SPE Brazil Flow Assurance Technology Congress
Rio de Janeiro, Brazil, November 15 – 18 2022

Obstruction in the Riser Due to a By-product of H_2S Scavenger Reaction

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Abstract
Tubarão Martelo (TBMT) field produces approximately 10,000 barrels of oil per day through five wells connected to the FPSO Bravo, which has been operating in the field since 2012. The TBMT field is located on the north coast of the state of Rio de Janeiro and has the highest levels of H_2S in the Campos Basin with values in producing wells ranging from 3900 to 11200 ppm in gas. Then, H_2S scavanger is added to lower the H_2S content and attend the plant integrity and security specifications. In 2017, a large pressure drop was detected in the Wet Christmas Tree (WCT) of well TBMT-8H and it was requiring the deactivation of the well's ESP. A study was carried out and it was concluded that there was an obstruction on the production line and the residue represented a by-product of the H_2S scavenger reaction. Meanwhile, several actions were taken to remove the obstruction, such as pressurization of the duct, operation with coiled tubing and ethanol injection. Therefore, this paper will describe the causes of this obstruction and the measures taken to clear the production pipeline of the well.

Keywords
Flow Assurance; Chemical Inhibitors; Hydrogen Sulfide

Introduction
Currently, Tubarão Martelo field (TBMT) produces approximately 10,000 barrels of oil per day through five wells connected to the FPSO Bravo, which has been operating in the field since 2012. In 2020, PetroRio acquired the FPSO and became the operator of TBMT.
TBMT field is located in the Campos Basin, on the north coast of the state of Rio de Janeiro, and has the highest levels of H_2S in the Basin with values in producing wells ranging from 12,000 to 18,000 ppv.
H_2S scavenger is added in the subsea so the oil can fit exportation standards and be stored in cargo tanks properly. It's also responsible for protecting the subsea in cases with partial pressure above the standard and the plant integrity and security.
In July 2017, a rapid and large pressure drop was detected in the Wet Christmas Tree (WCT) and upstream of the choke valve of well TBMT-8H, showing a significant reduction in flow. Thus, the well was closed to avoid possible damage to the Electrical Submersible Pump (ESP). Until then, the well was producing around two thousand barrels daily.
When the ESP was activated to return production from the well, extreme pressures (up to 46 bar) were obtained at the WCT [1] However, there was no increase in the pressure upstream of the choke valve in the subsea production flowline, so this occurrence indicates an obstruction in the line.
Several tests were carried out and it was confirmed that the obstruction was due to the accumulation of a mixture of inorganic deposits, generated by the use of hydrogen sulfide scavenger, with organic deposits, from the oil produced in the well. This is an unprecedented problem in Brazil, according to the experience and knowledge of the technical team [1] Therefore, this paper will describe the causes of this obstruction and the measures taken to clear the production pipeline of the well.

Methodology
This section will describe the actions taken to clear the line and the experimental procedure performed to analyze the residue extracted at the pig receiver.

Measures for Clearance
Several actions were taken to remove the obstruction. Initially, pressurization through the service line against the choke valve of the well was used, but it was not successful. Consequently, the

clearance actions became more complex, as reported below.

1. Pressurization of the ducts: First, water was injected to achieve higher pressures. As there was no increase in the inlet pressure of the duct unit applying 200 bar, it was decided to inject Diesel due to its compatibility with oil. Thus, there were pressurization cycles injecting Diesel reaching up to 275 bar, with a small removal of fluid [1] Finally, these attempts were unsuccessful to clear the line.
2. Coiled tubing operation: The operation of the coiled tubing was initiated for well cleanout stimulation. The technical team identified the most critical waste accumulation locals, one at the riser's Touch Down Point (TDP), a location inaccessible by the coiled tubing, and the other at the last bend downstream of the Mid Water Arch (MWA).
3. Ethanol injection: After analysis, it was confirmed that the final residue is “hard” and in contact with ethanol becomes softer. Therefore, it was decided to implement ethanol injection in the blocked pipeline. The total volume of ethanol injected was 130 m³ [1] corresponding to the volume of the service pipeline plus the production pipeline, in order to guarantee the passage of ethanol through the obstruction for a considerable time. The production pipeline from the TBMT-8H well remained aligned to the test separator for most of the time, as it was the safest way to maintain constant drainage. Samples were collected daily for analysis of density and centrifugation for sediments. After the ethanol injection was completed, the flushing operation began with the injection of fresh water. Samples were collected in the return line as well as in the pig receiver to monitor the flushing efficiency through the waste return. The tightness tests of the pipe sections of the production line were successfully carried out and the TBMT-8H well was started.

Experimental Analysis

Although the obstruction occurred in 2017, the presence of solids on the platform had previously been identified, as an example, in 2015 solids were found at different points of the oil processing unit of the platform and an investigation had been made. Therefore, two samples were collected and analyzed [2] . The first sample consisted of an emulsion collected in the electrostatic oil dehydrator (sample B) and the second sample consisted of a powdery solid that was collected at the gas outlet of the three-phase separator (sample B). The analysis was performed by gas chromatography with mass detector, inductive plasma optical emission spectrometry (ICP-OES), infrared absorption spectroscopy, x-ray fluorescence and CHN elemental analysis of the samples.

After the obstruction, the same experiment performed previously was carried out to analyze the residue collected from the TBMT-8H production line. Furthermore, another experimental analysis was performed by a different laboratory [3] . The evaluation of the solubility of residue from the well was carried out in different solvents, under specific temperatures. Some systems were sent for analysis in an infrared spectrometer with Fourier transform (FT-IR) for qualitative chemical analysis of the sample and in thermogravimetry, to investigate the presence of inorganic calcium carbonate in the residue and verification of the final residue content after degradation of the material.

Determination of the Scavenger Injection Rate

The gas cylinder, flow meter, reactor and H_2S analyzer were connected and the jacketed reactor was filled with a combination of Isopar M and brine (150 mL and 350 mL, respectively) with an overhead stirrer speed of 500rpm. The bubbling of H_2S and CO_2 was performed until outlet H_2S concentration reaches the feed concentration, and it was monitored with the lead acetate tape analyzer. A dose of 1000ppm of scavenger was injected and then samples of approximately 5 mL were retrieved at 5 minutes intervals and aged overnight in the oven at 60ºC[4] .

Results and Discussion

This section will show and discuss the results obtained in 2015 and 2017, which both residues are by-products of the reaction of the non-nitrogen scavenger with H_2S.

Identification of the residue

The gas chromatography was able to detect that, in the portion of the sample that was soluble in dichloromethane, 67.62% and 3.23% were saturated and sulfureted compounds, respectively. [2] . Solid analysis via GC-MS represents the fraction of the solid sample that was soluble in dichloromethane. The analysis was also able to detect the presence of trithiolane and tetrathiepane, cyclic polysulfides, in concentrations of 1.23% and 2.00% of the sample, but only 1.00% was composed by a nitrogenic compound named bromine butyl piperidinone. These compounds are illustrated in Figure 1.

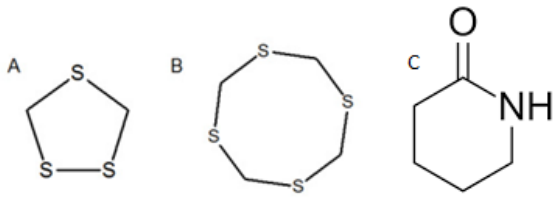

Figure 1. Molecular structure of trithiolane (A), tetrathiepane (B) and piperidinone (C) [2] .

Piperidinone is a very common molecule used in the formulation of corrosion and carbohydrate inhibitors.

The ICP-OES test revealed a 35.2% Sulfur content and, considering that the ash content test shows a less than 1% fraction of inorganic matter. The levels determined for the elements Na, Ca and Si add up to 0.24%, a value consistent with the one obtained in the test to determine the ash content. It's supposed that all this compound comes from the organic part of the sample [2] . Thus, this shows to be a mainly sulfureted and organic solid since the inorganic fraction has lower contribution in the chemical composition of the residue.

According to the results of infrared absorption spectroscopy presented in Figure 2 and Figure 3, the peaks between 3000 a 2850 cm^{-1} and 1470 a 1350 cm^{-1} can be related to the ones found in the analyzes of tritian [2] .

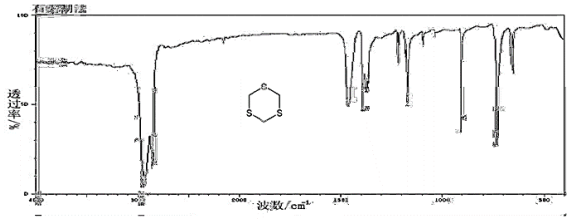

Figure 2. Infrared absorption spectroscopy results for tritian.

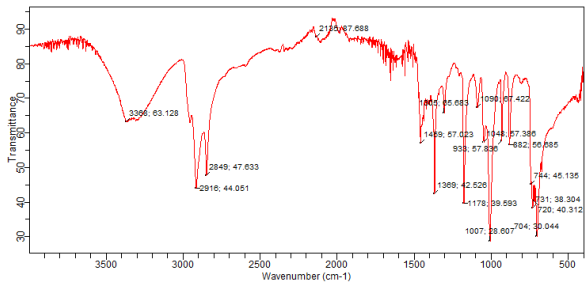

Figure 3. Infrared absorption spectroscopy results for the sample.

Considering a chemical reaction between triazine and H_2S, amorphous dithiazine will be formed and the percentage of nitrogen in the composition would be approx. 5% and 52% sulfur. The elemental analysis of C, N and H indicates a distribution of 43% in C, 7.3% in H and only 0.16% in N. As the analysis by ICP-EOS indicates the presence of 35.2% of S, by difference we can infer the Oxygen content present in the sample, as shown in Table 1. As only 0.16% of nitrogen was observed, the existence of amorphous dithiazine would only explain approximately 3% of the solid's composition [2] .

Table 1. Elemental analysis results of SAMPLE B.

Parameter	SAMPLE B results
Ashes (% m/m)	<1
Carbon (% m/m)	43 (±1)
Hydrogen (% m/m)	7.3 (±0.3)
Nitrogen (% m/m)	0.16 (± 0.01)
Sulfur (% m/m)	35.2
Oxygen (% m/m)	14.3

Regarding the experiment carried out by UFRJ after the obstruction, Table 2 shows the results of the value of mass reduction as a function of initial mass of 0.1g of residue that each solvent system caused on the residue [3] .

Table 2. Results of the mass reduction after solubilization in different solvent systems.

System	Mass Reduction (%)
Water	22.8
Diesel	34.3
Xylene	78.5
Xylene/diesel	61.3

It can be concluded that the sample solubilizes well in the xylene solvent, with a mass reduction of more than 75%. Increasing the solubilization time from 3 hours to 24 hours did not improve the sludge solubilization process. Figure 4 shows the FT-IR spectrum for the residue remained after solubilization in xylene for 3 hours [3] .

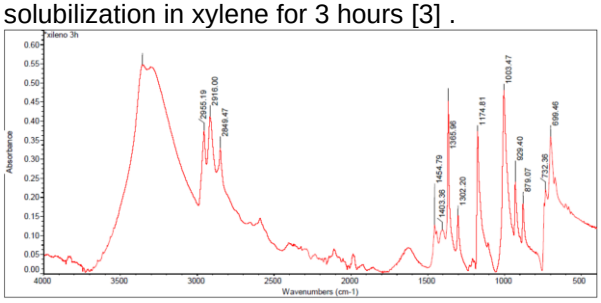

Figure 4. FT-IR / ATR spectrum of the residue remained after solubilization in xylene for 3 hours.

The analysis of the wavelengths of the main absorption bands was performed together with the possibilities of deformation of different groups possibly present in the residue. Through the physical-chemical characterization of the solid, it can be observed the presence of a mixture of materials, which contains aromatic compounds, amine-based compounds and sulfur compounds, and that there is a strong relationship between these results and the technical information received about the H_2S scavenger.

Measures for Clearance

As the pressurization method was unsuccessful, it was decided to operate the coiled tubing to clear the line. It was confirmed that there is a concentration of residue that blocked the location duct in the TDP region and in the section of the riser catenary. The result of this operation was not completely successful due to the presence of obstruction outside the reach of the equipment, but part of the residue was removed. Lastly, the ethanol injection had success and the TBMT-8H well returned to normal production.

In addition, a study was carried out to verify the maximum allowable pressure upstream of the choke in order to avoid stress corrosion at this point

[1] . For this study, two values of H2S concentration in the gas were considered for each TBMT well. According to the calculations performed, and considering the pressure values currently practiced, it was found that the operating pressures for the TBMT wells are within the acceptable limits for the standard. This standard applies to cases where the temperature is lower than 80 °C, as is the case of the arrival temperatures of the 4 wells. This standard also assumes a maximum partial pressure limit equal to 0.34 bara. For both values of H_2S concentration in the gas considered in the calculations, the pressure upstream of the choke of the TBMT 8H well is far below the maximum limit allowed by the standard. Therefore, it was recommended and implemented the interruption of the injection of H_2S scavenger in this well. With the return of production from the well, we verified a reduction in the head loss from the MWA to the choke, evidencing that at least part of the flow restrictions were removed.

Determination of the Scavenger Injection Rate

The curve showed in Figure 5 is used to determine the dose rate of the scavenger at different times. It is observed thar the H_2S concentration at the reactor outlet started to drop after adding the scavenger. Additionally, the lowest concentration was achieved at approximately 2min, followed by a gradually increases towards the inlet concentration.

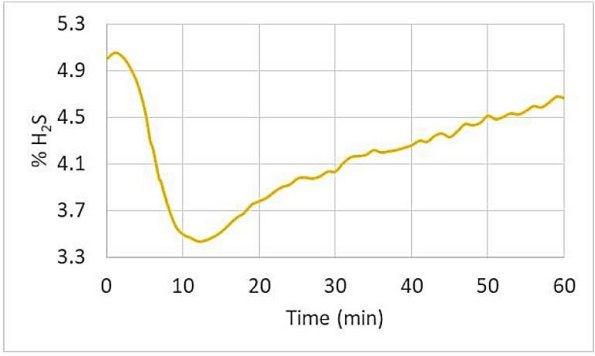

Figure 5. Reduction of H_2S at reactor outlet after the injection of scavenger [4] .

The samples collected after the injection of scavenger were observed for solids and determined the dose rate, as shown in the Table 3.

Table 3. Scavenger dose rate and amount of solids corresponding to each sample.

Sample ID	Liters Scavenger/ kg H_2S	Amount of solids
A	58	Trace
B	14	Low
C	7	Low
D	5	Medium
E	4	High

It can be concluded that the trace to low amount of solids were observed for initial set of samples A, B and C. However, significantly higher amount was observed for the last two samples (D and E) [4] .

Conclusions

Based on the analytic results, it is concluded that the sample is composed majority for sulfureted compounds with a preferentially cyclic chain due to the presence of trithiolane and tetrathiepane, which may even contain some aromatic and inorganic compounds, as Sodium, Calcium and Silicon. This sample represents a by-product of the reaction of a non-nitrogen scavenger with H_2S that has polythiomethylene bonds and, possibly, a cyclic chain with high sulfur content.

The operation performed with the coiled tubing was successful in unblocking the obstruction located at the last bend downstream of the MWA. Then, the operation was performed correctly, safely and without failures, but it did not prove to be sufficient. Conversely, the ethanol proved to be effective in softening the residues and cleaning the line.

In conclusion, the analysis of the influence of the rate of scavenger injection in the formation of this solid revealed that the lowest rate that generates an acceptable quantity of solids is 7 L scavenger/ kg H_2S, so that shouldn't damage the flowline.

Responsibility Notice

The authors are the only responsible for the paper content.

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