

Evaluation of Scale Inhibitors To Prevent Calcium Sulfate In Sulfate Removal Units

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ABSTRACT: Chemicals (scale inhibitor and biocide) are used to prevent the formation of CaSO_4 in the spiral wound modules (SWMs) of offshore sulfate removal units (SRUs). In these units, seawater is filtered by nanofiltration to remove sulfate ions. This study evaluated six scale inhibitors in the presence and absence of DBNPA-based biocide. Synthetic seawater was used, with an estimated ionic composition for the membrane surface. Assays were performed at 25°C, for 24 hours. The results showed that CaSO_4 precipitation kinetics occur quickly under these conditions, with doses of 5 to 1,000 mg/L for scale inhibitors and 200 to 2,000 for biocide. Static inhibition efficiency values for CaSO_4 with 800 mg/L of biocide at 25° C for 60min were as follows: KCl-based phosphonate complex (Inhibitor 5), 68%; phosphonate-based (Inhibitor 1), 64%; EDTA tetrasodium salt-based (Inhibitor 2), 63%; Aminophosphonic acid-based aqueous solution (Inhibitor 6), 44%; DETA phosphonate-based aqueous solution (Inhibitor 4), 28%; and phosphonic acid, [nitriltris(methylene)] tris-, sodium salt (Inhibitor 3), 0%. These findings demonstrate the importance of these chemicals in SRUs to prevent CaSO_4 formation on the membrane surface.

Keywords: Calcium sulfate, nanofiltration, scale inhibitor, seawater, sulfate removal unit.

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I. INTRODUCTION

Seawater is usually injected into oil reservoirs when conditions do not allow oil to be spontaneously produced [1,2]. Seawater injection raises oil pressure above reservoir pressure, enabling oil production [1,2]. However, seawater is an aqueous fluid with high sulfate levels (approximately 3,000 mg/L), thereby increasing the risk of sulfate deposits during oil production. Sulfate scales are precipitates with low water solubility and high adhesion capacity to several materials present in oil production. They are formed by the reaction between sulfate present in seawater and barium, calcium or strontium in formation water. An alternative to reduce the formation of sulfate scale in oil production is sulfate removal using a membrane system. In offshore oil production, these systems are known as Sulfate Removal Units (SRUs) [3]. These SRUs remove sulfate through specialized nanofiltration (NF) membranes. This technology has been applied on offshore platforms since 1988 [4], when the first SRU was implemented in the Brae field (North Sea). Effective sulfate removal by SRUs requires seawater to pass through a sequence of filtration systems (pretreatment and treatment). The pretreatment stage uses 5.0 μm pore size cartridge filters to remove particulates, suspended solids and biological material. In the following step, the seawater passes through the thin-film composite (TFC) polyamide nanofiltration membrane for sulfate removal. The first SRU in Brazil was developed for the Roncador field, in 2002 [5]. Until 2008, the technology was controlled by two companies, the Dow Chemical Company (DOW) and Marathon Oil Company. DOW was responsible for manufacturing SWMs with nanofiltration membranes and thin selective layers of nylon (initially using FilmTec NF-40 membrane elements), and Marathon Oil for the SRU process itself [4,5]. The nanofiltration membranes used in SRUs consist of three overlying layers: a 120 μm -thick polyester polymeric support with 200 μm pore size; a 40 μm -thick polysulfone middle layer with 15 nm pore size; and a 200 nm-thick polyamide thin film with a pore size of 1 nm [6]. The polyamide film is responsible for the selective retention of sulfate ions from seawater according to ion size and charge, primarily divalent ions or those larger than 1 nm. As such, the major ions retained by SRU nanofiltration membranes are sulfate and calcium [7, 8, 9].

However, sulfate removal by SRUs can lead to the accumulation of calcium and sulfate ions on the nanofiltration membrane surface. This is due to the concentration polarization phenomena and the effect of transport mechanisms through the nanofiltration membrane. Ionic concentration occurs at the membrane surface and prompts the formation of precipitates such as CaSO_4 on the polarization layer [10, 11, 12, 13]. Precipitate formation on the nanofiltration membrane surface reduces permeation efficiency and the lifetime of the membrane. In order to minimize this problem and avoid having to change the nanofiltration membranes after pretreatment, SRUs are dosed with scale inhibitors combined with biocides to prevent the formation of CaSO_4 precipitates inside the SWMs (on the nanofiltration membrane surface) [14]. However, some scale inhibitors combined with biocides decrease inhibitory efficiency. Thus, the aim of this study is to analyze certain scale inhibitors in the presence or absence of biocide, in order to identify the most effective scale inhibitor for sulfate removal and the best dosage, scale inhibitor and biocide combination to reduce the costs associated with membrane changes.

II. MATERIAL AND METHODS

2.1 Synthetic Seawater Composition

The Sample Used For Tests In This Study Was a synthetic aqueous solution with an ionic composition similar to that of seawater on the nanofiltration membrane surface of SRUs. In order to determine the ionic composition of seawater typically found at offshore SRUs, prior in situ monitoring of three streams of an SRU was carried out for one year: feed stream of the nanofiltration system downstream from pretreatment; permeate stream of the nanofiltration system; and the concentrate (SRU discharge) stream. Seawater samples cannot be collected directly from the nanofiltration membrane surface and as such, the ionic composition was estimated based on three parameters: ionic composition of the feed and permeate streams of the in situ SRU during operation; volume flow rate through the membrane (J_v) and polarization layer thickness (δ).

2.1.1 Ionic composition of the SRU feed and permeate streams

The aqueous streams present in SRUs are: feed stream, downstream from pretreatment, containing about 3,000 mg/L of sulfate ion; permeate stream, with sulfate levels lower than 100 mg/L; and the concentrate (SRU discharge) stream, with sulfate content of approximately 11,000 mg/L. The ionic composition of the feed and permeate streams was determined in order to estimate the ionic composition of the synthetic seawater (condition of the nanofiltration membrane surface). To that end, six aqueous samples were collected from an SRU located in the Campos Basin, Brazil, three from the feed stream and three from the permeate stream, every two months over a one-year period. A total of thirty-six aqueous samples were collected, eighteen from the feed stream and eighteen from the permeate stream. The feed stream was sampled downstream from pretreatment (downstream cartridge filters) and upstream from nanofiltration, and samples of the permeate stream were collected in the second stage from the same SRU. The samples were characterized by ion chromatography (IC) to determine bromide and sulfate content [15]; inductively coupled plasma optical emission spectrometry (ICP-OES), to analyze sodium, potassium, magnesium, calcium, barium, strontium and iron levels [16]; and potentiometry to measure total alkalinity [17], pH [18] and chloride [19]. In order to determine the ionic composition of these streams (feed and permeate), an arithmetic mean was calculated for each stream based on the eighteen results of the respective streams.

2.1.2 Volume flow rate through the membrane and polarization layer thickness

The volume flow rate through the membrane (J_v) and polarization layer thickness (δ) considered were 9.72×10^{-6} m/s [20] and 2.59×10^{-4} m [13], respectively. These data were determined based on the concentration polarization phenomena and the effect of transport mechanisms through the nanofiltration membrane. Thus, the ionic composition of seawater on the nanofiltration membrane can be calculated by Equation (1).

$$\delta = [\ln(C_{im} - C_{ip}) / (C_{if} - C_{ip})] \cdot D_i / J_v \quad (1)$$

Where δ is the thickness of the polarization layer; C_{im} the estimated ionic concentration on the membrane surface; C_{ip} the ionic concentration of the in situ permeate stream; C_{if} the ionic concentration of the in situ feed stream; D_i the ionic diffusion coefficient; and J_v is the volume flow rate through the membrane.

Although concentrate stream samples were also collected from the same SRU, they were not used in the estimate. These samples were used in thermodynamic simulations to determine the most critical condition for sulfate salt formation in the SWMs during sulfate removal by the SRU. Of the in situ streams (feed, permeate and concentrate), the concentrate is critical in terms of sulfate salt formation. However, the nanofiltration membrane surface can be considered more critical due to the concentration polarization phenomena. Thus, thermodynamic simulations were performed considering the three in situ SRU streams and the estimated stream (seawater with an estimated membrane surface ionic composition). The simulations were carried out using Multiscale 6.1 software [21], with results expressed as saturation index (SI) and precipitated mass (M_p) that can

form under the previously established conditions (different pressures and temperatures) [21].The saturation index varies according to thermodynamic conditions, ionic strength and ionic activity, according to Equation (2).

$$SI = a_A \cdot a_C / K_{psAC} \tag{2}$$

Where a_A is the activity of A (anion), a_C the activity of C (cation), and K_{psAC} the solubility product of AC.

Table 1 shows the different pressure conditions applied in the simulations, at 25°C.

Table 1- Pressure conditions for each SRU stream (in situ and estimated) studied, at 25°C.

Streams	Pressure (bar)
Feed (in situ)	18
Permeate (in situ)	1.0
Concentrate (in situ)	15
Membrane surface (estimated)	18

2.2Chemicals

Table 2 shows the main active component, concentration, pH and density of the scale inhibitors and biocide evaluated in this study.

Table 2 - Chemical specification

Inhibit or	Main active component	Percentage (w/v), %	pH (21°C)	Density (20°C), g/mL	Chemical structure
1	Phosphonate	40-60	2.1	1.11	
2	EDTA tetrasodiumsalt Sodiumhydroxide Citricacid	10-30 1-5 1-5	12.9	1.19	
3	Phosphonic acid, [nitriltris (methylene)] tris-, sodium salt	30-60	10-11	1.39-1.41	
4	Aqueous solution of DETA phosphonate	N.I.	1-3	1.08-1.13	
5	Phosphonatecomplex withKCl	5-10 1-3	4.5-5.5	1.10-1.15	
6	Aqueous solution of aminophosphonic acid	Notidenti fied	2-3	1.17-1.20	
Biocid e	DBNPA	20	2-3	1.20-1.30	

EDTA: Ethylenediaminetetraacetic acid; DETA: diethylenetriaminepenta(methylene phosphonic acid);

DBNPA: 2,2-Dibromo-3-nitrilopropionamide; N.I.: not identified.

Scale inhibitors 1 and 5, 4 and 6, and 2 and 3 exhibit similar characteristics, such as the pH range of the solution and functional groups in the main active component. Nevertheless, the six inhibitors were considered different in terms of their main active component different because the suppliers of the products do not provide their precise composition.

2.3Chemical interaction between chemicals and synthetic seawater

SRU nanofiltration systems are often dosed with chemicals. However, some chemicals may be intolerant to high calcium levels in seawater, primarily on the nanofiltration membrane surface. When a

chemical is calcium intolerant, the dosed aqueous solution exhibits turbidity or the formation of salt precipitates. A good inhibitor should interact with the high-calcium aqueous solution without precipitation. The main active component of the chemical products should retain its primary function; in the case of scale inhibitors, these should prevent saline precipitation. As such, in the event of chemical dosing in nanofiltration sulfate removal, interaction between the chemical and synthetic seawater should be evaluated. The aqueous fluid used in tests to assess chemical interaction was synthetic seawater with the ionic composition of the membrane surface estimated at 25°C, for 24 hours. However, sulfate and bicarbonate ions were not added to the aqueous fluid in order to prevent the influence of other salt precipitates such as sulfate or bicarbonate. This interaction was evaluated in separate assays, using only a dose of the scale inhibitor or biocide, or combined assays, with dosage of both the scale inhibitor and biocide. Scale inhibitor and biocide doses ranged from 5 to 1,000 mg/L and 200 to 2,000 mg/L, respectively. The doses used were higher than those typically applied in SRUs to assess calcium intolerance, in order to ensure satisfactory results at smaller doses. Visual observations of turbidity and pH measurement of the aqueous solution were performed at the moment of chemical dosing and after 1, 2, 3, 4, 5, 6, 12 and 24 hours. The 24 hours limit was established considering a possible shutdown of the sulfate removal unit.

Table 3 shows the test conditions applied to assess the chemical interaction between scale inhibitors and synthetic seawater.

Table 3: Assay conditions applied to assess the chemical interaction between scale inhibitors and synthetic seawater, with and without biocide

Assay	Chemicals	Concentrations, mg/L				
		Separate	Scale inhibitor	1,000	100	50
	Biocide	2,000	1,500	1,000	500	200
Combined	Scale inhibitor	1,000	100	50	25	5
	+ Biocide	+	+	+	+	+
		2,000	1,500	1,000	500	200

2.4 Evaluation of static inhibition efficiency for CaSO₄ in the presence or absence of biocide

These assays aimed to quantify the inhibition efficiency of the scale inhibitors for CaSO₄ in the presence or absence of biocide. Static inhibition efficiency was assessed by correlating the assays with and without scale inhibitors (blank test solution). The scale inhibitors selected for this study are commercially formulated products used in situ in SRU to inhibit CaSO₄ formation. The standard scale inhibitor dose in SRUs is 5 mg/L, regardless of the percentage of the main active component in the composition. Thus, the static inhibition efficiency of the chemical products was assessed as a function of the product in question. Separate and combined assays were conducted with scale inhibitor doses of 5, 10 and 15 mg/L and a biocide concentration of 800 mg/L. Scale inhibitor doses were based on the standard in situ SRU concentration (5 mg/L), with two additional higher doses (10 and 15 mg/L). Biocide concentration (800 mg/L) was defined according to the biocide concentration used in the second stage of the in situ SRU. The aqueous fluid used in these tests was synthetic seawater with the ionic composition of the nanofiltration membrane surface estimated according to the average obtained by in situ monitoring of an SRU. Table 4 shows the assay conditions (separate and combined) for static inhibition efficiency assessment of CaSO₄ in synthetic seawater, at 25°C for 60min, in the presence or absence of biocide.

Table 4 - Assay conditions for the assessment of static inhibition efficiency for CaSO₄, with and without biocide

Assays	Chemicals	Concentrations, mg/L		
		Separate	Scale inhibitor	5
	Biocide	800		
Combined	Scale inhibitor +	5	10	15
	Biocide	+	+	+
		800	800	800

Tests to evaluate static inhibition efficiency for CaSO₄ were performed in triplicate, in addition to the blank test, to obtain representative data for each condition. Aliquots were collected immediately after the chemical dosing in the aqueous solution and at 20, 40 and 60min to determine calcium concentration in the solution. The maximum time of 60min was established considering the rapid kinetics of CaSO₄ precipitation. Aliquots were collected using a sterile disposable syringe and filtration unit (Millex 0.45 µm).

Static inhibition efficiency for CaSO₄ was calculated using Equation (3).

$$\% \text{ EE (time)} = (C_{\text{assay}} - C_{\text{blk}}) * 100 / (C_{\text{blk}} - C_{\text{zero}}) \quad (3)$$

Where %EE is static inhibition efficiency for CaSO₄, in %, over a set period of time; C_{assay} the calcium concentration in aqueous solution after the assay, in mg/L, over a set period of time; C_{blk} the concentration in aqueous solution in the blank test, in mg/L, over a set period of time; and C_{zero} the concentration in aqueous solution at the start of the blank test, in mg/L.

III. RESULTS AND DISCUSSION

3.1 Synthetic seawater composition

The ionic composition of seawater on the membrane surface was estimated based on the ionic compositions of in situ streams (feed, permeate and concentrate), sampled in an offshore SRU located in the Campos Basin, Brazil. The ionic compositions of the in situ streams were defined using the arithmetic mean of eighteen samplings carried out for each stream, on different days over a one-year period. Three samples were taken from each stream every two months. Calculations were performed using the known ionic compositions of the in situ streams (feed and permeate), volume flow rate through the nanofiltration membrane ($J_v = 9.72 \cdot 10^{-6}$ m/s) and polarization layer thickness ($\delta = 2, 59 \cdot 10^{-4}$ m). Volume flow rate and polarization layer thickness were determined in studies conducted by Lee [20] and Bader [13] for the same conditions and membrane. The authors considered the concentration polarization phenomena and transport mechanism effects for nanofiltration [20, 13].

Table 5 shows the ionic compositions of the three in situ streams and the estimated ionic composition of the synthetic seawater.

Table 5: Ionic compositions of the feed, permeate and concentrate streams (in situ streams) and synthetic seawater

Elements	Feed	Permeate	Concentrate	Membrane Surface
	In situ stream	In situ	In situ stream	Estimated composition
Na ⁺ , mg/L	11,000	11,000	13,357	11,000
K ⁺ , mg/L	420	395	637	486
Ca ²⁺ , mg/L	420	255	1,133	4,266
Mg ²⁺ , mg/L	1,300	670	4,328	23,261
Sr ²⁺ , mg/L	8.6	4.9	22	95
Cl ⁻ , mg/L	20,000	20,000	26,719	18,766
Br ⁻ , mg/L	62	64	84	59
SO ₄ ²⁻ , mg/L	2,750	106	11,309	28,474
HCO ₃ ⁻ , mg/L	155	42	195	1,000
pH (21°C)	8.0	8.0	8.0	8.0
NaCl, mg/L	33,001	33,001	44,089	30,964

Using the estimated ionic composition, a sample of seawater was synthesized in the laboratory for use in the assays to evaluate the scale inhibitors in the presence or absence of biocide. Figure 2 shows the results of SI (saturation index) and M_p (precipitated mass) [21] for each of the SRU conditions.

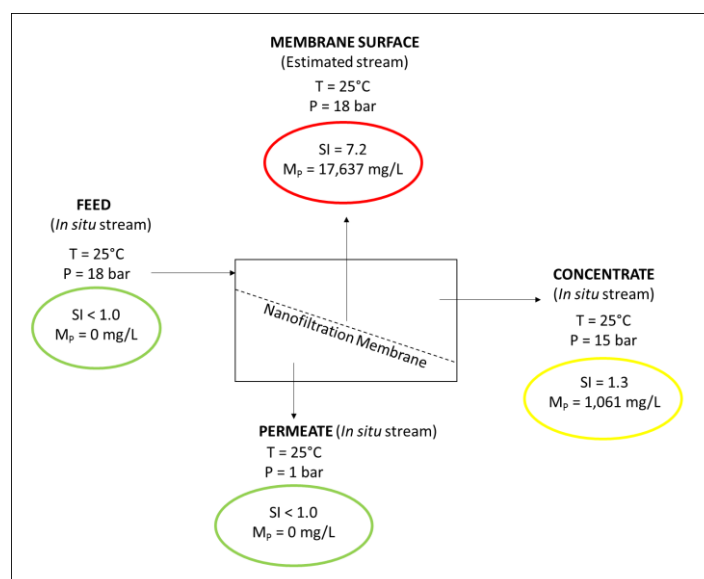


Fig.1 - Saturation index and precipitated mass, simulated in Multiscale 6.1 software, for each SRU condition for specific aqueous fluid, pressure and temperature

Thermodynamic simulations were performed in Multiscale 6.1 software using ionic compositions of the in situ SRU and an estimated composition (Table 5). The results (Figure 1) demonstrated that the membrane surface condition is the most critical for CaSO₄ formation (SI 7.2 and M_p 17,637 mg/L). In a system in equilibrium, SI is less than 1.0 and M_p is zero mg/L because no precipitation occurs (feed and permeate stream). All the SI and M_p results obtained in the simulations were related to CaSO₄ precipitation.

3.2 Kinetics of sulfate precipitation in synthetic seawater

The synthetic seawater was evaluated to determine calcium concentration in the aqueous solution at 25°C. The kinetics of CaSO₄ precipitation under these conditions are displayed in Figure 2.

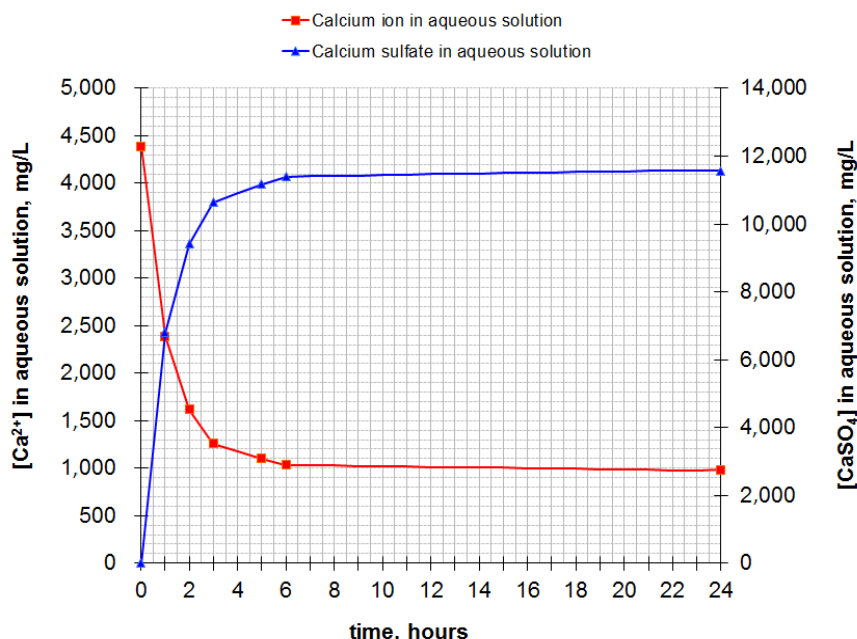


Fig.2 - Kinetics of CaSO₄ precipitation in synthetic seawater, with estimated ionic composition of the nanofiltration membrane surface (at 25°C for 24 hours).

CaSO₄ precipitation was 50% at 3 hours and 80% after 6 hours of the experiment. At 6 hours, almost all the calcium present in the aqueous solution precipitated in the form of CaSO₄.

3.3 Chemical interaction between chemicals and synthetic seawater

Tests conducted to analyze the chemical interaction between the chemicals (scale inhibitors and biocide) and synthetic seawater indicate that both can be used in synthetic seawater at 25°C. These chemicals interact with synthetic seawater by complexation and their primary function is to prevent calcium precipitation (turbidity) in aqueous solution (with a calcium content of 4266 mg/L). The results shown in Table 6 demonstrate that all chemicals studied here were tolerant to high calcium levels in synthetic seawater, at 25°C over 24 hours. Table 6: Turbidity of synthetic seawater with scale inhibitors with and without biocide, at 25°C during 24 hours

Separate Assays					
Turbidity (Ntu)					
[Inhibitor], Mg/L	1,000	100	50	25	5.0
Inhibitor 1	0.55	0.42	0.35	0.24	0.18
Inhibitor 2	0.75	0.38	0.25	0.14	0.12
Inhibitor 3	0.95	0.87	0.62	0.40	0.22
Inhibitor 4	0.88	0.86	0.75	0.72	0.60
Inhibitor 5	0.44	0.39	0.37	0.22	0.15
Inhibitor 6	0.76	0.69	0.55	0.52	0.46
[Biocide], Mg/L	2,000	1,500	1,000	500	200
Dbnpa-Based Biocide	0.62	0.58	0.55	0.47	0.42
Combined Assays					
Turbidity (Ntu)					
[Inhibitor], Mg/L	1,000	100	50	25	5.0
[Biocide], Mg/L	2,000	1,500	1,000	500	200
Inhibitor 1 + Biocide	1.05	0.95	0.87	0.74	0.68
Inhibitor 2 + Biocide	1.23	1.18	1.13	1.10	1.02
Inhibitor 3 + Biocide	1.84	1.82	1.64	1.41	1.36

Inhibitor 4 + Biocide	1.77	1.45	1.43	1.28	1.16
Inhibitor 5 + Biocide	0.89	0.81	0.70	0.64	0.55
Inhibitor 6 + Biocide	1.62	1.54	1.49	1.28	1.11

Chemical interaction was confirmed in separate and combined assays.

3.4 Evaluation of static inhibition efficiency for CaSO₄ in the presence or absence of biocide

Figures 3, 4, 5, 6, 7 and 8 display the static inhibition efficiency results for CaSO₄ of the six scale inhibitors at doses of 5, 10 and 15 mg/L, with and without the addition of 800 mg/L of biocide.

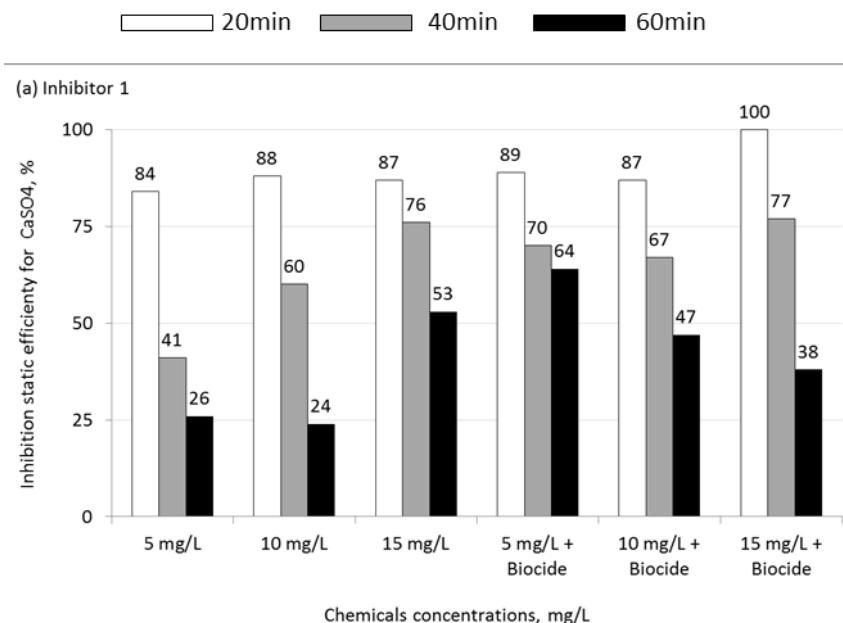


Fig.3 - Static inhibition efficiency for CaSO₄ of the Inhibitor 1 in synthetic seawater, with and without the addition of 800 mg/L biocide, at 25°C for 60 min.

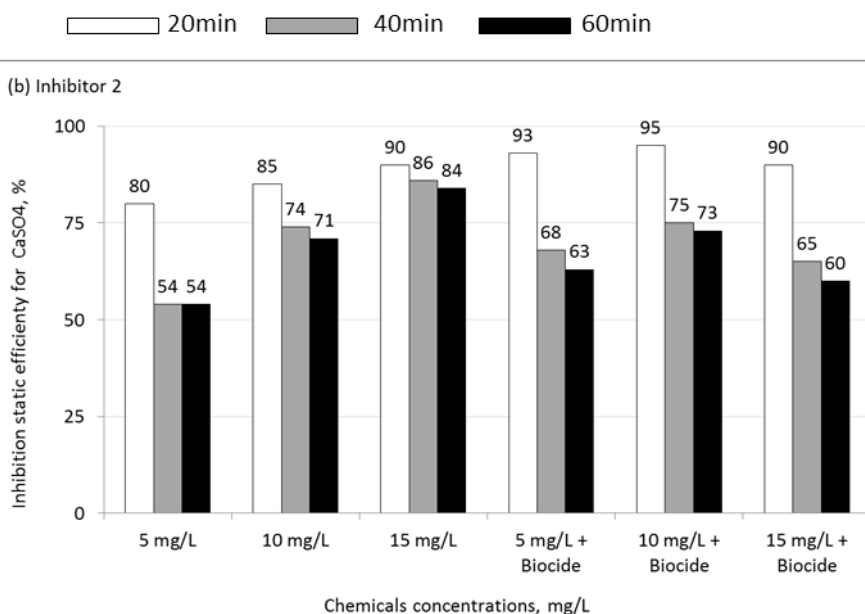


Fig.4 - Static inhibition efficiency for CaSO₄ of the Inhibitor 2 in synthetic seawater, with and without the addition of 800 mg/L biocide, at 25°C for 60 min.

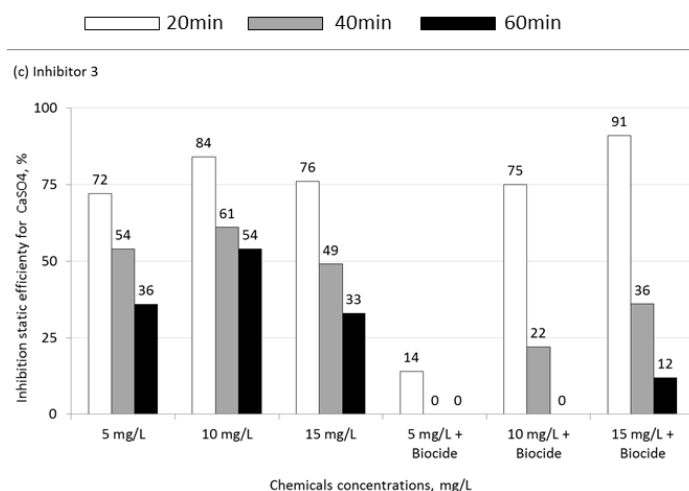


Fig.5 - Static inhibition efficiency for CaSO₄ of the Inhibitor 3 in synthetic seawater, with and without the addition of 800 mg/L biocide, at 25°C for 60 min.

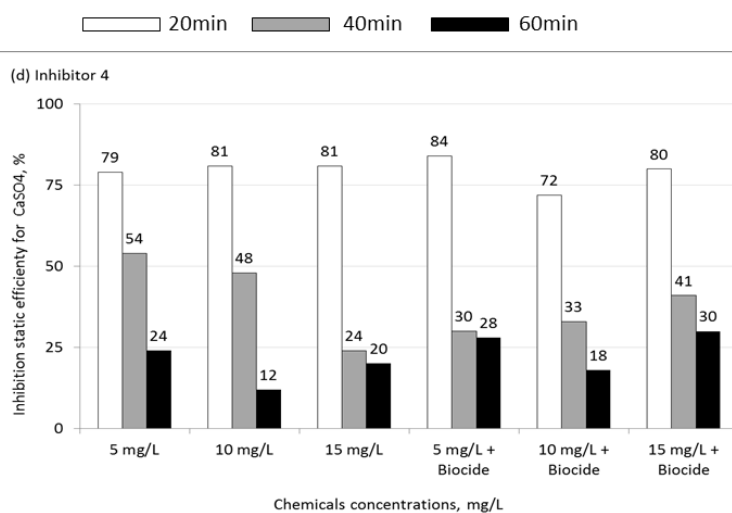


Fig.6 - Static inhibition efficiency for CaSO₄ of the Inhibitor 4 in synthetic seawater, with and without the addition of 800 mg/L biocide, at 25°C for 60 min.

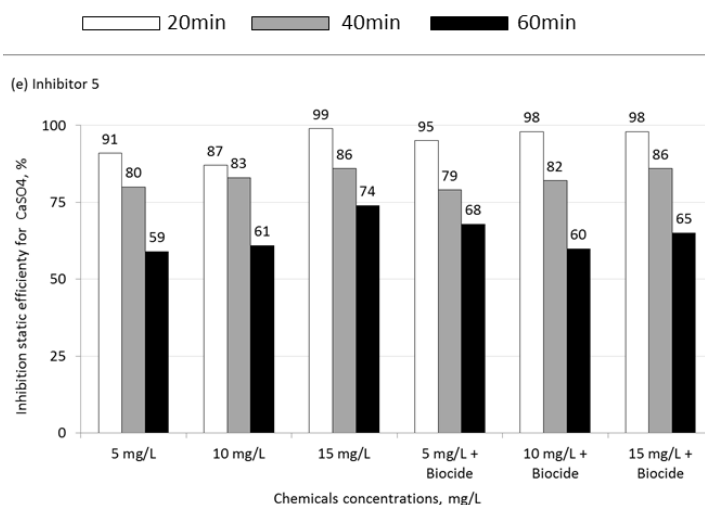


Fig.7 - Static inhibition efficiency for CaSO₄ of the Inhibitor 5 in synthetic seawater, with and without the addition of 800 mg/L biocide, at 25°C for 60 min.

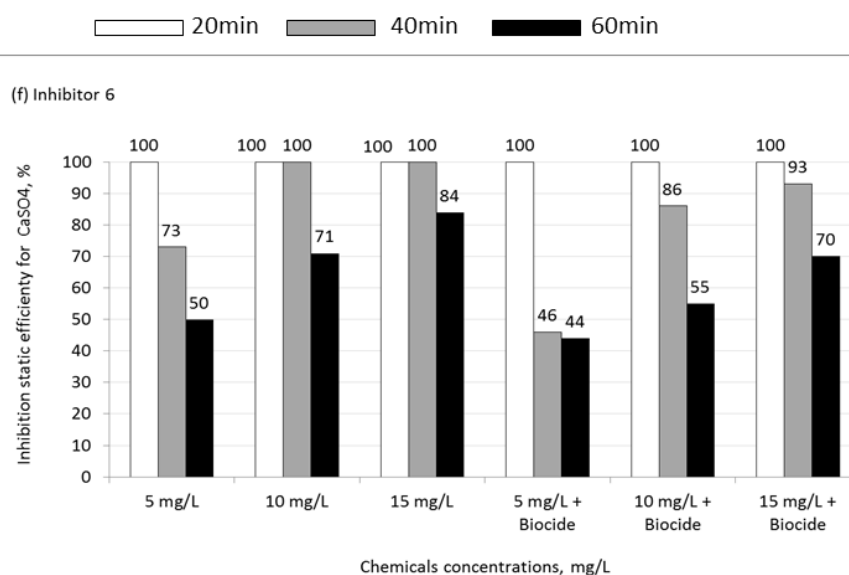


Fig.8 - Static inhibition efficiency for CaSO_4 of the Inhibitor 6 in synthetic seawater, with and without the addition of 800 mg/L biocide, at 25°C for 60 min.

Figures 3, 4, 5, 6, 7 and 8 indicates that the most efficient scale inhibitor was Inhibitor 5 (Figure 7), with 68% static inhibition efficiency for CaSO_4 at 60 min and the lowest inhibitor dose (5 mg/L) and 800 mg/L of biocide, at 25°C. Static inhibition efficiencies for CaSO_4 for the remaining scale inhibitors, tested under the same conditions, were 64% for Inhibitor 1 (Figure 3), 63% for Inhibitor 2 (Figure 4), 44% for Inhibitor 6 (Figure 8), and 28% for Inhibitor 4 (Figure 6). Inhibitor 3 was ineffective (Figure 5). The results show that phosphonate or EDTA-based scale inhibitors can be recommended for use in SRUs. It is important to note that DBNPA did not interfere in inhibitor performance for CaSO_4 under the conditions studied here. Inhibition efficiency remained the same or increased with the addition of 800 mg/L of biocide when compared to assays without biocide. Negative interference was observed for Inhibitor 3 and is therefore not recommended for use in SRU nanofiltration membrane systems.

IV. CONCLUSION

The present study analyzed several inhibitors, focusing on the kinetics of CaSO_4 precipitation, chemical interaction in saline solutions, and static inhibition efficiency for CaSO_4 in the presence or absence of biocide. The synthetic sample used in this study was estimated by monitoring the composition of SRU streams in situ. The initial calcium and sulfate concentrations in a sample were 4,266 mg/L and 28,474 mg/L, respectively. The kinetics of CaSO_4 precipitation under these conditions occurs rapidly, with 50% at 3 hours and 80% at 6 hours. The chemical interaction between the chemicals (scale inhibitor and biocide) and synthetic seawater showed no intolerance at doses of 5 to 1,000 mg/L for scale inhibitors and 200 to 2,000 for biocide, at 25°C over 24 hours. Six scale inhibitors were tested and the results of static inhibition efficiency for CaSO_4 with 800 mg/L of biocide at 25°C for 60 min were: Inhibitor 1, 64%; Inhibitor 2, 63%; Inhibitor 3, 0%; Inhibitor 4, 28%; Inhibitor 5, 68%; and Inhibitor 6, 44%. The inhibitors were evaluated separately (separate assays) and combined with 800 mg/L of biocide (combined assays). The best SRU scale inhibitors were phosphonate and the EDTA-based inhibitors (1, 2 and 5), and the worst was phosphonic acid, [nitritris(methylene)] tris-, sodium salt (Inhibitor 3).

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