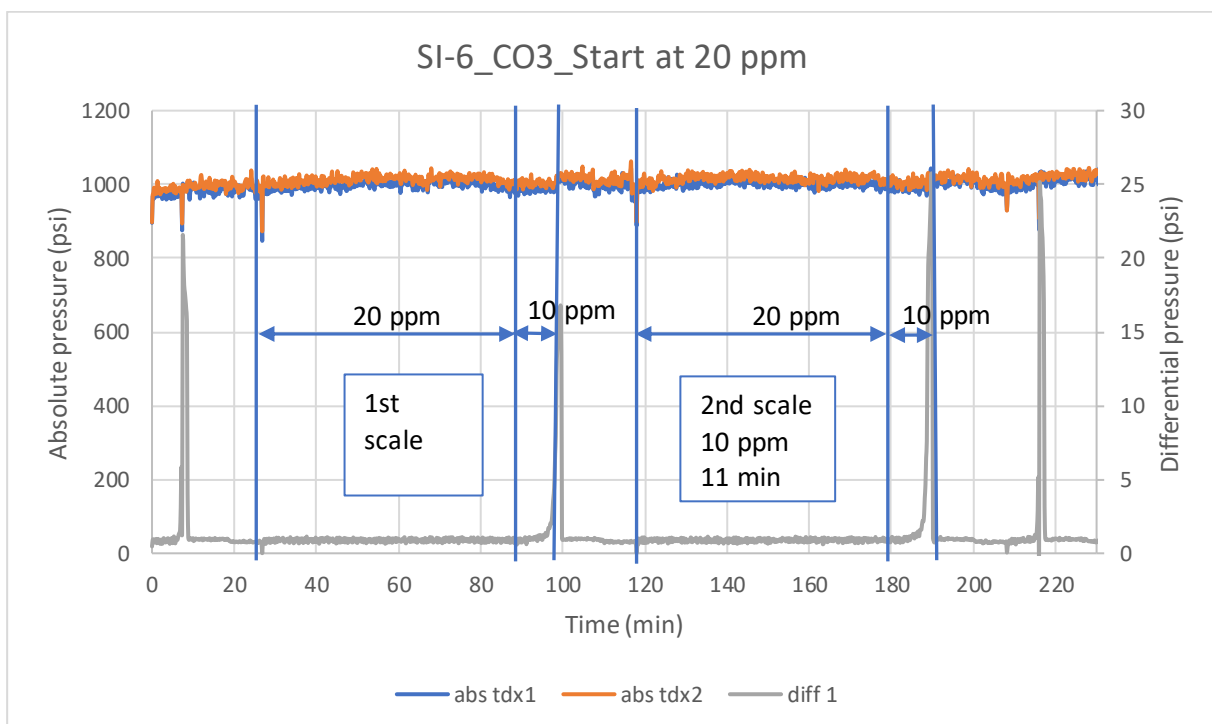
Graph 21 SI-5 tested for sulphate scale, start at 50 ppm.



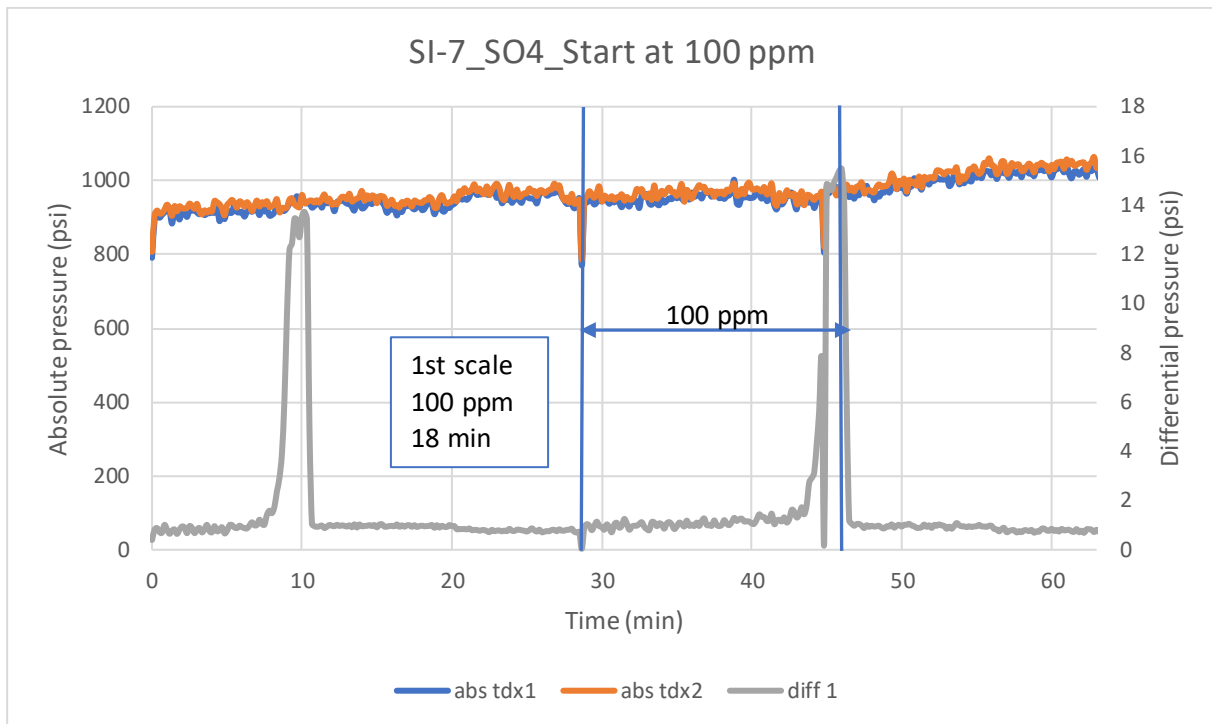
Graph 22 SI-5 tested for carbonate scale, start at 50 ppm.



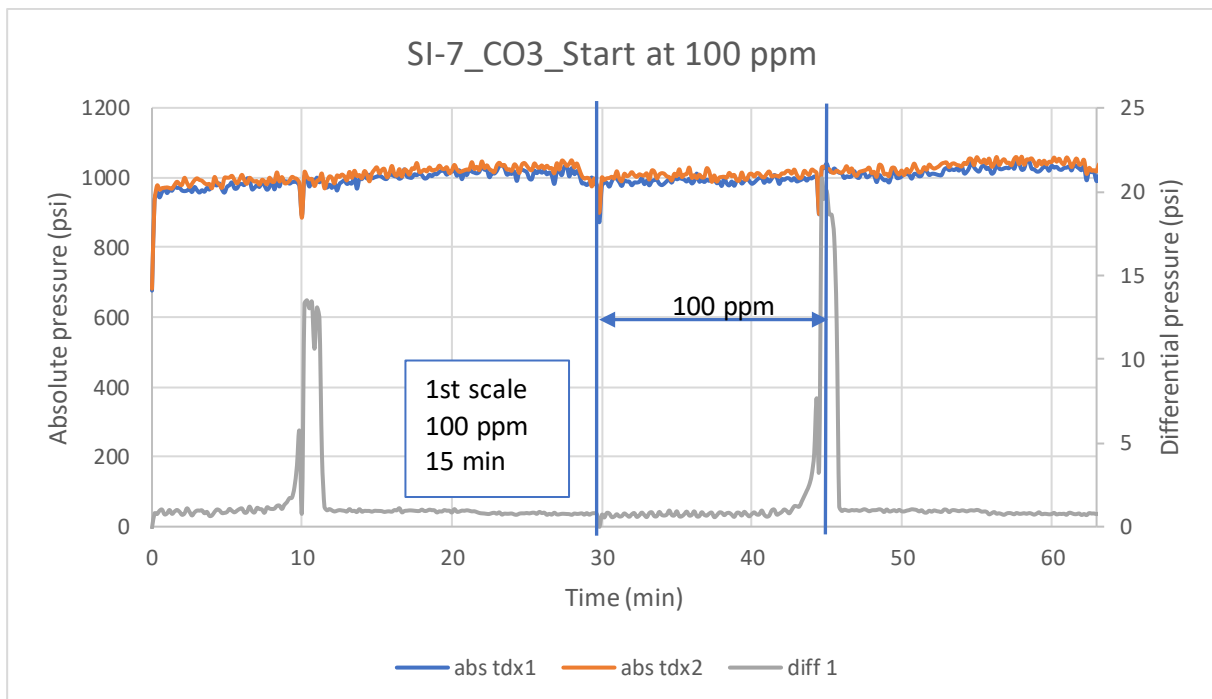
Graph 23 SI-6 tested for sulphate scale, start at 100 ppm.



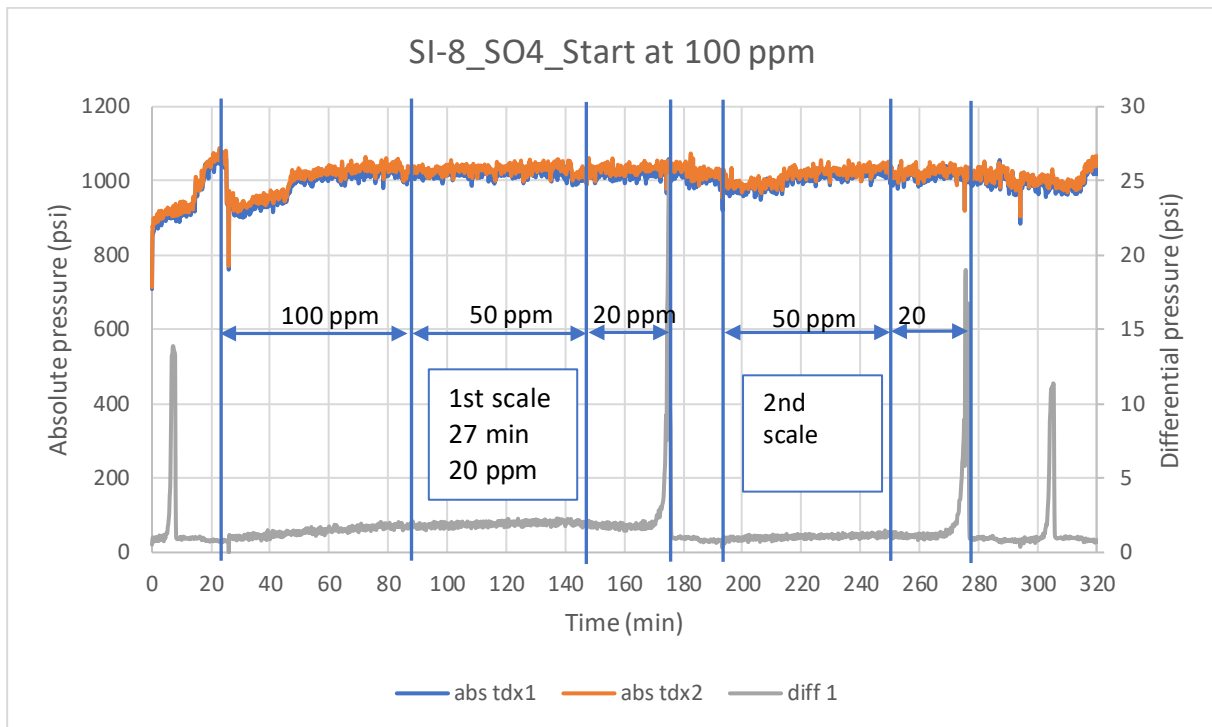
Graph 24 SI-6 tested for carbonate scale, started at 20 ppm.



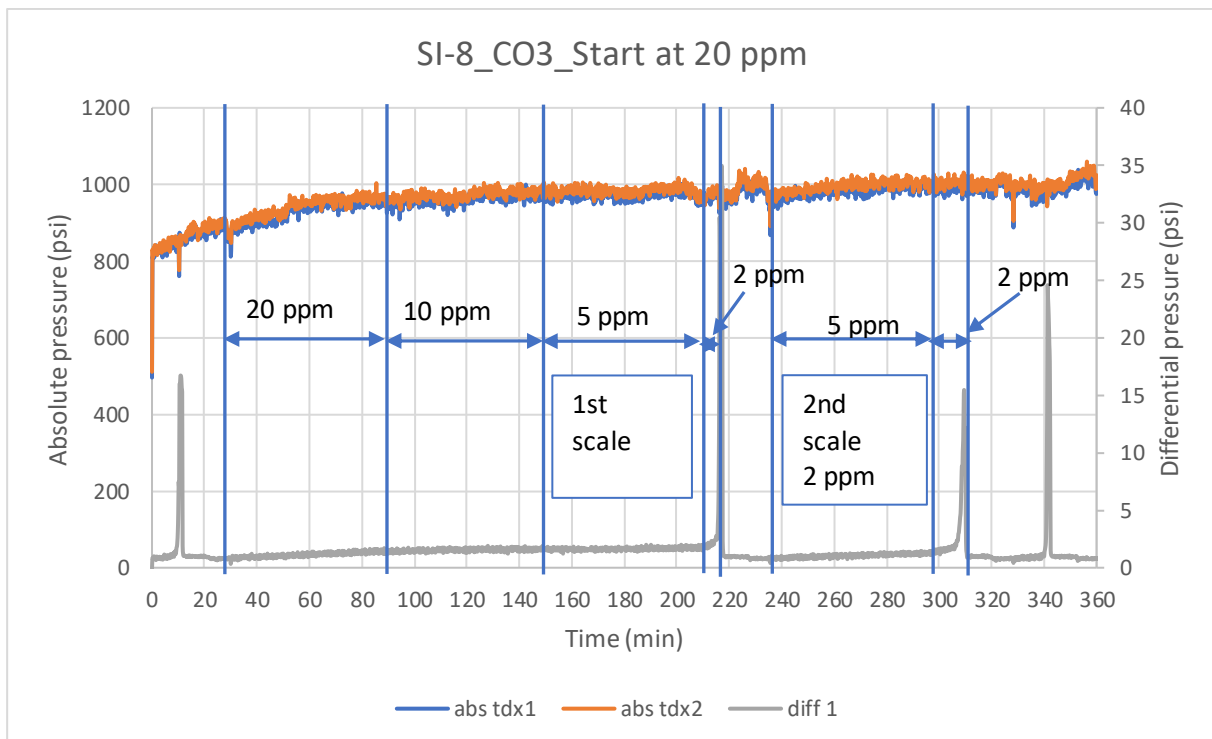
Graph 25 SI-7 tested for sulphate scale, start at 100 ppm.



Graph 26 SI-7 tested for sulphate, start at 100 ppm.



Graph 27 SI-8 tested for sulphate scale, start at 100 ppm.



Graph 28 SI-8 tested for carbonate scale, start at 20 ppm.