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New Product for Inhibition of Calcium Carbonate Scale in Natural Gas and Oil Facilities Based on *Aloe Vera*: Application in Venezuelan Oilfields

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Abstract

Scales are secondary deposits constituted by inorganic chemical compounds present in an anthropogenic system. They are generated by changes in the thermodynamic, kinetic and hydrodynamics conditions^[1] when formation fluids are produced, or by mutual physicochemical incompatibility between production and injection fluids. Therefore, they can jeopardize the integrity, good condition and useful lifetime of geological formations, producing and injection wells, surface facilities and pipelines, increasing the industry operation costs.

Generally, these problems had been mitigated by using conventional technologies based on chemical compounds (polyphosphate, carboxylic compounds, among others), that generate environmental liabilities and represent high costs for the industry.

Recently, PDVSA Intevep, S.A. has developed a scale inhibitor product based on *Aloe vera* plant chemical component^[2], that offers equal or in some cases better efficiency than conventional chemical treatments, on the same conditions of evaluation. In addition, it offers the potential benefits of a lower environmental impact.

In this study, the performance of this anti-scale polysaccharide-based product was evaluated in the laboratory, simulating oil and water transfer system from flow stations to tanks, producing wells with high water content and injection wells. After, the product was evaluated in pilot field tests in two wells during about 50 days each:

- (1) Barinas's production well with about 3200 BPD, 98% water and high scale tendency by Oddo-Thompson method at bottomhole.
- (2) Monagas's production well with about 2200 BPD, 74% water and high scale tendency by Stiff and Davis method at wellhead.

In both cases, the pilot field tests were successful. The scale inhibitor product developed was more efficient than commercial products used in those production wells.

Introduction

- Systems description

Produced oil properties are geographically heterogeneous across Venezuela. Figure 1 shows the geographical location of the selected wells for the *Aloe vera* based scale inhibitor field test. Said field tests were carried out in systems with high scaling tendencies from their failure histories and Saturation Indexes (SI).



Figure 1. Localization map

- Case Monagas at wellhead

The M-1 well was selected, where crude oil is secondarily recovered by a mechanism that includes water injection. Recurrent production problems are caused by mineral precipitation at the wellheads, specifically in the area after the redactor in the well's downward tunnel.

Operative conditions for the M-1 well are 2036 BBPD, 529 BNPD, 74% W&S and 22.3 API.

The M-1 well is one of 5 highly critical wells due to scale formation within all 72 wells throughout Eastern Venezuela. Currently a commercial chemical scale inhibitor product is being injected in the selected well at wellhead level.

The M-1 well is fitted with manometers at both wellhead and manifold level which allows the supervision of pressure falls through out the flow tunnel. It's also fitted for the collection of samples and has couponholders for a sequential inspection of an anti-scaling treatment trial.

- Case Barinas at bottomhole

At the B-1 well selected, oil is produced using a hydraulic pump production mechanism. Recurrent problems due to mineral precipitation at bottomhole are observed.

Operational conditions for the B-1 well are 2.699 BBPD, 94% W&S, 24.6 API, 30 RGP, wellhead pressure of 115 psi, bottomhole pressure of 3003 psi, 421.48 K temperature, release pressure 2161 psi, release temperature 416.48 K.

The failure history associated to scale formation shows that the well has been gone through several technical assessment in order to evaluate the quality of commercial scale inhibitory products that have been used; therefore a vast number of surface facilities are available for scale inhibitor products evaluation.

One of the most relevant surface facilities available at the B-1 well is a flow bypass which allows for the inspection of the product's behavior and efficiency without compromising production. Moreover it has couponholders which allow the installment of scale coupons for the study of scaling precipitate formation. It's fitted for the collection of samples and has a manometer at wellhead level. Scale inhibitor injection is carried out at the bottomhole through a capillar tubing; the well is equipped with two capillars which renders flexibility to the injection process.

Methodology

The production method, failure history and scale formation history for a given well was obtained, along with it's facilities. An inspection of the site where chemical treatment took place, was carried out, in order to verify all equipment is operable. Said inspection led to the selection of Wells B-1 and M-1 for the Barinas and Monagas field test respectively. The data was analyzed using Scalecorr v6.2 software^[3] for the determination of SI of the system.

The test was carried out for 51 days at B-1 well and 30 days at M-1 well. In both cases, water samples from the well were collected for calcium content determination thoughout the whole field test. Moreover, pressure data was recorded to check for a possible obstruction in the pipelines. For the Barinas case, visual inspections were carried out with a frequency of each and two weeks for the coupons and for the wellhead, respectively. For the Monagas case, weekly visual inspections were carried out for of coupons both at the well itself and at the manifold levels.

At the beginning of the *Aloe vera* based scale inhibitor injection, new scale coupons were installed and production data was recorded for a follow-up.

The scale samples were analyzed by Scanning Electron Microscopy (SEM, PHILLIPS XL30), Energy-dispersive X-ray spectroscopy (EDX, PHILLIPS XL30) and X-ray diffraction (XRD, PANalytical X'Pert PRO, with a copper cathode).

Results and discussion

- Case Monagas at wellhead

1. Scale tendency simulation

A water sample from the well was collected for an extended characterization, form which it's possible to simulate saturated conditions at different temperatures and study the formation of scaling precipitates. The characterization resulted in the following data: pH (at 298 K) 8.59; Conductivity 7307 μ S/cm; Total Alkalinity (as CaCO₃) 1337 ppm; Bicarbonate (HCO₃⁻) 1339 ppm; Carbonate (CO₃⁻) 96 ppm; Chloride (Cl⁻) 1879 ppm; Sulfate (SO₄⁻) 79.7 ppm; Calcium (Ca²⁺) 17.2 ppm; Barium (Ba²⁺) < 0.5 ppm; Strontium (Sr²⁺) < 0.5 ppm; Iron (Fe) 1.48 ppm; Magnesium (Mg²⁺) < 10.0 ppm; Potassium (K⁺) 16.2 ppm, Sodium (Na⁺) 1647 ppm, Dissolved solids 4343 ppm; Suspended solids 460 ppm; Total solids 4803 ppm.

The sample's SI was determined using the Stiff and Davis method^[4], which includes high ionic strengths, elevated dissolved solids levels and brines produced in oil wells. Figure 2 shows the SI simulation at different temperatures.



Figure 2. Monagas system's scaling tendency, simulated by the Stiff and Davis method

As seen in Figure 2, the scaling tendency of the system, under the conditions evaluated here, is at all times greater than zero, even at temperatures far lower than the temperature registrated for the pipeline (383.6 K). Therefore the systems are classified as "scaling".

2. Field test

The Monagas well field test had an overall duration of 30 days (4 weeks), and thus 4 inspections of the scale inhibitors coupons were performed, both at wellhead level and at manifold level. Figures 3 and 4 show the state of both scale coupons throughout all inspections.



Figure 3. Weekly inspections of the state of scale coupons at the well level



Figure 4. Weekly inspections of the state of scale coupons at the manifold level

Weekly inspections of the scale coupons led to define the recommended dosage for the inhibitor in the studied well at 3.0 gal/day. The conditions for pressure and temperature proved to be rather constant throughout the entire field test (Figure 5). The line's pressure had a variation range of just 20 psig (between 310 psig and 330 psig). The wellhead's pressure had a variation between 980 psig and 1000 psig. Temperature variation was ± 4.5 K. These results are in agreement with the evidence gathered through the inspections of the scale coupons. The lack of an increase in these operative condition variable would result in the absence of precipitated solids in the system, as was observed throughout the field test's weekly inspections.



Figure 5. Pressure and temperature of the field test with the Aloe vera based scale inhibitor

Moreover, results for calcium content are also in agreement with the observed evidence since the concentration data was relatively constant, and increased only slightly and transiently, as seen in Figure 6. Said figure also shows that calcium

content was at no point below the initial value, which would indicate a possible precipitate formation.



Figure 6. Calcium content of the field test with the Aloe vera based scale inhibitor

Since the amount present was insufficient precipitates it was not possible to characterize them. The comparison of the *Aloe vera*-based scale inhibitor field test's results with those of the previously used commercial scale inhibitor (Figure 7), strongly suggest that the *Aloe vera*-based scale inhibitor is far more efficient than the commercial scale inhibitor, since better results are obtained employing half the dosage.

Commercial Inhibitor	Aloe vera Inhibitor

Figure 7. Scale coupon comparison between commercial inhibitor and the Aloe vera-based scale inhibitor for the same test period

- Case Barinas at bottomhole

1. Scale tendency simulation

A water sample from the well was collected and was fully characterized. In conjunction with the production conditions the SI was determined. Chemical treatment injection took place at bottomhole, specifically at the artificial rise suction pump.

This system's scaling tendency simulation must be performed using Oddo-Thompson's method[4], which considers variables innate to at well's bottomhole. Calcium Carbonate's scaling tendencies were calculated throughall the well. Figure 8 shows the SI relative to well depth.

CaCO3 scale-proned zones (SI>0) are highlighted blue on Figure 8. The first zone is between 4000 and 6000 ft, this is also the area where the artificial rise pump is located (5000 ft specifically). Due to the high cost of this equipment and its importance, the injection of anti-scaling chemical treatment at the pumps suction is justified in order to guarantee its operational integrity during oil production.



Figure 8. SI based on the profile of the producing well

2. Field test

The first step taken was to dislodge and inspect the wellhead, finding coupons amounts of solids (Figure 9). It is important to point out that a commercial scaling inhibitor chemical treatment was already being used.



Figure 9. State of the wellhead of the selected well before the field test

Samples from the precipitate found at wellhead were collected to determine which chemical species were present. Through an organic extraction the precipitate's composition was found to be 5.13% of organic compounds, 0.32% of volatile and an inorganic fraction of 94.55%, which was then analyzed with SEM, EDX and XRD to determine the morphology and compounds present. SEM analysis (Figure 10a) did not elucidate any specific morphology in the samples; however EDX analysis (Figure 10b) detected the presence of Oxygen, Calcium and Carbon, which leads to the presence of compounds with these elements.



Figure 10. SEM and EDX of the solid sample found in the wellhead of the B-1 well before the start of the field test

To determine which species are present in the simple a XRD analysis was performed (Figure 11).



Figure 11. XRD of the solid sample found on the wellhead before the field test

After comparing the sample's spectrum with reference codes, it was concluded that the sample was composed by two Calcium Carbonate species: Calcite and Aragonite, which are the most thermodynamic stable forms of $CaCO_3$ under the system's condition.

After cleaning the wellhead, the *Aloe vera*-based scale inhibitor's field test was begun. Production started with 3200 barrels/day with a content of approximately 98% of water and sediments, and a scale inhibitor dosage of 2 gal/day (15.2 ppm). Fluid samples from the well were collected daily in order to determine the calcium content throughout the field test. Pressure at wellhead level was also recorded daily.

Twenty days after the field test began, the wellhead was dislodged and inspected along with the scale coupons. Figure 12 shows the absence of any precipitate in the wellhead, coupon and couponholder, which demonstrates the efficiency of the *Aloe vera*-based scale inhibitor up to the time of the inspection.



Figure 12. State of the wellhead, coupon and couponholder of the selected well at 20 days since the start of the field test at 20 days after the start of the field test

Further inspections were carried out after 35 and 51 days since the beginning of the field test. On both occasions the wellhead was free of any solid formations due to the precipitation of salts present in the well's water content. (Figure 13).



Figure 13. State of the wellhead at 35 (a) and 51 (b) days, respectively, since the beginning of the field test

Coupons and couponholders were also inspected and none of them showed the presence of precipitates.

Calcium content from the daily water samples is presented in figure 14. On statistical analysis was performed by t-student to remove data that did not conform to the linear setting with 99.99% confidence[5]. As can be seen, calcium concentrations varied through out the field test, the slope of the curve is positive, indicating a marked tendency to increase concentration of calcium in the water during the field test. Said behavior might be due normal variations innate to an oil reservoir in addition to calcium retention in the aqueous phase due to the inhibitory action of the product.



Figure 14. Variation in calcium content in production water associated with oil from the well during the field test

Conclusions

Under the present study conditions, it has been demonstrated that the scale inhibitor based on *Aloe vera* gel, is efficient in the prevention of scaling precipitate formation in the studied wells, showing a better performance than the commercial inhibitors to prevent/protect structures and systems for oil production.

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