

Exploring Modified Alendronic Acid as a New Inhibitor for Calcium-Based Oilfield Scales

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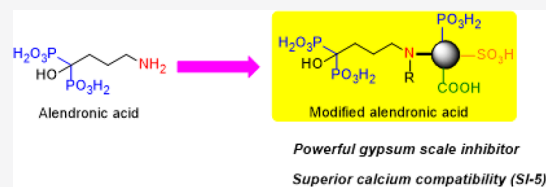
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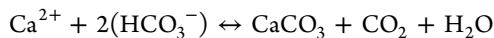
ABSTRACT: Organophosphorus compounds are well known as oilfield scale inhibitors. Earlier work showed that a series of new and well-known bone-targeting drugs incorporating non-toxic bisphosphonates (BPs) ($\text{PO}_3\text{H}_2\text{-C-PO}_3\text{H}_2$) gave good scale inhibition performance against calcite scale based on produced water from the Heidrun oilfield, Norwegian Sea, Norway. However, these chemicals showed only moderate calcium compatibility activity. In this project, we attempted to improve the inhibition performance and calcium tolerance of non-toxic BPs by introducing various functional groups (phosphonate (SI-2), sulfonates (SI-3 and SI-5), and carboxylates (SI-4, SI-6, and SI-7)) in the inhibitor structure backbone. All modified alendronic acid derivatives were screened for calcite and gypsum scale inhibition according to the NACE Standard TM0374-2007 protocol. We also report the calcite scale inhibition performance of all synthesized SIs according to the Heidrun oilfield, Norwegian Sea, Norway. In addition, the calcium tolerance and thermal stability activities of all synthesized SIs are reported. The tolerance results showed that all SIs gave better calcium compatibility than BPs reported earlier, with SI-5 giving the best results at high calcium concentrations (10,000 ppm). The corresponding attachment of an iminodi methylene/ethylene sulfonic moiety (i.e., SI-3 and SI-5) showed worse performance against gypsum scaling, whereas the methylenephosphonate derivative (SI-2) and the carboxylated derivatives (SI-4, SI-6, and SI-7) showed improved performance. For calcite scaling, the NACE standard test gave significantly lower inhibition results than the Heidrun-based produced water due to the former having a higher calcium concentration and calcite supersaturation. It was also found that SI-2, SI-5, and SI-7 showed good thermal stability at 130 °C for 1 week.



1. INTRODUCTION

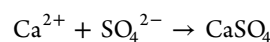
Scale formation is one of the main flow assurance problems faced in oil and gas production installations. It refers to the precipitation of inorganic minerals due to favored supersaturation conditions found in formation waters. This problem is more common in mature oilfields, where seawater is reinjected into the reservoir to enhance oil recovery (EOR). The difference in the ionic nature of seawater and formation water when mixed during this process leads to scale formation, particularly for sulfate scales. If scale is not treated early, it will potentially hinder the production process, causing an increase in operational expenses, and even worse, the potential loss of the well.^{1–4}

Carbonate and sulfate scales are commonly formed in the oil and gas industry. Calcite (CaCO_3) is the most thermodynamically stable polymorph of calcium carbonate. Calcite scale is formed due to the equilibrium between bicarbonate, carbonate, and carbon dioxide depending on the pressure and temperature in the petroleum reservoir.^{1,5} The chemical route for the calcite scale is presented as follows:



Gypsum (calcium sulfate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is formed when sulfate ions react with calcium ions and is considered the most

manageable group II sulfate scale. The following equation shows the formation of gypsum scale.^{1,6,7}



Various methods have been developed to mitigate scale deposits. Chemical treatment is the commonest technique for controlling inorganic scale in the petroleum industry. In particular, scale inhibition (prevention) is more beneficial and economical for squeeze treatment applications than scale removal (the cure). To prevent scale forming, scale inhibitors (SIs) are deployed in order to prevent nucleation, crystal growth, and the tendency for deposition of scale during production.^{2,8}

Organophosphorous-based scale inhibitors are widely utilized for oilfield scale management.^{9–11} There are several commercial SIs for carbonate and sulfate scales incorporating phosphonate groups ($-\text{PO}_3\text{H}_2$). These chemicals can be either polymeric or non-polymeric molecules. For example, non-

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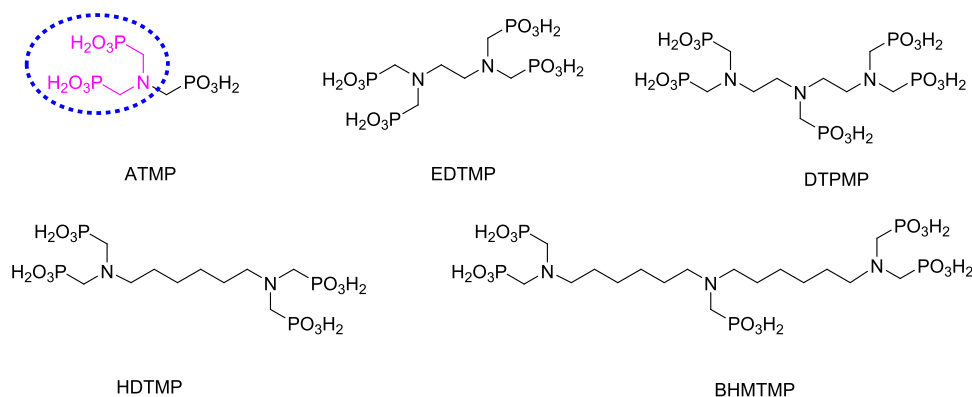


Figure 1. Examples of non-polymeric commercial aminomethylenephosphonate scale inhibitors in the oil and gas industry.

polymeric aminomethylenephosphonate compounds (Figure 1) showed excellent scale inhibition performance against calcite and sulfate scales under harsh oilfield conditions. It was reported that most aminomethylenephosphonate-based SIs are thermally stable and prolonged squeeze lifetime treatment.^{12,13}

However, many of these classes of phosphonate SIs show poor biodegradability, and they are often incompatible with oilfield brines.¹ Therefore, the need to design and develop environmentally friendly SIs is primarily driven by regulatory protocols matching environmental and economic concerns.¹⁴ In more recent years, our research group has developed and tested numerous green phosphonate-based SIs for oilfield applications.^{15–17} More recently, we have synthesized and tested a series of new and well-known bone-targeting drugs incorporating bisphosphonates (BPs) ($\text{PO}_3\text{H}_2\text{—C—PO}_3\text{H}_2$) as green SIs for calcite and barium sulfate (barite) scales.¹⁷ The chemical structures of the developed bisphosphonate (BP) SIs are given in Figure 2.¹⁷

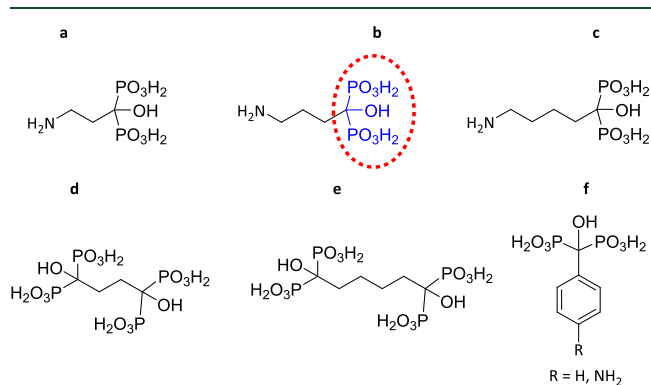


Figure 2. Chemical structures of pamidronic acid (a), alendronic acid (b), 5-amino-1-hydroxypentane-1,1-diylbis(phosphonic acid) (c), and a series of new green oilfield scale inhibitors bearing bisphosphonates (BPs) developed by our group (d–f).

In an earlier study, we have found that BPs gave good scale inhibition performance against calcite scale based on produced water from the Heidrun oilfield, Norwegian Sea, Norway.^{17,18} Moreover, these chemicals showed a moderate to poor inhibition efficiency for barite scale. The possible reason for this weak barite inhibition performance may be due to the limited number of phosphonate groups on their backbone structures. In addition, the lack of a nitrogen atom attached to the phosphonate groups may decrease the metal binding

abilities of the inhibitor. It was also found that BPs are incompatible with calcium ions under oilfield conditions.

In this project, we attempted to improve the calcium tolerance and inhibition performance of non-toxic BPs by introducing various functional groups in the inhibitor structure backbone. For the functionalization of BPs, we chose to use 4-amino-1-hydroxybutane-1,1-bisphosphonic acid (alendronic acid, SI-1) due to its superior calcite inhibition activity and environmental properties.¹⁷ Alendronic acid has an amino group at the end of the carbon chain. This motivated us to introduce several typical functional moieties onto the amino group that are found in scale inhibitors, such as phosphonate, carboxylate, and sulfonate.¹

Alendronic acid-capped aminomethylenephosphonates were synthesized via a Moedritzer–Irani reaction, giving ((4-hydroxy-4,4-diphosphonobutyl)azanediyl)dimethanephosphonic acid (SI-2).^{17,19} In addition, alendronic acid-capped sulfonates were prepared via the reaction of alendronic acid with formaldehyde-sodium bisulfite adduct, and vinyl sulfonic sodium salt to afford ((4-hydroxy-4,4-diphosphonobutyl)azanediyl)dimethanesulfonic acid (SI-3) and 2,2'-((4-hydroxy-4,4-diphosphonobutyl)azanediyl)bis(ethane-1-sulfonic acid) (SI-5), respectively. Moreover, we have introduced carboxylates onto the amino group by reacting alendronic acid with acrylic acid, maleic anhydride, and sodium chloroacetate, affording 3,3'-((4-hydroxy-4,4-diphosphonobutyl)azanediyl)dipropionic acid (SI-4), (4-hydroxy-4,4-diphosphonobutyl)aspartic acid (SI-6), and 2,2'-((4-hydroxy-4,4-diphosphonobutyl)azanediyl)diacetic acid (SI-7), respectively. All modified alendronic acid derivatives were screened for calcite and gypsum scale inhibition according to the NACE Standard TM0374-2007 protocol.^{20–22} We also report the calcite scale inhibition performance according to the Heidrun oilfield, Norwegian Sea, Norway. Furthermore, the calcium tolerance and thermal stability activities of all synthesized SIs are reported.

2. EXPERIMENTAL SECTION

2.1. Materials and Characterization. Chemicals used in this project were purchased from Tokyo Chemical Industry Co., Ltd., Sigma-Aldrich (Merck), VWR chemicals, and ACROS Organics. All solvents were used as purchased without further purification. Commercial scale inhibitors ATMP and PVS (molecular mass: 4000–6000) were obtained from Italmach Chemicals and Clariant Specialty Chemicals, respectively. The structures of the synthesized products were characterized by nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared (FTIR) spectroscopy. ¹H and ³¹P NMR chemical shifts were obtained in deuterium oxide

(D₂O), using a 400 MHz Bruker NMR spectrometer. The data was processed using TopSpin™ 3.2 software. Additionally, an Agilent Cary 630 FTIR spectrometer equipped with a diamond composite ATR (attenuated total reflectance) crystal was used. FTIR data was processed using MicroLab PC software.

2.2. Synthesis of Oilfield SIs. **2.2.1. Synthesis of Alendronic Acid (SI-1).** SI-1 was prepared by reacting 4-aminobutyric acid with phosphorus trichloride in the presence of methanesulfonic acid, as reported in our previously published article.¹⁷

2.2.1.1. 4-Amino-1-hydroxybutane-1,1-bisphosphonic Acid (SI-1). IR ν_{\max} (cm⁻¹): 3196 (NH₂), 3086 (OH), 919, 824 (PO₃). ¹H NMR (D₂O, 400 MHz) δ ppm: 2.96 (t, 2H, NH₂-CH₂-CH₂-), 1.99–1.89 (br, 4H, -CH₂-CH₂-C(OH)(PO₃H₂)₂). ³¹P NMR (D₂O, 162 MHz) δ ppm: 18.49.

2.2.2. Synthesis of ((4-Hydroxy-4,4-diphosphonobutyl)azanediyl)dimethanephosphonic Acid (SI-2). A 100 mL two-neck round-bottom flask equipped with a reflux condenser at 80 °C and magnetic stirring was loaded with alendronic acid (2.50 g, 10.04 mmol) and phosphorous acid (1.68 g, 20.48 mmol) together with 20 mL of deionized water. Hydrochloric acid (37%; 1.98 g, 54.24 mmol) was added dropwise to the solution. Then, formaldehyde (37%; 1.63 g, 54.23 mmol) was injected dropwise with a syringe through a rubber cork over 30 min. The reaction mixture was heated at 110 °C for 24 h under nitrogen. The crude solution was transferred to a 250 mL one-neck flask for solvent removal under *vacuo*. An oily product was obtained and then washed with acetone to give a suspension mixture. The suspension solution was filtered using a Büchner funnel, obtaining a white powder. For further purification, the crude product was dissolved in 25 mL of deionized water in a 100 mL two-neck Erlenmeyer flask. The pH of the mixture solution was then adjusted to 4.38 using 0.01 M HCl. The solution was heated under reflux at 110 °C overnight. The next day, it was filtered using a Büchner funnel to remove solid impurities. The filtrate was concentrated under reduced pressure, affording pale yellow crystals, SI-2.

2.2.2.1. (4-Hydroxy-4,4-diphosphonobutyl)azanediyl)-dimethanephosphonic Acid (SI-2). Yield: 56%. IR ν_{\max} (cm⁻¹): 3371 (OH), 1046, 898 (PO₃). ¹H NMR (D₂O, 400 MHz) δ ppm: 3.46–3.43 (d, 4H, 2 × -CH₂-PO₃H₂), 3.11–2.95 (br, 2H, -N-CH₂-CH₂-), 2.04–1.93 (br, 4H, -CH₂-CH₂-C(OH)(PO₃H₂)₂). ³¹P NMR (D₂O, 162.00 MHz) δ ppm: 17.71, 7.08.

2.2.3. ((4-Hydroxy-4,4-diphosphonobutyl)azanediyl)-dimethanesulfonic Acid (SI-3). A 100 mL two-neck flask equipped with a reflux condenser at 80 °C and magnetic stirring was loaded with alendronic acid (2.50 g, 10.04 mmol) and formaldehyde-sodium bisulfite adduct (2.83 g, 21.13 mmol) along with 30 mL of deionized water. The pH of the solution was adjusted to 11.67 by adding NaOH (50%) dropwise. The reaction vessel was stirred at 80 °C overnight under nitrogen. The crude solution was transferred to a 250 mL one-neck flask for solvent removal under reduced pressure, giving a white solid. For further purification, the product was dissolved in 25 mL of deionized water in a 100 mL Erlenmeyer flask. Then, the pH was adjusted to 5.87 using 0.01 M HCl. The solution was stirred under reflux at 110 °C overnight. The next day, it was filtered using a Büchner funnel to remove any solid impurities. The water phase in the filtrate was removed under *vacuo* to afford a sticky powder. The crude product was further washed with diethyl ether under vigorous stirring overnight. The solvent was evaporated under reduced pressure to give a pure white solid, SI-3.

2.2.3.1. ((4-Hydroxy-4,4-diphosphonobutyl)azanediyl)-dimethanesulfonic Acid (SI-3). Yield: 53%. IR ν_{\max} (cm⁻¹): 3373 (OH), 1162, 1027 (SO₃), 904, 776 (PO₃). ¹H NMR (D₂O, 400 MHz) δ ppm: 4.34 (s, 4H, 2 × -CH₂-SO₃H), 2.99 (t, 2H, -N-CH₂-CH₂-), 1.96–1.91 (br, 4H, -CH₂-CH₂-C(OH)(PO₃H₂)₂). ³¹P NMR (D₂O, 162.00 MHz) δ ppm: 17.91.

2.2.4. 3,3'-((4-Hydroxy-4,4-diphosphonobutyl)azanediyl)-dipropionic Acid (SI-4). A 100 mL two-neck flask equipped with a reflux condenser at 80 °C and magnetic stirring was loaded with alendronic acid (2.50 g, 10.04 mmol) and acrylic acid (1.45 g, 20.07 mmol) along with 30 mL of deionized water. The pH of the reaction solution was adjusted to 11.36 by adding NaOH (50%) dropwise.

The reaction vessel was heated at 80 °C overnight under nitrogen. The crude solution was then transferred to a 250 mL one-neck flask for solvent removal under vacuum to leave a white powder. For further purification, the product was dissolved in 25 mL of deionized water in a 100 mL two-necked Erlenmeyer flask. Then, the pH of the mixture was adjusted to 4.98 using 0.01 M HCl. The solution was heated under reflux at 110 °C overnight. The next day, it was filtered using a Büchner funnel to remove any solid impurities. The filtrate was concentrated under reduced pressure to afford a white solid, SI-4.

2.2.4.1. 3,3'-((4-Hydroxy-4,4-diphosphonobutyl)azanediyl)-dipropionic Acid (SI-4). Yield: 81%. IR ν_{\max} (cm⁻¹): 3428, 3361 (OH), 1578 (CO), 1052, 880 (PO₃). ¹H NMR (D₂O, 400 MHz) δ ppm: 3.32 (t, 4H, 2 × -CH₂-CH₂-COOH), 3.15 (t, 2H, -N-CH₂-CH₂-), 2.59 (t, 4H, 2 × -CH₂-CH₂-COOH), 2.01–1.94 (br, 4H, -CH₂-CH₂-C(OH)(PO₃H₂)₂). ³¹P NMR (D₂O, 162.00 MHz) δ ppm: 17.81.

2.2.5. 2,2'-((4-Hydroxy-4,4-diphosphonobutyl)azanediyl)bis-(ethane-1-sulfonic Acid) (SI-5). A 100 mL two-neck flask equipped with a reflux condenser at 80 °C and magnetic stirring was loaded with alendronic acid (2.50 g, 10.04 mmol) and vinyl sulfonic sodium salt (10.45 g, 80.29 mmol) along with 30 mL of deionized water. The pH of the reaction solution was further adjusted to 11.24 by adding NaOH (50%) dropwise. The reaction vessel was stirred overnight at 80 °C under nitrogen. Moreover, the crude solution was transferred to a 250 mL one-neck flask for solvent removal under reduced pressure. For further purification, the crude product was dissolved in 25 mL of deionized water in a 100 mL two-neck Erlenmeyer flask, and pH was adjusted to 5.89 using 0.01 M HCl. The solution was stirred under reflux at 110 °C overnight. The next day, it was filtered using a Büchner funnel to remove any solid impurities. The filtrate was removed under *vacuo* to afford a sticky powder. This sticky powder was washed with diethyl ether and followed by washing with methanol under vigorous stirring overnight. The methanol was evaporated under *vacuo*, affording a white solid, SI-5.

2.2.5.1. 2,2'-((4-Hydroxy-4,4-diphosphonobutyl)azanediyl)bis-(ethane-1-sulfonic Acid) (SI-5). Yield: 83%. IR ν_{\max} (cm⁻¹): 3459 (OH), 1179, 1042 (SO₃), 911, 745 (PO₃). ¹H NMR (D₂O, 400 MHz) δ ppm: 3.33 (t, 4H, 2 × -CH₂-CH₂-SO₃H), 3.27 (t, 2H, -N-CH₂-CH₂-), 3.15 (t, 4H, 2 × -CH₂-CH₂-SO₃H), 2.05–1.91 (br, 4H, -CH₂-CH₂-C(OH)(PO₃H₂)₂). ³¹P NMR (D₂O, 162.00 MHz) δ ppm: 17.78.

2.2.6. (4-Hydroxy-4,4-diphosphonobutyl)aspartic Acid (SI-6). A 100 mL two-neck flask equipped with a reflux condenser at 80 °C and magnetic stirring was loaded with alendronic acid (2.50 g, 10.04 mmol) and maleic anhydride (0.98 g, 10.04 mmol) along with 30 mL of deionized water. The pH of the mixture solution was adjusted to 11.15 by adding NaOH (50%) dropwise. The reaction vessel was heated at 120 °C overnight under nitrogen. The crude solution was then transferred to a 250 mL one-neck flask for solvent removal under reduced pressure. The obtained crude product was washed with acetone under stirring overnight and then filtered using a Büchner funnel to give a white powder. For further purification, the crude product was dissolved in 25 mL of deionized water in a 100 mL two-neck Erlenmeyer flask. The pH of the mixture solution was then adjusted to 4.58 using 0.01 M HCl. The solution was stirred under reflux at 110 °C overnight. The next day, it was filtered using a Büchner funnel to remove any solid impurities. The filtrate was concentrated under *vacuo* to leave a pure-beige solid, SI-6.

2.2.6.1. 4-((4-Hydroxy-4,4-diphosphonobutyl)amino)-4-oxobut-2-enoic Acid (SI-6). Yield: 43%. IR ν_{\max} (cm⁻¹): 3484, 3350 (OH), 1622, 1550 (CO), 1064, 860 (PO₃). ¹H NMR (D₂O, 400 MHz) δ ppm: 3.17–2.66 (br, 5H, -N-CH₂-CH₂- + -N-CH₂-CH₂-), 1.99–1.92 (br, 4H, -CH₂-CH₂-C(OH)(PO₃H₂)₂). ³¹P NMR (D₂O, 162.00 MHz) δ ppm: 17.82.

2.2.7. 2,2'-((4-Hydroxy-4,4-diphosphonobutyl)azanediyl)diacetic Acid (SI-7).²³ A 100 mL two-neck flask equipped with a reflux condenser at 80 °C and magnetic stirring was loaded with alendronic acid (2.50 g, 10.04 mmol) and sodium chloroacetate (2.34 g, 20.07 mmol) along with 30 mL of deionized water. The pH of the solution was adjusted to 11.47 by adding NaOH (50%) dropwise. The

reaction mixture was heated at 80 °C overnight. After that, the mixture was transferred to a 250 mL one-neck flask for solvent removal under reduced pressure to leave a sticky product. For further purification, the crude product was dissolved in 25 mL of deionized water in a 100 mL two-neck Erlenmeyer flask. The pH of the mixture solution was then adjusted to 4.63 using 0.01 M HCl. The solution was heated under reflux at 110 °C overnight. The next day, it was filtered using a Büchner funnel to remove any solid impurities. The filtrate was removed under *vacuo* and then washed with diethyl ether under vigorous stirring overnight. The solvent was evaporated under reduced pressure, giving a white powder, SI-7.

2.2.7.1. 2,2'-(4-Hydroxy-4,4-diphosphonobutyl)azanediyldiacetic Acid (SI-7). Yield: 72%. IR ν_{\max} (cm⁻¹): 3418 (OH), 1617 (CO), 1062, 905 (PO₃). ¹H NMR (D₂O, 400 MHz) δ ppm: 3.75 (s, 4H, 2x -N-CH₂-COOH), 3.22 (t, 2H, -N-CH₂-CH₂-), 1.99–1.89 (br, 4H, -CH₂-CH₂-C(OH)(PO₃H₂)₂). ³¹P NMR (D₂O, 162.00 MHz) δ ppm: 17.77.

2.3. Evaluation of the Scale Inhibition Performances.

Laboratory static test protocol was carried out for all new synthesized SIs for calcium carbonate (calcite) and calcium sulfate (gypsum) oilfield scales. The static antiscaling measurement was determined according to the NACE Standard TM0374-2007 protocol.^{24,25} For gypsum and calcite scales, the brines were prepared as described in Tables 1 and 2, respectively. We also screened these chemicals against

Table 1. Composition of Brine for Gypsum Scaling by NACE Standard TM0374-2007 Protocol²⁴

ion	ppm	component	brine 1 (g/L) ^a	brine 2 (g/L) ^b
Na ⁺	5900	NaCl	7.500	7.500
Ca ²⁺	3028	CaCl ₂ ·2H ₂ O	11.100	0
SO ₄ ²⁻	7209	Na ₂ SO ₄	0	10.660

^apH of the brine 1 is 5.5. ^bpH of the brine 2 is 5.5.

Table 2. Composition of Brine for Calcite Scaling by NACE Standard TM0374-2007 Protocol²⁴

ion	ppm	component	brine 1 (g/L) ^a	brine 2 (g/L) ^b
Na ⁺	25,964	NaCl	33.000	33.000
Ca ²⁺	3314	CaCl ₂ ·2H ₂ O	12.150	0
Mg ²⁺	440	MgCl ₂ ·6H ₂ O	3.680	0
HCO ₃ ⁻	5346	NaHCO ₃	0	7.360

^apH of the brine 1 is 5.5. ^bpH of the brine 2 is 7.1.

calcite scale according to the Heidrun oilfield, Norwegian Sea, Norway. The compositions of Heidrun brines (50:50 mix of formation water and seawater) are given in Table 3. Additionally, a 1000 ppm stock solution of SIs was prepared in 500 mL of deionized water, and the pH was adjusted between 4 and 6 to resemble a typical produced water from a petroleum reservoir (Table S1).

Cationic and anionic brines (B1 and B2, respectively) were prepared accordingly, as described in Tables 1–3. A total volume of 40 mL of 1:1 solution of cationic brine (B1) and anionic brine (B2)

Table 3. Composition for Calcite Scaling Based on Heidrun Oilfield Produced Water

ion	ppm	component	brine 1 (g/L) ^a	brine 2 (g/L) ^b
Na ⁺	39,020	NaCl	49.590	49.590
Ca ²⁺	2040	CaCl ₂ ·2H ₂ O	7.480	
Mg ²⁺	530	MgCl ₂ ·6H ₂ O	4.430	
K ⁺	1090	KCl	2.078	
Ba ²⁺	570	BaCl ₂ ·2H ₂ O	1.014	
Sr ²⁺	290	SrCl ₂ ·6H ₂ O	0.882	
HCO ₃ ⁻	1000	NaHCO ₃	0	2.760

^apH of the brine 1 is 5.5. ^bpH of the brine 2 is 7.1.

was used to produce the corresponding scale, e.g., calcite and gypsum. Consequently, in 50 mL Schott Duran glass bottles, different concentrations of SIs were dosed into known volumes of B1 and B2 by diluting a 1000 ppm stock solution of SI. Details of the procedure are shown in Table 4. Automated pipettes of 10 mL, 100

Table 4. Dosed Solutions for Static Performance Tests of SIs

SI concentration (ppm)	B1 (mL)	B2 (mL)	1000 ppm stock SI (mL)
100	20	16	4
50	20	18	2
20	20	19.2	0.8
10	20	19.6	0.4
5	20	19.8	0.2
2	20	19.92	0.08
1	20	19.96	0.04
0	20	20	0

μ L, and 1000 μ L (Thermo Fisher Scientific, USA) were used for this purpose. A series of SI concentrations are set to 100, 50, 20, 10, 5, 2, and 1 ppm (Table 4). Two blank samples were also prepared.

To determine the scaling time that samples are required to spend in the oven, a series of jar tests containing blank samples were performed prior to SI testing. The blank samples were placed in an oven at 80 °C for 1–6 and 24 h. These samples were then analyzed to determine the Ca²⁺ concentration in the solution via titration with EDTA using an ammonium purpurate (also known as murexide) indicator. These experiments were evaluated in triplicate to confirm the reproducibility of the obtained results. The standard deviation of all experiments was in the range of 1–5%. Unfortunately, the main drawback of this static jar test is the range variation of the obtained standard deviation. It was found that the ideal scaling time for forming the maximum amount of oilfield scale is 5 h over the test period (1–24 h), as shown in Figure 4. After this time, no significant change in the Ca²⁺ concentration retained in the solution was detected.

All samples containing SIs were prepared, mixed thoroughly, capped tightly, and then placed in a pre-heated oven at 80 °C and kept for 5 h. The Ca²⁺ concentration in each sample was determined following the procedure given by ASTM D-511.²⁶ The analysis consisted of withdrawing a 1 mL aliquot (without prior filtration) and diluting it to 50 mL with deionized water in a conic flask. Consequently, pH was adjusted to 12–13 with 100 μ L of NaOH 50%, and 200 μ L of murexide indicator were added. The titration setup consisted of a 25:0.05 mL glass burette (Hirschmann, Germany) and a lab disc (VWR, Germany) stirrer. The sample was then titrated with EDTA (0.01 M) until a color change from pink to purple occurred. The volume of EDTA consumed was recorded, and the Ca²⁺ concentration was estimated as shown in eq 1;

$$\text{Ca}^{2+}(\text{ppm}) = \frac{A \times B}{D} \times 40,100 \quad (1)$$

where *A* is the EDTA volume required to titrate Ca²⁺ in the sample (mL), *B* is the concentration of EDTA (mol/L), *D* is the volume of aliquot used (1 mL), and 40,100 represents the molecular weight of Ca²⁺ in mg/mol.

The scale inhibition efficiency is calculated based on the concentration of Ca²⁺ retained in solution relative to the blank at room temperature. The percent inhibition values were calculated as follows;²⁴

$$\% \text{inhibition} = \frac{C_a - C_b}{C_o - C_b} \times 100 \quad (2)$$

where *C_a* refers to the Ca²⁺ concentration in the sample after 5 h, *C_b* is the Ca²⁺ concentration in the blank after 5 h, and *C_o* is the Ca²⁺ concentration in the blank before precipitation. Each sample was titrated in triplicate.

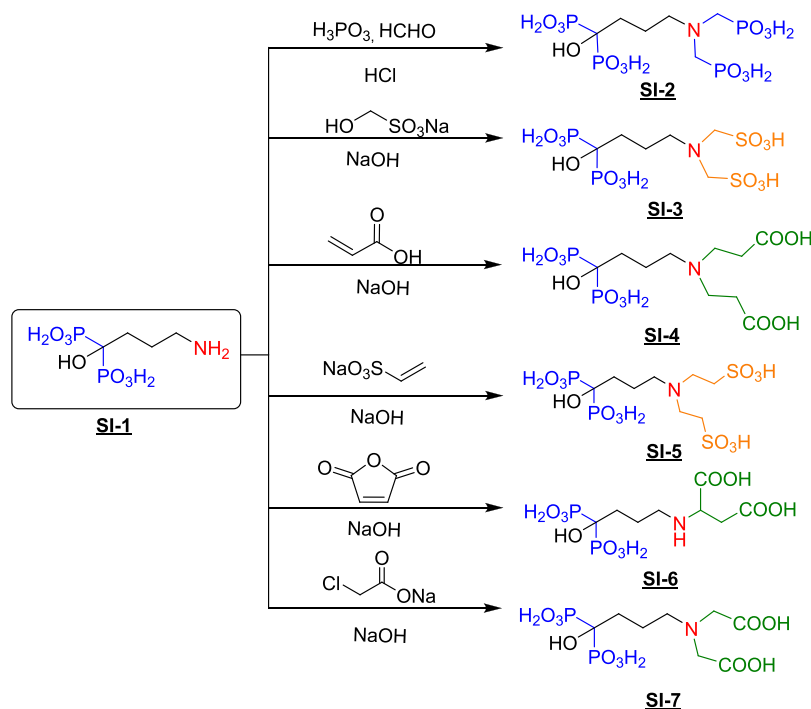


Figure 3. Schematic representation of the synthesis of modified alendronic acid as oilfield scale inhibitors.

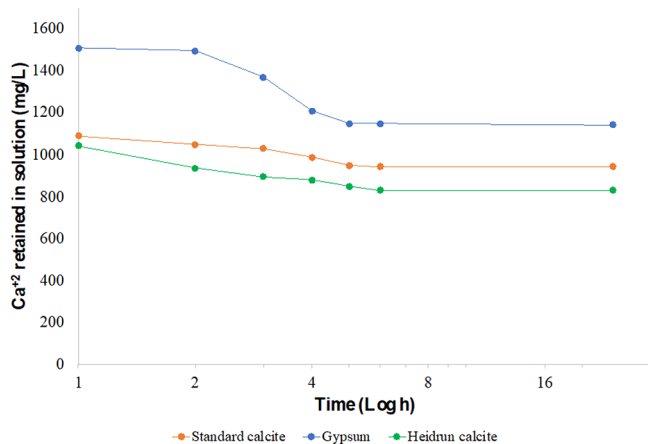


Figure 4. Duration test results for static bottle tests.

2.4. Calcium Compatibility Tests. The need to study the compatibility between SIs and brines is a critical factor for squeeze treatment applications.²⁷ Usually, formation water contains divalent cations such as Ca^{2+} , which at high concentrations of Ca^{2+} ions, could negatively affect the performance of the SI.¹ When this happens, there is a high tendency to form Ca^{2+} –SI complexes that precipitate and are expected to not be desirable during production. In some cases, the presence of Mg^{2+} ions also influences the performance of SIs. Thus, if the SI is incompatible with Ca^{2+} or Mg^{2+} , these complexes will be formed instead of inhibiting scale, causing a change in the physical and chemical structure of the SI, leading to formation damage, reduced productivity, and low profitability.^{28,29} From a general perspective, phosphonates are the least compatible with high $\text{Ca}^{2+}/\text{Mg}^{2+}$ concentrations, carboxylates are intermediate, and sulfonates are the most compatible.¹ Some aminomethylenephosphonates developed to be calcite and sulfate SIs have been claimed to have improved compatibility.²⁷

To evaluate the compatibility between Ca^{2+} ions and SIs, different concentrations of SI (100, 1000, 10,000, and 50,000 ppm) were tested at different Ca^{2+} ion concentrations (100, 1000, and 10,000 ppm) together with 30,000 ppm of NaCl (3 wt %) to simulate seawater

conditions, in 20 mL of deionized water. The pH of the solutions was further adjusted between 4 and 5. The bottles were then placed in an oven at 80 °C for 24 h. The appearance of the solutions was observed at mixing, after 30 min, 1 h, 4 h, and 24 h. SIs were considered compatible with Ca^{2+} when the visual appearance of the solution was clear after 24 h (Table S4).

2.5. Thermal Aging Test. An important characteristic of SIs evaluated for squeeze treatment applications is their ability to withstand and remain stable at high temperatures for long periods, as they would be subjected to the petroleum reservoir under harsh conditions.³⁰ Therefore, it is very useful to investigate the thermal stability properties for all synthesized SIs. Details of the thermal aging procedure are given below.

A 5 wt % solution of tested SIs in 20 mL of deionized water was added in a 50 mL sealed tube. The pHs of the mixture solutions were adjusted between 4.5 and 5.0. The sealed tubes were then sparged with nitrogen gas to mimic downhole anaerobic conditions. They were further heated up to 130 °C under stirring for 7 days. The obtained solutions were then diluted to 0.1% (1000 ppm) and stored in 1 L Schott bottles. Finally, the scale inhibition performance of the aged solutions was tested by the static bottle test method and compared to the respective non-aged SIs.

3. RESULTS AND DISCUSSION

3.1. Chemistry. A set of new aliphatic hydroxybisphosphonate SIs with different functional groups have been synthesized via various routes using alendronic acid as a starting compound. Alendronic acid (SI-1) is a well-known hydroxybisphosphonate drug for treating bone diseases.³¹ The low toxicity of alendronic acid motivated us to synthesize potentially environmentally acceptable SIs.

First, the amino group of alendronic acid was functionalized with methylenephosphonate groups using phosphorous acid, formaldehyde, and hydrochloric acid in water via the Moedritzer–Irani reaction to afford SI-2 (Figure 3). In addition, two sulfonic acid starting materials were used as capping agents to give alendronic acid with alkylsulfonate groups (alkyl = methyl and ethyl, for SI-3 and SI-5,

Table 5. Gypsum Inhibition Performance of Commercial SIs (PVS and ATMP) and SI-1 to SI-7

SI concentration (ppm)	% inhibition								
	PVS	ATMP	SI-1	SI-2	SI-3	SI-4	SI-5	SI-6	SI-7
100	98	97	100	100	100	99	95	100	98
50	96	93	97	99	97	99	92	100	98
20	95	90	96	97	85	99	86	98	97
10	95	87	96	96	65	99	68	95	97
5	93	87	83	94	42	97	32	93	97
2	91	87	82	93	13	97	24	90	94
1	89	85	75	80	13	96	15	85	94

respectively). Furthermore, alendronic acid-capped bis-alkyl-carboxylates (alkyl = methyl and ethyl, labeled SI-4 and SI-7, respectively) were synthesized via treatment with sodium chloroacetate or by Michael addition of acrylic acid. Moreover, alendronic acid-capped dicarboxylates (SI-6) were synthesized via the reaction of alendronic acid with maleic acid under alkaline conditions, as shown in Figure 3.

To characterize the modified alendronic acid derivatives, FTIR and NMR spectroscopy techniques were utilized. The FTIR spectra of SI-1 displayed a broad absorption peak at 3196 cm^{-1} attributed to the NH bond stretching vibration, a broad absorption peak at 3086 cm^{-1} representing the OH bond, and two peaks at 919 and 824 cm^{-1} revealing the BP groups ($-\text{PO}_3^-$). In addition, the FTIR spectrum of SI-2 displayed strong absorption peaks at 1046 and 898 cm^{-1} , indicating the presence of the capped phosphonate groups in the alendronic acid structure. It was also found that the OH band was observed at 3371 cm^{-1} without the presence of the NH bond. For SI-3 and SI-5, the SO absorption peaks were observed between 1027 and 1179 cm^{-1} . The carboxylated compounds SI-4, SI-6, and SI-7 revealed C=O peaks in the range of 1578–1617 cm^{-1} .

The ^1H NMR spectra of SI-2 in D_2O displayed a distinct doublet signal at δ 3.46–3.43 ppm corresponding to $-\text{CH}_2-\text{PO}_3\text{H}_2$, a broad peak at δ 3.11–2.95 ppm for $-\text{N}-\text{CH}_2-\text{CH}_2-$, and a broad multiplet at 2.04–1.93 ppm attributing to $-\text{CH}_2-\text{CH}_2-\text{C}(\text{OH})(\text{PO}_3\text{H}_2)_2$ protons. In addition, the ^{31}P NMR chemical shift (δ) of the BP ($-\text{CH}_2-\text{COH}(\text{PO}_3\text{H}_2)_2$) groups in SI-1 and all the modified structures showed a singlet signal between δ 17 and 18 ppm. In the case of SI-2, an additional singlet signal was obtained at δ 7.08 ppm corresponding to $-\text{N}-\text{CH}_2-\text{PO}_3\text{H}_2$. Thus, the obtained results in both FTIR and NMR spectra indicate that all compounds were successfully synthesized.

3.2. Static Scale Inhibition Performance and Long-Term Thermal Stability Tests. The calcium inhibition efficiencies of all modified alendronic acid derivatives (SI-2 to SI-7) were screened against gypsum and calcite scales and compared with unfunctionalized alendronic acid SI-1 and commercial oilfield SIs ATMP and PVS. Dosages of SIs of 100, 50, 20, 10, 5, 2, and 1 ppm were evaluated using static bottle tests at 80 $^\circ\text{C}$ for 5 h according to the NACE standard TM0374-2007 protocol.²⁴ For the thermal aging test, SI-2, SI-5, and SI-7 were selected as representatives of their respective functionalized groups (phosphonate, sulfonate, and carboxylate, respectively) for studying thermal stability activities in this project. A 5% solution of each SI was prepared and sparged with nitrogen to simulate anaerobic conditions. The solutions were kept at 130 $^\circ\text{C}$ for 7 days and then evaluated for gypsum and calcite scale inhibition.

3.2.1. Gypsum Scale. Table 5 summarizes the static scale inhibition performance of all synthesized SIs (SI-1 to SI-7) for gypsum scale compared to commercial SIs ATMP and PVS. Results show that both commercial SIs gave very good inhibition performance against the gypsum scale. For example, ATMP shows excellent inhibition performance against the gypsum scale at all SI concentrations (1–100 ppm). The maximum inhibition efficiency of 97% was detected at 100 ppm of ATMP, and the weakest inhibition efficiency was 85% at 1 ppm. In addition, PVS gave an excellent inhibition performance of 98% when the SI concentration was 100 ppm. It was also found that the low dosage of PVS (1 ppm) gave a good calcium inhibition performance of 89% in all repeated tests, as shown in Table 5.

For the synthesized BP SIs, the untreated alendronic acid (SI-1) displayed good to excellent inhibition for the gypsum scale. The highest scale inhibition rate was detected at high SI concentrations, and its performance slowly decreased at low concentrations. For example, the maximum inhibition efficiency of SI-1 was 100% at 100 ppm compared to ATMP and PVS under the same test conditions. In addition, an inhibition efficiency of 75% was determined at 1 ppm of SI.

For the modified alendronic acid, it was found that most of the capped alendronic acid derivatives with different functional groups (PO_3H_2 , COOH , and SO_3H) improved the inhibition performance against gypsum scale. Table 5 summarizes the calcium inhibition efficiencies of all functionalized alendronic acid derivatives (SI-2 to SI-7). Alendronic acid-capped aminomethylenephosphonates (SI-2) gave outstanding gypsum inhibition performance at all tested SI concentrations, remaining above 90% until 2 ppm. For example, the calcium inhibition efficiency was 100% at 100 ppm of SI-2. In addition, the iminodiphosphonate fragments into the alendronate molecule SI-2 providing better performance than all tested commercial SIs, except at 1 ppm where its performance dropped to 80%. Furthermore, SI-2 showed a better performance than unfunctionalized SI-1 at all tested SI concentrations. The static scale inhibition performance tests showed that the inhibition efficiency of 80% was reached at 1 ppm of SI-2 compared to an inhibition efficiency of 75% for SI-1 under the same test conditions (Figure 5). This indicates that the addition of aminomethylenephosphonate functional groups successfully improved scale inhibition performance.

For the modified SI-1 containing carboxylate groups, alendronic acid-capped bis-alkylcarboxylates (alkyl = methyl and ethyl, labeled SI-4 and SI-7, respectively) gave outstanding gypsum scale inhibition performances throughout the whole concentration range. The difference between SI-4 and SI-7 is the carbon chain length of the capping agent. Both products showed better inhibition performance than commercial SIs, exhibiting more than 90% inhibition at all SI dosages.

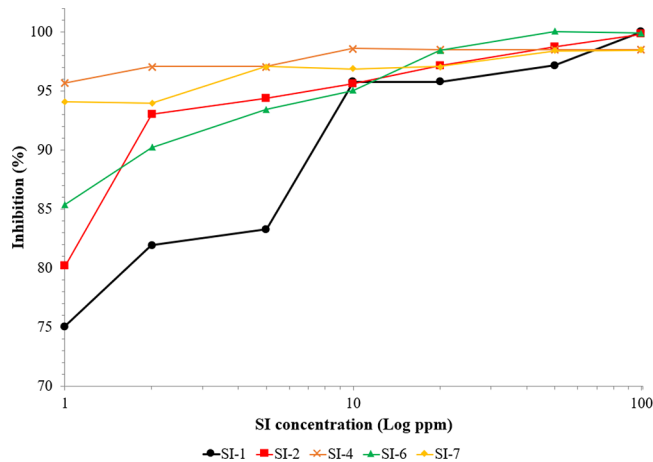


Figure 5. Gypsum inhibition performance of selected SI-based hydroxybisphosphonate groups.

Interestingly, **SI-4** and **SI-7** also displayed better performance compared to **SI-1** at low inhibitor concentrations (Figure 5). For example, **SI-4** shows excellent performance with an inhibition efficiency of 96% at 1 ppm. It has been reported that SIs containing carboxyl groups, especially polymeric, are particularly effective for gypsum scale control.^{32–34} It was also found that **SI-6** showed very good inhibition at all concentrations of SIs tested, providing more than 90% inhibition above 2 ppm. However, its performance dropped to 85% at 1 ppm. Compared to the commercial SIs, this is still good performance as **ATMP** presented the same inhibition at 1 ppm, while **PVS** showed 89% inhibition at the same concentration. In addition, it was found that **SI-6** gave better inhibition performance than **SI-1** at low SI concentrations (1–5 ppm).

The modified **SI-1** with alkylsulfonates (alkyl = methyl and ethyl, for **SI-3** and **SI-5**, respectively) also showed good inhibition performance at the higher tested concentrations (20–100 ppm), as shown in Table 5. However, **SI-3** and **SI-5** gave poor to moderate performance at low SI concentrations (1–10 ppm). For example, **SI-3** provided an inhibition efficiency of 13% at 1 and 2 ppm. The reason for this weakest performance is probably due to sulfonic groups forming weaker complexes with surface calcium ions in comparison to phosphonic or carboxylic groups.³⁵ This is why only polymeric sulfonated polymers such as **PVS** perform well as scale inhibitors.^{1,36,37}

Table 6 summarizes the calcium inhibition efficiencies of **SI-2**, **SI-5**, and **SI-7** after thermal aging at 130 °C for 7 days under anaerobic conditions against the gypsum system. Figure 6 shows the inhibition performances of the selected SIs (**SI-2**, **SI-5**, and **SI-7**) before and after thermal aging under the same test conditions. In Figure 6, the solid lines represent the inhibition efficacy of SIs before thermal aging, and the dashed lines represent the inhibition rate after thermal aging.

SI-2 remained relatively stable throughout the whole test after thermal aging (Table 6 and Figure 6). Before thermal aging, **SI-2** showed a decrease in inhibition performance from 93% at 2 ppm to 80% at 1 ppm. However, after thermal aging, this decrease in performance at low concentrations was not obtained. This was repeated in triplicate and gave the same result. Indeed, we do not currently have a clear explanation for this performance improvement after the aging test. This

Table 6. Gypsum Inhibition Performance of **SI-2**, **SI-5**, and **SI-7** after Thermal Aging (130 °C, 7 days)

SI concentration (ppm)	%Inhibition		
	SI-2 ^a	SI-5 ^a	SI-7 ^a
100	99	88	100
50	97	84	100
20	98	57	100
10	98	54	98
5	97	23	98
2	97	22	95
1	97	21	84

^aTested after heating at 130 °C over 7 days under anaerobic conditions.

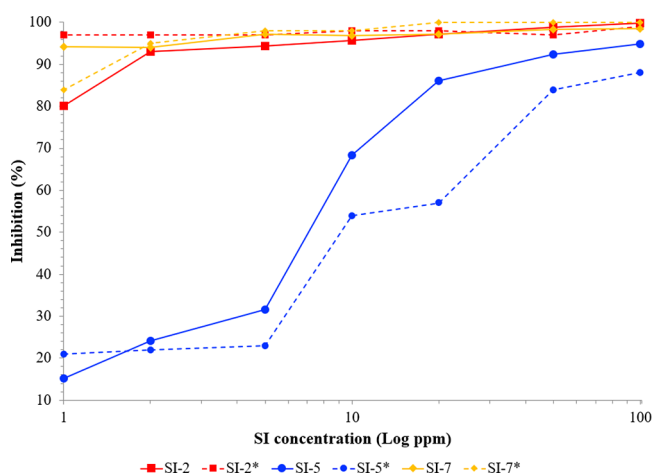


Figure 6. Gypsum inhibition performance of **SI-2**, **SI-5**, and **SI-7** after thermal aging. (*compounds tested after thermal aging).

highlights that the aminomethylenephosphonate **SI-2** was thermally stable against the gypsum scale.

The sulfonated **SI-5** gave a decrease in performance along the whole concentration range (1–100 ppm) even though the introduction of sulfonate groups often provides an improvement and thermal stability.³⁸ However, stability against gypsum scale formation was not obtained for **SI-5**. In contrast, the carboxylated **SI-7** maintained excellent inhibition performance after thermal aging. The inhibition performance of **SI-7** remained above 95% above 2 ppm after thermal aging for 1 week. It was also found that the inhibition efficiency for the same SI dropped from 94% at 1 ppm before thermal aging to 84% after thermal aging under the same test conditions.

3.2.2. Simplified Calcite Scale. Table 7 summarizes the inhibition performance results of the synthesized and commercial SIs against calcite scaling using a static bottle test at 80 °C for 5 h. A decrease in performance was obtained for all SIs in contrast to gypsum performance. All commercial SIs showed a significant decrease in performance at low concentrations. **PVS** remained as the SI with the highest inhibition performance. Its polymeric structure provides preferential affinity for Ca^{2+} and Mg^{2+} ions than non-polymeric compounds.^{28,29} However, **PVS** performance dropped from 97% at 100 ppm to 79% at 20 ppm and continued decreasing at lower concentrations. **ATMP** showed poor to moderate inhibition performance, reiterating the fact that phosphonated compounds cause incompatibility between SIs and Ca^{2+} ions, leading to precipitation of a Ca^{2+} –**ATMP** complexes. This has been similarly reported previously.^{15–17,27,38–41} It was also

Table 7. Calcite Inhibition Performance of Commercial SIs and SI-1 to SI-7

SI concentration (ppm)	% inhibition								
	PVS	ATMP	SI-1	SI-2	SI-3	SI-4	SI-5	SI-6	SI-7
100	97	85	76	56	84	82	75	75	80
50	92	70	73	50	71	72	74	67	72
20	79	64	63	38	57	63	58	57	64
10	54	59	62	34	40	55	32	52	61
5	43	53	45	28	27	49	25	41	46
2	12	50	26	2	16	16	10	16	19
1	5	28	10	0	12	1	4	6	3

Table 8. Heidrun Calcite Inhibition Performance of Commercial SIs and SI-1 to SI-7

SI concentration (ppm)	% inhibition								
	PVS	ATMP	SI-1	SI-2	SI-3	SI-4	SI-5	SI-6	SI-7
100	99	90	98	88	100	94	100	100	100
50	97	87	97	83	98	92	100	100	97
20	97	97	97	69	98	90	98	98	95
10	93	99	93	65	97	89	98	95	95
5	93	99	92	63	72	77	53	93	91
2	46	85	87	54	56	37	30	47	72
1	20	48	82	35	5	35	22	40	39

found that the untreated hydroxybisphosphonate SI (SI-1) provided a moderate scale inhibition performance at all SI concentrations (Table 7).

For the new modified hydroxybisphosphonate SIs containing pendant anionic functional groups (phosphonate, sulfonate, and carboxylate), all these chemicals gave poor to moderate inhibition efficacy according to this calcite system. For example, SI-2, which includes four phosphonate groups onto its structure backbone, showed the worst inhibition performance compared to the rest of hydroxybisphosphonate SIs. The main reason for this poor performance is the intolerance to high concentrations of calcium ions, forming a calcium–SI complex. The tolerance test of SI-2 showed poor calcium compatibility activities (see section 3.3 on calcium tolerance tests). The incompatibility of aminomethylene-phosphonates has been previously demonstrated and discussed thoroughly by our research group.^{13–19} The calcium concentration of this simplified calcite system is higher than the Heidrun calcite compositions, as shown in Tables 2 and 3. It was found that ATMP gave better performance compared to all BP SIs at low inhibitor dosages (1–5 ppm) for this calcite system.

Other modified SIs (SI-3 to SI-7) incorporating carboxylate and sulfonate groups displayed moderate inhibition performance. For example, SI-3, SI-4, and SI-7 afforded the best inhibition performance at high concentrations of SIs (100 ppm) in comparison with SI-1 under the same test conditions (Figure S1). However, the performance of all products was reduced at low concentrations of SIs (Table 7).

Furthermore, calcite inhibition performances of SI-2, SI-5, and SI-7 after thermal aging under anaerobic conditions over 7 days are presented in Table S2 and Figure S2. The obtained results showed that SI-2 increased in performance throughout the concentration ranges examined. Before thermal aging, the maximum inhibition exhibited by SI-2 was 56% at 100 ppm of SI. However, after thermal aging, a 77% inhibition was obtained at the same concentration. A similar trend was obtained even at low concentrations of SI. For example, before thermal aging, the inhibition performances of SI-2 were 0 and

2% at 1 and 2 ppm, respectively. While after thermal aging, these increased to 5 and 17%. Moreover, in the case of SI-5, inhibition performance remained relatively stable from 100 to 10 ppm. However, more noticeable decreases were observed at 2 and 1 ppm (Table S2 and Figure S2). In addition, it was found that SI-7 provided good thermal stability performance for simplified calcite scale, giving a slight loss of inhibition efficiency when heated up at 130 °C (Table S2 and Figure S2).

3.2.3. Heidrun Calcite Scale. We decided to evaluate further our new chemicals against calcite scaling according to more typical oilfield conditions in the Norwegian Sea. Thus, all commercial inhibitors and modified alendronic acid derivatives were also statically tested against calcite scale based on the water composition of produced fluids from the Heidrun platform in the Norwegian Sea. Table 8 shows the performance results for the commercial and synthesized products.

Compared to calcite scaling results with the NACE 0374-2007 system, we found that the inhibition efficiencies were significantly higher for all SIs for the Heidrun calcite scaling system. This is due to the Heidrun brine having lower calcium concentration and calcite supersaturation compared to the NACE system. It was found that PVS showed higher inhibition performance than for the previously tested simplified calcite system. This difference may be due to the slightly lower Ca²⁺ ion concentration in this brine mixture (1020 ppm) with respect to the brine mixture proposed by NACE 0374-2007 (1657 ppm).

The improved performance of ATMP with the Heidrun system is not only attributable to the lower calcite scaling supersaturation but also the lower calcium ion concentration that improved the compatibility properties between ATMP and the calcium ions. It was found that ATMP gave excellent inhibition efficacy in the range of 100–2 ppm of SI concentrations, as shown in Table 8. For example, the inhibition efficiency of ATMP reached 85% at 5 ppm.

For alendronic acid and its derivatives, most of these novel SIs afforded good inhibition performance up to 5 ppm against Heidrun calcite formation. However, SI-2 displayed poor to moderate inhibition performance over the tested SI concen-

trations. Presumably, the extra phosphonate groups made it less compatible with Ca^{2+} ions in solution than the parent SI-1, which decreases its inhibition efficiency by producing a calcium–SI precipitate.

SI-3, SI-5, SI-6, and SI-7 showed better performance than the parent compound SI-1 at concentrations of 100, 50, 20, and 10 ppm, almost reaching 100% in all cases (Figure 7).

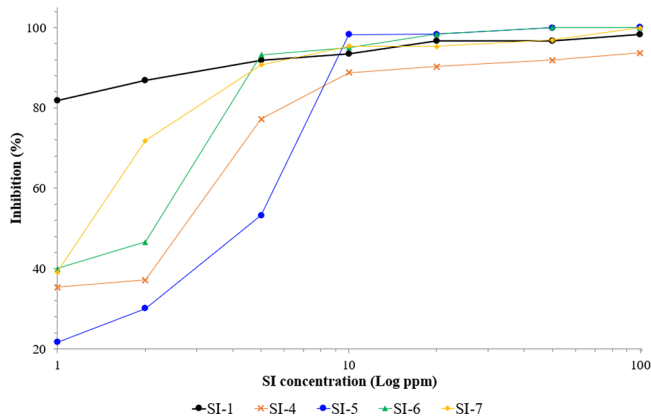


Figure 7. Heidrun calcite inhibition performance of selected SIs.

However, SI-3 decreased its inhibition at low concentrations, reaching a minimum inhibition of 5% at 1 ppm. Furthermore, SI-4 did not reach 100% inhibition at 100 ppm of SI but showed a higher inhibition rate at lower concentrations than SI-3 and SI-5. Again, these results reflect the higher compatibility between SI-based carboxyl groups with Ca^{2+} ions than SI-containing sulfonate groups.³⁵

Table 9 and Figure 8 present the inhibition performances of SI-2, SI-5, and SI-7 after thermal aging test under anaerobic

Table 9. Heidrun Calcite Inhibition Performances of SI-2, SI-5, and SI-7 after Thermal Aging

SI concentration (ppm)	% inhibition		
	SI-2 ^a	SI-5 ^a	SI-7 ^a
100	81	97	100
50	72	97	97
20	69	97	95
10	65	94	95
5	63	53	91
2	50	30	66
1	35	22	39

^aTested after heating at 130 °C for 7 days under anaerobic conditions.

conditions against calcite scale using synthetic brines with ionic composition from the Heidrun oilfield in the Norwegian Sea. Figure 8 highlights the comparison between the inhibition performances obtained before and after thermal aging of the studied SIs.

All three SIs showed only minor differences in performance after aging. For SI-2, a slight decrease in performance was obtained at 100 to 50 ppm before and after thermal aging tests. For example, the inhibition efficiency of SI-2 at 100 ppm went from 88% (before thermal aging) to 81% (after thermal aging). For SI-5, the performance before and after thermal aging remained above 90% inhibition in a range of 10–100 ppm. SI-7 was thermally stable at all tested concentrations after thermal

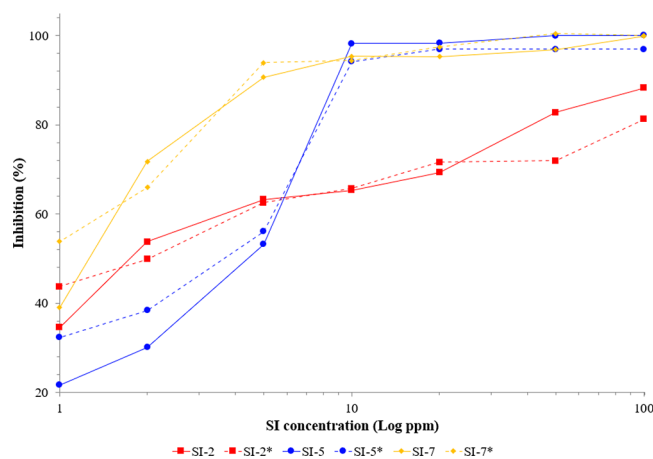


Figure 8. Heidrun calcite inhibition performances of SI-2, SI-5, and SI-7 after thermal aging. (*compounds tested after thermal aging).

aging. For example, Heidrun calcite scaling tests at 50 ppm showed 97% inhibition for both before and after thermal aging.

The above results showed that the nontolerant scale inhibitors (e.g., ATMP and SI-1) indicated much higher or similar inhibition efficacy than calcium-tolerant SIs (e.g., SI-3 and SI-5). It appears that when an SI gets disabled by the formation of insoluble calcium–SI phase and has no possibility to interact with gypsum or calcite, it still provides a better scale inhibition than a tolerant one, which does not form solids and is free for interaction with a gypsum or calcite surface. A possible explanation is provided from the results of Oshchepkov et al., which states that scale formation occurs in the bulk retentate phase via a heterogeneous nucleation process. Herewith, the background solid impurities (micro/nanodust) play a vital role as gypsum nucleation centers. Furthermore, non-tolerant antiscalants block via sorption exactly these nano/micro nucleation centers better than the tolerant ones, which are more soluble in general.^{21,22}

3.3. Calcium Tolerance Tests. As illustrated earlier, an important characteristic to consider when designing SIs is their compatibility with Ca^{2+} ions. Some SIs, especially phosphonates, tend to form Ca^{2+} –SI complexes that precipitate and could even cause formation damage downhole if squeezed incorrectly or obstruct the production line. In this research, calcium compatibility of the proposed SIs was evaluated by testing different concentrations of Ca^{2+} (100, 1000, and 10,000 ppm) against different concentrations of SIs (100, 1000, 10,000, and 50,000 ppm) at 80 °C under static and saline (3% NaCl) conditions. The pH of the solutions was adjusted between 4 and 5. Calcium compatibility was assessed by judging the appearance of the solutions as clear, hazy, or precipitative, after mixing and after 30 min, 1h, 4 h, and 24 h. SIs compatible with Ca^{2+} ions should show a clear solution appearance after 24 h at 80 °C. The calcium compatibility results of all SIs are provided in Table S3.

We have previously studied the calcium compatibility of SI-1 at the concentrations of inhibitor and calcium ions mentioned above.¹⁷ It was found that SI-1 provided poor calcium tolerance activities, as shown in Table S3. Therefore, one of our primary objectives in this project was to improve the calcium tolerance by introducing carboxylate and sulfonate groups in the inhibitor structural backbone.

The modified alendronic acid with carboxylate groups (SI-4, SI-6, and SI-7) successfully improved the calcium tolerance

properties compared to SI-1. For example, SI-4 and SI-7 afforded excellent compatibility at 1000 ppm Ca²⁺ ions and 50,000 ppm SI. However, both inhibitors (10,000–50,000 ppm) showed limited compatibility performance at high concentrations of calcium ions (10,000 ppm). Hazy solutions and precipitates were observed at these tested concentrations. It was also found that the phosphonated alendronic acid (SI-2) showed good compatibility at 100 ppm Ca²⁺ ions for all SI concentrations. However, SI-2 showed poor calcium tolerance at 1000 ppm Ca²⁺ ions. By visual observation, no clear solutions were obtained at all calcium/SI concentrations. Therefore, we decided to disregard this test at a high calcium ion concentration (10,000 ppm).

The functionalized alendronic acid with sulfonates (SI-3 and SI-5) exhibited good calcium tolerance efficacy at various concentrations of SIs and calcium ions. Significantly, the sulfonated SI-5 indicated outstanding compatibility with Ca²⁺ ions as the solutions remained clear after 24 h at all Ca²⁺ (up to 10,000 ppm) and SI concentrations (50,000 ppm). In addition, no haziness or precipitation was observed over the 24 h test period, as shown in Table 10.

Table 10. Calcium Tolerance Tests in 10,000 ppm Ca²⁺ and 30,000 ppm (3 wt %) NaCl for SI-5

dose (ppm)	appearance				
	after mixing	30 min	1 h	4 h	24 h
100	clear	clear	clear	clear	clear
1000	clear	clear	clear	clear	clear
10,000	clear	clear	clear	clear	clear
50,000	clear	clear	clear	clear	clear

4. CONCLUSIONS

We have synthesized a range of phosphonated, carboxylated, and sulfonated derivatives of the bis-phosphonate, alendronic acid (SI-1). They were evaluated for their performance against calcite and gypsum scaling using jar tests. The sulfonated derivatives of SI-1 (i.e., SI-3 and SI-5) showed worse performance against gypsum scaling, whereas the methylene-phosphonate derivative (SI-2) and the carboxylated derivatives (SI-4, SI-6, and SI-7) showed improved performance. In particular, SI-4 and SI-7 were better gypsum inhibitors at lower tested concentrations (down to 1 ppm) than the commercial inhibitors, PVS and ATMP. Anaerobic thermal aging at 130 °C did not show any loss of performance for SI-7 except at 1 ppm, whereas we unexpectedly observed an improvement in gypsum inhibition for SI-4.

For calcite scaling, the NACE standard test gave significantly lower inhibition results than the Heidrun-based produced water due to the former having a higher calcium concentration and calcite supersaturation. This is also reflected in the poorer result for the new phosphonated SI-2 with the NACE brine, which was exacerbated by the poor calcium compatibility. With Heidrun brine, several of the new SIs gave better scale inhibition performance, and SI-2, SI-5, and SI-7 did not lose inhibition efficiency after aging at 130 °C. SI-1 showed good calcite inhibition at lower inhibitor concentrations, better than the commercial SIs or any of the alendronic acid derivatives, but it showed very poor calcium compatibility. However, all SIs gave better compatibility, with SI-5 giving the best results at high calcium concentrations (10,000 ppm). Further work will

investigate the dynamic performance of the best alendronic acid derivatives, also for barite scaling.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.energyfuels.1c03936>.

(Figure S1) Simplified calcite inhibition performance of selected modified hydroxybisphosphonate SIs, (Figure S2) simplified calcite inhibition performances of SI-2, SI-5, and SI-7 after thermal aging (*compound tested after thermal aging), (Table S1) pH values of all tested SIs (SI-1 to SI-7) against an oilfield scale (gypsum, simplified calcite, and Heidrun calcite), (Table S2) simplified calcite inhibition performances of SI-2, SI-5, and SI-7 after thermal aging, (Table S3) Ca²⁺ tolerance tests at 30,000 ppm (3 wt %) NaCl for SI-1 to SI-7, (Table S4) calcium tolerance tests, appearance after 24 h, the ¹H and ³¹P NMR spectra of the modified alendronic acid derivatives, and the IR spectra of the modified alendronic acid derivatives (PDF)

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Notes

The authors declare no competing financial interest.

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