

## **Temperature Influence on High TAN Corrosion – A VGO Case Study**

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### **ABSTRACT**

High temperature activates and enhances the corrosive effects of sulfur compounds and naphthenic acids (NAP) inherently present in heavy crude oils. These corrosive processes involving sulfur and NAP have a significant impact on the distilling units integrity and consequently it becomes important to control and mitigate these corrosive effects. The main goal of this study was to investigate the temperature effect on NAP corrosivity in interaction with sulfur corrosion. Two distilling fractions with high NAP content were selected and tested in corrosion experiments done in a “flow-through” reactor at three distinct high temperatures similar or close to the operation conditions in oil distilling units. The factor time was also evaluated in this study as for each temperature level the test duration varied from 24 to 168 h. NAP corrosion and sulfur corrosion (sulfidation) were evaluated by measuring the iron and sulfur concentrations in samples collected during the tests. Scales (corrosion product) formed on metal samples, were analyzed using scanning electron microscopy and energy dispersive spectroscopy. The scales analysis and the collected kinetic data suggested that NAP and sulfur corrosion depend significantly on temperature variation but also on the chemical composition and on the concentrations in oil of two corrosive species.

**Keywords:** high temperature corrosion, naphthenic acids, sulfidation, test duration, oil distillation.

### **INTRODUCTION**

Oil refineries adjust constantly their production according to world oil production and availability, to the market demands and tendencies and under these conditions they try to keep simultaneously the balance between operating costs cost and margin benefits. There are several options in lowering the operating costs and one of these is the use of heavy crude oils which are cheap due to their acidity and high sulfur content. <sup>[1]</sup> The high content of naphthenic acids and of sulfur in heavy crudes makes them very corrosive when processed and as consequence refinery engineers adopt different strategies in mitigating and/or controlling the potential damaging effects of heavy crudes. Thus, light crudes are blended with heavy ones and transformed in high-value distillates, oil corrosivity is reduced by using corrosion inhibitors, or a

more costly option can be upgrading the metallurgy of the distilling units where corrosive processes are more intense and cause significant material losses.<sup>[2,3]</sup> An important tool in optimizing oil processing is the prediction of oil corrosivity by using corrosion models.<sup>[4]</sup> These models have to consider for their predictions the corrosive reactions of both naphthenic acid and sulfur species contained in crude oils and the factors that can influence these processes such as temperature, fluid velocity, viscosity, type of construction steel. This paper describes an experimental work that investigated the effect of time and temperature on the complex the sulfur-acid interactions in the scale formation and degradation processes.

## EXPERIMENTAL

### Experimental Instrumentation

As the goals of this research were aiming both to reproduce on lab scale the operating conditions in refinery distillation towers and also to decipher the intimate reaction mechanisms of the corrosion processes typical to these units, the experiments were conducted in a “flow-through” apparatus that met the selection criteria for these requirements. The “Flow-Trough-Mini-Autoclave” (FTMA) apparatus was selected for the experimental work and a schematic representation of it is presented in Figure 1. The FTMA can operate at temperatures up to 370°C (700°F) and on a pressure range of 0 to 1 MPa (0 - 150 psig).

Experimental fluids are pumped in the FTMA system through pumps towards the reactor that is heated with an electrical resistance. The tubular reactor contains the metal samples that are exposed to the testing fluids which are constantly and slowly pumped through the reactor during the test. As the fluid flow is set to a constant and very low flow rate, the FTMA flow regime can be considered almost stagnant and comparable to the static autoclave testing conditions. The “almost stagnant flow” conditions in the FTMA allow a constant replenishment of the testing fluid on the sample surfaces and prevent the accumulation of reaction byproducts in the reactor that might influence the corrosive process. A backpressure valve located downstream the reactor maintains the pressure high in the system thus keeping all components in liquid phase during testing. The FTMA has also a sampling port located downstream the reactor that allows the collection of fluid samples during the runs.

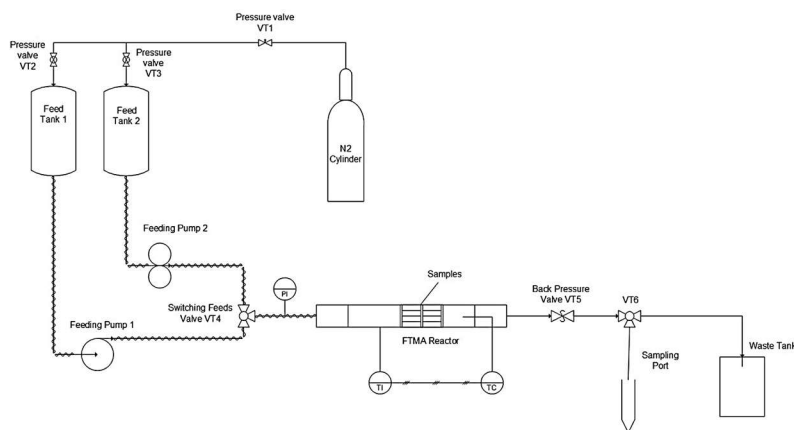


Figure 1. Flow Through Mini Autoclave (FTMA) – schematic representation of the “flow through” experimental apparatus.

## Experimental Materials

This experimental work was part of a research project and the selection of sample material, and the testing conditions were decided based on the project sponsors requirements. It was also the project sponsors who provided the testing fluids – two different distilling fractions – to be evaluated in the research work. The total acid number (TAN) and the total sulfur content of the two distilling fractions (VGO) are presented in Table 1. Metal samples with a rectangular shape were made of UNS K03006 carbon steel.

**Table 1**  
**List of the VGO used in “time and temperature” test series**

|   | <b>Test Fluid</b> | <b>TAN</b><br>(mg KOH/g oil) | <b>Sulfur content</b><br>(wt. %) |
|---|-------------------|------------------------------|----------------------------------|
| 1 | Fraction B        | 6.88                         | 0.76                             |
| 2 | Fraction C        | 1.51                         | 1.92                             |

## Experimental Conditions

The effect of time (test duration) and temperature on VGO corrosivity were the two test variables considered for this work. Four different test duration were selected i.e. 24, 48, 72, and 168h. Each of these four tests was conducted at three different temperatures. 288, 316, and 343°C. The pressure in the FTMA flow system was maintained at 100 psig and the oil flow rate was set to 1.5 cm<sup>3</sup>/min. The experimental conditions for all “time and temperature” test series are summarized in Table 2.

**Table 2**  
**Experimental conditions in “time and temperature” test series**

| <b>Experimental Fluid</b> | <b>TAN</b><br>(mg KOH/g oil) | <b>Sulfur content</b><br>(wt. %) | <b>Temp.</b>     | <b>Time</b><br>(h) | <b>Pressure</b><br>(psig) | <b>Oil Flow rate</b><br>(cm <sup>3</sup> /min) |
|---------------------------|------------------------------|----------------------------------|------------------|--------------------|---------------------------|------------------------------------------------|
| VGO                       | 1.51 – 6.88                  | 1.51 – 1.92                      | 343°C<br>(650°F) | 24, 48,<br>72, 168 | 100                       | 1.5                                            |
| VGO                       | 1.51 – 6.88                  | 1.51 – 1.92                      | 316°C<br>(600°F) | 24, 48,<br>72, 168 | 100                       | 1.5                                            |
| VGO                       | 1.51 – 6.88                  | 1.51 – 1.92                      | 288°C<br>(550°F) | 24, 48,<br>72, 168 | 100                       | 1.5                                            |

## Experimental Procedure

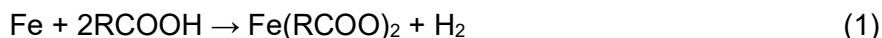
All samples used in the time and temperature tests were polished with 400 and 600 grit silicon carbide paper under isopropanol flush before testing. Further, samples were cleaned with acetone, dried under nitrogen flush, and weighed. After the test samples were cleaned thoroughly with toluene and acetone to remove the oil residues and then the scale formed on

their surfaces was mechanically removed with a stiff plastic brush and chemically by rinsing the samples successively in Clarke solution<sup>(5)</sup>. Samples were dried and weighed both after the scale was rubbed off and after they were dipped in the Clarke solution. Samples weight losses were used to calculate the corrosion rates. In every test some samples were not cleaned of the scale formed on their surface as they were saved for the electronic microscopy analysis.

The total sulfur content, the iron concentration, and the TAN were monitored during the tests by collecting oil samples and analyzing them with different analyzers. In all tests oil samples were collected at 1, 2, 3, 4, 5, 6, 9, 12, 24h intervals. In extended tests i.e. 48, 72, and 168h, the oil samples were collected at 24h intervals until the test end. The total sulfur content and soluble iron concentration in oil samples were measured using the High-Definition X-Ray Fluorescence (HDXRF) method, according to ASTM D4294, with an XRF analyzer. The oil acidity - Total Acid Number (TAN) was measured with a TAN titrator according to ASTM D664.

## RESULTS AND DISCUSSION

Chemical interactions at high temperature of the complex chemical compounds contained in crude oils and in their distilled derivatives make it difficult to generate a comprehensive mechanism of this specific corrosion. Therefore, the experimental work that attempts to decipher the corrosion mechanism of oil distilling fractions relies on limited data generated from samples weight losses, chemical analysis of the fluids, and structural and morphological information from the microscopic analysis of the scales formed on the samples. The mechanism of oil corrosive species, the naphthenic acids and sulfur compounds is summarized by three chemical reactions that explain the formation of corrosion byproducts (Reaction 1 and 2) and the “self-sustained” corrosive cycle in which acids are recomposed from these byproducts (Reaction 3).<sup>[3,6,7]</sup> This simplified mechanism assumes that sulfur compounds in oil thermally decompose and generate hydrogen sulfide which attack the metal immediately and forms the solid iron sulfide scale. Naphthenic acids attack the metal and form the iron naphthenates which are oil soluble and can be removed by the oil flow



The final result of naphthenic acid and sulfur corrosion was evaluated by calculating the corrosion rates based on samples weight losses. Figure 2 presents the corrosion rates measured for Fraction B (Figure 2(a)) and for Fraction C (Figure 2(b)) in “time and temperature” test series. Fraction B with a high TAN (6.88) and medium sulfur content (0.76 wt. %) showed a specific influence of the temperature on its corrosivity. Thus, as temperature decreased, the corrosion rates increased in Fraction B tests, regardless of the test duration. All corrosion rates decreased as test duration increased, a corrosion rate dependency of time that was noticed in other experiments too. In case of Fraction C that had a lower TAN (1.51) than B but a very high sulfur content (1.92 wt. %) the temperature decrease was followed by a decrease in the corrosion rates. The time increase in Fraction C tests decreased the corresponding corrosion rates. The decreasing temperature effect on Fraction B corrosivity was unpredicted and it was hoped that more information from the analytical data might explain this behavior.

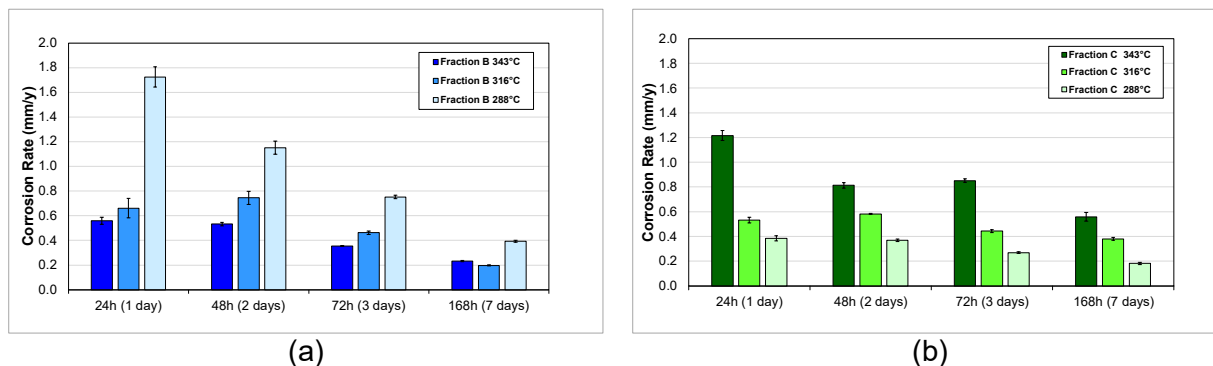


Figure 2. Corrosion rate comparison in “time and temperature” test series – Fraction B (a) vs. Fraction C (b).

It was assumed in this work that measuring the sulfur and the iron concentration in oil samples collected as the experiments were running, it would be possible to evaluate the intensity of the chemical reactions and the dynamics of byproduct formation. Thus, it was assumed that sulfur concentration can indicate when the sulfidation reaction is more intense and forms the iron sulfate scale. The iron concentration associated with the soluble iron naphthenate formation would similarly provide information of the intensity of the naphthenic acid attack. Both sulfur and soluble iron concentrations were measured using the High-Definition X-Ray Fluorescence (HDXRF) method, according to ASTM D4294.

The TAN of the oil samples was measured with a TAN titrator according to ASTM D664 and the values measured for tests done with Fraction B are presented and compared in Figure 3. Figure 3(a) shows the TAN values measured in the 24h test while Figure 3(b) shows the values measured in the 168h test. TAN values indicate that there was decreased of the acidity in the first hour of the test and then the values recovered and reached the same level as the original TAN of Fraction B which is the reference, and it is plotted at  $t = 0$ . Further, in the 168h test (Figure 3(b)) there was no significant difference between the TAN values measured during the run and the original TAN reference. This TAN data suggests that the naphthenic acid attack was constant as the test duration extended. TAN measurements indicate though that there was an increase of acidity during the first 3 hours of the tests done at the lower temperature of 288°C.

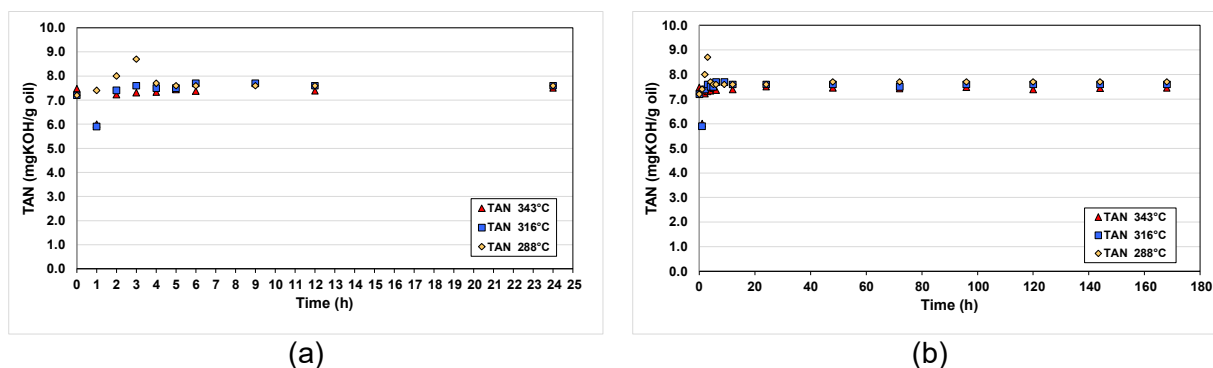


Figure 3. Total Acid Number (TAN) measurements in “time and temperature” series of tests using Fraction B (TAN - 6.88, S – 0.76), TAN values of the 24h test in (a) and of the 168h test in (b), respectively.

The XRF analytical results for oil samples collected in Fraction B test series show an interesting evolution of the soluble iron concentrations as function of the test temperature and time. Thus, in Figure 4 the plot summarizes the XRF measurements of the 168h test series with B having at  $t = 0$  the original iron concentration of the “neat” fraction as it was provided by the sponsor. The soluble iron concentrations measured for samples collected in 288°C test indicate a sharp increase of iron during the first 12h of the test followed by a decrease of these concentrations after 24h to a level that continues to be low and constant until the test ends. The high concentrations of soluble iron in the first four of the 288°C test might indicate a significant attack of the naphthenic acids against the metal.

A similar concentration increase for soluble iron is also shown in the first three hours of the test done at 316°C temperature. The iron concentration decreases during the next three hours of the test, reaching a low level after 9 hours and remaining constant for the rest of the test duration. The XRF data of the 343°C test plotted in Figure 4, indicate that at this temperature the soluble iron concentrations were very low from the beginning to the end of the test which might suggest a reduced activity of the naphthenic acids at 343°C. These assumptions regarding the possible correlations between the iron concentrations and the naphthenic acid attack against the metal will be further discussed in the scanning electron microscopy analysis.

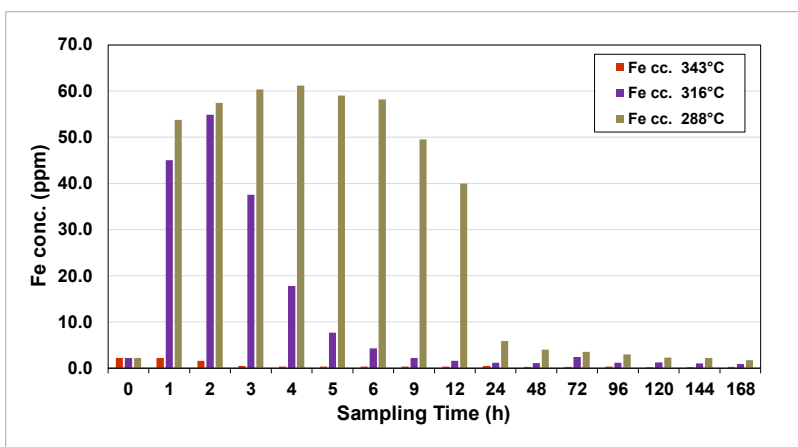


Figure 4. XRF measurements for soluble iron concentrations in “time and temperature” test series done with Fraction B (TAN - 6.88, S – 0.76 wt. %).

For the Fraction C the soluble iron concentrations measured in the “time and temperature” test series are plotted in Figure 5. The iron concentration of Fraction C plotted at  $t=0$  is the concentration of the “neat” fraction as it was provided by the sponsor. The XRF data measured in 288°C test shows that the soluble iron concentration increases slowly reaching a peak after 6 hours and then decreases to a level that remains constant for almost 60 hours. For the test done at 316°C, the iron concentration increases slightly in the first hours of the test and then decreases and remains constant for 40 hours.

The iron concentrations in the 343°C temperature test increase at the beginning of the test and then remain almost constant, with small variations towards the test end. If all iron concentrations measured in the Fraction C test series are compared to the “neat” value of the fraction (t=0) it can be concluded that only in the 288°C test there was a significant variation of the iron and consequently of the iron naphthenate. For the other two tests the iron concentrations did suggest that acids were reacting with the metal but not very intensely.

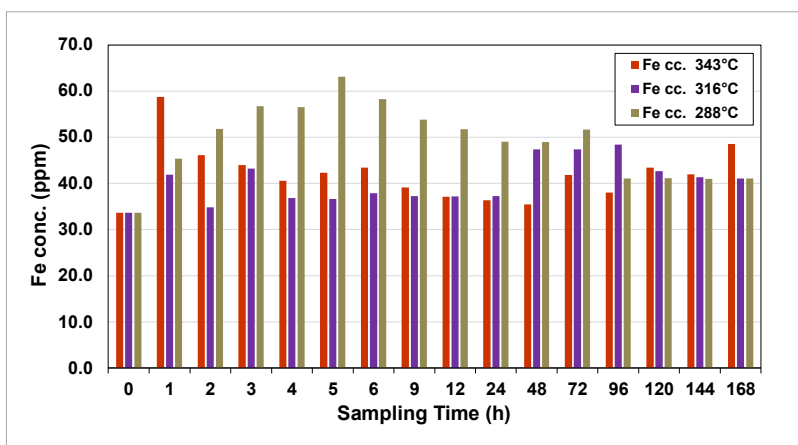
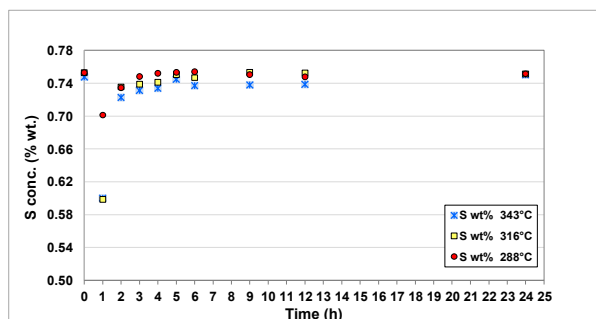
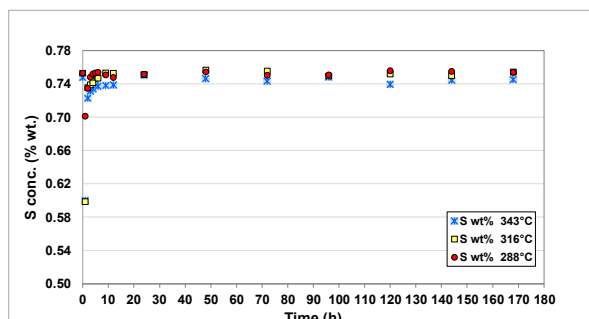


Figure 5. XRF measurements for soluble iron concentrations in “time and temperature” test series done with Fraction C (TAN – 1.51, S – 1.92 wt. %).

The XRF data for total sulfur concentrations plotted in Figure 6 for Fraction B test series and in Figure 7 for Fraction C series show similar trends in sulfur evolution for both fractions. For Fraction B there was significant drop in total sulfur concentration during the first hour of both tests done at 316°C and at 343°C suggesting an intense reaction of the sulfur species with the metal (Figure 6a). For the 288°C test there was a drop in sulfur concentration but not as significant as in the case of the other two higher temperature tests. The sulfur concentrations start to increase again after the first hour drop, reaching the initial level for all three distinct tests. There were no significant variations in the total sulfur concentrations after the first 24 hours of the longtime test.



(a)



(b)

Figure 6. XRF data for total sulfur concentrations measured in “time and temperature” series in tests using Fraction B (TAN - 6.88, S – 0.76 wt. %). Sulfur concentrations of the 24h test (a) and of the 168h test (b).

Fraction C with a very high total sulfur content (1.92 wt. %) behaved differently than Fraction B in the “time and temperature” test series. The total sulfur concentrations measured with the XRF in these tests are shown in Figure 7 (a) and (b). The total sulfur evolutions of Figure 7(a) suggest that in the 24h tests done with Fraction C the sulfur reactions with the metal were very intense during the first hour of the test done at 288°C temperature when the concentration dropped significantly. Sulfur concentration dropped in the tests at 316°C and at 343°C too but not as much as in the case of 288°C. Further, as the test continued, the sulfur concentration started to increase reaching the same value for all three distinct test cases after 4h. In the long-time tests (168h) plotted in Figure 7(b), the total sulfur evolution was similar to that of the 24h test.

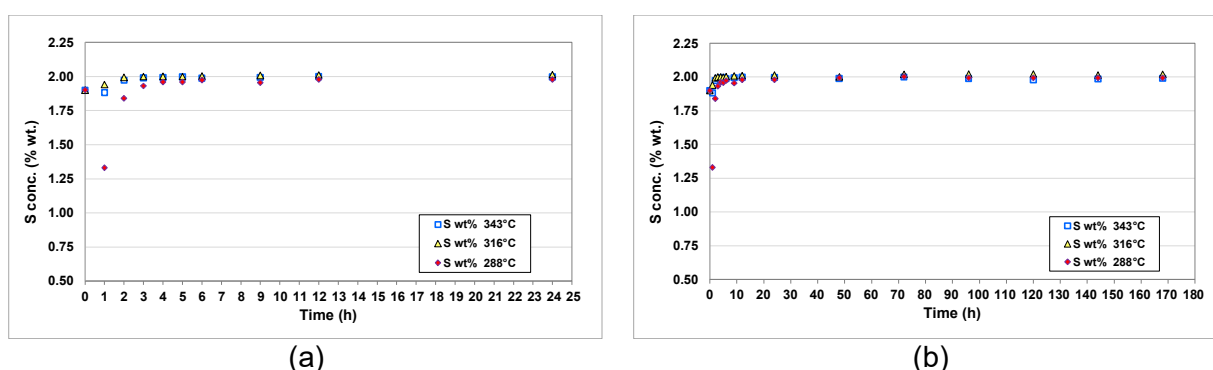


Figure 7. XRF data for total sulfur concentrations measured in “time and temperature” series in tests using Fraction C (TAN – 1.51, S – 1.96 wt. %). Sulfur concentrations of the 24h test (a) and of the 168h test (b).

## SEM/EDS Analysis of the Scale

The Scanning Electron Microscope (SEM) and the Energy Dispersive Spectroscopy (EDS) were used to analyze the scales formed on the samples used in the “time and temperature” test series. These cross-section images of the samples are compared in Figure 8 for tests done with Fraction B and in Figure 9 for tests done with Fraction C. The SEM images are arranged in each of the two figures, horizontally in the increasing order of the test duration and vertically in the decreasing order of the testing temperature.

SEM images of the samples collected in the 288°C temperature tests series done with Fraction B - Figure 8, bottom row – show that the naphthenic acid attack against the metal was very intense leaving large voids under the scale. The evidence of the intense naphthenic acid attack against the metal in these tests is also supported by the high iron concentrations that were measured in samples collected during the 288°C tests (Figure 4). High iron concentrations were measured also in the 316°C tests done with B and the SEM images of the scales formed at this temperature (Figure 8, middle row) show the voids left on the samples after the naphthenic acids attack.

Fraction C had a very high total sulfur content (1.92 wt.%) and formed thick multilayered scales on the samples. All SEM images of the scales formed on samples with Fraction C at different temperatures and time durations show scales consisting of multiple layers that were either strongly attached to each other or very loose and detached from the samples. These different morphologies of the scale layers explain the variation in iron concentrations that were measured with the XRF in fluid samples collected during the Fraction C test series. The scale formed and acted as a barrier reducing the acids diffusion to the metal, then as the test evolved, cracks were formed in the scales, the acids reached the metal and formed the soluble iron naphthenate that were entrained by the fluid flow.

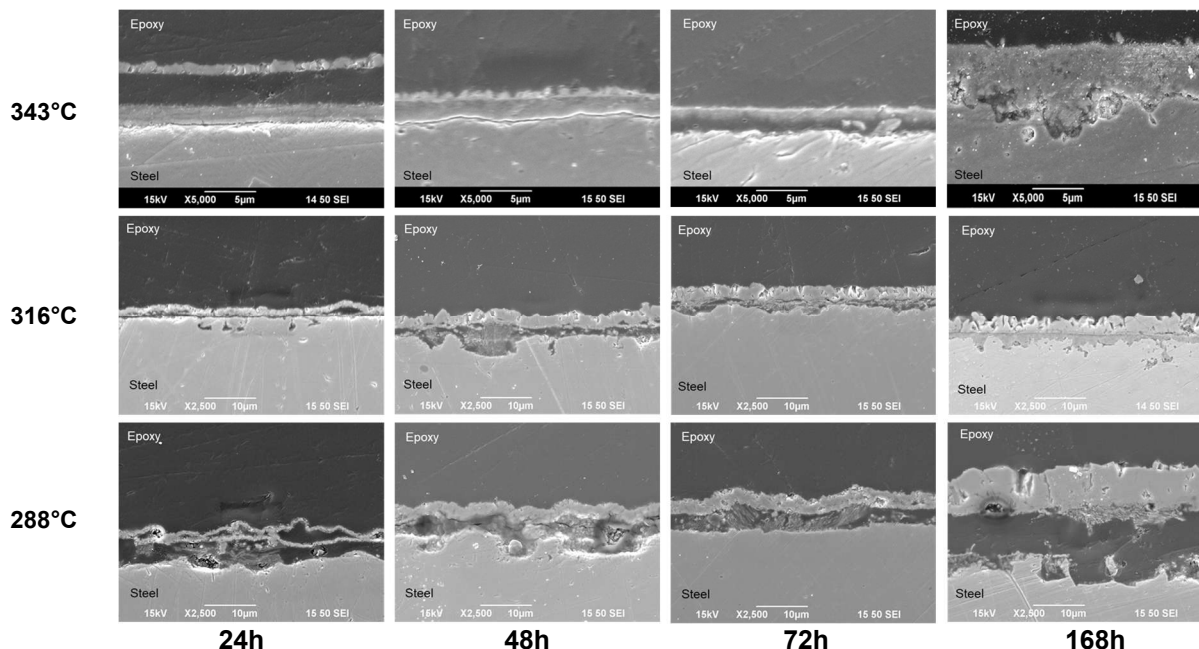


Figure 8. SEM images (cross-sections) of the scales formed with Fraction B at 343°C, 316°C, and 288°C temperatures in tests of different durations (24, 48, 72, and 168h).

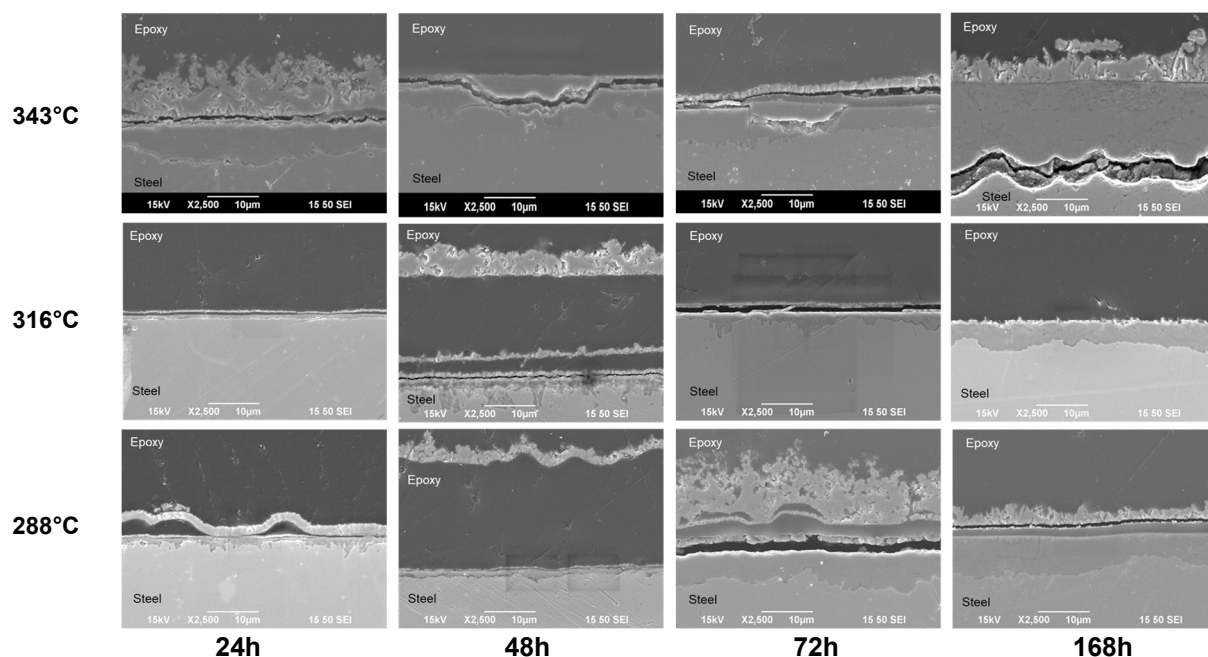


Figure 9. SEM images (cross-sections) of the scales formed with Fraction B at 343°C, 316°C, and 288°C temperatures in tests of different durations (24, 48, 72, and 168h).

## CONCLUSION

The effect of time and temperature on oil distillates (vacuum gas oils) was evaluated in a series of experiments of different time duration (24, 48, 72, and 168h) performed at three distinct temperatures close or similar to the operating conditions in distilling towers. The experiments conducted at three distinct temperatures 288°C, 316°C, and 343°C were using two VGO with a high TAN and sulfur content.

The evaluation included corrosion rate measurements, the XRD analysis of oil samples collected during the tests, and the SEM/EDS analysis of scales formed on the samples.

Fraction B with the highest TAN (6.88) and as the testing time increased the corresponding corrosion rates decreased in all considered temperature series. However, the corrosion rates increased for every specific test duration as the testing temperature decreased.

Fraction C had the highest sulfur content (1.92 wt.%) and in all time duration series the corrosion rates decreased as the experimental time increased. The decrease in the testing temperature was also lowering the corrosion rates in every testing time duration set.

The increasing corrosivity of Fraction B as the testing temperature decreased was also revealed by the high concentrations of soluble iron that were collected during the tests performed at lower temperature. The intensity of the naphthenic acid attack on the metal at low temperature was revealed in the SEM cross-section images of the samples used in the tests with Fraction B.

Although Fraction C had also a high TAN (1.51), the high sulfur content proved to be more corrosive and formed scales that limited the diffusion to the metal of the naphthenic acids and their destructive effect. Thus, the corrosion rates in tests done with Fraction C decreased as the

testing time increased and as the testing temperature was lower, the corresponding corrosion rates also decreased in these experiments.

Finally, it can be concluded that if the naphthenic acid content in an oil fraction is very high and the sulfur content is low, the corrosive effect of the acids is dominant, and it is able to overcome the scale formation process that might offer a limited protection to the metal surface. In contrast to the high TAN effect, if the sulfur content in the oil fraction is very high then the sulfur reaction can be fast and efficient in forming protective scales even at lower temperatures than the unit operating ones. Thus, it becomes possible for the scales to protect the metal surfaces and limit the naphthenic acid attack.

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