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Method Adaptation for Antiscaling Products Efficiency Measurement

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Abstract

Currently, mineral scales have become a quite common problem in oil extraction and production processes, making it extremely important to have an effective method that allows quantifying the efficiency of scale inhibitors. Based on this problem, an investigation was carried out whose objective was to determine the efficiency of scale inhibitors in production waters through the adaptation of the methodology proposed by Zhang, Wu, Li and Zhao in 2012. To do this, the physical-chemical characterization of three production water samples was performed, as well as two commercial inhibitors and one organic. Subsequently, the adaptation of the evaluative method for production water samples was generated and the behavior of pH as a function of the time generated by the scale inhibitors was studied, considering three different doses (50, 100 and 300 ppm). Additionally, a statistical comparison was made between the pH behavior obtained in this investigation with that obtained in the study carried out by Zhang, Wu, Li and Zhao. As a conclusion, it was obtained that the adaptation generated managed to reproduce the experimental criteria observed in the original proposal in each of the respective evaluations, thus becoming a simple methodology, with low costs associated with its assembly and which managed to adjust to the behavior of pH in function of the time evidenced in the base study, therefore it offers favorable results for measuring the efficiency of scale inhibitors in production waters.

Introduction

By their nature, hydrocarbon reservoirs contain combinations of liquid and/or gaseous hydrocarbons and water [1], commonly known as formation water, the latter being generally found in greater proportion [2] so it is quite common that there is a large production of it, especially with the elapsing of the reservoirs productive time.

Because of its compositional nature, the produced water from oil accumulations brings with it a variety of ionic constituents, which they are able to precipitate, thereby generating a scaling formation [1, 3-4] which is generally associated with minerals precipitation, however the scaling phenomenon also take place because the water that moves through the production system becomes supersaturated with mineral components due to incompatibility between it, injection water [5-6] or any other process water [7], bringing as a direct consequence that there is a flow rate gradual reduction in a well or surface equipment [8-9], causing subsequent operational problems in the production system [10].

To prevent this type of situation, a method that mitigates the scale formation generated by the deposited minerals should be used. Malavé et al. [11] state that this phenomenon can be prevented by controlling the operational parameters (pressure, temperature, flow, among others) or using specific chemical.

Among the chemical treatments, the use of scale inhibitor agents stands out [12-14], which have become one of the industry's preferred methods for maintaining well productivity due to their efficiency in preventing the carbonate and sulfate scale formation in areas near the well, pipes and wellheads [15].

Therefore, it is important to have an effective method that allows evaluating the antiscaling products performance, being the NACE TM0374-2016 Standard [16] an example of this. This standard allows the efficiency to be measured through a jar test in static condition; similarly, Hernández et al. [17] established a "New methodology for evaluation of scale inhibitor products based on existing models" where they evaluated the chemical products performance after subjecting them to various experimental conditions that allowed measuring their efficiency in an integral way.

In addition, Zhang et al. [18] developed a study called "A new evaluation method of scale inhibitors for controlling calcium carbonate scale in reverse osmosis system based on pH measurement". The objective of this study was to evaluate the performance of these agents in synthetic waters, by continuous pH measurement, using as an experimental criterion that the scale formation occurs when the pH declines, and then, on the basis of the calcium carbonate supersaturation calculation, they were able to quantify the efficiency of referred chemical agent with respect to the scale formation; based for this on the titration to a synthetic water sample (with an established concentration of calcium chloride) with sodium bicarbonate of defined concentration.

Although the authors provided a simple method, whose experimental assembly entails low costs and provides reliable data according to the reproducibility criteria used in their study, this methodology does not cover the production waters compositional diversity because synthetic water samples with known concentration were used, generating ideal results that are not consistent with the real processes that have taken place in the oil industry.

In this research, Zhang et al. [18] methodology was adapted to production water samples in order to have a procedure to measure the calcium carbonate scale inhibitors efficiency, on a more representative scale of the ionic concentrations found in production waters, in order to direct the technique to the actual processes occurring in the oil production activities. For this reason, it was taken as a hypothetical premise that the adaptation generated would give favourable results for measurement the scale inhibitors efficiency in production waters against the calcium carbonate formation.

Three production waters samples were characterized, as well as two commercial inhibitors and one of an organic nature. After this, we proceeded to generate the proposal adaptation through the study of pH behaviour as a function of time in each water sample at determined chemical agent dosages and finally the inhibitors behaviour was compared with that obtained by Zhang et al. [18] through the analysis of variance (ANOVA) in order to establish the fit between these, based on the arithmetic means found in both studies.

Materials and Methods

Characterization of production water samples

A set of physico-chemical tests were carried out in order to characterize two samples of production water from El Furrial oilfield (samples 1 and 2) and the other from Oritupano oilfield (sample 3). These tests were conducted at Hydrocarbon Processing, Drilling and Reservoir Laboratories of Petroleum Engineering Department, Universidad de Oriente, Núcleo de Monagas, Campus Los Guaritos; and Soil Laboratory, Universidad de Oriente, Núcleo de Monagas, Campus Juanico, located in Monagas state, Venezuela.

The physical tests performed were: density [19], content of total, dissolved and suspended solids [20] and conductivity [21]. Consequently, for chemical characterization the following properties were determined: pH [22], chloride content [23], calcium hardness [24] and alkalinity [25].

Also, the Langelier Saturation Index [26] was quantified in order to know the scaling or corrosive nature of the production water samples.

Characterization of the scale inhibitor products

Two commercial inhibitors were physically characterized, the first (1) is a mixture of methyl alcohol, phosphonic acid salt and acetic acid and the second product (2) is an acrylate polymer used as a calcium and magnesium carbonate scale inhibitor. Additionally, a third (3) chemical agent of an organic nature based on linseed gel (Linum usitatissimum) was used, developed in a previous research by Hernández & Rodriguez [27]. The characterization tests carried out on the products were: density [19], pH [22], conductivity [21] and viscosity [28]. The tests carried out on the water samples and the inhibitor products were performed in triplicate, in order to have a better results reliability level.

Scale inhibitor evaluation method adaptation according to the ionic concentration determined to each sample of production water

Zhang et al. [18] proposed a methodology based on titration with sodium bicarbonate (previously defined concentration) to 150 mL of synthetic water with a titration rate equal to 2 mL for every 2 minutes at a temperature of 25 °C; reaching to study the behaviour of pH as a function of time applying 1 ppm of the inhibitor to be evaluated through this experimental test. After this, they proceeded to determine the calcium carbonate supersaturation (S) in a purely empirical way, thus quantifying the evaluated chemical efficiency. The experimental setup of the present study (Figure 1) consisted of a hot plate (Magnestir Lab-Line), a 250 mL burette (Cole Parmer), a 100 mL beaker with magnetic stirrer and a portable digital pH meter (Sartorius, model PT-10).

Figure 1 Experimental setup of the methodology used.

The adaptation generated in this research was constituted by the establishment of an equation that allowed knowing the ideal sodium bicarbonate

concentration to use as a titrant in each characterized production water sample, this equation was:

$$[B_s] = 1.5181 \times [Ca^{2+}] \qquad (1)$$

Where:

[Bs]= sodium bicarbonate concentration (ppm)

[Ca^{2+}]= calcium ion contribution determined in each production water sample (ppm)

Similarly, an initial sample volume was established quantified through:

$$V = \frac{[B_s]\left(\frac{g}{L}\right) \times 150}{25.2} \qquad (2)$$

Where:

V = initial volume of sample to be used in the titration (mL)

Then, the study was carried out based on the pH behaviour as a function of time in production water samples at 50, 100 and 300 ppm dosages of the chemical treatments studied, and the tests were performed in triplicate. Thus, allowing to quantify *S* through the following equations:

$$S = \frac{A \times B}{Ksp} \qquad (3)$$

Where:

Ksp = calcium carbonate solubility constant (4.8×10^{-9} mol/L)

$$A = \frac{\left[Ca^{2+}\left(\frac{mol}{L}\right)\right] \times V}{V_f} \qquad (4)$$

Where:

Vf = solution final volume before precipitation

$$B = \frac{4.69 \times 10^{-11} \times \left[\frac{[B_s]\left(\frac{mol}{L}\right) \times V_t}{V_f}\right]}{10^{-pH_c}} \qquad (5)$$

Where:

4.69×10^{-11}= equilibrium constant according to the calcium carbonate precipitation reaction

Vt= Volume of spent titrant (mL)

pHc= solution pH at the precipitation instant

Finally, a new equation was established for the efficiency determination based on the scale precipitation time, which was the following:

$$E = \frac{t_p}{t_{mp}} \times 100 \qquad (6)$$

Where:

E= efficiency (%)

tp= precipitation time to evaluate (min)

tmp= maximum precipitation time in the water sample (min)

Statistical comparison of the results obtained through the Zhang, Wu, Li and Zhao method adaptation in production waters with those obtained in synthetic waters

Through the computer program *Statgraphics Centurion* XVI, this statistical analysis was carried out, which allowed us to validate the similarity between both behaviours through a simple analysis of variance (ANOVA). Similarly, a multifactorial analysis of variance was performed on each of the quantified efficiencies in order to establish which factors,

between water sample, dosage and inhibitor type, affected the quantified efficiency in each of the samples.

Results

Figure 2 presents the methodological adaptation structure generated for the evaluative method proposed by Zhang et al. [18] which allowed quantifying the scale inhibiting agent's efficiency as a function of the precipitation time exhibited by the water samples.
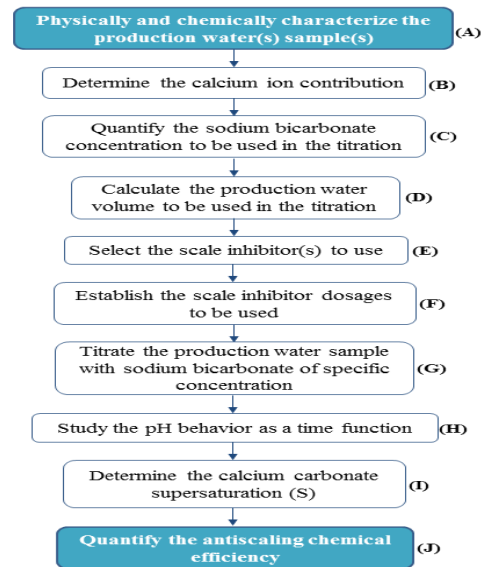

Figure 2 Zhang, Wu, Li and Zhao method adaptation diagram.

The production water samples physicochemical characterization **(A)** allowed us to know the high scaling capacity they have because, as seen in Table 1, all the properties combined with each other validate what was expressed. Thus, as established in the COVENIN 2771-91 standard [24] related to the calcium hardness values exhibited by the three samples, these can be classified as awfully hard water, which allows carbonate compounds to react with the calcium present and precipitate in insoluble compound form [29-30].

Also, the pH values and Langelier Saturation Index (LSI) of the water samples give them a highly scaling capacity, this because in pH terms, they all obtained values greater than 7 classifying them as alkaline solutions, being precisely in this type of solutions where the calcium carbonate precipitation tendency is increased [31]. Regarding the LSI, the samples are classified as scaling because this value is greater than zero (0) in all cases.

Table 1 shows a particularly important property in this investigation called calcium ion contribution **(B)** which allowed quantifying the sodium bicarbonate concentration to be used as a titrant **(C)** for the subsequent determination of the initial sample volume to use in titration **(D)**; obtaining sodium bicarbonate concentrations equal to 1.5; 0.8 and 0.5 g/L for production water samples 1, 2 and 3, respectively.

Table 1 Physicochemical properties of production water samples.

Property	Measurement unit	Production water 1	Production water 2	Production water 3
Density	g/mL	1.0803	1.0237	1.0033
Total solids	ppm	53,000	52,000	8,000
Dissolved solids	ppm	49,000	46,000	7,000
Suspended solids	ppm	4,000	6,000	1,000
Conductivity	mS/cm	49.6	30.2	9.7
Calcium hardness	ppm	2.480	1.280	800
Calcium ion contribution	ppm	992	512	320
Total alkalinity	ppm	400	300	1.800
Parcial alkalinity	ppm	0	0	400
Bicarbonate ions	ppm	488	366	2.196
Carbonate ions	ppm	0	0	240
Chlorides	ppm	18,795.76	17,396	2,499
pH	Adim.	7.12	7.18	8.72
pHs	Adim.	6.17	6.59	5.93
Langelier Saturation Index (LSI)	Adim.	0.9421	0.59	2.7885

The previous values are low when compared with those used by Hernández et al. [17] which were 2.52 g/L and 5.52 g/L or the one used by Sousa et al. (2016) who used 2.1 g/L in its titration, however it should be considered that previous research was based on evaluating the scale inhibitors efficiency in synthetic waters, while in this study production waters were used and clearly there is a large compositional difference.

The initial volumes calculated were 8.9, 4.8 and 3 mL for the analysed water samples (1, 2 and 3); these volumes exhibit a behaviour that is directly proportional to the sodium bicarbonate concentration, thus guaranteeing that the pH behaviour is fulfilled as a function of the time observed in the original proposal.

The inhibitors selected for this study **(E)** were characterized obtaining the values in Table 2. They show that the commercial products and the bioinhibitor are acidic substances (pH<7), whose density, in the commercial products, was higher than the density of common water, due to their compositional nature whose function is to prevent the scale precipitation process [5].

Table 2 Physicochemical properties of scale inhibitors.

Property	Measurement unit	Commercial inhibitor 1	Commercial inhibitor 2	Bioinhibitor
Density	g/mL	1.2253	1.0368	0.9969
pH	Adim.	5.6	5.42	4.48
Viscosity	cP	13.98	2.95	7.50
Electric conductivity	mS/cm	47.8	44.5	1.013

The natural antiscaling exhibited a density slightly lower than a common water (1.00 g/mL), because distilled water was used for its formulation, which by nature is water free of solids and salts [32]. These properties together with the others reported in Table 2 show the antiscaling capacity of each product.

For each characterized chemical agent, three dosages were established: 50, 100 and 300 ppm **(F)**, thus being able to carry out the respective titration **(G)**, which allowed studying the pH behaviour as a time function in each production water sample **(H)**. It should be noted that this behaviour is since adding sodium bicarbonate to the solution increases its alkalinity, because the ions responsible for this property are carbonates and bicarbonates [33], so the solution pH increases when adding sodium bicarbonate because it becomes more alkaline.

In reference to the above, if pH decreases, it indicates that there was a loss of carbonate ions that is related to the calcium carbonate precipitation. This is shown more clearly in Figure 3 specifically for water sample number 1. This graph shows that the longest precipitation time is seen in the 300 ppm dose of commercial inhibitor 1, because it was able to extend the flocculation threshold up to 74 minutes.

Now, if the previous statement is compared with what happened in the research by Zhang et al. [18], a notable difference is observed because in this study highest flocculation threshold was located around 32 minutes; the difference between two thresholds is related to the chemical product dosages used in each investigation, because in the original proposal 1 ppm of each agent was used while in the present research doses up to 300 times higher were used.

Also, Figure 4 shows that commercial product 2 showed higher performance in water sample 2, because in all its dosages it was able to increase the flocculation threshold in a longer time, compared to the other chemical agents, resulting in higher threshold at dose of 100 ppm for this antiscaling, whose precipitation time was in 66 minutes.
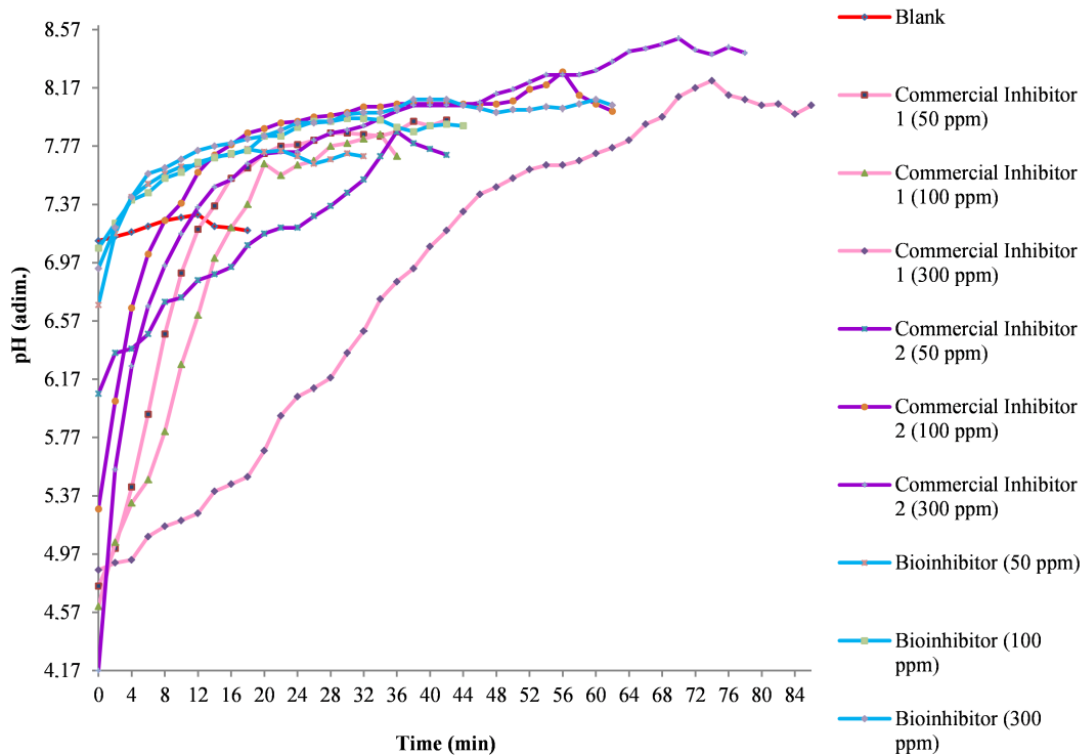
Figure 3 pH behaviour as a function of time in the production water sample 1.
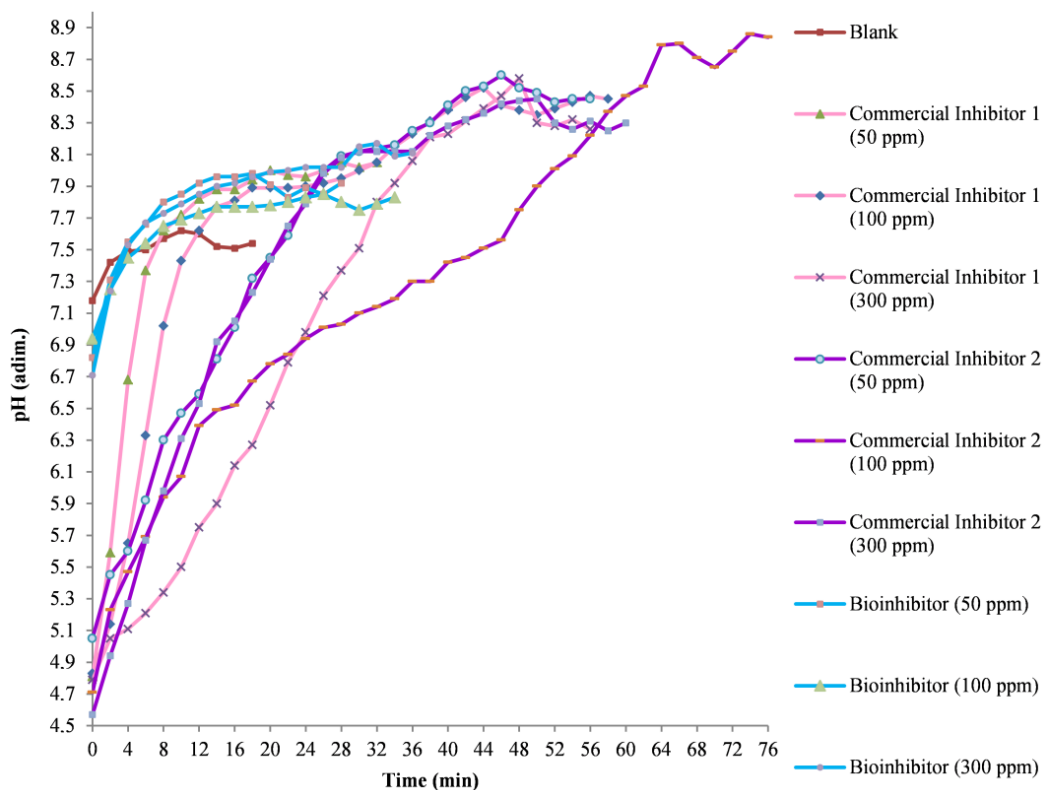

Figure 4 pH behaviour as a function of time in the production water sample 2.

Regarding sample 3 and its pH behaviour as a function of time, illustrated in Figure 5, it can be stated that the drop in pH occurred in a shorter time if compared to the other two samples, this phenomenon of early precipitation occurs because this sample is the only one that has carbonate ions in solution, which allows the calcium carbonate supersaturation point to be obtained faster [34], in addition to this, the cause of this phenomenon could be associated with high scaling capacity of this sample, obtaining the highest LSI (2.7885).

Also, in Figure 5 it is observed that in the sample without added chemical product (blank) the mineral scale was precipitated when the first 2 mL of sodium bicarbonate was placed, which gives it a high degree of supersaturation at initial conditions. Therefore, the worst performance was obtained by the bioproduct, because it was not able to reduce the degree of sample supersaturation, a situation that is causally related because bioinhibitors due to their organic

nature do not have the same action capacity if it is compared with a synthetic nature product [15].

Otherwise, the commercial products did show optimal performance, being able to lower the initial water sample pH, thus giving it a greater capacity to tolerate additional carbonate ions in solution, specifically the commercial inhibitor 1 at 300 ppm delayed the calcium carbonate precipitation for up to 16 minutes showing a precipitation pH equal to 8.39

just now when the first pH drop occurred. Regarding this specific point, it is observed how, once it is reached, the system starts a phase of increase and decrease in pH generating a loop effect, which was also evidenced in the study developed by Hernández et al. [17] with the particularity that in this research the effect occurred before reaching the supersaturation point.
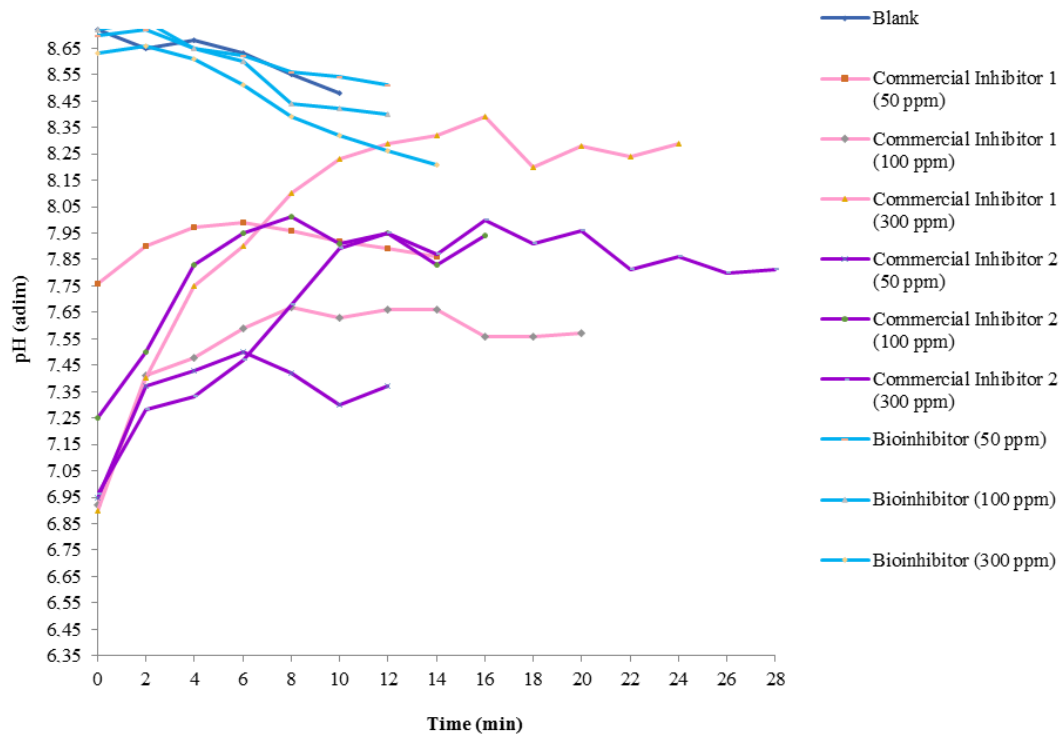

Figure 5 pH behaviour as a function of time in the production water sample 3.

Once the previous behaviour had been analysed, the water samples calcium carbonate supersaturation (*S*) was calculated **(I)**, concluding that, due to certain inconsistencies shown in Table 3, the antiscaling product with the highest *S* should not be considered as more efficient, as considered by Zhang et al. [18], because there is no relationship between this variable and the precipitation time (tc).

Table 3 shows that the highest supersaturation for water sample 1 (*S*= 140) is found at a 300 ppm dose of commercial inhibitor 2 with a precipitation time of 70 minutes. Now, if it is compared with the dose of commercial inhibitor 1, the precipitation time was 74 minutes, 4 minutes higher than the previous one, however, at this dose of the referred product an S equal to 68 is perceived, thus having a clear difference if the same efficiency criteria as the original proposal were used.

All this is explained because the equation to quantify *S* is sensitized to give a higher value in those doses that achieve higher precipitation pH even when the flocculation threshold is higher in other doses; inconsistencies of this type are observed in the proposal by Zhang et al. [18] specifically between ATMP and TPTO-150 scale inhibitors (Table 3).

For the aforementioned, Sousa et al. (2016) used the Zhang et al. [18] methodology but equating the solution pH with inhibitor to the solution pH without inhibitor (blank), thus guaranteeing that the pH of all the dosed samples starts from the same point, being more efficient the one that is further from the initial pH.
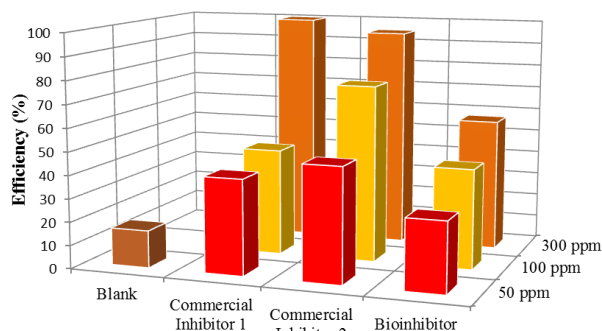
About water sample 2, Table 3 shows that the highest S is found in the 100 ppm dose of commercial inhibitor 2, this being consistent with that shown in Figure 3 respect to the highest flocculation threshold exhibited, however it is observed that for this water sample the organic inhibitor has a higher *S* at the 50 ppm dose with a precipitation time (tc) of 18 minutes compared to the 100 ppm dose of this same product whose tc was 26 minutes.

On the other hand, the supersaturation results in water sample 3 show in a more pronounced way the fact that the equation used to calculate *S* does not consider the precipitation time because for three doses of the bioinhibitor precipitation time was 2 minutes, while supersaturation shows different values, a similar situation occurred in the results reported by Zhang et al. [18] between the PTP-0100 inhibitor and HPMA inhibitor.

Table 3 Inconsistencies between supersaturation (S) and precipitation time shown by the production water samples.
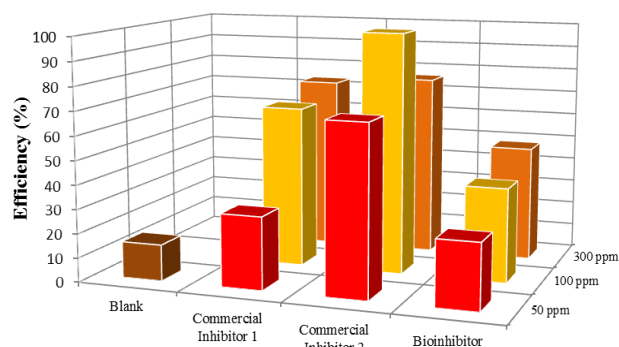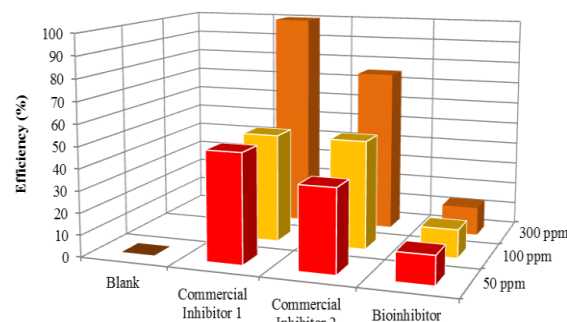
Inhibitor	Dose [ppm]	Volume of sodium bicarbonate used [mL]	Precipitation time (t_c) [min]	Precipitation pH (pH_c)[adim.]	S [adim.]
Production water 1					
Commercial 1	300	74	74	8.22	68
Commercial 2	300	70	70	8.51	140
Production water 2					
Commercial 2	100	66	66	8.80	47
Bioinhibitor	50	18	18	7.98	19
Bioinhibitor	100	26	26	7.85	11
Production water 3					
Bioinhibitor	50	2	2	8.72	59
Bioinhibitor	100	2	2	8.75	63
Bioinhibitor	300	2	2	8.66	51
Results obtained by Zhang et al. (2012)					
ATMP	1	24	24	8.11	403
TPTO – 150	1	20	20	8.23	461
HPMA	1	12	12	8.11	232
PTP – 0100	1	12	12	8.28	346

Finishing the methodological sequence shown in Figure 1, the chemical agent efficiencies **(J)** in the production water samples 1, 2 and 3 were calculated, showing the results in Figures 6, 7 and 8 respectively. Thus, showing in Figure 6 that commercial product 1 at 300 ppm dose was the most efficient; Figure 6 also shows the products evaluated efficiencies in water sample 1 which were directly proportional to the doses used, typical behaviour in scale inhibitor efficiency studies. This intensifies the premise where product with the longest precipitation time is considered the most efficient.

The water sample 2 efficiencies are shown in Figure 7, noting commercial inhibitor 2 at 100 ppm doses as the most efficient product, it is also illustrated that for commercial inhibitor 1 and the bioinhibitor agent the efficiency is directly proportional to the dose used; however, this behaviour does not occur in commercial product 2, obtaining greater efficiency at 100 ppm dose compared to the 300 ppm dose. This could be due to an excess of chemical product depending on the ionic concentration and the initial water sample volume, causing the salts present in the product to dissociate, contributing to the scale formation.

Figure 6 Inhibitors efficiency results in production water sample 1.

Figure 7 Inhibitors efficiency results in production water sample 2.

In contrast to the above, Figure 8 shows the commercial inhibitor product 1 (at a 300 ppm dose) as the most efficient for water sample 3. In addition, commercial product 2 showed behaviour directly proportional to the dose used, while commercial additive 1 showed an equal efficiency value for the dose of 50 and 100 ppm, because none of these doses was able to lower the pH enough to allow the sample to move away from the supersaturation point that it had at initial conditions. The bioinhibitor constant behaviour in efficiency terms is due to the precipitation times equality at three doses used.

Figure 8 Inhibitors efficiency results in production water sample 3.

In order to validate the pH behaviour obtained in this research, a statistical comparison was made with the behaviour of the Argo inhibitor, which was the product with the best performance in original proposal [18]. Appreciating the results obtained in Table 4, it is evidenced that according to the simple variance analysis in each water sample there was a significant statistical difference because the P-value in all cases is less than 0.05 because in this study the evaluation conditions were quite different from those used in the base proposal (different doses, different nature water and different chemical products).

Table 4 Comparative statistical analysis between the pH behavior produced by the inhibitor Argo in the original proposal and the pH behavior obtained in the production water samples.

Production water 1			
Analysis of Variance (ANOVA)			
F-ratio		**P-Value**	
10.66		0.0000	
Multiple range test			
Inhibitor	Dose (ppm)	Arithmetic average	Homogeneous groups
Commercial 1	300	6.903	X
Commercial 1	100	6.977	XX
Commercial 2	50	7.165	XX
Commercial 1	50	7.316	XX
Bioinhibitor	50	7.627	XX
Bioinhibitor	100	7.767	X
Commercial 2	100	7.819	X
Commercial 2	300	7.871	X
Bioinhibitor	300	7.898	X
Argo		8.045	X
Production water 2			
Analysis of Variance (ANOVA)			
F-ratio		**P-Value**	
2.26		0.0192	
Multiple range test			
Inhibitor	Dose (ppm)	Arithmetic average	Homogeneous groups
Commercial 1	300	7.135	X
Commercial 2	100	7.415	XX
Commercial 2	300	7.574	XXX
Commercial 2	50	7.635	XX
Commercial 1	50	7.659	XXX
Bioinhibitor	100	7.709	XX
Bioinhibitor	50	7.814	XX
Commercial 1	100	7.834	X
Bioinhibitor	300	7.898	X
Argo		8.045	X
Production water 3			
Analysis of Variance (ANOVA)			
F-ratio		**P-Value**	
40.21		0.0000	
Multiple range test			
Inhibitor	Dose (ppm)	Arithmetic average	Homogeneous groups
Commercial 2	50	7.398	X
Commercial 1	100	7.579	X
Commercial 2	300	7.759	X
Commercial 2	100	7.865	XX
Commercial 1	50	7.927	XX
Argo		8.045	XX
Commercial 1	300	8.116	X
Bioinhibitor	300	8.423	X
Bioinhibitor	100	8.543	X
Bioinhibitor	50	8.6	X

However, according to Dagnino [35], when in an analysis of variance, the P-value is less than 0.05; a multiple-range test must be applied to establish which the different groups are. For this reason, the results obtained from this analysis for each water sample are observed in Table 4, noting, the Argo inhibitor average efficiency in water sample 1 does not have a significant difference with five (5) different levels of the scale inhibitors doses used in this research,

because the Argo inhibitor shares the same column of "X" with these five levels.

As for the production water sample 2, it exhibits the best adjustment, because in it seven pH behaviours shown by the evaluated inhibitors did not have statistically significant differences when compared with the Argo inhibitor. Finally, it is observed that in water sample 3 there was an adjustment only in two levels, specifically those referred to commercial inhibitor 1 at the doses of 50 and 300 ppm.

The results obtained in the multiple-range tests validate the pH behaviour determined in this research and support that there was an adjustment in 14 of the 27 levels contemplated in the statistical analysis, thus generating a similarity with the pH performance produced by Argo in the study by Zhang et al. [18]

despite having been evaluated in different saline environments.

Additionally, a multifactorial analysis of variance was carried out on the quantified efficiencies, determining according is shown in Table 5 that the dosage and inhibitors used in this research had a significant effect on the efficiency, because when applying different dosages this varies due to the greater volume of added chemical product, while the inhibitor type significant effect with respect to the dependent variable (efficiency) is due to the fact that we worked with three chemical products with totally different characteristics and properties, which gave better performance in those with commercial characteristics. On the other hand, the water sample type did not have a significant effect on the quantified efficiency (P-value > 0.05) (Table 5).

Table 5 Comparative statistical analysis between the pH behavior produced by the inhibitor Argo in the original proposal and the pH behavior obtained in the production water samples.

Effects	Sum of squares	F-ratio	P-Value
Dosage	4,645.41	9.76	0.0011
Inhibitor type	7,406.52	15.56	0.0001
Water sample	1,283.63	2.7	0.0919

The adapted methodology gave favourable results for measuring the calcium carbonate scale inhibitors efficiency in production waters, not showing significant statistical differences for 52% of the total levels compared to the original proposal according to pH behaviour.

Conclusions

The adaptation carried out allowed to simulate pH behaviour as a time function evidenced in the original proposal, giving acceptable results for measuring the scale inhibitors efficiency in production waters, using the longest precipitation time as an efficiency criterion, which is lower in those water samples that have carbonate ions in solution in initial conditions, due to the high saturation degree that these ions confer on the water, however, in order to optimize the methodology proposed in this research, it is recommended to propose a new equation for the efficiency determination in which the precipitation time and calcium carbonate supersaturation are related, in addition to expanding the action field of this methodology by defining a titrant agent that allows evaluating the scale inhibitors efficiency using water that generates calcium sulfate scale.

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Conflicts of interest

There are no conflicts to declare.

References

[1] S. Kumar, T.K. Naiya, and T. Kumar, Developments in oilfield scale handling towards green technology-A review, Journal of Petroleum Science and Engineering. 169 (2018) 428–444. https://doi.org/10.1016/j.petrol.2018.05.068.

[2] B. Bailey et al., Water control, Oilfield Review. 2 (2000) 30-51. http://www.academia.edu/download/36044468/Coning_Slumberger_Technology.pdf.

[3] Y. Liu et al., An assay method to determine mineral scale inhibitor efficiency in produced water, Journal of Petroleum Science and Engineering. 143 (2016) 103–112. http://dx.doi.org/10.1016/j.petrol.2016.02.024.

[4] Z. Amjad and K.D. Demadis, Mineral Scales and Deposits: Scientific and Technological Approaches, Elsevier, Amsterdam, Netherlands, 2015. https://books.google.co.ve/books?hl=es&lr=&id=JxCdBAAAQBAJ&oi=fnd&pg=PP1&ots=EOBAtlHmcj&sig=jP2-si-gbJS8_a7EN-zholbKNdc&redir_esc=y#v=onepage&q&f=false.

[5] A.X. Salamanca Sánchez, Evaluación de un inhibidor de incrustación para evitar taponamiento de las líneas de producción en una plataforma petrolera, Fundación Universidad de América, Colombia, 2018. http://52.0.229.99/bitstream/20.500.11839/7213/1/6112785-2018-2-IQ.pdf.

[6] S.M. Ghaderi, R. Kharrat, and H.A. Tahmasebi, Experimental and Theoretical Study of Calcium Sulphate Precipitation in Porous Media Using Glass Micromodel, Oil & Gas Science and Technology –

Revue d'IFP Energies nouvelles. 64, 4 (2009) 489-501. https://doi.org/10.2516/ogst/2009018.

[7] Z. Kiaei and A Haghtalab, Experimental study of using Ca-DTPMP nanoparticles in inhibition of $CaCO_3$ scaling in a bulk water process, Desalination. 338 (2014) 84-92. https://doi.org/10.1016/j.desal.2014.01.027.

[8] S. Hajirezaie, X. Wu, M.R. Soltanian, and S. Sakhad, Numerical simulation of mineral precipitation in hydrocarbon reservoirs and wellbores, Fuel. 238 (2019) 462-472. https://doi.org/10.1016/j.fuel.2018.10.101.

[9] T. Kumar, S. Vishwanatham, and S.S. Kundu, A laboratory study on pteroyl-L-glutamic acid as a scale prevention inhibitor of calcium carbonate in aqueous solution of synthetic produced water, Journal of Petroleum Science and Engineering. 71 (2010) 1-7. https://doi.org/10.1016/j.petrol.2009.11.014.

[10] C. León Vanegas, H. Buendia, and L. Carrillo, Evaluación y selección de un inhibidor multiscale para prevenir la formación de incrustaciones inorgánicas en un campo petrolero colombiano, Revista Fuentes: El Reventón Energético. 14, 2 (2016) 111-120. https://doi.org/10.18273/revfue.v14n2-2016010.

[11] D. Malavé, T. Marín, V. Acevedo, and M. Parra, Extracto de Okra (*Abelmoschus esculentus*) como aditivo inhibidor de carbonato de calcio en aguas de producción del Campo El Furrial, Estado Monagas, Venezuela, Revista Tecnológica ESPOL – RTE. 29, 2 (2016) 1-11. http://www.rte.espol.edu.ec/index.php/tecnologica/article/view/416/342.

[12] G. Ruan , A.T. Kan, M.B. Tomson, and P. Zhang, Facile one-pot synthesis of metal-phosphonate colloidal scale inhibitor: Synthesis and laboratory evaluation, Fuel. 282 (2020) 1-9. https://doi.org/10.1016/j.fuel.2020.118855.

[13] M. F. Sousa, F. Signorelli, and C. A. Bertran, Fast evaluation of inhibitors for calcium carbonate scale based on pH continuous measurements in jar test at high salinity condition, Journal of Petroleum Science and Engineering. 147 (2016) 468–473. http://dx.doi.org/10.1016/j.petrol.2016.09.007.

[14] M. Chaussemier et al., State of art of natural inhibitors of calcium carbonate scaling. A review article, Desalination. 356 (2015) 47–55. https://doi.org/10.1016/j.desal.2014.10.014.

[15] A. Wilson, The Importance of Scale-Inhibitor Analysis - A State-of-the-Art Overview, Journal of Petroleum Technology. 68, 9 (2016) 107–109. https://doi.org/10.2118/0916-0107-jpt.

[16] National Association of Corrosion Engineers (NACE), NACE Standard TM0374-2016: Standard Test Method: Laboratory Screening Tests to Determine the Ability of Scale Inhibitors to Prevent the Precipitation of Calcium Sulfate and Calcium Carbonate from Solution (for Oil and Gas Production Systems), NACE, Houston, Texas, U.S.A, 2016. https://store.nace.org/tm0374-2016G.

[17] V. Hernández Pinto, M. Rodríguez Muchati, and L. Castillo Campos, Nueva metodología para la evaluación de productos inhibidores de incrustación basada en modelos existentes, TecnoLógicas. 23, 49 (2020) 161-184. https://doi.org/10.22430/22565337.1648.

[18] X. Zhang, W. Wu, D. Li, and G. Zhao, A new evaluation method of scale inhibitors for controlling $CaCO_3$ scale in reverse osmosis system based on pH measurement, Advanced Materials Research. 356-360 (2012) 2146-2152. http://dx.doi.org/10.4028/www.scientific.net/AMR.356-360.2146.

[19] ASTM International, ASTM D369: Standard Test Method for Specific Gravity of Creosote Fractions and Residue, ASTM International, West Conshohocken, PA., 2002. https://www.astm.org/Standards/D369.htm.

[20] Comisión Venezolana de Normas Industriales, COVENIN 2461-87 Aguas naturales, industriales y residuales. Determinación de sólidos, Primera ed., Fondonorma, Caracas, Venezuela, 1987. http://www.sencamer.gob.ve/sencamer/normas/2461-87.pdf.

[21] ASTM International, ASTM D1125-95: Test Methods for Electrical Conductivity and Resistivity of Water, ASTM International, West Conshohocken, PA., 2009. https://doi.org/10.1520/D1125-95R09.

[22] American Public Health Association, APHA 4500-H+ B: Standard Methods for the Examination of Water and Waterwaste: pH, electrometric method, 18th ed., APHA, Washington D.C., U.S.A., 1992. https://www.edgeanalytical.com/wp-content/uploads/Waste_SM4500-H+.pdf.

[23] Comisión Venezolana de Normas Industriales, COVENIN 3141-95 Aguas naturales, industriales y residuales. Determinación de cloruros, Fondonorma, Caracas, Venezuela, 1995. http://www.sencamer.gob.ve/sencamer/normas/3141-95.pdf.

[24] Comisión Venezolana de Normas Industriales, COVENIN 2771-91 Aguas naturales, industriales y residuales. Determinación de dureza, Fondonorma, Caracas, Venezuela, 1991. http://www.sencamer.gob.ve/sencamer/normas/2771-91.pdf.

[25] American Public Health Association, APHA 2320 A: Standard Methods for the Examination of Water and Waterwaste: Alkalinity, 18th ed., APHA, Washington, D.C., U.S.A, 1992. https://law.resource.org/pub/us/cfr/ibr/002/apha.method.2320.1992.html.

[26] W.F. Langelier, Chemical equilibria in water treatment, Journal of the American Water Works Association. 38, 2 (1946) 169-178. https://www.jstor.org/stable/23349196?seq=1.

[27] M. Hernández and A. Rodriguez, Inhibidor de incrustaciones mejorado a base de mucílago de linaza (*Linum usitatissimum*), Universidad de Oriente, Núcleo de Monagas, Monagas, Venezuela, 2021.

[28] ASTM International, ASTM D2196-18, Standard Test Methods for Rheological Properties of Non-Newtonian Materials by Rotational Viscometer, ASTM International, West Conshohocken, PA., U.S.A., 2018. https://www.astm.org/DATABASE.CART/HISTORIC AL/D2196-18.htm.

[29] Z. Zhang, A.T. Kan, M.B. Tomson, and P. Zhang, Laboratory investigation of co-precipitation of $CaCO_3$/$BaCO_3$ mineral scale solids at oilfield operating conditions: Impact of brine chemistry, Oil & Gas Science and Technology - Rev. IFP Energies nouvelles. 75 (2020) 1-9. https://doi.org/10.2516/ogst/2020075.

[30] Q. Wang et al., Laboratory study on efficiency of three calcium carbonate scale inhibitors in the presence of EOR chemicals, Petroleum. 4 (2018) 375-384.
https://doi.org/10.1016/j.petlm.2018.03.003.

[31] M. Kobr, R. Huizar, and O. Campos, Evaluación hidrogeológica de pozos a través de registros geofísicos (fundamentos), Primera ed., Universidad Autónoma de México, México, 2005. https://books.google.es/books?hl=es&lr=&id=vb2 hNjEKgTUC&oi=fnd&pg=PA7&dq=Kobr,+M.,+Huiz ar,+R.,+%26+Campos,+O.+(2005).+Evaluaci%C3%B 3n+hidrogeol%C3%B3gica+de+pozos+a+trav%C3% A9s+de+registros+geof%C3%ADsicos+(.

[32] Diccionarios Oxford-Complutense, Química, Primera reimpresión ed., Editorial Complutense, España, 2003. https://books.google.co.ve/books?id=VmdvQfFbq 9UC&printsec=frontcover&hl=es&source=gbs_ge_ summary_r&cad=0#v=onepage&q&f=false.

[33] J. Porras, P. Nieto, C. Álvarez, A. Fernández, and M. Gimeno, Calidad y contaminación de aguas subterráneas en España, IGME, España, 1985. http://aguas.igme.es/igme/publica/libro43/lib43. htm.

[34] M. Rigola Lapeña, Tratamiento de aguas industriales: Aguas de proceso y residuales, Alfaomega Marcombo, Barcelona, España, 1990. https://books.google.es/books?id=fQcXUq9WFC8 C&printsec=frontcover&hl=es&source=gbs_ge_su mmary_r&cad=0#v=onepage&q&f=false.

[35] J. Dagnino, Análisis de Varianza, Revista Chilena de Anestesia. 43 (2014) 306-310. https://revistachilenadeanestesia.cl/PII/revchilan estv43n04.07.pdf.