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Sulfur/TAN Ratio Effect on Iron Sulfide (FeS) Scale Properties Challenged in Continuous Oil Flow

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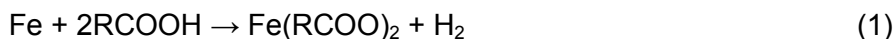Athens, OH 45701
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ABSTRACT

Naphthenic (NAP) acids and sulfur compounds are important corrosive species contained in low quality crudes and can cause significant equipment damage when such crudes are processed. Although the two corrosive species have a synergistic effect at high temperatures their corrosion products can influence the extent of the damage. Thus the iron sulfide (FeS) scales formed as sulfur reacts with iron can hinder the NAP acid diffusion to the metal limiting their corrosive effect. The FeS scale properties are influenced by different factors such as the types of sulfur compounds in oil (sulfides, disulfides, mercaptans, thiophenes), NAP acid interactions, temperature, flow conditions - all factors that are difficult to control. This experimental work intended to evaluate the properties of FeS scales formed from model sulfur compounds (sulfides and mercaptans) in interaction with NAP acids using the "pretreatment – challenge" test protocol. According to this protocol FeS scales were formed on metal samples from mercaptans/mercaptans and sulfides on different ratios/concentrations in the presence of NAP acids at high temperature. Further, preformed scales were exposed to a constant NAP acid attack under high temperature and continuous flow conditions. Samples metal losses and scale SEM/EDS analysis were used to characterize the protective properties of FeS scales.

Keywords: sulfur, naphthenic acid, Total Acid Number (TAN), corrosion, model compounds, high temperature

INTRODUCTION

Highly corrosive effects at high temperature of some heavy crude oils are the result of complex interactions between naphthenic (NAP) acid and sulfur (S) compounds they contain.[1,2] The mechanism of NAP acid and sulfidic corrosion is not well understood but it is generally accepted by refinery engineers and scientists that it is described by three chemical reactions. [3]

In Reaction 1 NAP acids react with the iron forming the iron naphthenates that are oil soluble and as a consequence they are constantly removed from the metal by the oil flow. The S compounds thermally decompose forming hydrogen sulfide (H_2S) that reacts almost instantly with the iron forming iron sulfide (FeS), a solid corrosion product which builds up on metal surfaces as multilayered scales (Reaction 2). The corrosion byproducts iron naphthenates and H_2S react with each other rebuilding the NAP acids and forming more solid FeS (Reaction 3).

$$Fe + 2RCOOH \rightarrow Fe(RCOO)_2 + H_2 \qquad (1)$$

$$Fe + H_2S \rightarrow FeS + H_2 \qquad (2)$$

$$Fe(RCOO)_2 + H_2S \leftrightharpoons FeS + 2RCOOH \qquad (3)$$

All these reactions occur in distilling towers at temperatures between 220 and 400ºC with NAP acid corrosion reaching its highest intensity around 340ºC. Sulfidic corrosion also occurring in the same temperature range has its highest effect maximum at 425ºC and it is mainly caused by the interaction of H_2S with the metal. As H_2S is generated in thermal decomposition of S species in oil, such as sulfides, disulfides, and mercaptans, different studies focused on investigating the corrosive effects of each of these species in order to generate better predictions for crude corrosivity. [4-8] The experimental results of sulfidic corrosion studies have practical applications for oil refineries in setting the guidelines for oil blending and reducing their corrosive effects.

The current study investigated the corrosive effect of sulfur components (mercaptans and sulfides) and NAP acids under different mixing ratios. As the NAP acid concentration is expressed by the Total Acid Number (TAN) and sulfur in oil is measured as weight percent, several S/TAN ratios were selected for these experiments. The goal of this work was to understand better how different S/TAN ratios can influence the oil corrosivity and the ability of these model oils to form protective scales against the acidic attack. Therefore the experiments were carried out using a specific testing protocol - the "pretreatment-challenge" designed to evaluate the protective properties of scales formed in crude fractions or in model oils that mimic such fractions. The following sections will describe and discuss the experimental method and the results generated in the S/TAN ratio experiments.

EXPERIMENTAL

Experimental Procedure

The "pretreatment-challenge" testing protocol was designed as a screening tool to evaluate the crude oils corrosivity by assessing the protective properties of scales such crudes generate at high temperatures.[9] The protocol consists of two distinct phases performed in different experimental equipment. Thus the scales are formed on metal samples, from crude fractions, at high temperature, in a static autoclave, during the "pretreatment" phase. Following the "pretreatment" is the "challenge" phase when the scales formed on samples are exposed to model oil spiked with NAP acids, under high temperature and high velocity conditions. At the end of the two phases the oil corrosivity and scale protectiveness are evaluated by measuring the corrosion rates of samples submitted to this testing protocol.

Two sets of tests were performed using the same S/TAN ratios and same testing protocol. One set of tests used for sample "pretreatment" solutions were prepared from n-octadecyl mercaptan (C18-SH), commercial NAP acids and mineral white oil as solvent. In the second set of tests dodecyl sulfide (DDS) and n-octadecyl mercaptan (C18-SH) were dissolved with the same NAP acids in mineral oil and used in "pretreatment".

The concentration values for sulfur and NAP acids in the S/TAN ratio experiments were selected based on experimental results generated in previous experimental work and on field experience. Thus it was decided that the TAN should be the constant and the total sulfur content should be the variable. However in real crude oils not all sulfur species are reactive. Therefore the sulfur concentrations were calculated based on the oil refinery "rule of thumb" that only one third of total sulfur content in oil is considered as the reactive corrosive sulfur species. Based on the above considerations for the constant TAN value of 1.75, in S/TAN ratio 1:1 the sulfur content was 0.58 wt%. The S/TAN ratio was selected as reference and it was used to calculate the sulfur content for all other ratios and is presented in Table 1.

In experiments that used both mercaptan (CH18-SH) and sulfide (DDS) for "pretreatment" the sulfur content was 20% mercaptan and 80% sulfide.

Table 1
S/TAN ratios selected for "pretreatment" with mercaptans and sulfides.

	S/TAN Ratio	Sulfur content (wt.%)	TAN (mg KOH / g oil)
1	**0.33 : 1**	0.19	1.75
2	**1 : 1**	**0.58**	1.75
3	**2 : 1**	1.17	1.75
4	**3 : 1**	1.75	1.75
5	**4 : 1**	2.23	1.75

Experimental Materials

The experimental solutions for the S/TAN ratio "pretreatment" were prepared by dissolving n-octadecyl mercaptan, 96% purity (C18-SH), dodecyl sulfide, 96% purity (DDS) and commercial naphthenic acids in paraffinic white oil. Solutions used in "challenge" tests were prepared using the same naphthenic acids and paraffinic white oil. All "challenge" solutions had the same TAN = 3.5.

Metal samples with ring geometry OD = 81.75 mm were made of UNS K03006 carbon steel (CS) and of UNS K41545 alloy steel (5Cr). Six rings were used in every "pretreatment-challenge" experiment (3 rings of each steel type). The rings were polished before the tests with silicon carbide (SiC) paper of 400 and 600 grit, under isopropanol flush. After polishing, the rings were rinsed with acetone, dried under a nitrogen flush and weighed on an analytical balance. The geometric dimensions of each ring were measured with a caliper and recorded. When the tests were completed the samples were removed from the experimental apparatus and processed for corrosion rates evaluation. Samples were rinsed with organic solvents (toluene and acetone) then the scales formed on the samples were removed mechanically (brushing, wiping) and chemically (Clarke solution).[10] At the end of the clarking procedure the samples final weight was measured, recorded, and used in corrosion rate calculations.

Experimental Equipment

"Pretreatment" phase was carried out in a static 1L autoclave with a magnetic stirrer that could be operated at temperatures up to 370ºC. A schematic representation of the autoclave and of the samples arrangement for the "pretreatment" is shown in Figure 1. The scales formed on samples during "pretreatment" were "challenged" with NAP acids (TAN 3.5) in a "flow through"

apparatus – the "High Velocity Rig" (HVR) – that was specially designed to reproduce shear stress and velocity conditions from transfer lines. Figure 2 shows a schematic representation of the HVR loop. The loop includes a rotating cylinder autoclave where samples are spun at 2000 rpm which corresponds to a peripheral velocity of 8.5 m/s at the samples outer surface. The HVR autoclave can be operated at pressures from 0 to 3.4 MPa and temperatures up to 370ºC. The HVR metering pump provides a constant fluid flow of fresh feed in a range from 5 to 20 cm^3/min. All testing fluids were purged with nitrogen prior to testing. All autoclave "pretreatment" and HVR "challenge" tests had identical durations of 24 h. The experimental conditions of "pretreatment" and "challenge" tests are summarized in Table 2.
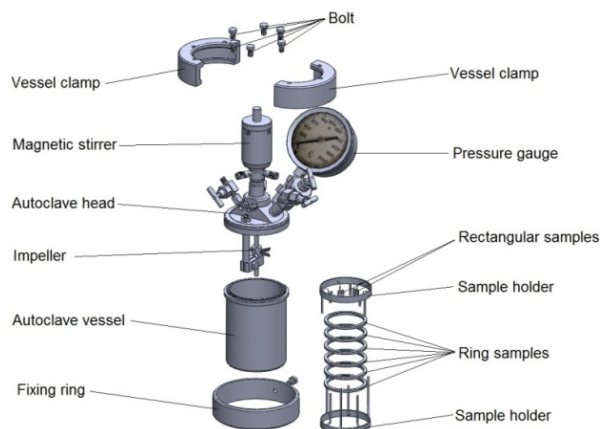

Figure 1: Static autoclave. Main components and samples set-up for the "pretreatment" experimental phase.
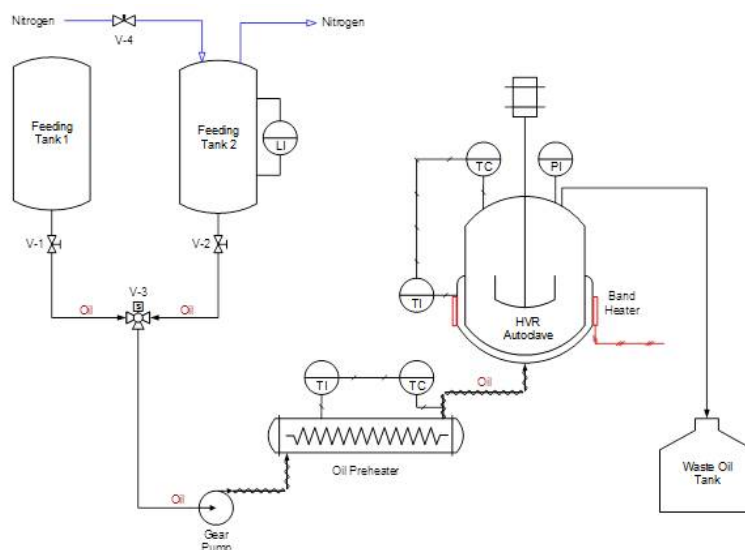

Figure 2: Schematic representation of the High Velocity Rig (HVR), the "flow through" loop used in "challenge" phase.

Table 2
Experimental conditions in static autoclave and in the HVR during the "pretreatment-challenge" experiments.

Test Phase	TAN (mg KOH / g oil)	Sulfur content (wt %)	Temp. (ºC)	Time (h)	Pressure (MPa)	Peripher. velocity (m/s)	Rotation (rpm)
Pretreatment	1.75	0.19 – 2.23	343	24	Autogenous generated	0	0
Challenge	3.5	0	343	24	1.034	8.5	2000

Scales formed on the samples were examined and analyzed using a scanning electron microscope (SEM) coupled with an energy dispersive X-ray spectrometer (EDS).

Hydrogen Sulfide Measurements

Both mercaptan and sulfide thermally decompose during "pretreatment" at high temperature generating hydrogen sulfide (H_2S) that reacts with iron or with the iron naphthenates (Reactions 2 and 3). Not all the generated H_2S will participate in these two reactions but will dissolve in the oil or accumulates in the autoclave headspace during pretreatment tests. The concentrations of H_2S that was found in the autoclave headspace at the end of the "pretreatment" tests were measured using a specialized micro gas-chromatograph. The H_2S samples were collected from autoclaves in special sampling bags.

Experimental Calculations

Sample corrosion rates were calculated based on their weight loss during the tests. The weight loss generated by NAP acid and sulfidic corrosion is expressed as the difference between sample weights before the test (initial weight) and after the test (final weight) and it is calculated using 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]

Equation 1 considers the initial weight of the fresh polished samples at the beginning of the test. However, the samples according to the testing protocol are exposed to NAP and sulfidic corrosion during the "pretreatment" and then to the NAP acid attack during the "challenge". In order to evaluate the scale protective properties against the NAP acid attack a separation must be made between the samples metal losses during each of the two distinct experimental phases. Thus separate "pretreatment" reference tests were done and the samples

corresponding metal loss was evaluated. This "pretreatment" reference metal loss was subtracted from samples weight before any experimental phase and this new value was used in Equation 1 to calculate the corrosion rate produced by NAP acids during the "challenge". In this way it became possible to separate the NAP acid corrosive effect during the "challenge" from the corrosive effect of species used in "pretreatment".

Iron sulfide formed in the direct reaction of H_2S with the iron (Reaction 2) or with the iron naphthenates (Reaction 3) built up as multilayered scales on the metal surfaces. It was assumed that the FeS scales were homogenous and uniformly covered the samples. Based on these assumptions a theoretical scale thickness was calculated using Equation 2.

$$\delta_A = \frac{(W_{Rub} - FW)}{\rho_{FeS} \cdot A_T} \cdot 10^6$$

(2)

where:

δ_A – adherent scale thickness [µm]
W_{Rub} – rub weight [kg]
FW – final weight (after last clarking) [kg]
ρ_{FeS} – iron sulfide density [kg/m^3]
A_T – sample total area exposed to corrosive fluids [m^2]

Equation 2 evaluates the thickness only for the scale that was removed during the clarking procedure as this scale was resilient and resisted the mechanical removal procedure. It is considered that this strongly adherent scale has protective properties compared to the fragile layer of scale that was easily removed by mechanical means (wiping, brushing) during sample processing after the tests.

RESULTS AND DISCUSSION

Corrosion rates were plotted separately for "pretreatment" and for "challenge" tests. The "pretreatment" corrosion rates plotted in Figure 3 compares the effect of the two different testing solutions on CS samples (a) and on 5Cr samples (b). In "pretreatment" tests the two different test solutions (mercaptan vs. mercaptan and sulfide) had no effect on CS corrosion rates (Figure 3 (a)). It was the S/TAN ratio that influenced the CS corrosion rates. As the sulfur ratio increased from 0.33 to 2 the corrosion rates also increased. Beyond a S/TAN ratio of 2:1 increasing the "pretreatment" sulfur content generated a slight decrease in samples corrosion rate. A similar correlation between samples corrosion rates and sulfur content increase was noticed in the case of 5Cr (Figure 3 (b)). For 5Cr samples the corrosion rates were highest in the "pretreatment" with mercaptans and sulfide at S/TAN of 3:1. All other 5Cr corrosion rates showed similar trends to the CS samples.

"Challenge" phase data are plotted in Figure 4 (a) for CS and (b) for 5Cr samples. These "challenge" corrosion rates exclude the metal loss that occurs in the "pretreatment" phase. The plots of Figure 5 include CS and 5Cr "pure TAN 3.5 corrosion" rates. These specific corrosion rates were measured in separate TAN 3.5 "challenge" tests done in the HVR on CS and 5Cr samples that were not exposed to any "pretreatment" prior to the test (bare samples). The "pure TAN 3.5 corrosion" rates are used as reference in evaluating the scales protective properties or the lack thereof.

"Challenge" corrosion rates for CS plotted in Figure 4 (a) indicate that scales formed in "pretreatment" with mercaptan and sulfide, which offered some limited protection up to S/TAN

ratio of 2:1 at which point the scale protectiveness degraded for higher ratios. The "pretreatment" with mercaptan solutions also formed protective scales on CS up to the S/TAN ratio of 4:1 when scales failed completely in protecting the CS samples against the TAN 3.5 "challenge". In the case of 5Cr samples the "challenge" data indicates that only scales formed with sulfide and mercaptan at S/TAN ratio of 1:1 were protective for these samples. All other scales formed in these S/TAN ratio tests failed in protecting the 5Cr samples. Further, in the case of 5Cr, the samples "pretreated" in high S/TAN ratio solutions were damaged more in the TAN 3.5 challenges.
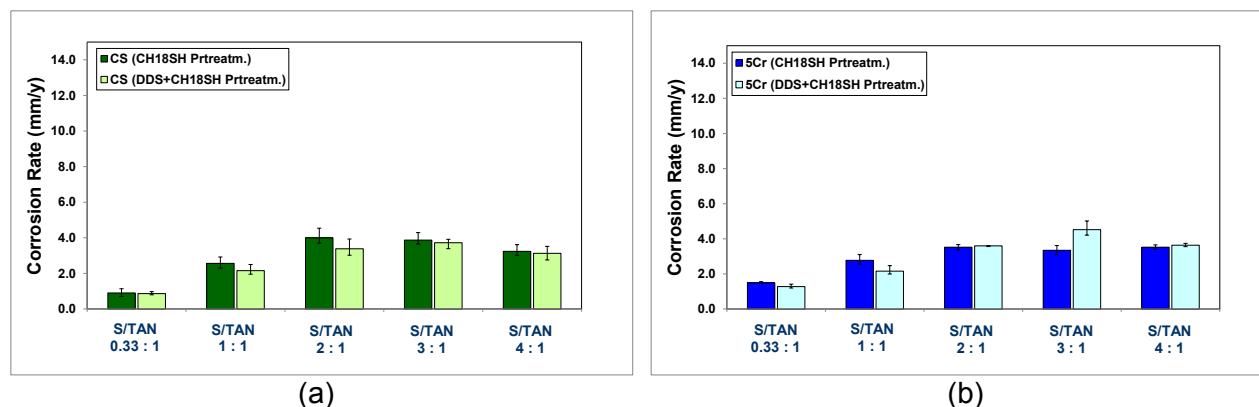

(a)   (b)

Figure 3: "Pretreatment" Corrosion Rates. Comparison of CS (a) and 5Cr (b) corrosion rates measured in "pretreatment" S/TAN ratio tests done with "CH18-SH & NAP" or with "CH18-SH, DDS & NAP" solutions on different S/TAN ratios.

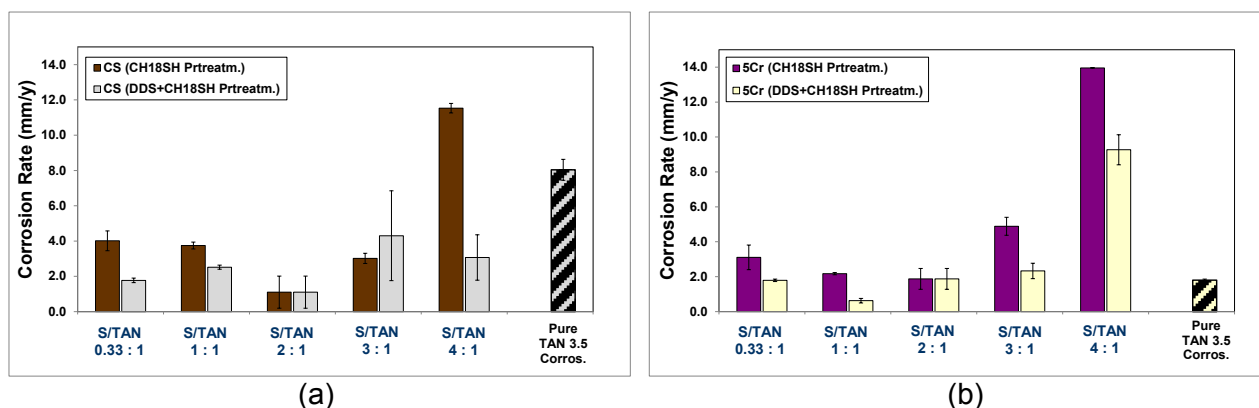(a)   (b)

Figure 4: "Challenge" Corrosion Rates. Comparison of CS (a) and 5Cr (b) corrosion rates "challenged" with NAP acids (TAN 3.5). CS and 5Cr samples were "pretreated" with "CH18-SH & NAP" or with "CH18-SH, DDS & NAP" solutions on different S/TAN ratios.

All corrosion data presented here suggests that in autoclave experiments the S/TAN ratio solutions were corrosive up to a 2:1 or 3:1 ratio and then the higher sulfur content was decreasing the corrosivity or did not change it for both types of samples. As FeS scales were formed in all "pretreatment" tests, it was sought to find any possible correlations between scale thickness and corrosion rates of samples they covered. In Figure 5 (a) CS and 5Cr corrosion rates and scale thickness are compared for "pretreatment" tests performed with mercaptan and NAP acids. The plotted data of this figure shows that as sulfur content increased over the 2:1 ratio, the samples corrosion rate and their corresponding scale thicknesses decreased, a trend that suggests a decline of corrosive processes. A similar evolution of corrosion rates and scale

thickness is shown in Figure 5 (b) which summarizes the experimental data in "pretreatment" tests done with mercaptan, sulfide, and NAP acid solutions. In the case of Figure 5 (b), the inflection point for the decline of corrosive processes is the S/TAN ratio of 3:1.

The comparison of CS and 5Cr corrosion rates and scale thicknesses for the "challenge" tests are presented in Figure 6 (a) and (b). All scales formed in mercaptan and NAP acids had similar low thicknesses after they were "challenged" with TAN 3.5 in the HVR (Figure 6 (a)). However, scale thicknesses compared to their corresponding sample corrosion rates suggest that there were differences in protective properties and these differences were caused by scale structure and chemical composition. The comparisons of "challenged" corrosion rates and scales formed with mercaptan, sulfides, and NAP acids are shown in Figure 6 (b). In the case of the scale formed with mercaptan and NAP acids and later "challenged" there was no obvious correlation between thickness of scales formed with mercaptan, sulfide, and NAP acid that survived the "challenge" and the corrosion rates of samples measured in these tests. "Challenged" scales were not protective and had similar, comparable, and low thicknesses regardless of the S/TAN ratio when they formed.
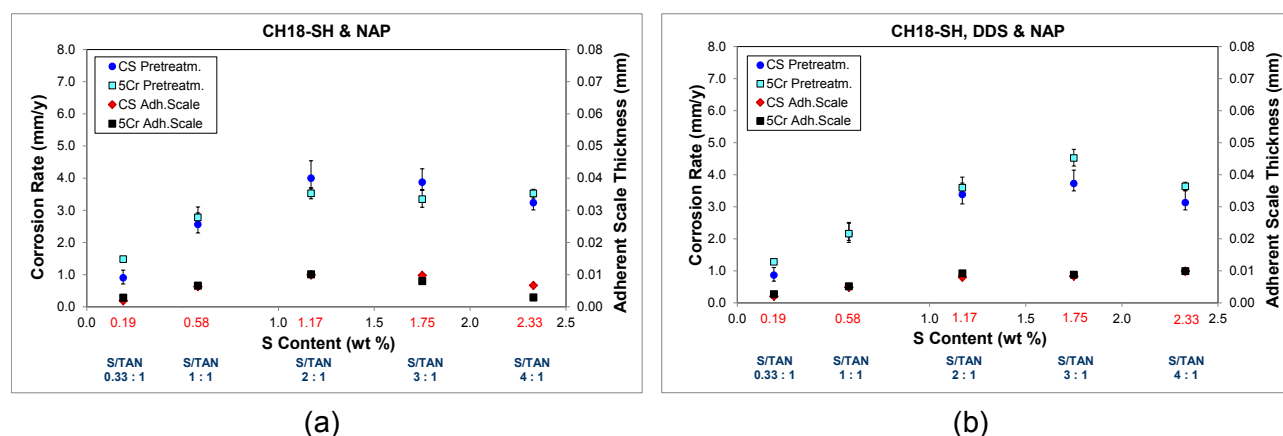

(a)

(b)

Figure 5: CS & 5Cr Corrosion rates vs. scale thicknesses in "pretreatment" tests - samples "pretreated" with "CH18-SH & NAP" (a) and samples "pretreated" with "CH18-SH, DDS & NAP" (b) solutions.
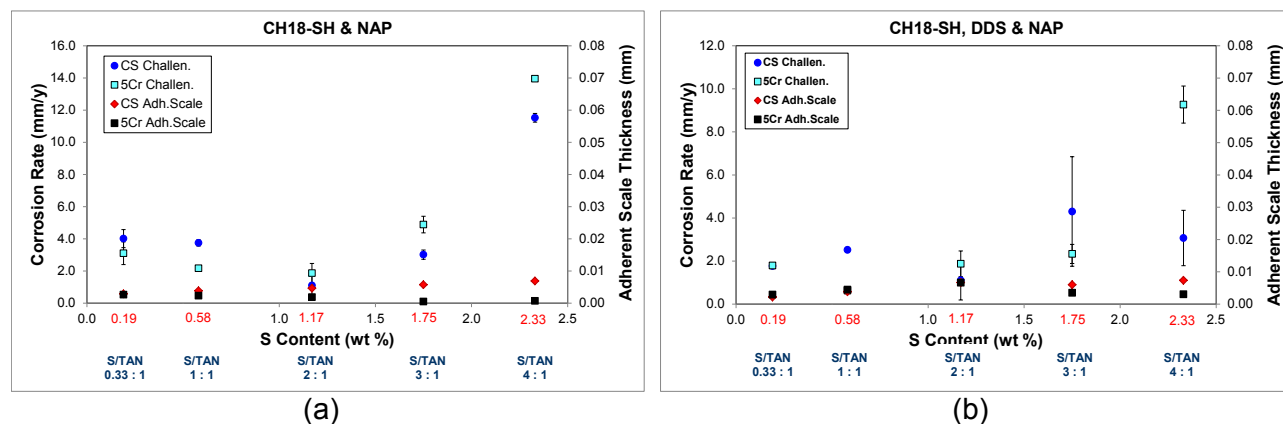

(a)

(b)

Figure 6: CS & 5Cr Corrosion rates vs. scale thicknesses in "challenge" tests – before the TAN 3.5 "challenge" samples were "pretreated" with "CH18-SH & NAP" (a) or with "CH18-SH, DDS & NAP" (b) solutions.

H$_2$S concentration in the autoclave headspace was measured for every "pretreatment" test. The gas samples were collected at the end of the 24 h test and then measured with a micro gas-chromatograph. Before collecting the gas samples the autoclave pressure was recorded. All H$_2$S concentrations and the autoclave pressure before sample collections are summarized in Table 3. The H$_2$S data plotted in Figure 7 show that gas concentrations in the autoclave increased as the sulfur content of the "pretreatment" solution increased. More H$_2$S was generated in "pretreatments" done with mercaptan, sulfide, and NAP acid solutions than in the tests with mercaptan and acid. It can be assumed that the high H$_2$S concentrations for high S/TAN ratios (3:1 and 4:1) would suggest highly corrosive solutions. However, contrary to this assumption corrosion rates of CS and 5Cr measured in these tests were lower which suggests that the scale formed on samples protected them from corrosive H$_2$S generated in excess.

Table 3
H$_2$S concentrations measured at the end of the autoclave "pretreatment" tests.

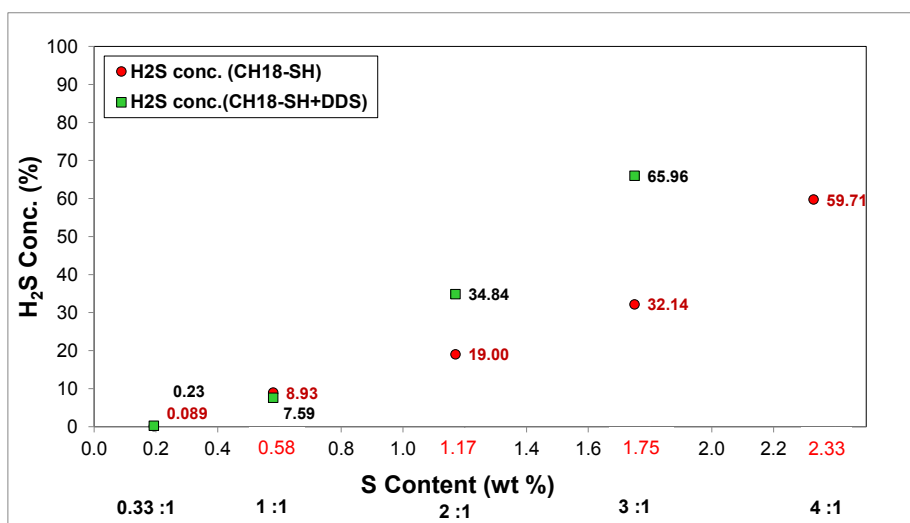|	S/TAN Ratio	Sulfur content (wt.%)	TAN (mg KOH / g oil)	CH18-SH & NAP		CH18-SH, DDS & NAP	
				H$_2$S conc. (v %)	Pressure (MPa)	H$_2$S conc. (v %)	Pressure (MPa)
1	0.33 : 1	0.19	1.75	0.089	2.758	0.23	2.068
2	1 : 1	0.58	1.75	8.93	3.309	7.59	3.309
3	2 : 1	1.17	1.75	19.00	3.585	34.84	3.998
4	3 : 1	1.75	1.75	32.14	3.998	65.96	3.998
5	4 : 1	2.23	1.75	59.71	3.998	-	4.412

Figure 7: H$_2$S concentrations as a function of S/TAN ratio. The H$_2$S concentrations were measured at the end of the autoclave "pretreatment" tests done with "CH18-SH and NAP" and with "CH18-SH, DDS, and NAP" solutions, respectively.
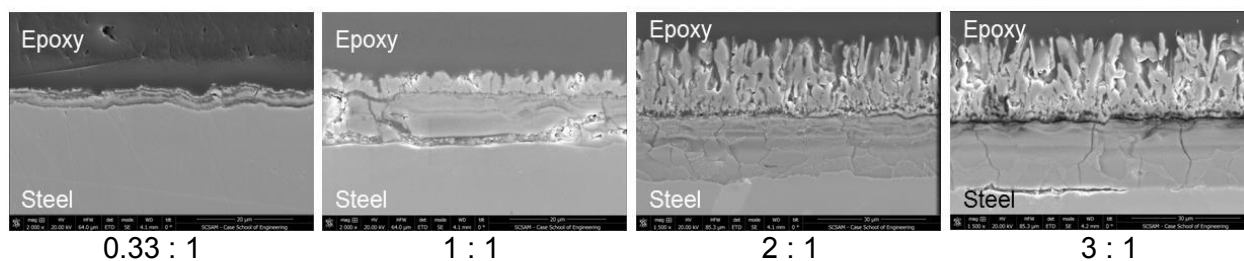
SEM Scale Analysis

All calculated data for the scales formed in S/TAN ratio experiments showed that scale thickness cannot be correlated with corrosion rates of the samples on which these scales were formed using different "pretreatment" solutions. The explanation for differences in scale protective properties can be suggested by the SEM cross-section images of these scales embedded in epoxy resin.

The SEM images of scales formed on CS with mercaptan and NAP acid or with mercaptan, sulfide and NAP acid indicate that all scales consisted of multiple layers of different structures (Figure 8). For both "pretreatment" solutions, the inner layers are compact with a homogenous structure but fragmented by fine cracks. The top layers consist of large FeS crystals that become longer as the S/TAN ratio of the "pretreatment" solution increases. In the case of "pretreatment" with mercaptan and sulfide at S/TAN ratio of 3:1 the top layer is missing and only a few large crystals were found on the compact inner layer (Figure 8, bottom right image).

Figure 9 shows the SEM images of multilayered scales formed on 5Cr samples in "pretreatment" with mercaptan and NAP acids and with mercaptan, sulfides, and NAP acid. As in the case of CS samples the scale that mercaptan or mercaptan and sulfide formed on 5Cr increased as the S/TAN ratio increased too. Scale inner layers were compact and homogenous but fragmented by multiple cracks. The SEM images of scales formed with mercaptan and NAP acid show delaminated top layers of thin FeS. The delamination suggests that top layers were loose and could be easily removed during "challenges". Scales formed with mercaptan, sulfide, and NAP acid on 5Cr were very similar to those formed with mercaptan only.

For the SEM analysis of the "challenged" scales formed in S/TAN ratio experiments only two examples were selected; the scales formed on 5Cr at 1:1 and 3:1 ratios with each of the two solutions. At S/TAN ratio of 1:1 the mercaptan and sulfide formed the most protective scale on 5Cr in this test series but failed in generating a scale of similar quality at S/TAN ratio of 3:1 as corresponding corrosion rates indicate in Figure 4 (b). The SEM images of 5Cr samples of Figure 10 (a) show a very thick multilayered scale for the 1:1 ratio that survived the TAN 3.5 "challenge" and protected the metal. However, the scale formed at a 3:1 ratio fragmented and partially removed from the metal as shown in Figure 10 (b). The scales formed with mercaptan and NAP acid on 5Cr and then "challenged" with TAN 3.5 are shown in the SEM images (c) 1:1 ratio and (d) 3:1 ratio (Figure 10). Both scales appear to be very fragmented with voids in their structure which explains the high corrosion rates measured in these tests.

CH18-SH & NAP

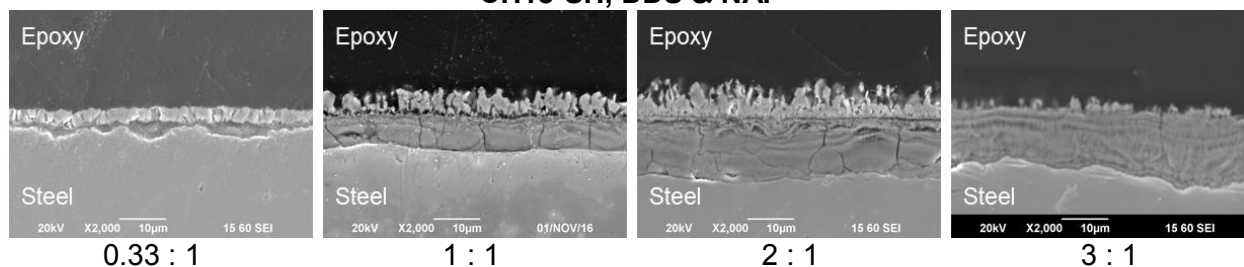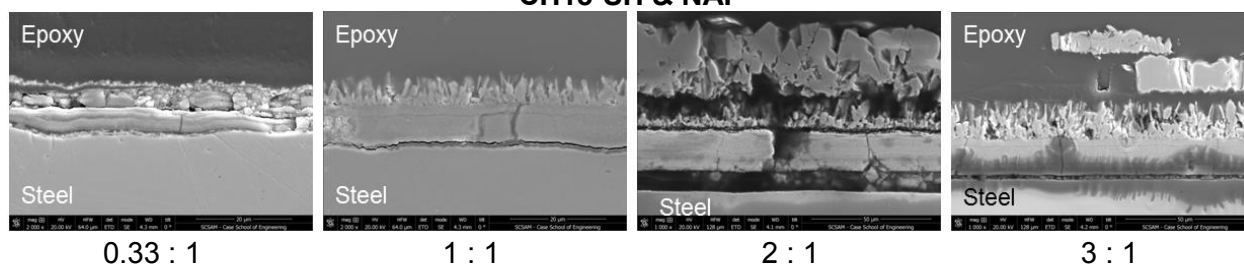|			
0.33 : 1	1 : 1	2 : 1	3 : 1

CH18-SH, DDS & NAP

0.33 : 1	1 : 1	2 : 1	3 : 1

Figure 8: SEM cross-section images of "pretreatment" scales formed on CS samples on different S/TAN ratios.

CH18-SH & NAP

0.33 : 1	1 : 1	2 : 1	3 : 1

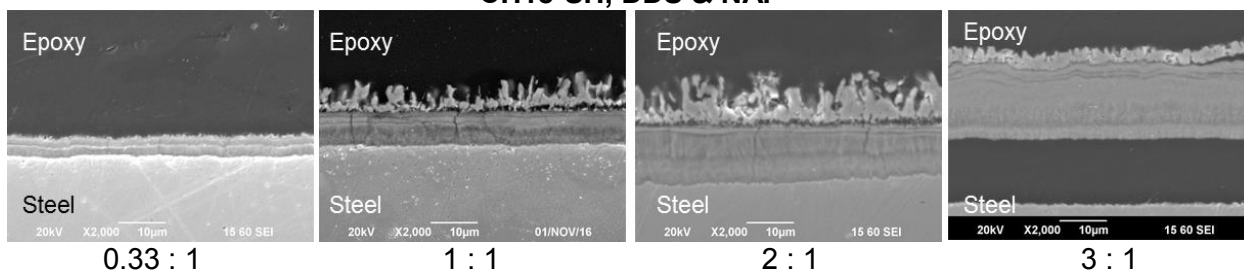**CH18-SH, DDS & NAP**

0.33 : 1	1 : 1	2 : 1	3 : 1

Figure 9: SEM cross-section images of scales formed on 5Cr samples in "pretreatment" tests with different S/TAN ratios.

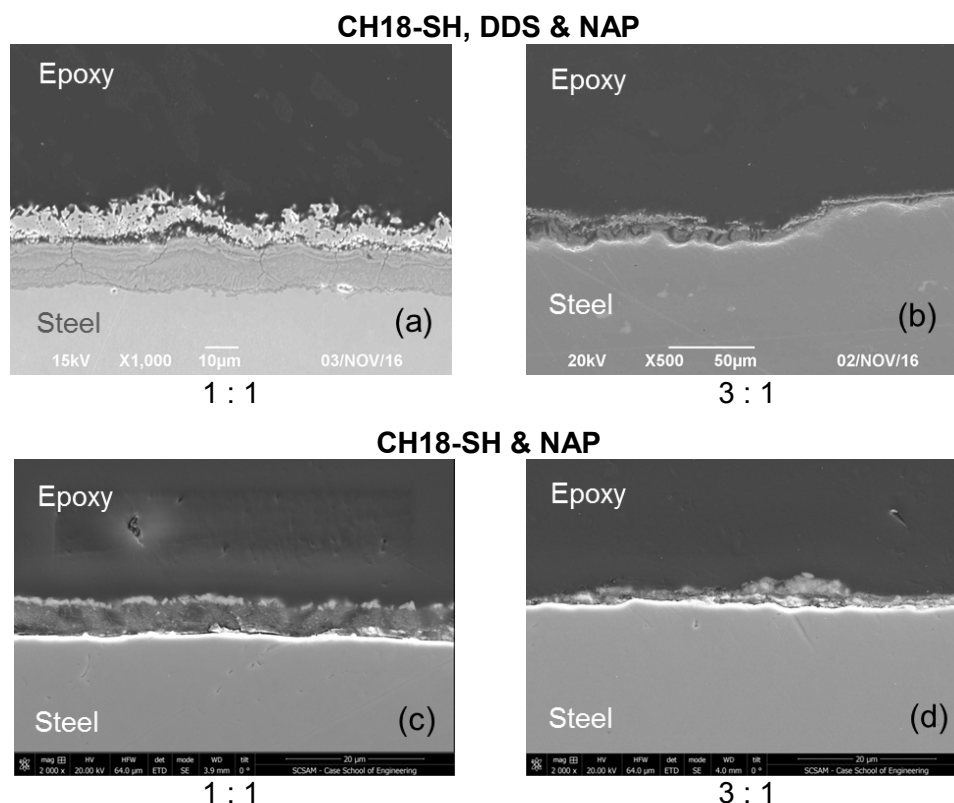**CH18-SH, DDS & NAP**

CH18-SH & NAP

Figure 10: SEM cross-sections images of scales on 5Cr samples after the TAN 3.5 challenge. Scales were formed at S/TAN ratios of 1:1 and 3:1 with mercaptan, sulfide, and NAP acids (a & b) and with mercaptan and NAP acid (c & d).

CONCLUSIONS

- Properties of scales formed in mercaptan and NAP acids or in mercaptan, sulfide, and NAP acids were evaluated using the "pretreatment-challenge" testing protocol. The scales were formed on steel samples during the "pretreatment", from the sulfur compounds and NAP acids mixed at different S/TAN ratios and then, in the "challenge" the scales were exposed to a continuous NAP acid attack (TAN 3.5) to test the protective properties of these scales.

- Both types of sulfur and NAP acid solutions had similar effects in "pretreatment" tests. As the S/TAN ratios increased (0.33:1 to 3:1) sample corrosion rates and scale thicknesses increased too. Beyond a S/TAN ratio of 3:1 there was a decline in corrosion rates and scale thickness suggesting a reduction in corrosive processes.

- "Challenge" data indicated that only the scales formed in sulfide, mercaptan, and NAP acids were able to offer a limited protection to CS samples but no protection for 5Cr. All other scales were not protective on the two steel type samples. "Challenge" data analysis suggests that CS and 5Cr corrosion rates have parabolic evolution as a function of the S/TAN ratio used in "pretreatment". High corrosion rates at 0.33:1 ratio decrease towards 2:1 ratio and then sharply increase at 3:1 and 4:1 ratios. This trend of CS and

5Cr corrosion rates might suggest that scales formed at high S/TAN ratios "trap" more acid during the "challenge" that damage the metal.

- The SEM images collected on cross-sections of the scales formed in "pretreatment" indicate that scale thickness increases with the sulfur content in solution, become very thick at high ratios (3:1 and 4:1) and have a very fragmented and porous structure. Similar SEM images of "challenged" samples indicate the extent of the NAP acid attack against the metal and the thin fragmented scale that "survived" on the sample surfaces.
- Hydrogen sulfide generation increased as the sulfur content became higher in the "pretreatment" solutions but the H_2S levels could not be correlated with solution corrosivity.
- Although the S/TAN ratio experiments using model compounds were carried out at sulfur and TAN contents much higher than the ones used in refinery practice, they provide good information on the influence of mercaptans, sulfides, and naphthenic acids on iron sulfide scale properties formed under these testing conditions.

ACKNOWLEDGEMENTS

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