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Sulfur and Naphthenic Acid Interactions in a Snapshot of Refinery Distillates

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ABSTRACT

Sulfur organic compounds contained in crude oils create significant material damage when such oils are processed at high temperatures in distilling towers. These sulfur corrosive damages are enhanced when naphthenic acids are also present in the processed oils. Therefore, the destructive corrosive effects of sulfur compounds and naphthenic acids have to be controlled, mitigated, and estimated/predicted to operate safely the distilling units of oil refineries.

A snapshot of refinery distillates was evaluated as part of the experimental work using a specific experimental protocol “pretreatment - challenge” designed to estimate the combined corrosive effects of naphthenic acids and sulfur compounds in oil. This protocol estimates the corrosive processes by evaluating the protectiveness of scales preformed (“pretreatment”) in oil fractions on metal samples against naphthenic acid corrosive attack (“challenge”). The study also investigated the possible connections between fractions corrosivity, and the hydrogen sulfide generated during their experimental evaluation.

The refinery distillates selected for this evaluation were obtained from the same oil and were collected from the same vacuum distilling unit over several days. The distilling tower was operated as pulling Light Vacuum Gas Oil (LVGO), 100N, 325N, and High Vacuum Gas Oil (HVGO) streams that were blended back together as “gas oil”.

Keywords: sulfur, naphthenic acid, hydrogen sulfide, high temperature corrosion, laboratory methods.

INTRODUCTION

Crude oils have a complex chemical composition that influences their corrosivity when they are processed at high temperatures in oil refineries. There are several groups of chemical compounds contained in crude oils that become very corrosive mainly in the distilling towers where different fractions are separated from oil at high temperature. Among these corrosive components, the sulfur species in oil thermally decompose generating hydrogen sulfide, a gaseous compound that can attack rapidly the metal or it is the specific sulfur compounds that react directly with the metal. Besides the corrosive sulfur species, most of the heavy crude oils also contain naphthenic acids (NAP) which are corrosive too at high temperatures.[1,2,3] Therefore, when such crudes are processed, their damaging effect is the result of the simultaneous corrosive actions of sulfur and NAP. The intimate mechanism of sulfur and NAP corrosion is not well known or understood as the chemical composition of oils varies from region to region, and the interactions between sulfur and NAP as well as their interactions with the metal are difficult to be analyzed and quantified with the current available analytical methods and instrumentation. Thus, controlling and mitigating the corrosive effects in oil refineries becomes a challenging task for engineers.[4] They have different strategies for controlling the corrosive effects of sulfur compounds and NAP such as blending crude oils of different qualities, removing acids from oils, using corrosion inhibitors, using high quality alloys, predicting the crudes corrosivity by using corrosion models, and performing specific corrosivity tests on lab scale.[5,6,7,8,9]

The specific lab corrosion tests represent an attractive option in studying and understating the corrosive mechanism of sulfur and NAP because they have a short time duration, do not require large volumes of crude oil/distillates, and by using simultaneously different types of alloys they can provide a significant amount of analytical data. This paper presents an experimental evaluation of a snapshot of refinery distillates, a research work that was performed as part of the Naphthenic Acid Corrosion Joint Industry Project (NAP JIP) at Ohio University.

EXPERIMENTAL

Experimental Procedure and Instrumentation

The refinery snapshot distillates were evaluated experimentally by using the "pretreatment-challenge" test protocol developed previously at Ohio University.[10] "Pretreatment – challenge" testing protocol is designed to evaluate protective properties of scales formed from crude fractions on metal surfaces at high temperature. The protocol consists of two successive experimental phases ("pretreatment" and "challenge") done in separate instrumental apparatuses – static autoclave (AUT) and a flow through system – the High Velocity Rig (HVR).

During the autoclave "pretreatment" scales are formed on metal samples immersed in crude fractions. After "pretreatment", the metal samples covered with scales are extracted from the static autoclave and inserted on the rotating cylinder of the HVR autoclave where they will be rotated at high temperature under a constant flow of white oil spiked with NAP acids. Thus, during the HVR "challenge" the "preformed" scales are exposed to a constant attack of naphthenic (NAP) acids (dissolved in oil) and simultaneously to high temperature and high velocity (shear stress). Corrosion rates are calculated based on samples' weight loss during the test. Separate "pretreatment only" tests are run for every tested crude fraction. By subtracting the metal loss corresponding to the "pretreatment" test from the initial weight of samples that are exposed to a complete "pretreatment – challenge" experiment, it becomes possible to calculate the corresponding metal loss for the "challenge" phase only. Thus, the NAP acid effect on pretreated samples and their covering scales can be separated from corrosive effects and metal loses corresponding to the "pretreatment" phase. Scale protective properties are further evaluated by comparing corrosion rates of samples "pretreated" in crude fraction and “challenged” with NAP acids to corrosion rates of similar samples that were only exposed to NAP acids corrosion without any previous “pretreatment”.

Experimental Instrumentation.

Sulfur containing compounds in crude fractions decompose during the autoclave “pretreatment” and generate hydrogen sulfide (H_2S) that partially reacts with the metal samples. The concentrations of the H_2S that was accumulating in the autoclave headspace during the “pretreatment” test were measured with a MicroGC VARIAN 490 (Agilent) at the end of the test.

The HVR used in the “challenge” phase of the protocol is a “once flow through” apparatus” where samples are exposed to high temperature and high velocity conditions similar to those of refineries transfer lines. The schematic HVR flow system presented in Figure 1 includes the autoclave where the ring samples inserted on a ring are rotated with 2000 rpm under the constant oil flow. This high rotation corresponds to a peripheral velocity of 8.5 m/s on the samples outer surfaces. The HVR autoclave can be operated at temperatures up to 370ºC (700ºF) and on a pressure range of 0 to 3.4 MPa (0 - 500 psig). The testing fluids (“challenge” solution) are purged with nitrogen in their feeding containers before being pumped into the flow system. The testing fluids are kept in liquid form in the autoclave by using a backpressure valve located downstream the autoclave. The 1L static autoclaves (Parr Instruments Series 4520) presented in Figure 2 are used for the “pretreatment” phase of the testing protocol. The static autoclaves have a magnetic drive that entrains an impeller which keeps the solutions homogenous during the tests. The operating conditions of the 1L static autoclaves are temperatures up to 370ºC (700ºF) and a maximum pressure of 13.1 MPa (1900 psi). Before starting the test, the autoclave headspace is purged with nitrogen for removing the oxygen (air).

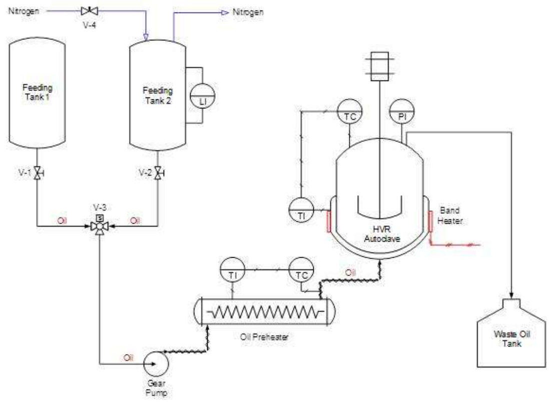

Figure 1: The “flow-through system” – the High Velocity Rig (HVR) used in the “challenge” experimental phase.

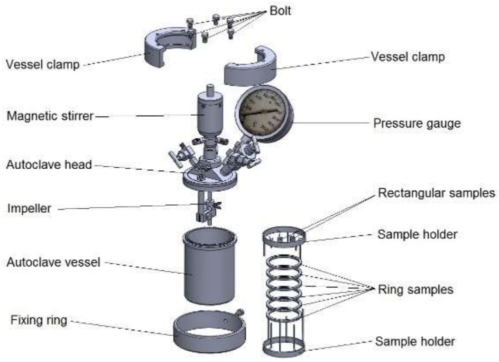

Figure 2: 1L Static autoclave used in the "pretreatment" experimental phase.

The experimental conditions used in this experimental evaluation of the refinery distillates are summarized in Table 1.

Table 1
Experimental conditions for the "pretreatment-challenge" tests.

Test Phase	**TAN** (mg KOH / g oil)	**Sulfur content** (wt %)	**Temp.**	**Time** (h)	**Pressure** (psig)	**Rotation** (rpm)
"Pretreatment"	0.27 – 4.47	0.1 – 0.82	343ºC (650ºF)	24	200	0
"Challenge"	3.5	0	343ºC (650ºF)	24	150	2000

Experimental Materials

The selected refinery distillates listed in Table 2 were tested in the static autoclaves during the "pretreatment" phase of this experimental evaluation. These refinery distillates have medium to high sulfur contents (0.27 – 4.47 wt %), low to high TAN concentrations (0.1 – 0.82), and they were obtained from the same oil. All vacuum distillates were collected from the same vacuum distilling unit over several days. The distilling tower was operated as pulling Light Vacuum Gas Oil (LVGO), 100N, 325N, and Heavy Vacuum Gas Oil (HVGO) streams that were blended back together as "gas oil". Besides the vacuum distillates, the evaluation included also the fractions Kero, Diesel, and Automotive Gas Oil (AGO) obtained from the same raw crude oil. The "challenge" solution used for testing the protective qualities of the scales formed in refinery distillates was prepared by dissolving naphthenic acids (TCI America, CAS # 1338-24-5) in mineral oil (Tufflo 6056) - Table 3. The TAN level of the "challenge" solution was TAN = 3.5, a value selected based on the experimental results of the previous work done in this research project.

Metal samples used as screening materials were made of UNS K03006 carbon steel (CS) and of UNS K41545 alloy steel (5Cr). The samples they had a ring shape with the outer diameter OD = 81.76 mm. Rectangular samples made of identical steel types were also used in the autoclave "pretreatment" phase for further SEM/EDS analysis needs.

Table 2
Total sulfur and TAN contents of the selected refinery distillates.

	Fraction Type	**S content** (wt %)	**TAN** (mg KOH / g oil)
1	Kero	0.27	0.10
2	Diesel	0.90	0.29
3	LVGO	1.32	0.40
4	AGO	1.40	0.51
5	100N	1.96	0.75
6	325N	2.13	0.70
7	HVGO	2.38	0.65

Table 3
Chemical products used for the acidic "challenge" solution.

	Chemical product	**Specific Gravity** (kg/m^{-3})	**S content** (wt %)	**TAN** (mg KOH / g oil)
1	**Tufflo 6056**	0.86	0	0
2	**Naphthenic acids**	0.98	0	216

All samples were polished before the tests with 400 and 600 grit silicon-carbide (SiC) paper under isopropanol flush, then they were dried under nitrogen flush and weighed. Samples geometrical dimensions were measured with a caliper. The samples were later inserted on a special holder (Figure 2) and the set-up was immersed in the experimental fluid contained in the autoclave vessel. The autoclave was sealed, inserted into a heater, and heated to the preset temperature of the "pretreatment" phase. CS and 5Cr samples were extracted from the static autoclave after "pretreatment" and further inserted in the HVR autoclave for the "challenge" phase. After "challenge" phase ended, the samples were removed from the HVR rotating cylinder and processed for corrosion rates evaluation. This final procedural step included rinsing the samples several times with toluene and acetone to remove completely the oil residues from their surfaces. Following the solvent rinsing the samples were weighed then the samples were brushed with a stiff plastic brush and weighed again. The scale fragments left on samples after mechanical processing (rinsing and brushing) were finally chemically removed by successive rinsing of the samples in the Clarke solution (ASTM G 1-90).[11] The final weight of each sample was recorded and used to calculate the corrosion rate.

Experimental Calculation - Corrosion Rates

"Pretreatment – challenge" test protocol evaluates the scale protective properties by measuring the corrosion rates of samples "pretreated" in crude fractions and then exposed to NAP acid attack of a given TAN concentration. All corrosion rates expressed in mm/y are calculated based on samples weight losses using the Equation (1):

$$CR = \frac{(IW - FW)}{\rho_{Fe} \cdot A_S \cdot t} \cdot 24 \cdot 365 \cdot 1000 \qquad (1)$$

where

CR - corrosion rate [mm/y]
IW – initial weight [kg]
FW – final weight (after last clarking) [kg]
ρ_{Fe} – Steel density [kg/m^3]
A_s – sample area exposed to corrosive fluids [m^2]
t – time of the experiment [h]

As it was mentioned previously, the "pretreatment-challenge" consists of two distinct experimental phases, each one of them with a corresponding metal loss of the samples. In order to separate the corrosive effects of the two experimental phases ("pretreatment" and "challenge"), distinct "pretreatment only" reference tests have to be performed. In such "pretreatment" reference tests it becomes possible to measure only the metal loss corresponding to this experimental phase. The average metal loss evaluated in separate "pretreatment" reference tests is subtracted from every sample initial weight (IW) that will be "challenged" in the HVR after the "pretreatment" (scale formation). Thus, this new value (sample weight – average pretreatment loss) will be used in Equation 1 to calculate the final corrosion rate. In such manner it becomes possible to evaluate and calculate the "net corrosive effect" of NAP acid on scale protectiveness (i.e. CR of pretreated samples and then NAP challenged).

RESULTS AND DISCUSSION

Experimental Results – Corrosion Rates Evaluation

The intimate mechanism of sulfur and NAP corrosion is not well known although there were many research studies dedicated to this important topic for the oil refining industry. Generally, it is accepted and published in the literature that the sulfur – NAP corrosion mechanism can be summarized by three generic chemical reactions. NAP react with the metal forming iron naphthenate, an oil soluble reaction by-product and hydrogen (Equation 2). The sulfur compounds in oil thermally decompose and form H_2S that reacts very fast with the metal and forms iron sulfide (FeS), a solid reaction by-product that builds up the metal surfaces as a scale (Equation 3). The H_2S formed in excess reacts with the iron naphthenates reconstituting the original NAP and forming more FeS (Equation 4). With the newly reconstituted NAP, the sulfur – NAP corrosion cycle continues, damaging further the metal surfaces exposed to these corrodents.[2,3,12]

Previous experimental studies investigating the FeS scale formation processes identified that the scales formed from crude fractions at high temperatures had a complex chemical composition consisting of distinct layers of FeS and iron oxides. The presence of iron oxides in the scale structure offered special protective properties to these scales in particular cases. It was hypothesized that iron naphthenates at high temperatures decomposed and formed ketones and wűstite (FeO) as in Equation 5. However, wűstite is an unstable product that at same high temperature switched to magnetite (Fe_3O_4) and alpha-Fe (Equation 6). All these experimental findings support the use of the "pretreatment - challenge" testing protocol as an useful tool in predicting the crude fractions corrosivity.[13,14,15,16]

$$\mathrm{Fe + 2RCOOH \rightarrow Fe(RCOO)_2 + H_2} \tag{2}$$

$$\mathrm{Fe + H_2S \rightarrow FeS + H_2} \tag{3}$$

$$\mathrm{Fe(RCOO)_2 + H_2S \rightleftharpoons FeS + 2RCOOH} \tag{4}$$

$$\mathrm{Fe(RCOO)_2 \rightarrow FeO + RCOR + CO_2} \tag{5}$$

$$\mathrm{4FeO \rightarrow Fe_3O_4 + \alpha\text{-}Fe} \tag{6}$$

CS and 5Cr samples were exposed simultaneously to sulfur species and NAP corrosive actions in the autoclave "pretreatment" experiments and a comparison of corrosion rates for the two steel types is presented in Figure 3. The results are presented in the increasing order of the distillates total sulfur content. The plotted data suggests that corrosion rates increased as the total sulfur content of the distillate became higher. The comparison in Figure 6 also shows no significant differences between the individual corrosion rates of each of the two alloys, both showing similar values in every test.

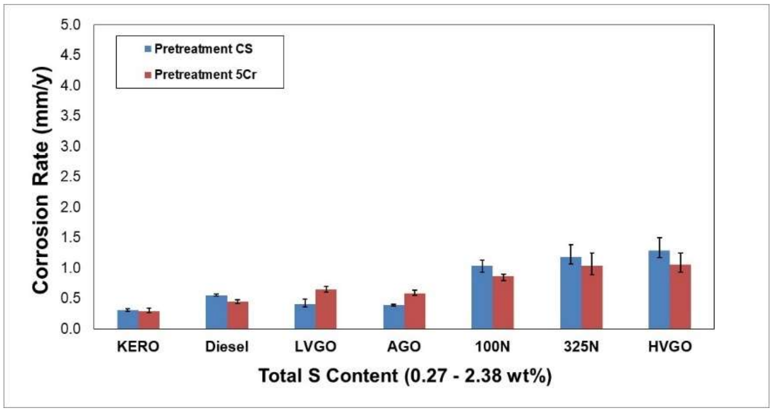

Figure 3: Comparison of CS and 5Cr corrosion rates measured in "pretreatment" tests using selected refinery distillates.

The "pretreated" samples were further exposed to the NAP attack in the "challenge" phase to evaluate their protective properties or the lack of it. "Challenge" corrosion rates for CS samples are compared in Figure 4 to those measured in the "pretreatment" phase for the same steel type. The comparison indicates that scales formed on CS with the selected distillates were not able to withstand the NAP attack during the "challenge" offering no protection to the metal surfaces they covered.

A similar comparison was done for the 5Cr samples in Figure 5 where "challenge" corrosion rates are plotted versus the "pretreatment" corrosion rates. In case of 5Cr samples this corrosion rates comparison indicates clearly which scales were protective and which were not. Thus, the scales formed by distillates "Diesel" and "100N" were very protective whereas the other scales either offered a limited protection against NAP challenges ("Kero", "LVGO", and AGO") or no protection as in the case of "325N" and "HVGO".

The differences in protectiveness for the scales formed on the CS and 5Cr samples might be related to the scale morphology and chemical composition, two particularities that will be discussed and analyzed in the following paragraphs.

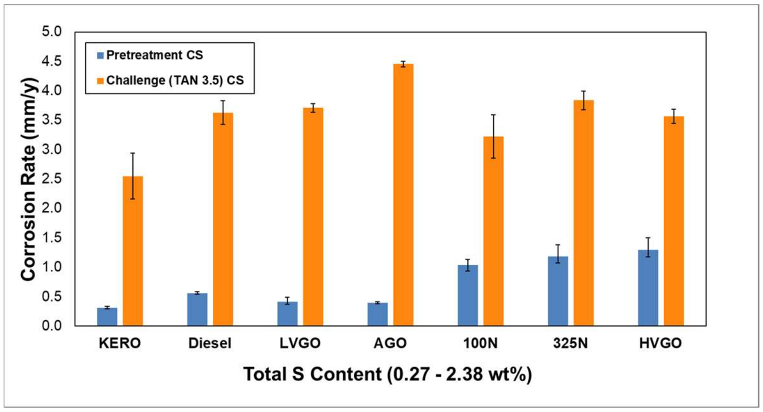

Figure 4 Comparison of CS corrosion rates measured in "Pretreatment" reference and "TAN 3.5 Challenge" tests. Samples exposed to the "TAN 3.5 Challenge" were pretreated in selected refinery distillates.

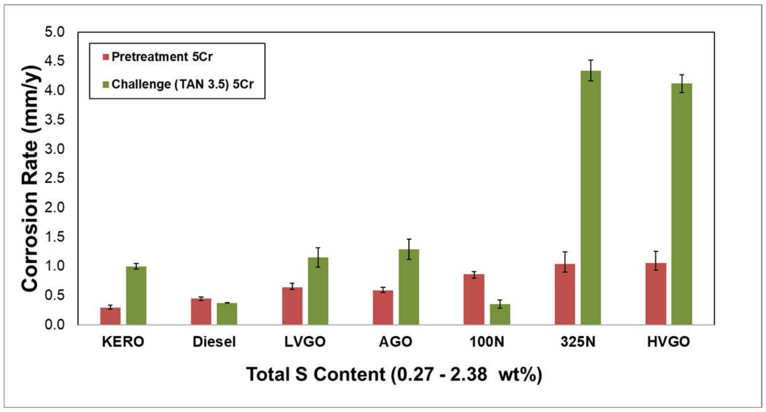

Figure 5: Comparison of 5Cr corrosion rates measured in "Pretreatment" reference and "TAN 3.5 Challenge" tests. Samples exposed to the "TAN 3.5 Challenge" were pretreated in selected refinery distillates.

Experimental results - H_2S Generation and Measurements

The sulfur compounds in the refinery distillates thermally decomposed and generated hydrogen sulfide (H_2S) during the "pretreatment" in thee autoclave tests. The H_2S generated during tests reacted partially with the metal samples and some of it accumulated in the autoclave headspace. As one of the goals of this investigation was to find possible correlations between fractions corrosivity and the H_2S, gaseous samples were collected at the end of each "pretreatment" test. These gaseous samples were analyzed with a micro gas-chromatograph (MicroGC) to measure the H_2S concentration. Table 4 summarizes the H_2S concentrations measured in the gas samples collected from autoclave "pretreatment" tests with distillates. Table 4 also presents the autogenous pressure generated in autoclave headspace at the end of each test. All pressure values were recorded before the sampling procedure of the gas.

Table 4

H_2S concentrations and pressure values in AUT headspace recorded at the end of “pretreatment” tests with refinery distillates.

	Fraction Type	**S content** (wt. %)	**Pressure** (psig)	**H_2S conc.** (%)
1	Kero	0.27	360	0.038
2	Diesel	0.9	400	0.234
3	LVGO	1.32	410	0.88
4	AGO	1.4	390	0.701
5	100N	1.96	420	0.512
6	325N	2.13	400	0.957
7	HVGO	2.38	440	2.813

The H_2S concentrations in “pretreatment” test were plotted versus distillated total sulfur content of the fractions in Figure 6. The data in Figure 6 shows how the distillates with a higher total S wt% generated more H_2S than those distillates with a lower total S wt%. This H2S evolution as a function of fraction total sulfur content cannot be correlated precisely with the corrosivity of those respective fractions. Thus, fractions corrosion rates in autoclave test were in some cases comparable i.e. 100N, 325N, and HVGO whereas the concentrations of H2S these fractions generated were increasing significantly. The comparison of fractions corrosion rates versus H2S concentrations in autoclave tests is presented in Figure 7.

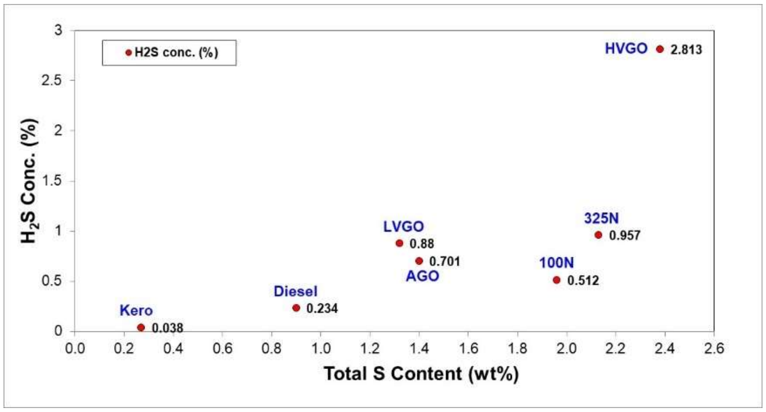

Figure 6: H_2S concentrations plotted as a function of total sulfur content of the refinery distillates. Values recorded in “pretreatment” tests.

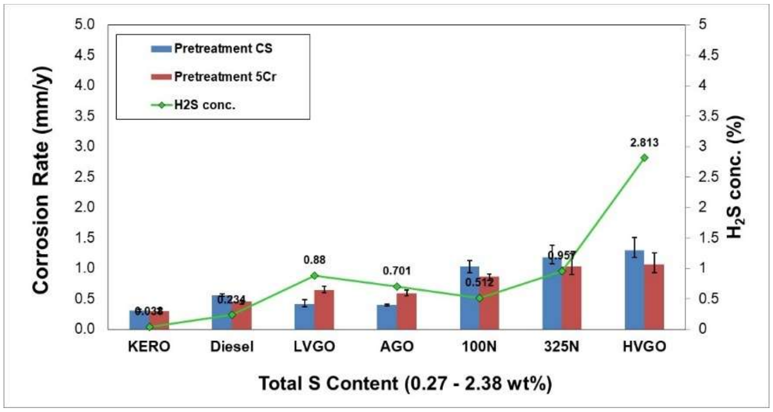

Figure 7: H_2S concentrations versus samples corrosion rates measured in the "pretreatment" tests.

Scale SEM/EDS Analysis

Corrosion evaluation of the refinery distillates included also the analysis of the chemical composition and structure of the scales they formed on CS and 5Cr samples. These structural analyses were performed using the Scanning Electron Microscope (SEM) and the Energy Dispersive Spectroscopy (EDS) for chemical elemental analysis. The samples collected from each test ("pretreatment" and "challenge") were embedded in epoxy, polished, and their cross-section was then analyzed with the SEM/EDS.

The SEM images of the scales formed on CS samples are compared in Figure 8. The scale formed in "pretreatment" tests (top row) are compared to the scales "challenged" with NAP (TAN = 3.5) in presented in the bottom row. On the SEM images of the samples the epoxy region was labeled "E" and steel region "S". All SEM images were arranged in the increasing order of the distillates sulfur content. The "pretreatment" scales had all a multilayer structure, with cracks, consisting of crystals of different dimensions. The scale thickness increased as the total sulfur content of the originating distillate increased. The "challenged" scales shown in the bottom row were able to preserve the multilayered structure in some cases following the NAP attack, or they were completely removed from the sample surfaces as in the cases of "100N" and "325N" distillates. Although the scales that survived the NAP "challenge" preserve their structure they allowed the NAP diffusion through their layers and the acids attacked the metal leaving large voids under the scales (distillates "Diesel", "LVGO", "AGO", and "HVGO"). The SEM images of the "challenged" scales on CS explain the high corrosion rates measured in these experiments. "HVGO" and "325N" formed very thick scales but they were not offering any protection to the CS samples they covered.

The scales formed on 5Cr samples are presented and compared in a similar way in the SEM images of Figure 9. All distillates formed multilayered scales, consisting of crystals with different dimensions, on the 5Cr samples during the "pretreatment" tests as it is shown in the top row of SEM images. The scale structures were also fragmented similar to the scales on CS. For the 5 Cr samples the scale thickness could not be correlated with the sulfur content of the distillates. "Kero" and "Diesel" formed scales comparable to those formed by "100N" and "325N". The "challenged" scales on 5Cr (bottom row) were damaged significantly by the NAP attack in case of "325N" and "HVGO" distillates. These scales were left fragmented and highly porous by the acids which explains their lack of protectiveness and the high corrosion rates for these samples.

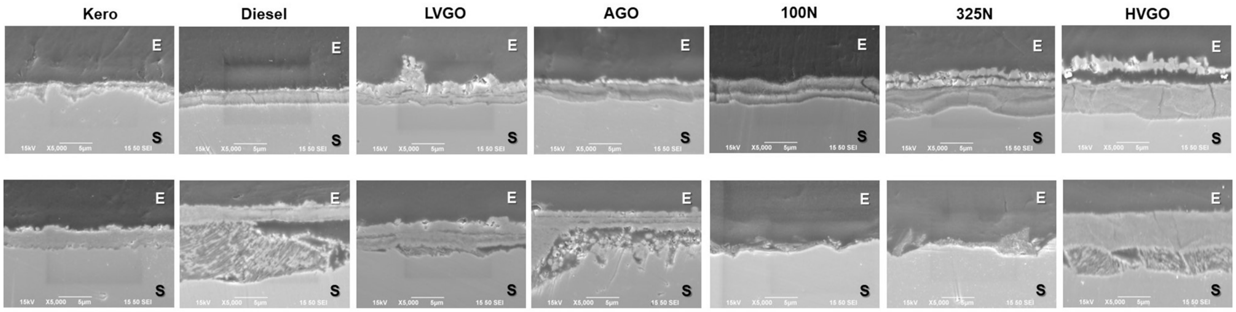

Figure 8: CS samples. Cross-section SEM images comparison – "pretreatment" and "TAN 3.5 challenge" scales. "Pretreatment" images -top row vs. "Challenge" images – bottom row. The results are presented in the increasing order of the distillates total sulfur content.

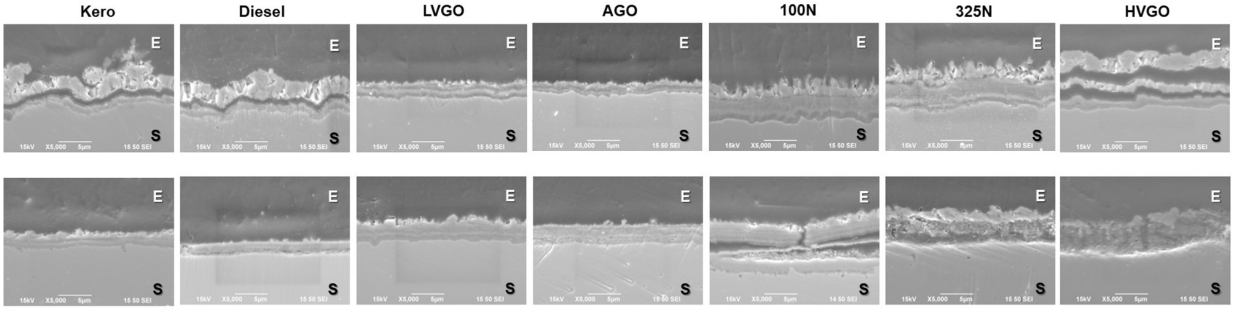

Figure 9: 5Cr samples. Cross-section SEM images comparison – "pretreatment" and "TAN 3.5 challenge" scales. "Pretreatment" images -top row vs. "Challenge" images – bottom row. The results are presented in the increasing order of the distillates total sulfur content.

The EDS elemental mapping of all the scales formed on CS in the "pretreatment" tests is shown in Figure 10. For a better understanding of the analysis the epoxy region was labeled "E", the steel "S", and the chemical elements - iron "Fe", sulfur "S", and oxygen "O". The elemental mapping confirms that "pretreatment" scale on CS consisted of FeS and had also some traces of iron oxide. The oxygen was detected clearly in the scales of "Kero", "Diesel", "LVGO", and "AGO" which might suggest that iron oxide was formed in these layers. The presence of iron oxide in the scales of the four distillates might be correlated with the low corrosion rates measured for CS in "pretreatment" tests. However, the iron oxide formed in the four distillates scales did not offer any protection against the NAP when these samples were later "challenged" with the TAN 3.5 solution.

The elemental analysis of the scales formed on 5Cr samples in the "treatment" tests is presented in Figure 11. This analysis of these scales identified also the chromium (labeled "Cr") along all other elements (Fe, S, and O). The elemental mapping in Figure 11 suggests that a chromium oxide was formed on the samples. This chromium oxide appears clearly in the case of "Kero" where the oxygen layer overlaps the chromium layer in the same section of the image. This oxygen – chromium overlap is also distinct for the other scales shown in this comparison. The presence of the chromium oxide in the scale structure can explain the better protectiveness of scales against the NAP attack and the lower corrosion rates of the 5Cr samples in the "challenge".

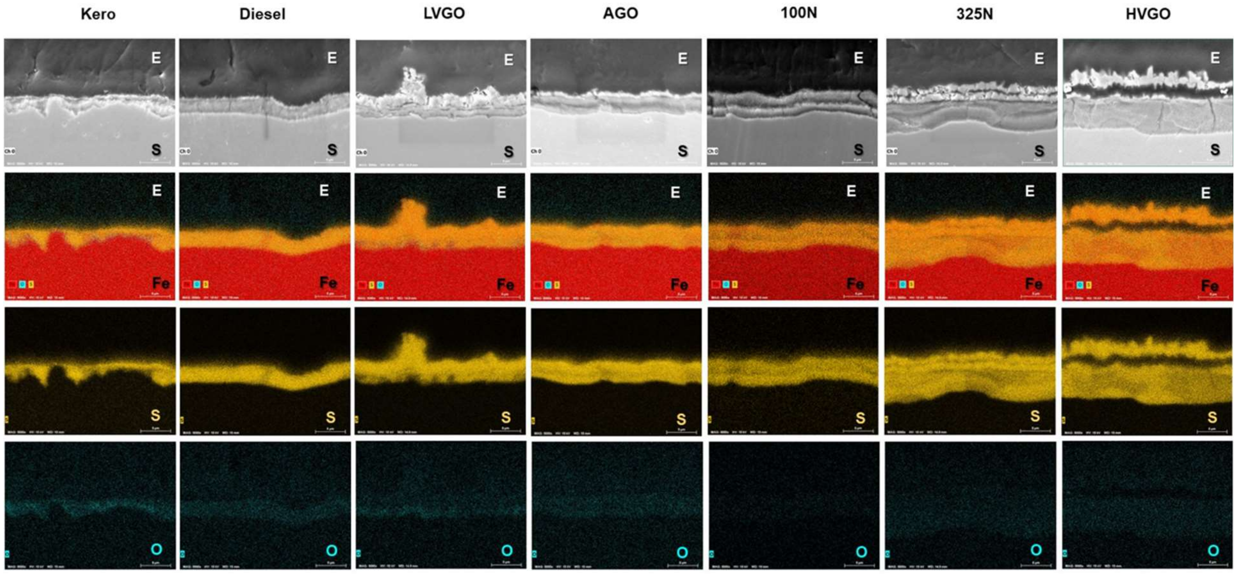

Figure 10: EDS mapping analysis – Scales formed on CS samples in "pretreatment" tests. The results are presented in the increasing order of the distillates total sulfur content.

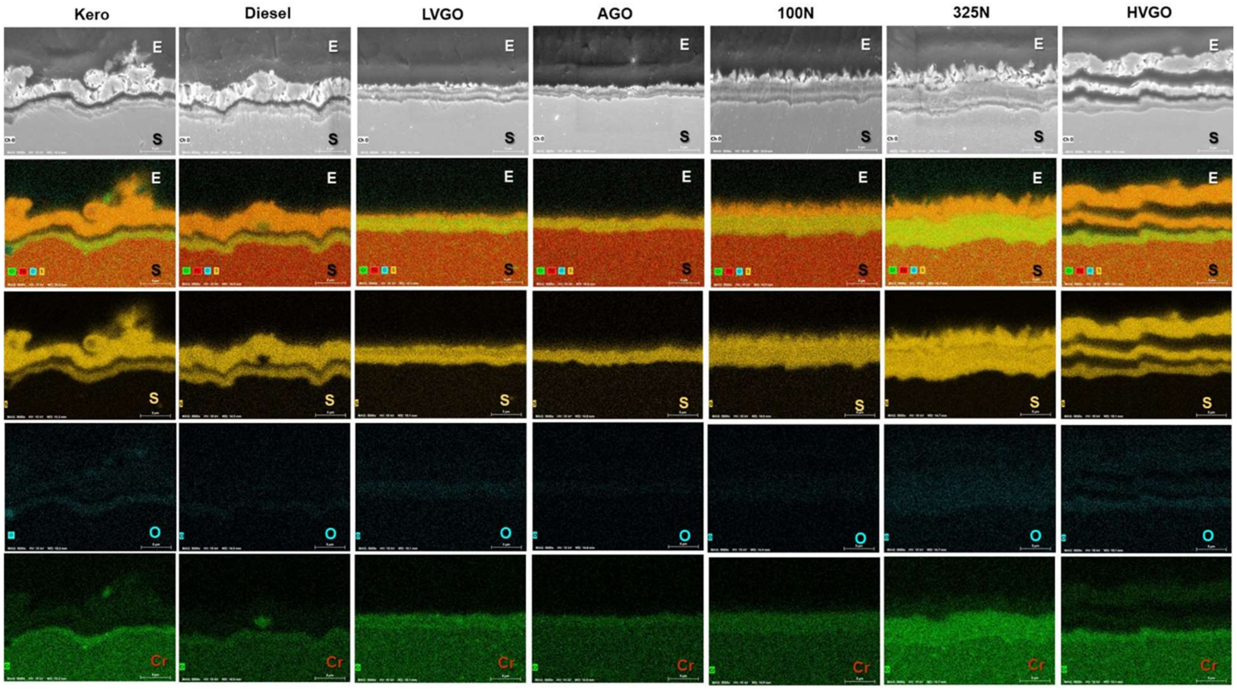

Figure 11: EDS mapping analysis – Scales formed on 5Cr samples in "pretreatment" tests. The results are presented in the increasing order of the distillates total sulfur content.

CONCLUSIONS

A set of selected distillates originating from the same raw crude oil were investigated experimentally using a specific testing protocol – the "pretreatment - challenge". The testing protocol evaluated the distillates corrosivity and their capability of forming protective scales against the NAP corrosive attack.

The experimental data indicated that the distillates corrosivity could not be correlated with their natural sulfur and NAP content. The total sulfur content of the distillates was only partially related to the H_2S concentrations measured in the autoclave headspace at the end of the "pretreatment". It was found that the H2S concentration could not be correlated with the fractions corrosivity.

All distillates formed on CS and 5Cr scales that consisted mainly of iron sulfide and some iron and chromium oxides. The protection offered by these scales to the metal samples against NAP attack was different from fraction to fraction for each type of steel. The scales were not protective for CS samples and in case of the 5Cr samples only the distillates with less than 2% total sulfur content offered some limited protection against the NAP challenges.

The SEM/EDS analysis showed that all scales formed during "pretreatment" were made of multiple successive layers and consisted mainly of iron sulfide with some traces of iron oxide and chromium oxide. The oxygen layer presence that suggests the formation of metal oxides was detected in scales formed on both CS and 5Cr samples, in "pretreatment" tests of distillates with less that 2% total sulfur content.

The evaluation of the snapshot distillates showed that in spite of the fact that all fractions were obtained from same raw crude oil, they behaved differently under identical test conditions that were selected as close as possible to field operation conditions.

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