

NAPHTHENIC ACID CORROSION OF MILD STEEL IN THE PRESENCE OF SULFIDE SCALES FORMED IN CRUDE OIL FRACTIONS AT HIGH TEMPERATURE

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ABSTRACT

Increasing demand on the oil market has raised interest in oils with high naphthenic acid (NAP) concentration. These oils were previously considered of lower quality due to their corrosive character. Processing such oils at elevated temperatures encountered in refineries (300-350°C) may cause aggressive corrosive attack on the inside walls of equipment such as pipes and distillation towers. Naphthenic acid corrosion attack is a non-aqueous corrosion process and can be retarded by sulfur containing compounds inherently present in crude oil fractions in the form of soluble sulfides. Although these sulfides can be corrosive as well, they can also form iron sulfide scale on the metal surfaces potentially offering a degree of protection against naphthenic acid attack. However the iron sulfide scales can be removed from metal surfaces under the combined effects of high velocity flow and NAP attack. This research project has focused on the role of iron sulfide scales formed in different crude oil fractions on samples made from mild as well as chromium containing steels. They were exposed to naphthenic acid attack under high flow rates at high temperature.

Keywords: naphthenic acid, corrosion, sulfide scales, high temperature, crude oil fractions.

INTRODUCTION

Oil production, transportation and its processing in refineries raises a multitude of challenges for the industry, and all of them can be expressed in terms of economic costs and benefits. One option to reduce costs is to process the so called “opportunity crudes” also referred to as “lower quality” corrosive crudes with high naphthenic acid and sulfur content. However, in spite of the fact that these acidic crudes are less expensive, their processing in refineries raises a concern about the potential corrosion problems. Thus, refinery engineers have to adopt special strategy for mitigating acidic crude oil corrosivity effects by modifying the refinery unit’s design and procedures and by opting for better materials for the critical components. In order to make these kinds of decisions with more confidence it is important to better our understanding of the mechanism of naphthenic acid corrosion and its interaction with sulfidic corrosion.

This study starts from the hypothesis that sulfur containing compounds can mitigate naphthenic acid corrosion by building iron sulfide scales on metal surfaces. However the iron sulfide scale protective effect is limited under combined effect of strong acidic attack and high velocity conditions. Therefore, the study focuses on finding the limits where iron sulfide scales formed by crude oil fractions are protective against naphthenic acid attack under high temperature and velocity conditions.

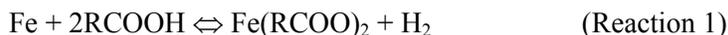
LITERATURE REVIEW

Processing acidic crudes in refineries was always associated with high corrosion rates especially in atmospheric and vacuum distillation columns, side strippers, furnaces, piping, and overhead systems¹. Naphthenic acid corrosion products also produce fouling in heat-exchangers, atmospheric and vacuum units and poison the catalytic conversion units causing their breakdown¹.

Among the most typical corrosive agents in oil, naphthenic acids prove to be one of the most aggressive and as a consequence numerous studies focused on investigating their corrosive effects. W.A. Derungs wrote one of the first papers about naphthenic acid corrosion in 1956 and mentioned that it was difficult to differentiate between naphthenic acid and sulfide corrosion which were both aggressive at elevated temperatures. He considered that the most important factors influencing naphthenic acid corrosion are: the acid concentration in oil, high temperatures and high velocities². Later J. Gutzeit did the first laboratory tests on corrosion kinetics of naphthenic acids corrosion and correlated them to refinery corrosion data. He made the observation that naphthenic acid corrosion process occurred only in liquid phase and that pressure had little influence³.

In 1987 R.L. Piehl wrote in his paper that FeS scales formed in distilling towers and heat exchangers had a protective role against naphthenic acid corrosive attacks. He suggested that that there was a competition between the sulfidic and naphthenic acid corrosion processes and variations in corrosion rates were dependent on sulfur and NAP acids concentrations in processed crudes⁴.

Combined corrosive effects of naphthenic acids and sulfur containing compounds were summarized in the following chemical reactions⁵⁻⁷:



In Reaction (1) iron naphthenates are formed as products of direct reaction between naphthenic acids and the steel and, being oil soluble, they are entrained by the fluid flow. At the same time hydrogen sulfide (or some other soluble sulfide containing species) reacts with the metal (Reaction 2) forming solid iron sulfide which is deposited on the metal surface. Hydrogen sulfide can react with iron naphthenates (Reaction 3) to form iron sulfide scale and regenerate the naphthenic acids.

According to most of the authors in the literature, these three reactions represent the accepted scenario of NAP corrosion mechanism in sulfur containing crudes. However naphthenic acid corrosion processes are more complicated and are affected by many other factors: *i.e.* temperature, velocity, acid and sulfur content in the oil, pressure, etc. Further text will briefly describe the most important factors influencing naphthenic acid corrosion as they are presented in the open literature.

The Effect of Naphthenic Acid Concentration

Naphthenic acid concentration is frequently expressed by the total acid number (TAN) which represent the number of milligrams of KOH used to neutralize the acid present in one gram of oil. TAN is measured either

using a colorimetric procedure (ASTM⁽¹⁾ D 974) or a potentiometric method (ASTM D 664)^{4,7}. Although it is the most used method in refineries, the latter method is less accurate because it measures not only the organic acids but also the acidity generated by other compounds contained in the oil (*i.e.* H₂S, CO₂, MgCl₂, and CaCl₂)^{4,6}. According to the current literature, measured TAN values using the potentiometric method may be up to 80% higher than values obtained using the colorimetric method for the same oil⁴.

In spite of these inconsistencies, TAN is still used to characterize crude oil acidity and estimate its corrosive potential. Thus crude oils with TAN values higher than 0.5 are considered corrosive when processed in atmospheric distilling towers, whereas in vacuum distilling towers crude oils are believed to be corrosive if their TAN value is between 1.5 and 2^{4,7}.

Effect of Sulfur Containing Compounds

Although not all sulfur compounds are equally corrosive (nor protective) it was widely accepted for practical reasons to classify crude oils according to their total sulfur content. Thus oils with less than 1 wt% sulfur content generally known as “sweet crudes” are of good quality whereas the so called “sour crudes” containing more than 0.5 wt% sulfur are deemed to be of lower quality and represent the main cause of sulfidic corrosion in refineries^{6,8,9}. Many crude oils contains some amount of H₂S which is highly corrosive but also generates insoluble iron sulfide as a protective corrosion product^{3,5,10,11}. On the other hand the combined effect of naphthenic acids and high flow velocities can lead to damage of the iron sulfide scale, thereby increasing the corrosion rate by leaving the steel surface exposed to direct acidic attack^{11,12}.

Effect of Temperature

Naphthenic acids become corrosive around 220°C (430°F) and reach their highest activity at 350°C (662°F). Over 400°C (750°F) no evidence of NAP corrosion was reported due to naphthenic acid decomposition at high temperature^{2,3,4}.

Experiments investigating temperature effect on naphthenic acid corrosion were done by Gutzeit who found that corrosion rate triples with every 55°C increase in temperature. Gutzeit suggested that NAP corrosion kinetics follows the Arrhenius equation and it is controlled by a chemisorption mechanism³. His assumption on naphthenic acid corrosion kinetics were later challenged by Slavcheva *et al.* who suggested that oil composition is the main factor influencing the activation energies and thus controlling corrosion kinetics^{5,6}. Piehl suggested that NAP acids distribution in crude oils is function of their true boiling points (TBP). Thus if TBP's of naphthenic acids in oil are known it would be easy to predict where in the plant they will reach highest concentrations and cause corrosion⁴.

Effect of Vaporization-Condensation

Apparently naphthenic acids have the most severe effects at temperatures close to their boiling points. Based on field observations and laboratory tests, Derungs determined that highest corrosion rates of naphthenic acids occurred at their condensation points. He also noticed that there was no corrosion when naphthenic acids were totally transformed into the vapor phase². Gutzeit also did vaporization-condensation experiments with naphthenic acids and found that in the vapor phase corrosion was caused by a condensate film formed on metal surface and not by the vapors³. He concluded that naphthenic acids were corrosive only in liquid phase. However Slavceva *et al.* suggested that even if naphthenic acids were close to their boiling points, their corrosivity was influenced by the dilution of the acids in hydrocarbons with similar boiling points^{6,7}.

Effect of Velocity

¹ ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428

Under severe flow conditions protective iron sulfide film can be physically removed by the shear stresses resulting in the exposure of the metal surface to further naphthenic acid attack. High corrosion rates caused by high flow rates and turbulences were identified in return bends, tube inlets of furnaces, and bends of transfer lines^{13,14}. First literature references of flow effect in naphthenic acid corrosion mentioned that fluid velocities in distilling units were dependent on volatility of the products, pressure, and steam injection^{3,4,14}. Later studies investigated the role of shear stress on scale integrity under acidic corrosion conditions and it was found that oils with a high sulfur and NAP acid content vaporized less and were more sensitive to velocity effects^{8,11,12,15,16}.

Effect of Acid Structure

Starting from the hypothesis that naphthenic acid carboxylic group activity is influenced by the rest of the molecule that included one or more cyclic structures Slavcheva *et al.* investigated any possible correlation between NAP acid molecular structure and their corrosive activity^{5,6}. They found that corrosion rates increased with molecular weight for simple naphthenic acid structures but decreased when molecular structures become bigger and more complicated. Based on these experimental observations the authors final assumption was that steric hindrance decreased naphthenic acid corrosion by preventing adsorption of acid molecules on metal surface. Therefore crude oils with similar or identical TAN values would lead to different corrosive effects.¹⁷

Effect of Pressure

According to the literature^{2,4,5}, pressure had little or no effect on naphthenic acid corrosion. However in vacuum distilling units any pressure variation (*i.e.* by steam injection) can influence the vaporization of naphthenic acids and consequently their corrosivity.

IRON SULFIDE SCALE FORMATION AND REMOVAL

As the abovementioned literature review shows many of the previous research focused on naphthenic acid or sulfur corrosion due to their high impact on refinery design and exploitation. The present research effort will differ in trying to “decipher” the corrosion reaction mechanism that involves simultaneous presence of both naphthenic acid and sulfur corrosion, Based on the previous practical observations and experiments, this study starts from the hypothesis that sulfur containing compounds mitigate corrosion by forming iron sulfide scale on the metal surface. However this effect diminishes under combined effect of strong acidic attack and high velocity when the scale loses its protectiveness. In order to verify this hypothesis it was decided to form iron sulfide scales and attack (“challenge”) them with crude oil fractions containing naphthenic acids under experimental conditions close to those found in distillation towers. In the experiments described below the iron sulfide scale was performed on steel samples by using real crude oil fractions containing significant amounts of sulfur compounds and little naphthenic acid. These were then “challenged” by model oils containing no sulfur but with higher naphthenic acid content.

The following sections will describe the experimental setup and procedures in detail followed by a discussion of the results for both model oil and real fraction tests.

EXPERIMENTAL

Experimental Setting and Procedure

Experimental apparatus used for naphthenic acid corrosion tests called the High Velocity Rig (HVR) is schematically presented in FIGURE 1. The HVR is designed to reproduce the flow, pressure, temperature and shear stresses conditions usually encountered in liquid side streams of atmospheric and vacuum distillation units. The main part of the HVR loop is an autoclave where ring samples made from steel are mounted on a rotating cylinder and flushed with testing fluids at high temperature. Operating pressure of the autoclave is from 0 to 500 psig and temperature up to 370°C (700°F). The fluid flow rate provided by the HVR pump is controllable over the

range of 5 to 20 cm³/min. Ring samples are rotated in the autoclave at 2000 rpm during the experiments. The entire experimental rig and the fluids used are purged with an inert gas before the tests.

The test protocol calls for pre-treating (pre-sulfidation) the steel ring sample *ex-situ* in sulfur containing fluids which form iron sulfide scale on the steel surface. Ex-situ pre-sulfidation of the steel rings is done in separate autoclaves at the same high temperature 370°C (700°F) as used in the subsequent challenge phase. The HVR is used for challenging the pre-sulfided steel rings in a sulfur-free environment. All the tested crude oil fractions and their total corrosive sulfur and acidic contents are listed in TABLE 1.

Ring samples are fabricated from carbon steel (CS) and 5Cr steel (5Cr, 0.5 Mo) and with the outer diameter OD = 81.75 mm. Six ring samples were used in every test (3 of each steel type). Before every test, samples were polished using 400 and 600-grit silicon carbide (SiC) paper under isopropanol flushing, then dried with nitrogen, and finally weighed before being inserted into the autoclave. Corrosion rates were evaluated by sample weight loss measured as the difference between sample weight before and after the tests. Samples final weight was evaluated at the end of every test by removing iron sulfide scale completely from the steel surfaces using mechanical and chemical means. The very loose scale was mechanically removed from sample surfaces by rinsing them with organic solvents (toluene and acetone) and then brushing with a stiff plastic brush. At the end of mechanical cleaning samples were weighed again. Strongly adherent scale that survived the mechanical cleaning was chemically removed later using Clarke solution⁽²⁾ (ASTM G 1-90) when the final weighing was done.

Two samples (one of each steel type) were saved at the end of every test and prepared for further analysis that included scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX).

Experimental Design

The main goal of this project was to evaluate the protectiveness of pre-formed iron sulfide scales against naphthenic acid corrosive attack. In order to achieve this goal, experiments included two stages: 24-hour pre-treatment or “pre-sulfidation” stage when iron sulfide scales were generated on steel sample surfaces by exposure in model oils or real crude fractions, and then the attack or “challenge” stage when scales were exposed to model oil containing naphthenic acids. Since the challenge phase contained no sulfur there was no opportunity for scale repair. Tested crude oil fractions cover a range of sulfur and naphthenic acid concentrations. Moreover, their compositions in terms of trace metals varied. Therefore, there was no expectation that the iron sulfide scales they form would provide similar protection from NAP corrosion. Consistent with pre-sulfidation time, it was decided to challenge these scales only at a “low” (TAN 3.5) and a “high” (TAN 6.5) level. These challenges were run for 24 hr for each TAN level using white (model) oil (no sulfur; no acid) spiked with a commercial naphthenic acid. All test conditions used in crude oil fractions experiments are summarized in TABLE 2.

Separate sulfidation-only “reference” tests were conducted for each of the tested crude oil fractions. Corresponding metal weight losses of samples due to corrosion and weight gains generated by iron sulfide scale formation were subtracted from final values of samples obtained in the complete tests which included both sulfidation and challenge stages. Thus it was possible to distinguish the effects of naphthenic acid attacks on a steel surface covered by iron sulfide.

Experimental Data Calculations

Corrosion rates of the samples were evaluated by weight loss, calculating the difference of samples weight before and after the test, according to Equation (1), with the final result being expressed in *mm/y*:

² ASTM G 1-90 “Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens”.(West Conshohocken, PA, Annual Book of ASTM Standards, Vol 03.02, 1990)

$$CR = \frac{(IW - FW)}{\rho_{Fe} \times A_c \times t} \times 24 \times 365 \times 1000 \quad (1)$$

where

CR - the corrosion rate [mm/y],

IW - initial weight [kg],

FW – final weight (after final clarking) [kg],

ρ_{Fe} - iron density [kg/m³],

A_c - sample area exposed to acidic oil during challenge (outer ring area) [m²],

t - time of the experiment [hr].

Because the experiments consist of two separate phases *i.e.* sulfidation followed by challenge, final corrosion rates have to express exclusively the effect of NAP acid corrosion. Therefore in Equation (1) initial weight IW used for calculations represents the difference between initial weight of samples before any experimental phase and the weight loss corresponding to separately run sulfidation phase. Thus the weight loss of interest *i.e.* caused by naphthenic acids attack excludes the weight losses of presulfidation. From weight loss measurements, a hypothetical scale thickness was calculated for both “total” and “adherent” scale by assuming that the iron sulfide scale was perfectly compact and dense. It is referred to below as the “calculated scale thickness”. Total scale includes both the loose scale that could be removed by simple mechanical means (rubbing, brushing) and the strongly adherent scale which could be removed only chemically (Clarke solution). The total scale was calculated with Equation (2) using weight difference between weight after solvent rinsing and final weight of the sample.

$$\delta_T = \frac{(W_{Rinse} - FW)}{\rho_{FeS} \times A_T} \times 10^6 \quad (2)$$

where

δ_T - thickness of total scale [μm],

W_{Rinse} - rinse weight, weight after solvent rinse, rubbing, brushing [kg],

FW – final weight (after final clarking) [kg],

ρ_{FeS} – iron sulfide density [kg/m³],

A_T – total area of the sample (total ring area) [m²].

Finally, the adherent scale was evaluated using the weight difference between sample weight after rubbing (mechanical removal) and sample final weight after last cleaning with Clarke solution (“clarking”) - Equation (3).

$$\delta_A = \frac{(W_{Rub} - FW)}{\rho_{FeS} \times A_T} \times 10^6 \quad (3)$$

where

δ_A - thickness of adherent scale [μm],

W_{Rub} - rinse weight [kg],

FW – final weight (after final clarking) [kg],

ρ_{FeS} – iron sulfide density [kg/m³],

A_T – total area of the sample (total ring area) [m²].

All graphical representation referring to corrosion rates or scale thicknesses that were included in this paper were normalized with the same value (due to confidentiality clauses required by the sponsoring company) to enable effective comparison and analysis of the results.

RESULTS AND DISCUSSION

Compared to model oils, the real crude oil fractions represent very complex mixtures containing hydrocarbons and organic compounds like acids, phenols, sulfides, etc. It is the interaction between these different compounds that influence crude fractions reactivity and corrosive effects on metals. Thus iron sulfide scales generated with real crudes in this project offered different protection against naphthenic acids attack for the two steel types. As a consequence of these differences in scale protectiveness, in many cases same experiment had to be repeated even three times in order to confirm the trend for a given crude oil fraction. Final results in some cases have a high margin of error but in spite of all these variations all the test results are presented below including the cases where variability is high. Thus it becomes possible to have a more complete picture of iron sulfide scales protectiveness formed in various crude oil fractions.

All tested crude oil fractions are provided by the sponsor⁽³⁾ and their corresponding acid and sulfur contents are presented in TABLE 1. Experimental conditions used for testing these crude fractions are summarized in TABLE 2.

Corrosion Rate Results

Corrosion rates were plotted for each of the tested crude oil fractions by showing together the results obtained in the NAP challenge phase and those from the sulfidation phase (also called also the “reference” tests), that were conducted separately for each crude fraction. Challenge phase data presented in FIGURE 2 and in following figures exclude the metal loss that occurs in sulfidation phase. Fraction “D” test results will be presented in detail and for all other tested crude fraction experimental data will be summarized in two graphs that offer a complete view. Thus in FIGURE 2 corrosion rates of “low” and “high” TAN challenges are compared to those of sulfidation reference tests for fraction “D” (TAN 0.2 and S:0.7%). It includes experimental data for both steel types (carbon steel and 5Cr steel). From FIGURE 2 results it can be seen that iron sulfide scale formed with fraction “D” was able to protect only against TAN 3.5 (low) naphthenic acid challenge and failed to protect in case of TAN 6.5 (high) challenge. Thus corrosion rates measured for TAN 3.5 challenge were the similar both for carbon steel and 5Cr steel samples and in the same range with sulfidation reference test results. Higher TAN 6.5 challenge corrosion results were spread over a large range without the possibility to separate clearly the two steel types. Although there are considerable differences of corrosion rates in “low” and “high” TAN challenge tests, iron sulfide scales formed on these samples have almost the same thickness regardless the level of the challenge (FIGURE 3 and FIGURE 4). FIGURE 3 presents the scale thicknesses measured on carbon steel and FIGURE 4 the scale thicknesses on 5Cr steel samples.

The final corrosion rates for all the tested crude fractions and model oil are summarized in Figure 5 for carbon steel and Figure 6 for 5Cr steel. Both figures include also the “pure TAN” corrosion rate that was generated under pure naphthenic acids attack in the absence of sulfur, representing the maximum expected corrosion rate under the given set of conditions. Some general conclusions can be drawn:

- For all crude oil fractions tested as well as the model oil, the pre-sulfidation resulted in sulfide scale which was somewhat protective resulting in a lower corrosion rate compared to that seen on a bare metal.
- Corrosion rates seen after pre-sulfidation with crude oil fractions were different and varied unpredictably when compared to those obtained in a model oil.

³ ExxonMobil Research and Engineering Company

The following observations can be made upon reviewing of FIGURE 5 for carbon steel:

- The TAN 6.5 challenge always resulted in a higher corrosion rate than the TAN 3.5 challenge.
- None of the crude oil fractions have formed a sulfide scale that could withstand the TAN 6.5 challenge.
- When considering the TAN 3.5 challenge, pre-sulfidation with crude oil fractions A, C, D did provide considerable protection. Scale formed in crude fractions B, and E provided similar but reduced level corrosion protection. Thus TAN 3.5 challenge differentiates the protectiveness of iron sulfide scales formed on carbon steel.

From FIGURE 6 for the 5Cr steel it can be seen that:

- The TAN 6.5 challenge results in a higher corrosion rate than the TAN 3.5 challenge for crude oil fraction B. For the other crude oil fractions, results for the different TAN values are close within experimental variability.
- Crude oil fractions A, C, D formed protective scales which were very protective and withstood the challenge by TAN 6.5.
- When considering the TAN 3.5 challenge, pre-sulfidation with crude oil fractions A, C, and D resulted in very good protection and very low corrosion rate while pre-sulfidation with crude oil fractions B and E did significantly reduced the corrosion rate but not as much as with the other crude oil fractions.
- Comparing the two challenges data it is obvious that in case of 5Cr steel it was TAN 6.5 challenge that differentiate the protectiveness of iron sulfide scales formed on steel surface.

Test results demonstrated that it is difficult to predict protectiveness of iron sulfide scale based only on sulfur content of crude oil fractions generating the scales. As a general conclusion, it can be said that in the case of all crude oil fractions tested, the iron sulfide scales could protect the steel against TAN 3.5 challenge to a similar degree. The TAN 6.5 challenge clearly differentiated between more and less protective scales.

Iron Sulfide Scale Analysis

All the experimental data presented above demonstrate the protective role of iron sulfide scales against naphthenic acids corrosive effects. Scale thicknesses were analyzed as function of corresponding test corrosion rates in order to assess whether there are any possible correlations between these experimental data. FIGURE 7 presents total and adherent scales as function of carbon steel corrosion rates resulting from a TAN 3.5 challenge. As the plot shows, there is no correlation between the final carbon steel corrosion rate and scale thickness. For crude oil fractions A, C, and D that have similar corrosion rate values, the adherent scale is the same but also similar to crude oil fraction B which has the highest corrosion rate.

FIGURE 8 presents similar data for the 5Cr steel and leads to the same conclusion: there is no correlation between scale thickness and corrosion rate. Crude oil fractions A and C have similar corrosion rate values but their scale thicknesses are very different, other crude oil fractions resulted in varying corrosion rates and different scale thicknesses.

SEM images of cross-sections for these iron sulfide scales also show differences in scale porosities and structures. There is no evidence that iron sulfide scale structure can be correlated to corrosion rate of the metal covered with this scale. This is very well illustrated in case of fractions C and E when corrosion rate values are very similar for consistent metallurgy and TAN challenge (FIGURE 5 and FIGURE 6) but iron sulfide scales have different structures in spite of corrosion rate similarity.

Comparing the SEM images of scales formed on carbon steel (FIGURE 9) structural differences become very clear. Scale formed on carbon steel with crude oil fraction C (FIGURE 9 image *a*) is thick and consists of

multiple layers with various porosities whereas crude oil fraction E formed a thin porous iron sulfide scale on similar carbon steel samples (FIGURE 9 image *b*).

SEM images of scale formed on 5Cr steel with the same crude oil fractions C and E also present structural differences although 5Cr steel corrosion rates are similar for both fractions in case of TAN 6.5 challenge (FIGURE 10). Challenged scale formed with crude oil fraction C on 5Cr steel is thick with multiple layers that have a compact appearance (FIGURE 10 image *a*). Scale formed with crude oil fraction E on 5Cr steel and later challenged also consists of several layers but is more porous when compared to scale formed by C (FIGURE 10 image *b*).

For all other iron sulfide scales generated with crude oil fractions, the SEM images of cross-sections show similar structures to those that have already been presented. In all cases iron sulfide scales consist of several successive layers with fragmented aspect but these structures can not be easily related to scale protective qualities against NAP acid corrosive attack.

CONCLUSIONS AND FUTURE WORK

- ❖ Corrosion of steel in real crude oil fractions was tested according to a new protocol – first by pre-sulfidation in a low TAN environment to form a protective scale, then by challenge in a low and high TAN containing oil in order to verify the protective properties of iron sulfide scales formed with these crude fractions.
- ❖ Most crude oil fractions generated rather protective scale against a low TAN 3.5 challenge and only a few of them maintained that protection in high TAN 6.5 challenge. In general a more protective iron sulfide scale was formed on 5Cr steel compared to carbon steel. All these experimental findings demonstrate that it is difficult to predict iron sulfide scales properties and corrosion rates based exclusively on naphthenic acid concentration and sulfur content in crude oil fractions. However based on these experimental data it is possible to develop a testing protocol for assessing protectiveness of iron sulfide scales formed with real crude oil fractions and challenged with naphthenic acid containing oil.
- ❖ There was no obvious correlation between the iron sulfide scale thickness/morphology and the protection provided to mitigate naphthenic acid corrosion.

These data are being incorporated into a model that enables the prediction of liquid fraction corrosivity in refinery crude units. Based on these results, it is evident that this model will need to incorporate the mechanism of protection by iron sulfide scale against naphthenic acid corrosion.

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REFERENCES

1. Kapusta, S.D.; Ooms, A.; Smith, A.; Van den Berg, F.; Fort, W.; Safe processing of Acid Crudes. *Corr. Paper 04637*, 2004, pp.1-19
2. Derungs, W.A.; Naphthenic Acid Corrosion – An Old Enemy of the Petroleum Industry. *Corr.* 1956, *12*, pp.617-622.
3. Gutzeit, J.; Naphthenic Acid Corrosion in Oil Refineries. *Mater.Perform.*, 1977, *16*, pp.24-35.

4. Piehl, R.L.; Naphtenic acid corrosion in crude distillation units. *Mater. Perform.* 1988, 27 (1), pp.37-43.
5. Turnbull, A.; Slavcheva, E.; Shone, B.; Factors controlling naphtenic acid corrosion. *Corr.*, 1998, 54 (11), pp.922-930.
6. Slavcheva, E.; Shone, B.; Turnbull, A.; Review of naphtenic acid corrosion in oil refining. *Br. Corr.J.* 1999, 34 (2), pp.125-131.
7. Babaian-Kibala, E.; Craig H.L.; Rusk, G.L.; Quinter R.C.; Summers M.A.; Naphthenic Acid Corrosion in Refinery Settings. *Mater. Perform.* 1993, pp.50-55.
8. Kane, R.D.; Cayard, M.S.; Understanding Critical Factors that Influence Refinery Crude Corrosiveness. *Mater. Perform.* 1999, July, pp.48-54.
9. Speight, J.G.; *The Chemistry and Technology of Petroleum* 3rd Ed. Marcel Dekker, New York 1999, pp 244f
10. Tebbal, S., Kane, R.D., "Assessment of Crude Oil Corrosivity". *Corr. Paper No.578*, 1998, pp.1-11. (Houston, TX: NACE, 1998)
11. Kane, R.D.; Cayard, M.S. "A comprehensive Study on Naphthenic Acid Corrosion". *Corr. Paper No.02555*, 2002, pp.1-16. (Houston, TX: NACE, 2002)
12. Tebbal, S.; Kane, R.D.; "Review of Critical Factors Affecting Crude Corrosivity". *Corr. Paper No.607*, 1996, pp.1-10. (Houston, TX: NACE, 1996)
13. Craig H.L.; "Naphthenic Acid Corrosion in the Refinery". *Corr. Paper No.333*, 1995, pp.120-141. (Houston, TX: NACE, 1995)
14. Craig H.L.; "Temperature and Velocity Effects in Naphthenic Acid Corrosion". *Corrosion Paper No.603*, 1996, pp.1-13. (Houston, TX: NACE, 1996)
15. Pritchard, A.M.; Graham, A.; Rance, A.; "Use of a Rotating Cylinder System to determine the Corrosivities of Acid Crudes". *Corr. Paper No. 01525*, 2001, pp.1-8. (Houston, TX: NACE, 2001)
16. Smart, N.R.; Rance, A.P.; "Pritchard, A.M.; Laboratory Investigation of Naphthenic Acid Corrosion under Flowing Conditions". *Corr. Paper No. 02484*, 2002, pp.1-23. (Houston, TX: NACE, 2002)
17. Messer, B.; Tarleton, B.; Beaton, M.; Phillips T.; "New Theory for Naphthenic Acid Corrosivity of Athabasca Oilsands Crudes". *Corr. Paper No. 04634*, 2004, pp.1-11. (Houston, TX: NACE, 2004)

TABLE 1
MODEL OILS AND REAL CRUDE OIL FRACTIONS USED IN SULFIDATION-CHALLENGE TESTS

	Tested Fluid	Total Acid Number (mg KOH/gr oil)	Corrosive Sulfur (%wt)
1.	White Oil (Model oil)	0	0
2.	Yellow Oil (Model oil)	0	0.25
3.	Naphthenic acids	~230	0
4.	Fraction A	1.75	0.18
5.	Fraction B	<0.1	0.6
6.	Fraction C	1	1.51
7.	Fraction D	0.2	0.7
8.	Fraction E	0.2	0.92

Note: Fluids 1 and 2 have no appreciable naphthenic acid or metals. For the results in Figures 2-5, the TAN level in fluid 2 was increased to 0.1 using commercial naphthenic acid.

TABLE 2
GENERAL TEST CONDITIONS FOR SULFIDATION AND CHALLENGE TESTS DONE USING REAL CRUDE OIL FRACTIONS

Test phase	Sulfur content (%w/w)	TAN	Temp.	Time (hr)	Pressure (psig)	Rotation (rpm)
Sulfidation (Autoclave)	0.25-1.51	0.1-1.75	343°C (650°F)	24	200	0
Challenge (HVR)	0	3.5	343°C (650°F)	24	150	~2000
	0	6.5	343°C (650°F)	24	150	~2000

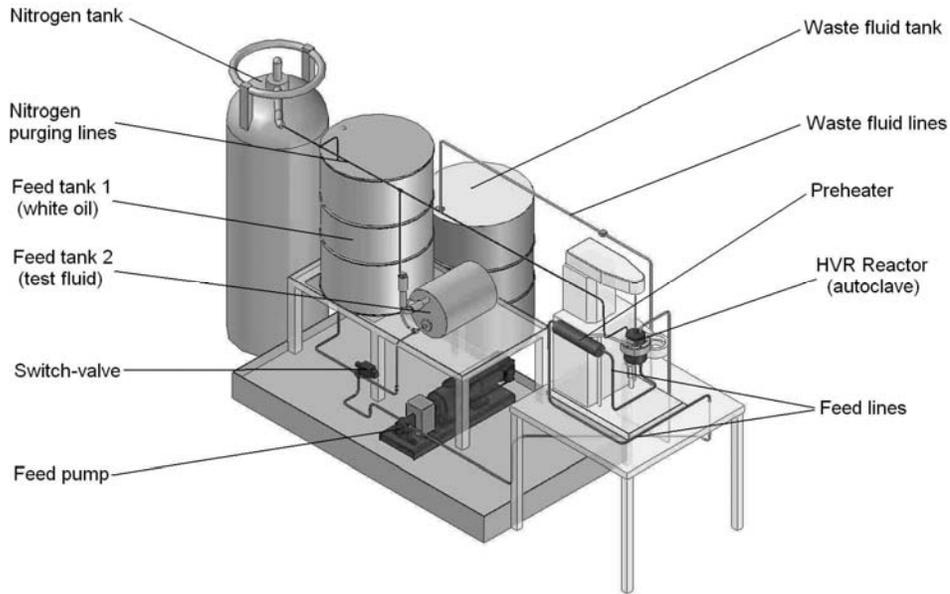


FIGURE 1. High Velocity Rig used for naphthenic acid corrosion tests under high velocity and temperature conditions. The HVR autoclave was used for challenging with naphthenic acids pre-formed iron sulfide scales on CS and 5Cr samples.

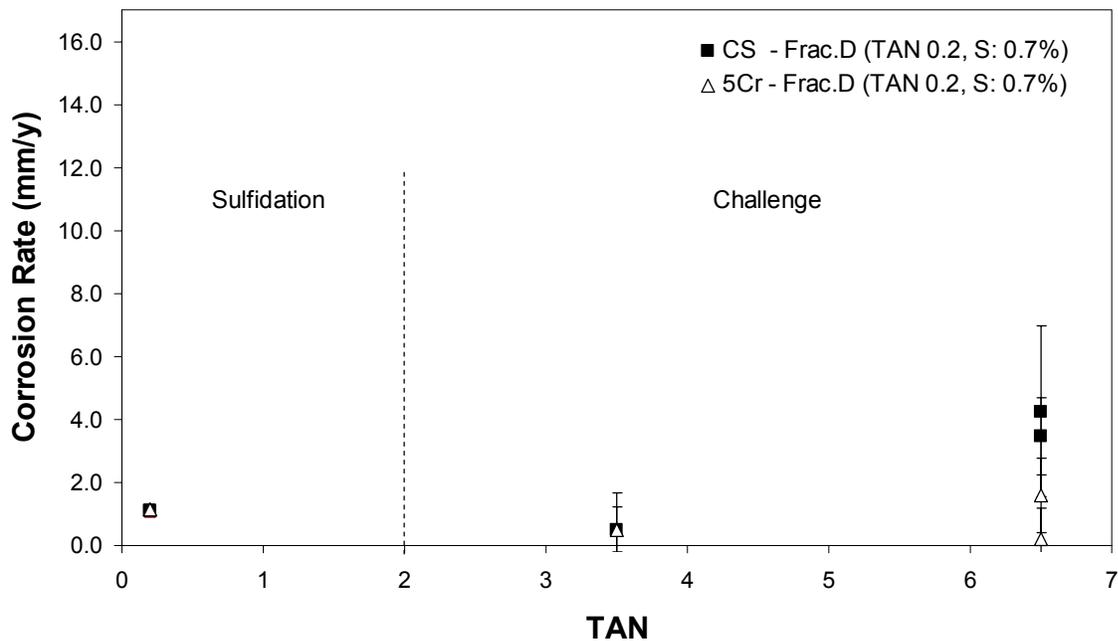


FIGURE 2. Comparison of corrosion rates for carbon steel and 5Cr steel samples pretreated in crude oil fraction D and then challenged with naphthenic acids of TAN 3.5 and TAN 6.5 concentrations. The graph includes corrosion rates of the two steel types generated exclusively in crude oil fraction D sulfidation test. These corrosion rates are plotted on the left part of the graph “Sulfidation” separated from “Challenge” part including corrosion rates generated exclusively with naphthenic acids only.

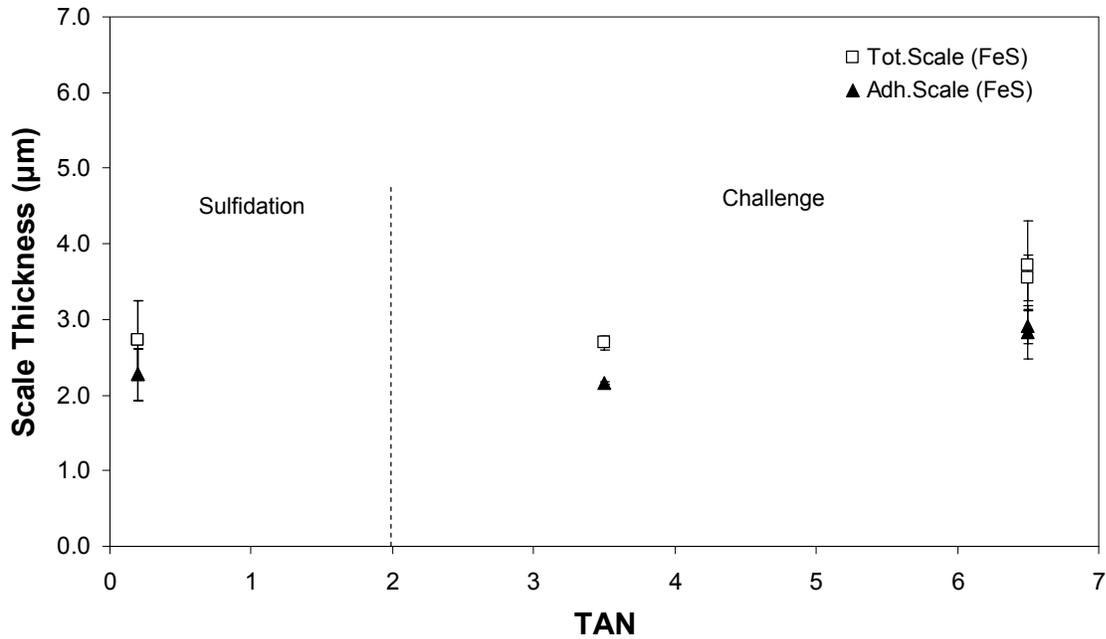


FIGURE 3. Iron sulfide scale thicknesses evaluated on carbon steel samples in tests using fraction D (TAN 0.2 and 0.7% sulfur). The graph shows separately the scale thickness measured on samples at the end of sulfidation test (Sulfidation) and the scale thickness that was found on samples after the “low” and “high” TAN challenges (Challenge).

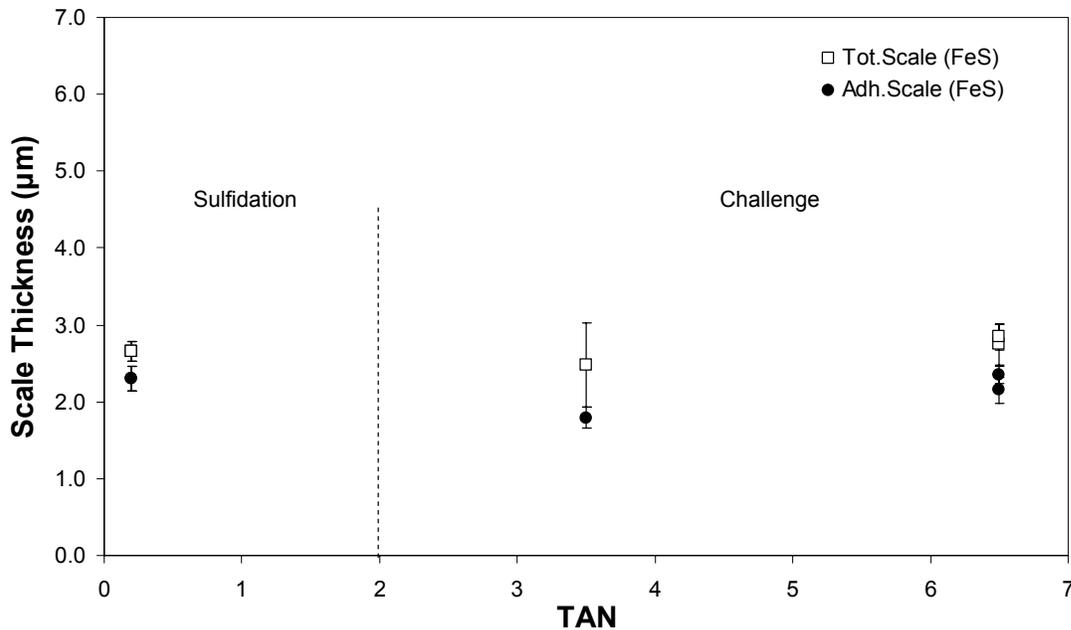


FIGURE 4. Iron sulfide scale thicknesses evaluated on 5Cr samples in tests using fraction D (TAN 0.2 and 0.7% sulfur). The graph shows separately the scale thickness measured on samples at the end of sulfidation test (Sulfidation) and the scale thickness that was found on samples after the “low” and “high” TAN challenges (Challenge).

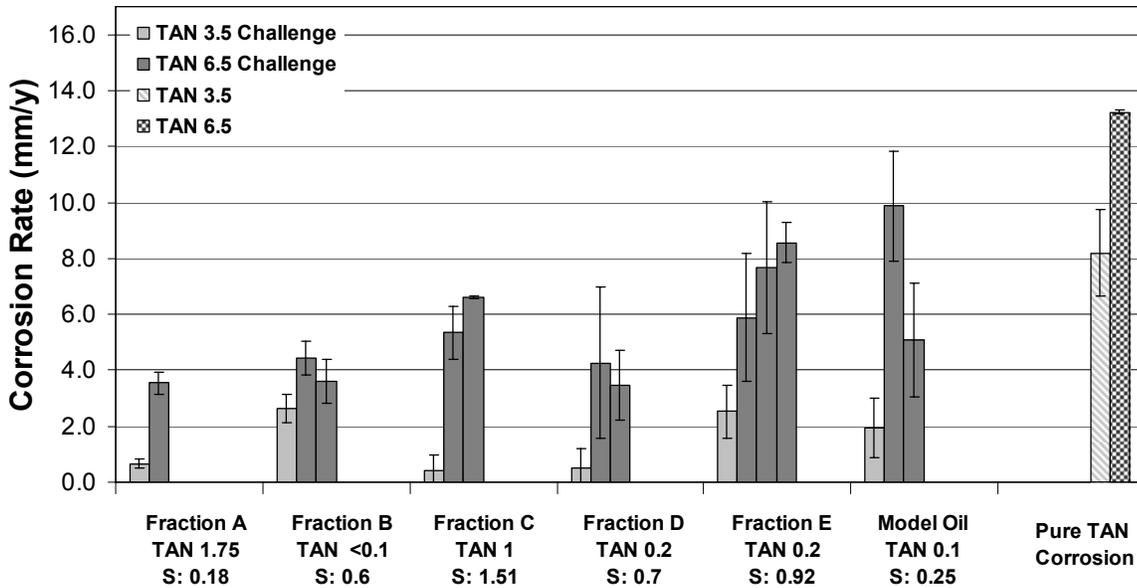


FIGURE 5. Corrosion rates for CS samples that were pre-sulfidized in autoclave with crude oil fractions and then challenged at high velocity with naphthenic acids at TAN 3.5 and TAN 6.5. Plot includes also corrosion rates generated with pure naphthenic acids dissolved in white oil (sulfur free environment) at identical temperature and velocity conditions to all other tests.

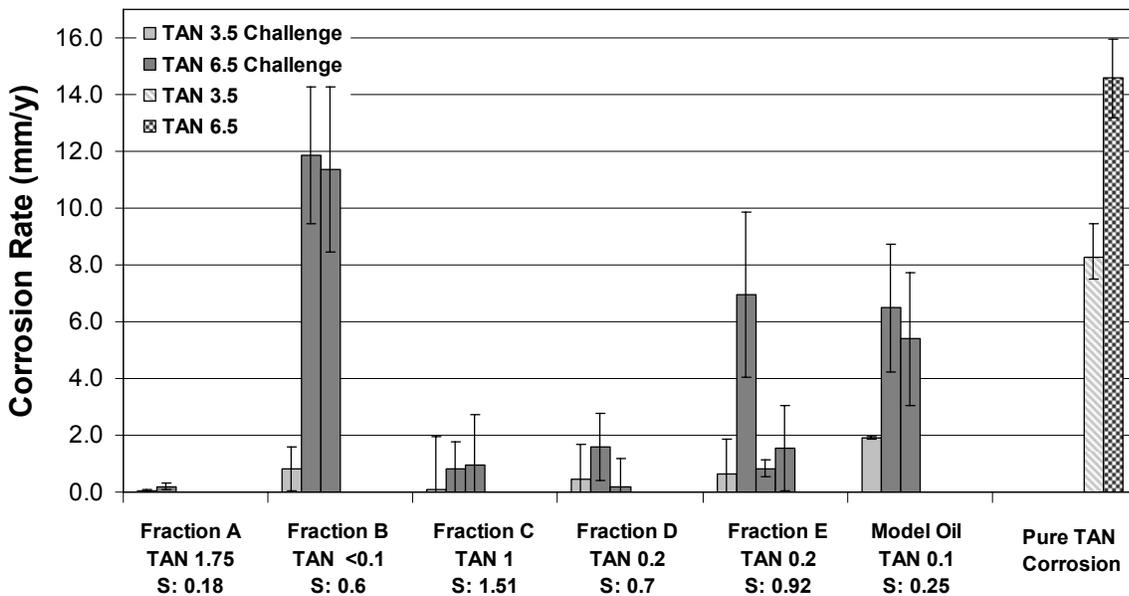


FIGURE 6. Corrosion rates for 5Cr samples that were pre-sulfidized in autoclave with crude oil fractions and then challenged at high velocity with naphthenic acids at TAN 3.5 and TAN 6.5. Plot includes also corrosion rates generated with pure naphthenic acids dissolved in white oil (sulfur free environment) at identical temperature and velocity conditions to all other tests.

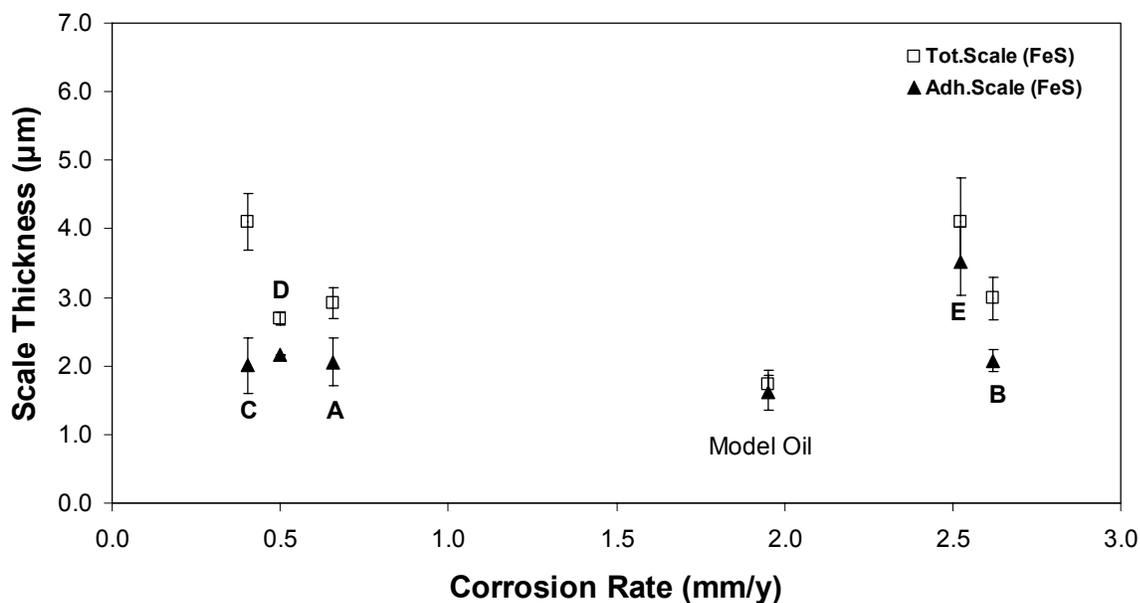


FIGURE 7. Total and adherent scale thickness represented as function of CS corrosion rates. Corrosion rates are generated in tests that challenged with TAN 3.5 CS samples pretreated with crude oil fractions. Tested crude oil fractions that generated the iron sulfide scales are indicated with their corresponding letter (A – E) for every set of scale thickness data.

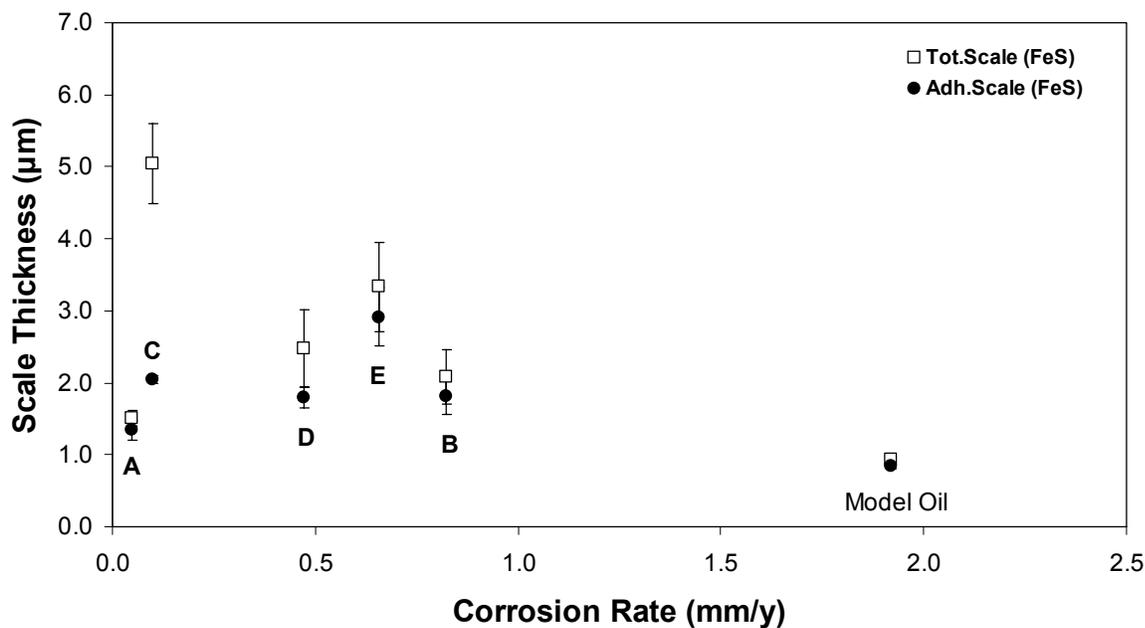
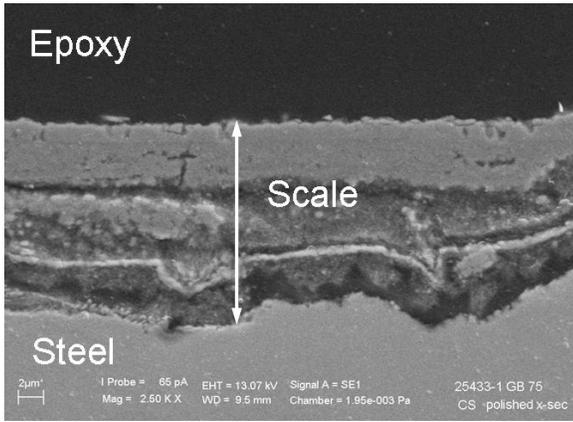
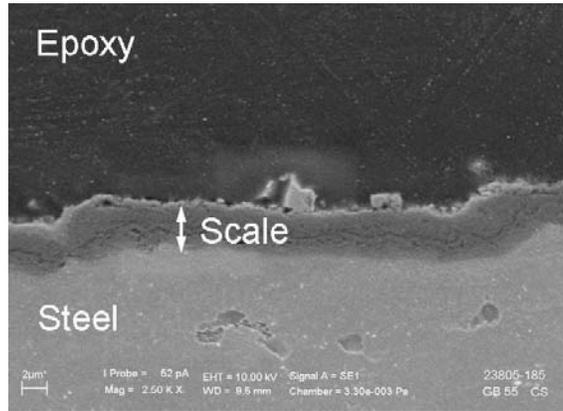


FIGURE 8. Total and adherent scale thickness represented as function of 5Cr corrosion rates. Corrosion rates are generated in tests that challenged with TAN 3.5 5Cr samples pretreated with crude oil fraction. Tested crude oil fractions that generated the iron sulfide scales are labeled with their corresponding letter (A – E) for every set of scale thickness data

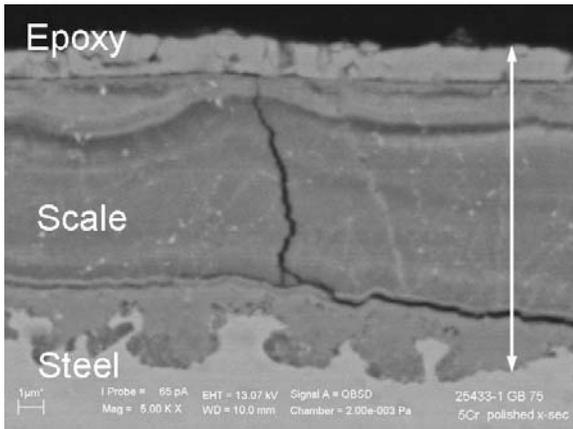


(a)

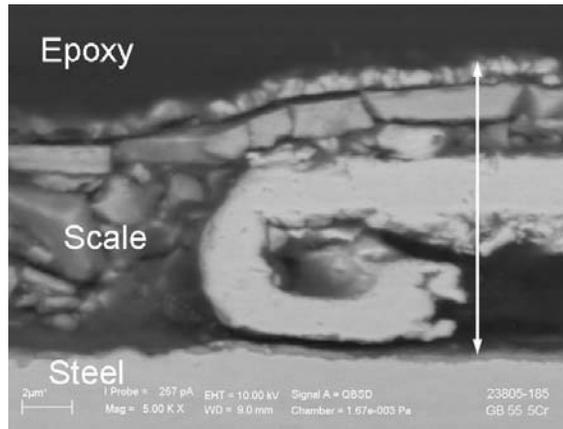


(b)

FIGURE 9. Backscattered SEM images represent cross-sections on CS samples pre-sulfidized with crude oil fractions C (image a) and E (image b). Both samples are challenged with TAN 6.5. Image a shows a multilayer porous thick iron sulfide scale formed with crude oil fraction C. Image b presents the thin porous scale formed by crude oil fraction E. Magnification in both images is 2500 X.



(a)



(b)

FIGURE 10. Backscattered SEM images represent cross-sections on 5Cr samples pre-sulfidized with crude oil fractions C (image a) and E (image b). Both samples are challenged with TAN 6.5. Image a shows a multilayer, compact, and thick iron sulfide scale formed with crude oil fraction C. Image b presents the iron sulfide scale formed with crude oil fraction E. Scale is also thick but layers are fragmented showing a significant porous structure. Magnification in both images is 5000 X.