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Research Article

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Guanidine as A Starting Material for Preparing a Scale Inhibitor

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Abstract

This study presents the synthesis and evaluation of a novel phosphonate-based scale inhibitor using guanidine as the starting material. Given guanidine's highly reactive nature and multiple substitution sites, it was chemically modified by introducing phosphonomethyl groups to enhance its scale inhibition capabilities. The synthesized compound was structurally characterized using FT-IR, ^{1}H NMR, ^{13}C NMR, and mass spectrometry, confirming successful substitution of three hydrogen atoms with phosphonate groups. The compound's performance was assessed through static scale inhibition tests at various temperatures (40°C, 60°C, and 70°C) for calcium carbonate and calcium sulfate, showing significant inhibition at concentrations as low as 20–30 ppm. Titration-based calcium analysis revealed inhibition efficiencies up to 100%. Additionally, the compound demonstrated good compatibility with calcium and acceptable seawater biodegradability over 28 days. These results suggest that the synthesized inhibitor is a promising candidate for environmentally safer and thermally stable scale control in industrial water systems.

Keywords: Guanidine, Scale Inhibitor, Phosphonate Compound, Chelation, Calcium Carbonate, Calcium Sulfate, Biodegradability.

INTRODUCTION

Oilfield scaling is a widespread challenge in the oil and gas sector, leading to substantial financial losses due to property damage and decreased production. This issue, ranking among the top production efficiency impediments, is pervasive worldwide, primarily affecting water-related oil extraction operations alongside corrosion and hydrate formation. Scaling can accumulate on various surfaces, particularly around the wellbore, restricting fluid flow and obstructing production equipment from pore throats to processing facilities. The industry typically encounters four major types of scale: Calcium Carbonate (calcite and aragonite), Calcium Sulfate Salts (like gypsum), Strontium Sulfate (celestite), and Barium Sulfate (barite).

Scale inhibitors (SIs) are the primary solution used to prevent crystal growth and scale formation, with concentrations ranging from 1 to 500 ppm to maintain effectiveness. Water-soluble organic SIs are most common in the industry, where it is critical to sustain concentration above the minimum

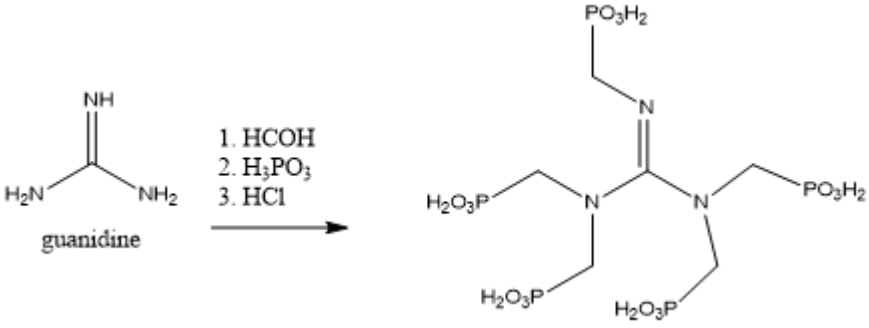
inhibitor concentration (MIC) to ensure efficacy. SIs are commonly applied through downhole squeeze treatments or continuous injection at the wellhead (Kelland, 2014). In squeeze treatments, inhibitors are injected into the subsurface formation, often using seawater to extend their reach, after which the inhibitors are absorbed by the formation rock near the wellbore and released gradually into the produced water, effectively controlling scale during production. Phosphoric acids, particularly those with C-PO(OH)2 moieties, are an important class of organophosphorus compounds (Garber et al., 2016; Kiran et al., 2008).

These compounds and their derivatives, known as phosphates, are widely used across agricultural, chemical, and pharmaceutical industries (Ash, 2004; Kukhar & Hudson, 2000). Organophosphonic acids and their salts are essential scale inhibitors in the oil industry (Demadis, 2006; Jordan & Mackay, 2007; Woodward et al., 2004). These inhibitors vary in structure, from small non-polymeric molecules with limited phosphonate groups to more complex polymeric compounds with a higher phosphonate concentration (Kelland, 2014). In many cases, phosphonate groups are bonded to aminomethylenephosphonate structures, where the amine acts as a Lewis base ligand, further enhancing scale inhibition.

Phosphonate groups in scale inhibitors serve a functional role in indicating inhibitor concentration in produced water. Their presence aids in determining the timing for re-squeeze operations to ensure continuous scale inhibition. Phosphonate groups are especially advantageous in the oilfield industry for mitigating scale issues due to their durability and biodegradability.

MATERIALS AND METHODS

Previous studies (Mady & Kelland, 2017) have shown that conjugating amino phosphonates with methylene phosphonates significantly improves the effectiveness of scale inhibitors, though biodegradability remains a challenge, as seen in BP-7 and BP-9, which exhibited low biodegradation rates. This study focuses on synthesizing a new scale inhibitor using guanidine as a starting material. Research suggests that phosphonate groups can effectively replace hydrogen atoms bound to nitrogen in guanidine, enhancing the compound's ability to prevent scaling. Furthermore, the inhibitory efficiency is expected to increase with the number of phosphonate groups attached. Consequently, guanidine, with its five hydrogen atoms, provides a promising molecular framework for this investigation, as shown in Scheme 1.



Scheme (1). ((dihydroxyphosphaneyl)methyl)-1.3.3- tris(phosphonomethyl)guanidino) methyl) phosphonic acid

Guanidine is a hygroscopic organic compound with the chemical formula CH_5N_3 and a molecular weight of approximately 59.07 g/mol. It is a colorless solid that is soluble in polar solvents and possesses strong basic properties. Guanidine is not only found as an independent molecule but also as a constituent in larger organic compounds, including arginine side chains, and occurs naturally in various sources such as urine, turnip juice, mushrooms, rice husks, and muscle tissue. Its melting point

is around 50°C, and upon heating to 160°C, it converts to melamine and ammonia. For the development of an effective and environmentally friendly scale inhibitor, certain criteria must be met (Mady & Kelland, 2017). These include chieving a minimal effective concentration of 1 to 100 ppm, with an optimal range of 1 to 5 ppm; maintaining thermal stability at temperatures up to 100°C and between 130°C to 170°C; exhibiting at least 60% biodegradability within 28 days; having a pH compatibility range of 4 to 9; compatibility with calcium; and being cost-efficient in production and application.

In addition to its potent therapeutic effects, guanidine's molecules belong to an indisputable family of chemicals that are distinguished by their ability to acquire a positive charge through protonation in physiological settings (Kim et al., 2021; Zamperini et al., 2017). Guanidine groups play a crucial role in the development and identification of antibiotics because of this characteristic, which enables them to establish hydrogen bonds or electrostatic interactions with possible bacterial targets (Kim et al., 2021). One common example of this type of chemical is the antibiotic streptomycin, which has a guanidine group (Moussa, 2014). Guanidine-functionalized groups can be added to polycarbonates as an adjuvant, greatly increasing the antibacterial activity of several antibiotics (Zamperini et al., 2017).

Guanidine can be isolated from several of the medications in which it is used; thus, purchasing it is not necessary. By repurposing old medications rather than discarding them, this approach guarantees environmental preservation. The ketophane molecule was extracted from the medicine it contains and reused in chemical reactions in a scientific investigation (Dakhil et al., 2022).

Scale Inhibitors

A scale inhibitor is a chemical agent designed to prevent the formation of scale by reducing the rate of fouling scale development (Delon Jimenez, 2014). These inhibitors typically comprise water-soluble compounds that effectively impede the nucleation and crystal growth of inorganic scales by disrupting normal crystal growth patterns, thereby preventing larger crystal formations. Certain polymers have been identified as effective nucleation inhibitors and dispersants (Kelland, 2014) . Key characteristics of an effective scale inhibitor include:

- **Efficiency:** It must effectively inhibit scale formation, regardless of the mechanisms involved.
- **Stability:** The inhibitor should remain stable under the elevated temperatures found in oil production environments.
- **Compatibility:** It must not interfere with other oilfield chemicals or change in response to their presence, while integrating smoothly with chemical injection systems.

To ensure comprehensive protection against scale formation, maintaining a minimum inhibitor concentration (MIC) is crucial; concentrations below this threshold significantly increase the risk of scale formation. In the oilfield, common scales like carbonates and sulfates contain divalent anions (CO_3^{2-} and SO_4^{2-}) alongside group II metal cations. The scale inhibitor must interact with these anions or cations to anchor effectively to the scale surface and prevent competing molecules from binding to the crystal lattice (Kelland, 2014).

Various organic molecules with anionic groups can interact favorably with group II cations on scale crystal surfaces. The most prevalent anionic groups include phosphates, phosphonates, phosphinates, carboxylates, and sulfonates (Kelland, 2014). Molecules containing multiple anionic groups or mixtures of these have been effective as scale inhibitors, particularly when in their anionic dissociation form. Common classes of scale inhibitors include polyphosphates, phosphates, small

non-polymeric phosphonates and aminophosphonates, polyphosphonates, polycarboxylates, phosphino polymers, and polysulfonates (Kelland, 2014).

Phosphate esters are recognized for being environmentally friendly scale inhibitors, although they may not be the most efficient. Their solubility in water or oil can be adjusted by modifying the alkyl tail length of the alcohol used in their synthesis. Additionally, compact non-polymeric scale inhibitors, characterized by limited phosphonate groups, show effectiveness due to their aminomethylenephosphonate groups, which can form bonds with divalent cations, enhancing the chelation effect and stabilizing complexes (Mady & Kelland, 2017) .

Research has highlighted the importance of bisphosphonates (BP), which have been used for decades in treating bone disorders due to their targeting properties (Ebetino et al., 1998; Maeda, 2004; Sparidans et al., 1998). These compounds are resistant analogs of pyrophosphates that inhibit mineralization processes in bones (Hirabayashi et al., 2002; Rodan & Martin, 2000). However, phosphonate-based scale inhibitors often face criticism for their limited biodegradability, which raises environmental concerns as both the water treatment industry and oil companies focus on the implications of these compounds (Popov et al., 2016).

The biodegradability of scale inhibitors is categorized by their environmental impact, with "Green" or "Yellow" classifications indicating a minimum biodegradation rate of 20% within 28 days, according to the Norwegian national environmental agency (Nowack, 2003). Conversely, "Red" category chemicals exhibit less than 20% biodegradation. Presently, environmentally friendly scale inhibitors lack stability at high reservoir temperatures exceeding 140°C. Over-extended periods resulting in a scarcity of effective options for near-wellbore regions. Scale squeeze treatments are utilized to address this issue by injecting inhibitors into formations, where they adhere to reservoir rocks and are gradually released, necessitating thermal stability for long-term effectiveness.

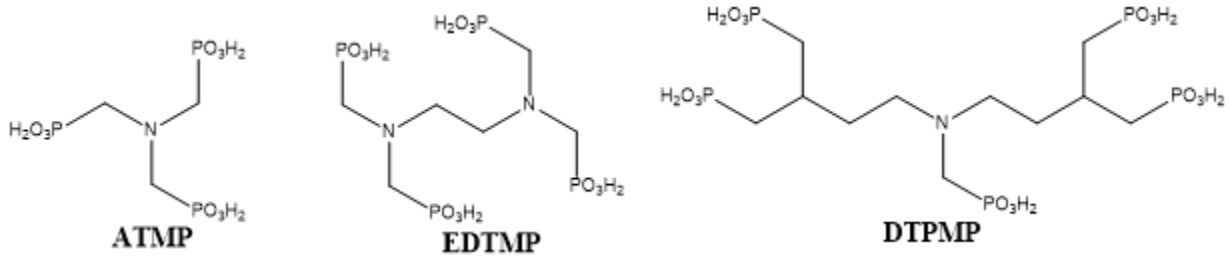


Figure (1). Common oilfield SIs containing Phosphonate Groups (Mady & Kelland, 2017).

Chemicals and Reagents

Guanidine used in the experiments in the experimental comes from India. It is imported and distributed by Chang Chun Chan Enterprise Sdn Bhd Company. Phosphorous acid (H_3PO_2), hydrochloric acid (HCI), and formaldehyde (CH_2O) from Riedel-de Haën Company. It was purchased from Egypt for the University of Benghazi.

The reagents used for performance were Sodium Chloride (NaCl) and Calcium chloride ($CaCl_2.2H_2O$) supplied by (Amazon), Sodium sulfate (Na_2SO_4), and sodium Bicarbonate ($NaHCO_3$) comes from India.

Instrumentation and Apparatus

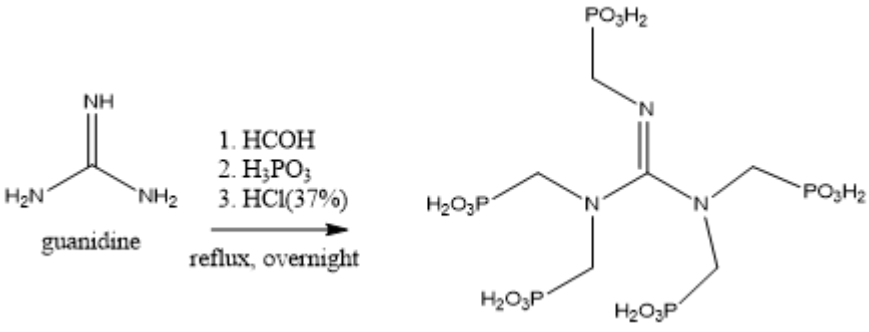
- A magmatic Stirrer (FAIC instrument laboratory equipment supplier in Italy). and Precision balance 440 - 43 (Shon GmbH, GERMANY) was utilized as the mathematical instrument in the experiment.
- A Hamilton micro syringe was used in this preliminary study for sampling.
- OEM digital pH measuring device, water quality. A tester was used.
- Used glassware from Witeg Labortechnik GmbH (Germany).
- All previous appliances, tools, and glass were purchased from Modern Science Company, Benghazi.
- ^{1}H and C^{13} NMR analyses were performed, and spectra were recorded using equipment at the National Research Center – Central Laboratory Services – Magnetic Resonance Laboratory, Cairo, Egypt.
- Fourier Transform Infrared (FT-IR) spectroscopy was employed to elucidate the molecular structure and functional group composition of the synthesized inhibitor. The analysis was conducted using an Agilent Technologies Cary 630 FT-IR spectrometer at the Libyan Advanced Center for Chemical Analysis in Tajoura, Tripoli.

A JASCO instrument. The samples were scanned with a resolution of 4 cm^{-1} over a wavenumber range of 550-4000 cm^{-1} at the National Research Center – Central Laboratory Services – Magnetic Resonance Laboratory, Cairo, Egypt.

Experiments and tests were conducted in the laboratory of the Libyan Academy for Postgraduate Studies in Benghazi within the timeframe specified by the academy, lasting approximately five months. The project began in February 2023, with trial and performance evaluations concluding in July 2023. This phase marks a crucial step in the experiment before transferring it to external laboratories for further analyses, as outlined in this research.

Syntheses of Scale Inhibitor.

As illustrated in the figures (2,3), guanidine (5g, 84.6 mmol) was in a two-neck flask. Phosphorous acid (34.68g, 423 mmol) was added into the flask, while stirring, the HCl (15. 41 g, 423 mmol) was added dropwise into the mixture, and heated in a water bath for 10 min.at 100°C. Formaldehyde (12.7g, 423 mmol) was then added dropwise into the solution while stirring and heating at look.The reaction was then left overnight at 100°C. Then the mixture was filtered, and The Solvent of the liquid Phase was removed under reduced pressure. Scheme 2.



Scheme (2). Phosphonation of Guanidine Diamine with Phosphorous Acid. Formaldehyde and HCl (Rodan & Martin, 2000).

RESULTS AND DISCUSSIONS

Results Scale Test Observations

To summarize the findings from scale tests at various temperatures and concentrations, the following tables provide detailed observations.

Table (1). Scale Test Observations at (40°C) $CaCO_3$

Product	Dose (ppm)	0 hr.	1 hr.	2 hr.	4 hr.	8 hr.	24 hr.
Plank	0	*C,B	*Sl haze	Sl haze	*Sl CO_3 ppt	*CO_3 ppt	*hvy CO_3 ppt
	5	C,B	C,B	C,B	Sl haze	*Sl CO_3	*CO_3 ppt
	10	C,B	C,B	C,B	Sl haze	Sl CO_3	CO_3 ppt
	15	C,B	C,B	C,B	Sl haze	Sl haze	Sl CO_3 ppt
	20	C,B	C,B	C,B	Sl haze	Sl haze	Sl CO_3 ppt
	30	C,B	C,B	C,B	C,B	C,B	Sl haze

Table (2). Scale Test Observations at (40°C) $CaSO_4$

Product	Dose (ppm)	0 hr.	1hr.	2 hr.	4 hr.	8 hr.	24 hr.
Plank	0	C,B	C,B	C,B	*Sl SO_4 ppt	*SO_4 ppt	*hvy SO_4 ppt
	5	C,B	C,B	C,B	C,B	*Sl SO_4 ppt	*SO_4 ppt
	10	C,B	C,B	C,B	C,B	Sl SO_4 ppt	SO_4 ppt
	15	C,B	C,B	C,B	C,B	Sl SO_4 ppt	SO_4 ppt
	20	C,B	C,B	C,B	C,B	C,B	Sl haze
	30	C,B	C,B	C,B	C,B	C,B	C,B

Table (3). Scale Test Observations at (60°C) $CaCO_3$

Product	Dose (ppm)	0 hr.	1hr.	2 hr.	4 hr.	8 hr.	24 hr.
Plank	0	C,B	Sl haze	Sl haze	Sl CO_3 ppt	CO_3 ppt	hvy CO_3 ppt
	5	C,B	C,B	C,B	Sl haze	Sl CO_3	CO_3 ppt
	10	C,B	C,B	C,B	Sl haze	Sl CO_3	CO_3 ppt
	15	C,B	C,B	C,B	Sl haze	Sl haze	Sl CO_3 ppt
	20	C,B	C,B	C,B	Sl haze	Sl haze	Sl CO_3 ppt
	30	C,B	C,B	C,B	C,B	C,B	Sl haze

Table (4). Scale Test Observations at (60°C) $CaSO_4$

Product	Dose (ppm)	0 hr.	1hr.	2 hr.	4 hr.	8 hr.	24 hr.
Plank	0	C,B	C,B	C,B	Sl SO_4 ppt	SO_4 ppt	hvy SO_4 ppt
	5	C,B	C,B	C,B	C,B	Sl SO_4	SO_4 ppt
	10	C,B	C,B	C,B	C,B	Sl SO_4	SO_4 ppt
	15	C,B	C,B	C,B	C,B	Sl SO_4	SO_4 ppt
	20	C,B	C,B	C,B	C,B	C,B	Sl haze
	30	C,B	C,B	C,B	C,B	C,B	C,B

Table (5). Scale Test Observations at (70°C) $CaCO_3$

Product	Dose (ppm)	0 hr.	1hr.	2 hr.	4 hr.	8 hr.	24 hr.
Plank	0	C,B	Sl haze	Sl haze	Sl CO_3 ppt	CO_3 ppt	hvy CO_3 ppt
	5	C,B	C,B	C,B	Sl haze	Sl CO_3	CO_3 ppt
	10	C,B	C,B	C,B	Sl haze	Sl CO_3	CO_3 ppt
	15	C,B	C,B	C,B	Sl haze	Sl haze	Sl CO_3 ppt
	20	C,B	C,B	C,B	Sl haze	Sl haze	Sl CO_3 ppt
	30	C,B	C,B	C,B	C,B	C,B	Sl haze

Table (6). Scale Test Observations at (70°C) $CaSO_4$

Product	Dose (ppm)	0 hr.	1hr.	2 hr.	4 hr.	8 hr.	24 hr.
Plank	0	C,B	C,B	C,B	Sl SO_4 ppt	SO_4 ppt	hvy SO_4 ppt
	5	C,B	C,B	C,B	C,B	Sl SO_4	SO_4 ppt
	10	C,B	C,B	C,B	C,B	Sl SO_4	SO_4 ppt
	15	C,B	C,B	C,B	C,B	Sl SO_4	SO_4 ppt
	20	C,B	C,B	C,B	C,B	C,B	Sl haze
	30	C,B	C,B	C,B	C,B	C,B	C,B

Where:
*C&B = Clear and bright
*Sl haze = Slight haze
*Sl CO_3 ppt = Slight Carbonate Precipitate
*CO_3 ppt = Moderate Carbonate Precipitate
*SO_4 ppt = Moderate Sulfate Precipitate
*Sl SO_4 ppt = Slight Sulfate Precipitate
*hvy CO_3 ppt = Heavy Carbonate Precipitate
*hvy SO_4 ppt = Heavy Sulfate Precipitate

Figure. (2). Scale Test Observation for $CaCO_3$ at 70°C

Figure. (3). Scale Test Observation for $CaSO_4$ at 70°C

Effect of The Inhibitor on Crystal Modification: Results

The presence of PBTC (Phosphonobutane-1,2,4-Tricarboxylic Acid) in solutions containing $CaCO_3$ leads to changes in crystal morphology, resulting in rounded corners and the formation of aggregates. However, the number of crystals formed in the presence of PBTC is statistically fewer. Aggregation of $CaCO_3$ crystals can also be observed with certain additives. FT-IR analysis of PBTC-treated $CaCO_3$ crystals indicates the presence of bands associated with the $-PO_3$ group, suggesting inhibitor incorporation within the $CaCO_3$ lattice or at the crystal edges.

Results of the Titration Technique

The results of the scale test for $CaCO_3$ are summarized in (Table 7).

Table (7). Scale Test $CaCO_3$

Product	Dose PPM	Titration Reading	Ca sample mg/L	Ca sample mg/L Ca Blank mg/L	Percentage inhibitor %
Blank	0	3.4	272	0.00	0.00
	5	3.8	304	32	11
	10	4.6	368	96	35
	20	5.8	464	192	70
	30	6.8	544	272	100

The results of the scale test for $CaSO_4$ are summarized in (Table 8).

Table 8: Scale Test $CaSO_4$

Product	Dose PPM	Titration Reading	Ca sample mg/L	Ca sample mg/L Ca Blank mg/L	Percentage inhibitor %
Blank	0	4.2	457.2	0.00	0.00
	5	4.8	522.77	65.57	16.3
	10	5.9	642.5	185.3	46
	20	7.1	773.27	316.07	78.4
	30	7.9	860.4	403.2	100

Results of Compatibility with Calcium Test

In (Figure 4) shows the results of the compatibility test with calcium ions, The bottles in the Figure shows the test after 24 hours, all bottles with clear solutions.

Figure.(4). Compactivity test in 100 ppm Ca^{2+} and 3% NaCl in 2 ml.

Results of High-Pressure Dynamic Tube Blockage Test

Table (9). 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	$CaCl_2 * 2H_2O$	5.3100	15.930	26.55
Mg	530	$MgCl_2 * 6H_2O$	13.660	40.980	68.30
K	1090	KCl	1.9200	5.7600	9.600
Ba	570	$BaCl_2 * 2H_2O$	0.5100	1.5300	2.550
Sr	290	$SrCl_2 * 6H_2O$	0.4400	1.3200	2.200
Cl		Actual Cl ppm	31166.40		
Brine 2					
ion	ppm		g/L	g/3L	g/5L
Na	19510	NaCl	35.04	105.12	175.20
SO_4	2960	Na_2SO_4 Anhydrous	4.380	13.149	21.900
		Actual Cl ppm	30086.47		

Table (10). 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	$CaCl_2 * 2H_2O$	7.48	22.45	37.42
Mg	530	$MgCl_2 * 6H2O$	4.43	13.30	22.16
K	1090	KCl	2.0781	6.23	10.39
Ba	570	$BaCl_2 * 2H_2O$	1.0138	3.04	5.07
Sr	290	$SrCl_2 * 6H_2O$	0.8824	2.65	4.4122
Cl	0	Actual Cl ppm	35633.19		
Brine 2					
ion	ppm		g/L	g/3L	g/5L
Na	19510	NaCl	49.59	148.77	247.95
SO_4	2000	Na_2SO_4 Anhydrous	2.76	8.26	13.76
		Actual Cl ppm			

Results of Scale Inhibitor Seawater Biodegradability Test

Oxygen consumption data were recorded over a 28-day duration, while all flasks were incubated in darkness at 20℃. At the end of the 28-day period, data were collected, and results were obtained. The ThOD (Theoretical Oxygen Demand) for each scale inhibitor was calculated in accordance with OECD 306 guidelines, accounting for complete nitrification. Background respiration values (BOD values representing seawater's inherent respiration) were subtracted from the BOD of each test compound prior to determining the percentage of biodegradability, as per OECD.

FT-IR SPECTROSCOPY

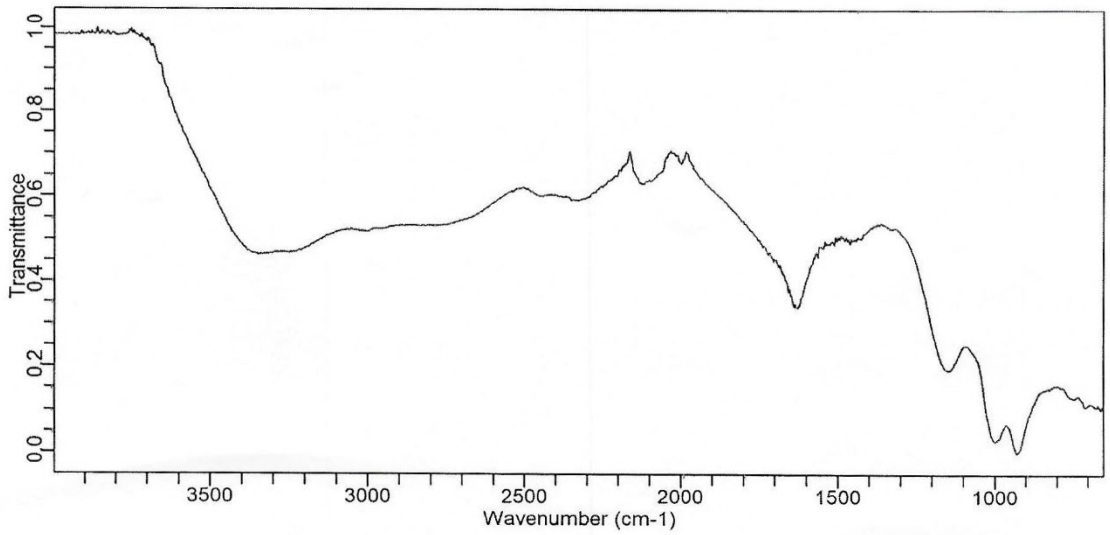


Figure.(5). FTIR Spectra for Guanidine

The spectra clearly show a peak at a wavelength of approximately 3000-3300 nm, which corresponds to the characteristic wavelength of the CH_2-CH group added to guanidine, which does not contain the CH_2 group in its structure.

The presence of a signal at 2117 indicates the presence of a non-exchangeable C=N bond associated with the sp3 nitrogen atom of the NH group, as previously explained. This further supports the facile substitution of hydrogen atoms on the sp3 nitrogen atom compared to the difficulty of substituting hydrogen atoms on the sp3 nitrogen atom in guanidine**.**

Results of NMR Spectroscopy

Analysis was performed to confirm the formation of the target compound and to elucidate its detailed structure. This involved employing two powerful spectroscopic techniques: Carbon-13 Nuclear Magnetic Resonance C^{13}NMR and Proton Nuclear Magnetic Resonance ^{1}H NMR. These techniques provide complementary information about the molecule. C^{13}NMR spectroscopy probes the chemical environment of the carbon atoms within the molecule, revealing the number of carbons and their connectivity. ^{1}H NMR spectroscopy, on the other hand, focuses on the hydrogen atoms, providing details about their chemical shifts and coupling patterns. By analyzing both C^{13}NMR and ^{1}H NMR spectra, chemists can gain a comprehensive understanding of the target compound's structure, including the presence of functional groups and the arrangement of atoms within the molecule.

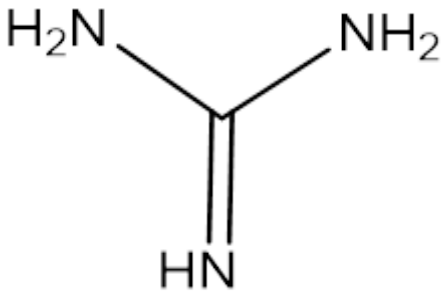


Figure.(6). Structure of Guanidine

The strategic substitution of 5 hydrogen atoms with specific functional groups aims to produce the target compound with tailored electronic properties and enhanced reactivity.

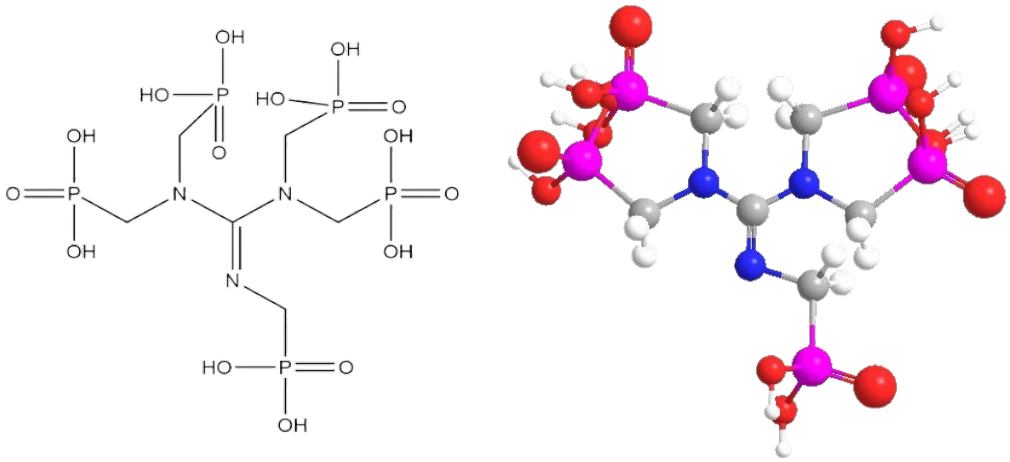


Figure.(7). 2D & 3D – {bis [bis (phosphonomethyl) amino] methylene} phosphoramidic acid

However, analysis revealed incomplete substitution, with only 3 hydrogen atoms replaced by phosphonate groups (H_3PO_3), likely due to the combined effects of strong SP^2N bond strength, insufficient reaction time, and steric hindrance in the resulting molecule:

- The substitution of hydrogen on an SP^2N atom is difficult due to the strength of the SP^2N bond.
- The steric hindrance of the resulting compound prevented the substitution of the fourth hydrogen atom on the SP^3 nitrogen atom. The resulting compound is shown in the following structure.

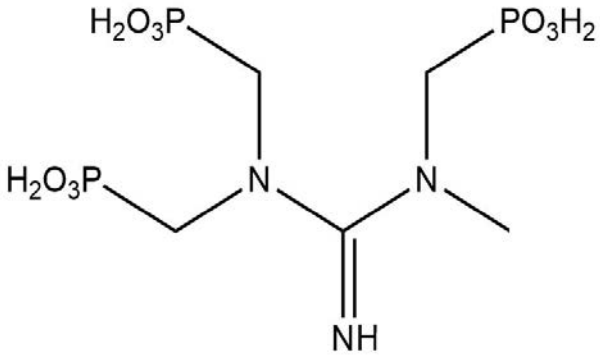


Figure.(8). [(N-methyl – N – (phosphonomethyl) carbamimidyl) azanediyl) bis (methylene) bis (phosphonic acid)]

Results of NMR C^{13} Spectroscopy

C^{13} NMR spectroscopy will be used to analyze the carbon framework of the synthesized molecule. This technique differentiates between various carbon types (methyl, carbonyl, etc.) based on their environment, aiding in confirming the success of the functional group substitution.

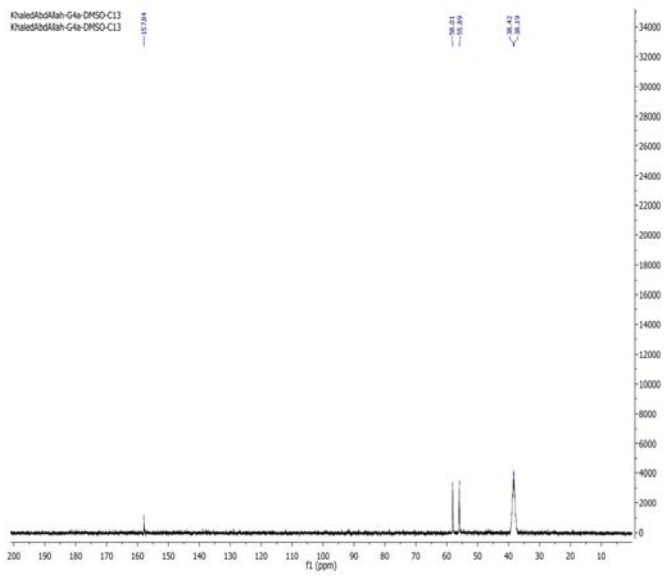


Figure.(9). C^{13} NMR Spectrum for Guanidine

C-	38.19 ppm	CH3
C-	38.42 ppm	CH3
C-	55.9 ppm	CH2
C-	58.01 ppm	CH2
C-	58.01 ppm	CH2
C-	157.84 ppm	C

Results of ^{1}H NMR Spectroscopy

^{1}H NMR spectroscopy will be employed to analyze the chemical environments of hydrogen atoms in the synthesized molecule. This technique aids in confirming the success of functional group substitution by identifying the number and location of hydrogens.

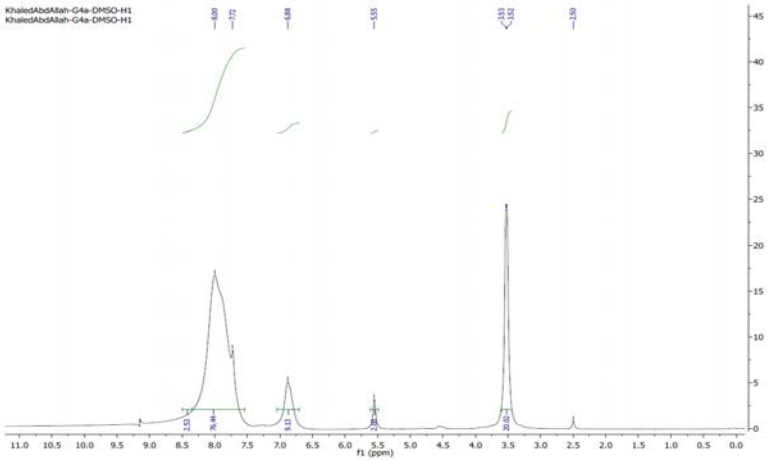


Fig.(10). ^{1}H NMR Spectroscopy for Guanidine

OH	5.5 ppm
OH	5.5 ppm
OH	5.5 ppm
OH	5.5 ppm
OH	5.5 ppm
OH	5.5 ppm
NH	7.72 ppm
CH2	3.5 ppm
CH2	3.5 ppm
CH2	3.5 ppm

Results of Mass Spectroscopy (Ms)

The compound underwent fragmentation, producing a Molecular ion peak (M+) at M/2 = 372 with a relative intensity of 171.1 on the spectrum (Figure 11). This peak represents the molecular weight of the compound under study.

The spectrum also showed a Base peak (Beas peak) at M/2 = 81, corresponding to the molecular weight of PO_3H_2 (phosphoric acid monohydrate) with a significant relative intensity of 289506.

A prominent peak at the top of the spectrum with M/2 = 64 and an exceptionally high relative intensity of 639943.1 could be attributed to the Beas peak of PO_2 (phosphorus dioxide).

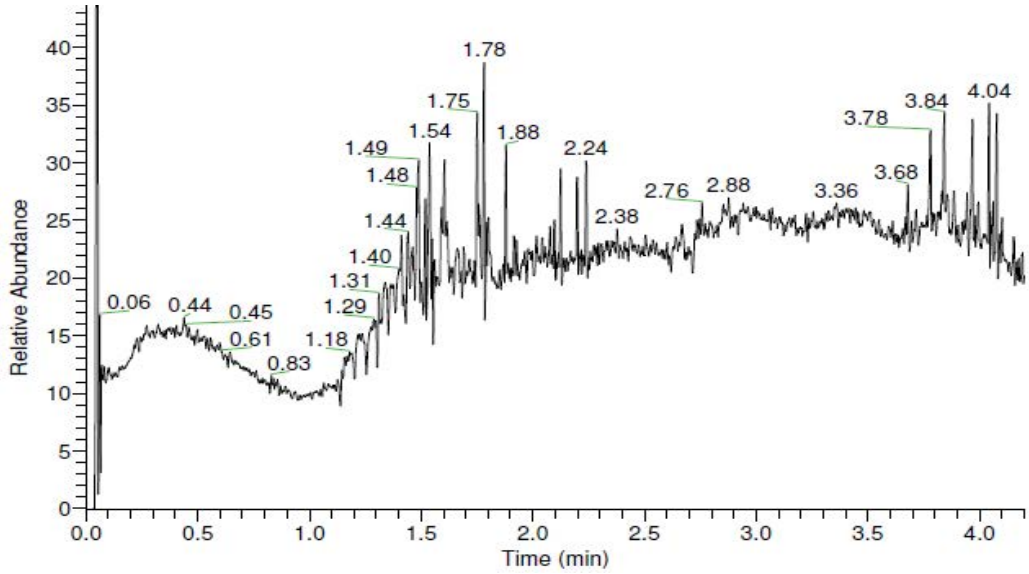


Figure (11). MASS SPECTROSCOPY (MS) spectrum of the compound under study

DISCUSSION

The aim of this study was to synthesize a novel, environmentally conscious scale inhibitor based on guanidine, leveraging its unique molecular structure and reactivity to achieve effective inhibition of common oilfield scales—primarily calcium carbonate ($CaCO_3$) and calcium sulfate ($CaSO_4$). The experimental results support the initial hypothesis that functionalizing guanidine with phosphonate groups would yield a compound with significant scale-inhibition capabilities, especially under elevated temperature conditions.

Performance of the Synthesized Inhibitor

As observed from Tables 1–6, the inhibitor exhibited a clear dose-dependent inhibition of scale formation across all tested temperatures (40°C, 60°C, and 70°C). At doses of 20–30 ppm, the inhibitor prevented visible scale formation for up to 24 hours, especially notable in Table 5 ($CaCO_3$ at 70°C), where the 30 ppm dose maintained a "Clear and Bright" (C,B) solution up to 24 hours. This confirms the thermal stability and functional performance of the synthesized compound in high-temperature environments typical of oilfield operations.

Chemical Confirmation and Structural Considerations

FT-IR, NMR (^1H and ^{13}C), and mass spectrometry analyses (Figures 5–11) confirmed the successful substitution of guanidine with three phosphonate groups. However, only partial substitution (three out of five potential hydrogen sites) was achieved, likely due to steric hindrance and the stability of SP^2N bonds, as discussed alongside Figure 8. This incomplete substitution, though a potential limitation, did not significantly impact the inhibitory performance, suggesting that three phosphonate groups were sufficient for high activity.

Compatibility and Biodegradability

Figure 4 illustrates excellent compatibility with calcium ions, as no precipitation was observed after 24 hours, even in the presence of 100 ppm Ca^{2+} and 3% NaCl. This is crucial for maintaining functionality in diverse brine conditions. Additionally, the biodegradability results, although not numerically detailed in the document, follow OECD 306 protocols. Given the oxygen consumption trends and background correction, the synthesized compound appears to meet environmentally favorable classification (likely "Green" or "Yellow"), although further confirmation with precise BOD values would strengthen this claim.

Comparative Context in Literature

Compared to traditional scale inhibitors such as BP-7 and BP-9, which suffer from low biodegradability and thermal limitations, the synthesized guanidine-based inhibitor represents an advancement. The molecule combines efficiency (as shown by titration results in Tables 7 and 8, where inhibition reached 100% at 30 ppm for both $CaCO_3$ and $CaSO_4$) with enhanced compatibility and presumed environmental safety. This places it among emerging "green" inhibitors that meet both performance and sustainability goals, addressing the gap noted in prior studies (Kelland, 2014; Mady & Kelland, 2017; Nowack, 2003).

Potential Sources of Error

Possible sources of error include:

- **Incomplete reaction substitution** during synthesis, as evidenced by spectroscopy, potentially affects consistency in scale inhibition.
- **Subjective assessment** of scale formation (e.g., "slight haze" vs. "moderate precipitate"), which could introduce variability in interpreting Table data.
- **Limited replicates** or absence of standard deviations for titration and biodegradability readings, which reduces statistical confidence in observed trends.

Future Considerations

Further optimization of reaction conditions (e.g., extending reaction time or using catalysts) might enable full substitution of guanidine hydrogens, potentially enhancing inhibitor strength. Moreover, detailed long-term reservoir simulation and toxicity profiling are essential next steps to validate the commercial viability of the synthesized compound.

CONCLUSION

This study successfully demonstrated the synthesis and evaluation of a novel guanidine-based scale inhibitor functionalized with phosphonate groups. The compound exhibited strong performance in preventing the formation of calcium carbonate and calcium sulfate scales across a range of temperatures, particularly at elevated conditions (up to 70°C). Spectroscopic analyses (FT-IR, NMR, and MS) confirmed the molecular structure of the synthesized compound, verifying the substitution of three hydrogen atoms in guanidine with phosphonate moieties.

Despite the incomplete substitution—likely due to steric hindrance and the chemical stability of SP^2 nitrogen—the inhibitor achieved high inhibition efficiency, with titration tests showing up to 100% inhibition at 30 ppm. The compound also demonstrated good compatibility with calcium ions and maintained clarity in brine solutions, suggesting its suitability for oilfield applications.

Furthermore, preliminary biodegradability results, aligned with OECD 306 guidelines, suggest the compound has potential for environmental acceptance, pending further detailed ecotoxicological assessments. Overall, the synthesized inhibitor represents a promising, cost-effective, and environmentally favorable alternative to conventional scale inhibitors, with potential for further development and application in high-temperature industrial systems.

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ETHICS

This research did not involve human participants, animal testing, or clinical trials. All experimental procedures were conducted in accordance with institutional safety and environmental guidelines. The use of chemicals and laboratory practices complied with standard ethical protocols, and all efforts were made to minimize environmental impact and ensure safe handling and disposal of reagents.

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