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Breaking Barriers: Advancements in Scale Inhibition for Pre-Salt Reservoirs

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Abstract
The rise in produced water, fueled by the maturation of aging fields, particularly in regions such as the Brazilian pre-salt, has presented a myriad of intricate technological hurdles in ensuring fluid flow reliability. Scale buildup, a persistent challenge, results in decreased flow rates, equipment degradation, corrosion, and compromised thermal conductivity. To combat scale accumulation under harsh conditions (e.g., high temperatures, salinity, elevated bivalent ion levels, CO_2 concentrations). Formulating inhibitors necessitates a thorough consideration of specific operational parameters. This study introduces new classes of scale inhibitor for pre-salt conditions and compares them with conventional technologies Assessment methodologies encompass static bottle experiments, dynamic loop trials (DSL), kinetic turbidity assessments (KTT), bivalent ion tolerance examinations, biodegradability evaluations, and thermogravimetric analyses (TGA). The new scale inhibitors demonstrate outstanding efficacy in preventing multiple scale formations, surpassing incumbent technologies at 15 parts per million (ppm). The innovative product exhibits robust tolerance to bivalent ions, superior thermal stability, and compatibility with thermodynamic hydrate inhibitors, coupled with heightened biodegradability.

Keywords
Scale inhibitor; pre-salt; calcium carbonate

Introduction
The surge in produced water, propelled by the maturation of aging fields, particularly in locales like the Brazilian pre-salt, has introduced a plethora of intricate technological hurdles in ensuring smooth flow. As these challenges mount, it becomes imperative to delve into the intricate mechanisms underlying scale formation in the upstream oil and gas sector. Recognized as one of the most formidable issues, scale formation triggers a cascade of problems including decreased flow, equipment erosion, corrosion, and compromised thermal efficiency within the system [1]. Amidst the complex landscape of the oil and gas industry, common inorganic scales like calcium carbonate, sulfate salts of calcium, strontium, and barium are widely acknowledged [2].
However, recent operational scenarios have paved the way for the emergence of unconventional scales, necessitating a nuanced approach to scale inhibition strategies. [3]. Amidst these challenges, the selection of appropriate chemicals for injection in oil production necessitates a comprehensive grasp of specific operational conditions. Developing effective scale inhibitors capable of withstanding extreme conditions such as high temperatures, elevated salinity, increased bivalent ion concentration, and high CO_2 levels is imperative [3].
There are numerous technical criteria to consider for the development of scale inhibitors, suggesting the need to innovate a new generation of inhibitors that meet these characteristics. This study proposes a methodology for chemical selection and outlines the development of highly adaptable scale inhibitors. These novel scale inhibitors were assessed under Brazilian pre-salt conditions and juxtaposed with conventional technologies utilized for scale inhibition.

Methodology
In this study, we utilize conventional techniques to assess the efficacy of scale inhibitors under highly challenging circumstances (temperature = 135°C, salinity = 180,000 ppm, calcium = 7,200 ppm). Furthermore, we conduct biodegradability assessments and thermogravimetric analyses to ascertain chemical durability.
Conventional polyamino polyether methylene phosphonic acid (PAPEMP) and novel scale inhibitors with codifications SI-1, SI-2 and SI-3 were used as collected, both supplied by Dorf Ketal. Monoethylene glycol with codification MEG (99.5% purity) and hydrated ethanol with codification EtOH (95.0% purity) were also supplied by Dorf Ketal.
For static and dynamic efficiency, synthetic brine (summarized in Tab. 1) was prepared using different salts from Vetec S.A., graded as analytical

grade, including sodium chloride, calcium chloride dihydrate, magnesium chloride hexahydrate, barium chloride dihydrate, strontium chloride hexahydrate, potassium chloride, sodium sulfate, sodium bicarbonate, sodium acetate, and sodium bromide.

Table 1. Synthetic brine composition used for the experiments.

Ion	Concentration (mg/L)
Na^+	57,169
Ca^{2+}	7,182
Mg^{2+}	1,415
K^+	2,999
Sr^{2+}	947
Ba^{2+}	37
Cl^-	106,544
SO_4^{2-}	541
HCO_3^-	1,128
pH	6.5
Total dissolved solids	179,288

Static Bottle Test

The standard static bottle test is well-known technique in the industry which is used to determine scale inhibitor efficiency under static conditions, according to NACE TM0197-2010. The metal ions concentration left in solution is monitored by inductively coupled plasma (ICP-OES). Efficiency of scale inhibitors (in dosage of 10 ppm) was determined comparing metal ion concentration measured in a scaling blank (i.e., without scale inhibitor) and a non-scaling control solution, according to Eq. (1).

$$\%\ \text{Inhibition efficiency} = \left(\frac{C_{SI} - C_B}{C_0 - C_B}\right) \times 100 \quad (1)$$

C_{SI} = metal concentration in sample with inhibitor;
C_0 = metal concentration in unscaled sample;
C_B = metal concentration in sample w/out inhibitor.

Dynamic Scale Loop Test

Dynamic scale loop (DSL) tests were conducted to evaluate performance data of scale inhibitor, under dynamic conditions, using automated apparatus PMAC HTHP series, built by PMAC Scientific Ltd., Scotland. The differential pressure across this scaling coil (ΔP) is recorded as a function of time, the pass criteria is related to the ability of scale inhibitor to keep a flat-line at concentration of 15 ppm of active acid (< 1 psi rise in ΔP over 60 min).

Brine Compatibility

Bivalent ions tolerance tests were carried based on modified method NACE TM0197-2010. In a similar manner to standard bottle test, anionic (without scaling anions) and cationic synthetic brines were mixed in the presence of scale inhibitors (pH range of 6 to 7) in dosages of up to 50,000 ppm of active. The samples are observed visually and aspect of solution is recorded.

Kinetic Turbidity Test

The kinetic turbidity tests (KTT) were conducted using in-house equipment. The turbidity meter sample cuvette also has temperature control (90°C) and magnetic stirring (900 rpm). As brines are introduced into the cells, the scaling behavior of the brine and inhibited brines are recorded over time.

Biodegradability Test

The biodegradation data were obtained by OECD 306 procedure which provides, specifically chemical substances biodegradability in seawater. The positive and negative controls are used. The seawater used in the test was collected at Pedrinhas (Macaé, Brasil). For each scale inhibitor, as is the product, the biological oxygen demand (BOD) was measured over 28 days.

Thermal Stability

Thermogravimetric analyzer TGA 55 (TA Instruments) was applied to investigate the thermal stability of scale inhibitor. The samples of dry scale inhibitors were subjected to a linear ramp from 155°C to 700°C at 5°C/min. The thermal stability of scale inhibitors in water was also investigated. Thermal aging of scale inhibitors, as is the product, was carried out in an oven at 135°C up to 6 hours.

Solvent Compatibility

The ability of scale inhibitors to stabilize in alcoholic solvent, such as monoethylene glycol (MEG) and ethanol (EtOH), known as thermodynamic hydrate inhibitors (THIs) were invetigated.
The tests were carried formulating scale inhibitor with THIs mixture – MEG:EtOH (4:11 w/w), in weight ratio of THIs:SI (15:1), then visual aspect of solution is recorded.

Results and Discussion

The scale prediction, based on the Pitzer theory (Tab. 2) identified various scales, including calcite, strontianite, anhydrite, celestite, and barite. Novel scale inhibitors (SI-1, SI-2, and SI-3) were tested against conventional ones in static bottle tests using synthetic brine.

Table 2. Scaling prediction of synthetic brine at 135°C and 120.4 psi.

Scale	Saturation Index	Potential amount of precipitation (mg/L)
Calcite	1.84	298
Anhydrite	0.25	326
Barite	0.88	54
Strontianite	1.26	330
Celestite	0.69	709

The results of scale inhibition efficiency are shown in Tab. 3. Conventional scale inhibitor PAPEMP provides low protection (< 90%) against calcium scale, strontium scale, and barium scale. Conversely, the novel scale inhibitors SI-1 and SI-3

provided good efficiency for calcite and barite (≥ 90%). SI-2 showed the best inhibition related to strontium scale. The scale inhibitor SI-1 has slightly better inhibition efficiency by showing good protection against all scale cations evaluated.

Table 3. Static bottle test results at 135°C (24h).

Inhibition Efficiency (%)	Calcium	Strontium	Barium
PAPEMP	56	83	87
SI-1	100	91	100
SI-2	60	100	91
SI-3	96	83	96

The results of DSL tests are shown in Fig. 1 with the graphical representations. The blank runs using a 50-50 mixture of anionic and cationic synthetic brines failed immediately after the synthetic brines were mixed. The ΔP of conventional scale inhibitor PAPEMP increased up to 1 psi at about 9.9 min in the presence of 15 ppm of active acid. On the other hand, the new scale inhibitors SI-1, SI-2, and SI-3 showed excellent scale inhibition when compared to the conventional scale inhibitors, the baseline kept flirting and showing low scale tendency, presenting ΔP lower than 0.5 psi in across 60.0 minutes at same dosage of active acid.

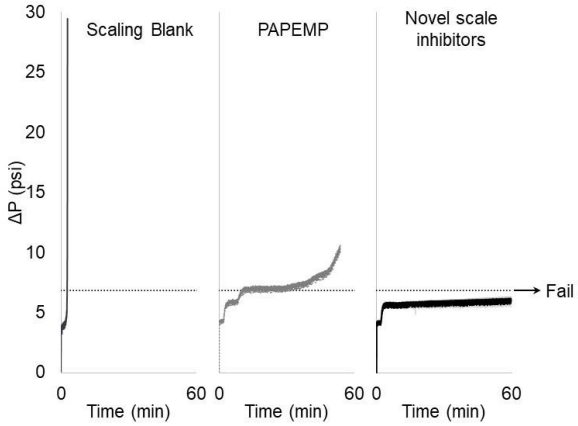

Figure 1. DSL performance results at 135°C.

A typical behavior for scaling blank was observed in KTT test (Fig. 2), in which a rapid increase in turbidity is evidenced as scale particles form and decreases with time due to the lowering of the supersaturation of solution after precipitation of inorganic scales. Scale inhibitors SI-1 and SI-3 shows very flat line, as PAPEMP, indicating that the scale growth is controlled over the extent of the duration of experiment, by action of these molecules preferably on nucleation inhibition mechanism. Although the PAPEMP molecule presented similar behavior as SI-1 and SI-3 using KTT experiments, DSL results showed improvements in efficiency of new molecules. Despite the DSL induces highly nucleation tendency (favoring nucleation-delay mechanism of the products), it is suggested that the new molecules SI-1, SI-2 and SI-3 can act effectively retarding the scale growth combining different action mechanism (like as dispersive effect and growth controller). This phenomenon is more evident on the scale inhibitor SI-2, that behaved both as dispersant and growth controller. The KTT shows an initial increase in turbidity, lower than scaling blank, followed by a plateau, which suggests complete control of the scale growth at that stage.

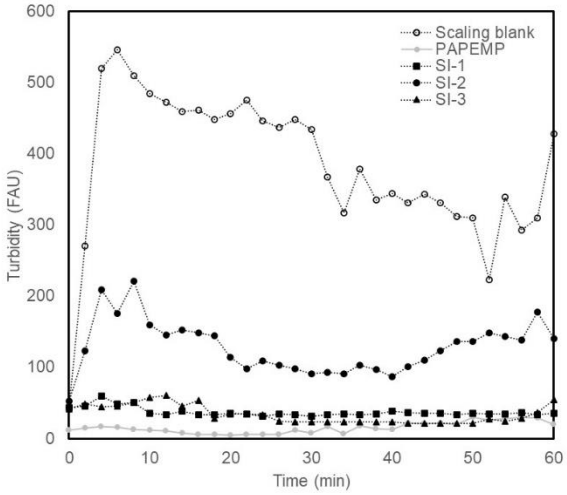

Figure 2. KTT inhibition mechanism investigation.

The brine compatibility of newly developed scale inhibitors was compared to PAPEMP. It was found that new scale inhibitor SI-1, SI-2, and SI-3 showed an excellent brine compatibility by showing no precipitation (Tab. 4) with all concentrations up to 50,000 ppm of active acid over 24 hours test period.

Table 4. Brine compatibility test of scale inhibitor with field's water.

Scale inhibitor	Dose of active (ppm)		
	5,000	25,000	50,000
PAPEMP	Clear	Haze	Haze
SI-1	Clear	Clear	Clear
SI-2	Clear	Clear	Clear
SI-3	Clear	Clear	Clear

The biodegradation test data of new scale inhibitors SI-1, and SI-3 were measured and compared to PAPEMP and sodium benzoate as the biodegradable reference in the seawater sample, as shown in Fig. 3. The reference chemical sodium benzoate presented biodegradation of about 94% in 28 days. The results showed biodegradation of 37% in 28 days for PAPEMP. The new scale inhibitors showed highest biodegradation rate of 48% and 46% in 28 days for SI-1 and SI-3 respectively, and therefore considered to be inherently biodegradable and environmentally more friendly that conventional technologies based on the biodegradation criteria for OECD 306 test. These two new scale inhibitors SI-1 and SI-3 showed a relative increase in biodegradation of 30% and 24% respectively, when compared to the conventional scale inhibitor, such as PAPEMP over 28 days.

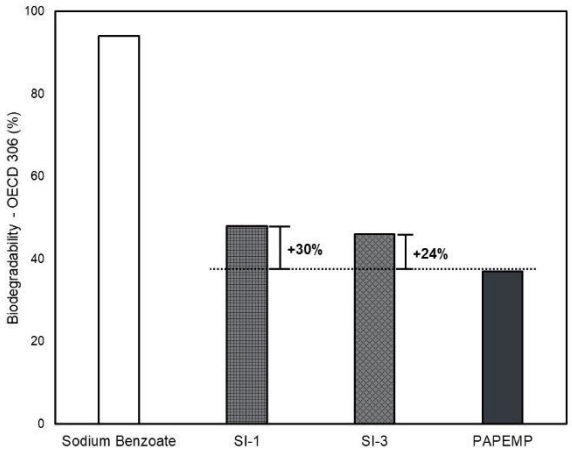

Figure 3. Biodegradability data measured by the OECD 306 procedure over 28 days.

Thermal stability of the samples of dry scale inhibitors was verified by TGA using temperature program indicated in the experimental procedure section. The results of thermal stability are shown in with the thermogram (Fig. 4). The new scale inhibitor SI-1, and PAPEMP begin to decompose above 155°C with multiple onset and end set temperatures and revealed two main stages with major mass losses with similar decomposition profile.

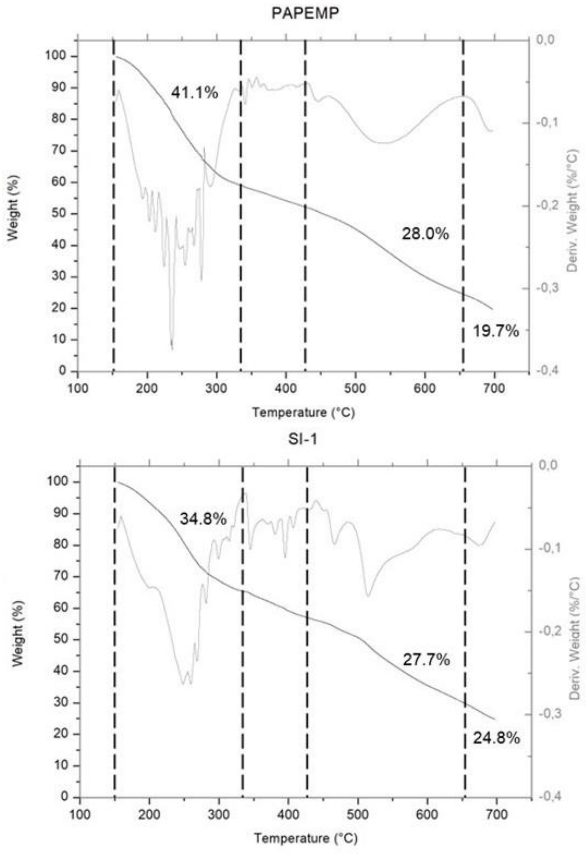

Figure 4. Thermogram TG curve and DTG curve of scale inhibitors.

The compatibility of new scale inhibitors was compared to conventional PAPEMP in the presence of THI solution. Figure 5 showed that, despite having a slight precipitate, scale inhibitors SI-1 showed better compatibility than PAPEMP. Scale inhibitors SI-2, and SI-3 exhibited better solubility within THI-rich solution, making them more suitable for subsea application.

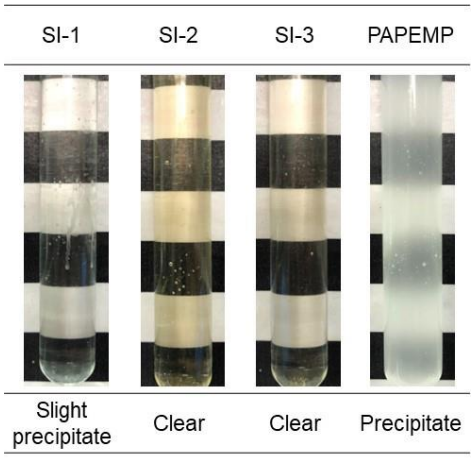

Figure 5. Chemical compatibility test of scale inhibitors with THIs.

Conclusions

The newly developed chemistry boasts a unique molecular structure with carefully chosen chemical properties, enabling effective management of calcium carbonate, barium sulfate, calcium sulfate, and strontium sulfate formation during mineral scale buildup. Crafting scale inhibitors that can handle diverse scales is crucial for water treatment in challenging environments like oilfields and geothermal applications. These new inhibitors are designed to act as efficient threshold inhibitors even under extreme conditions, demonstrating remarkable adaptability and promising performance. As the oil and gas industry landscape evolves, these advancements provide a hopeful solution to the complex challenges of scale formation and inhibition.

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Responsibility Notice

The authors are the only responsible for the paper content.

References

[1] Mpelwa, M.; Tang, S.F.; *Petroleum Science* 16(4), 830–849, 2019.

[2] Mady, M.F.; Bayat, P.; Kelland, M.A.; *Industrial and Engineering Chemistry Research* 59(21), 9808–9818, 2020.

[3] Beltrao, R.L.C.; Sombra, C.L.; Lage, A.C.V.M.; Fagundes Netto, J.R.; Henriques, C.C.D.; *Offshore Technology Conference* 19880, 1–11, 2009.