

ANALYSIS OF CORROSION SCALES FORMED ON STEEL AT HIGH TEMPERATURES IN HYDROCARBONS CONTAINING MODEL NAPHTHENIC ACIDS AND SULFUR COMPOUNDS

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ABSTRACT

Corrosive naphthenic acids and sulfur compounds in crude oils present a major challenge for refineries from a corrosion perspective. Although it is accepted that some sulfur compounds may form protective FeS scales on the metal surface and deter corrosion, attempting to correlate the characteristics of FeS scale with its protective properties has not been successful. Given the complex chemical compositions of real crudes, model sulfur compound and model naphthenic acids were used to mimic the corrosion by crude fractions in the present study. The iron sulfide scale formed by the model sulfur/acid compounds was challenged by naphthenic acids to examine its protectiveness against corrosion. Moreover, the scale was analyzed with TEM/EDS technique and a layer of iron oxide was found when naphthenic acids were present in the solution. The iron oxide layer appeared to be important for maintaining protection against naphthenic acid corrosion and further analysis revealed that it was composed of magnetite.

Key words: naphthenic acids, iron sulfide scales, iron oxide, high temperature corrosion, crude fractions, model sulfur compounds

INTRODUCTION

The high content of corrosive naphthenic acids and sulfur compounds represents an engineering challenge for refineries that are processing “opportunity crudes” which are characterized by the ease of procurement and discounted price. However, corrosive species in “opportunity crudes” may lead to severe corrosion of facilities, which may be mitigated by blending crudes, upgrading materials, and/or

adding inhibitors.^[1] It is widely accepted that the corrosion from naphthenic acids (NAP) and sulfur compounds takes place via the following reactions:^[2]



where RCOOH represents a generic naphthenic acid and H₂S represents the sulfur containing compounds in the crude. The iron naphthenates (Fe(RCOO)₂) generated in the naphthenic acid corrosion (Reaction 1) are oil soluble and they are removed by the oil flow, whereas the iron sulfide (FeS) generated in Reaction 2 (sulfidation reaction) is a solid product that is laid down as a scale on the metal surfaces. It is common wisdom in the oil industry that the iron sulfide film may protect the metal against naphthenic acid corrosive attack under certain conditions. The two reactions (1 and 2) represent the main corrosive reactions in crude oil, a process that continues due to Reaction 3 when reactive species are regenerated and reintroduced in the corrosive reaction cycle.

However, the naphthenic acids and sulfur compounds in real crudes are very complex and there are many authors in the literature who focused their studies on crude oil composition. For instance, Dzidic found that a mixture of California crudes possessed naphthenic acids (C_nH_{2n+z}O₂) with carbon number (n) from 10 to 30 and an index of hydrogen deficiency (z) from 0 to -12.^[3] Similarly to naphthenic acids, the sulfur compounds in the real crudes are complicated and do not always directly relate to the H₂S evolution behavior or crude oils as some authors suggested in their works.^{[1], [4]}

The complex composition of crude oil makes it difficult to evaluate accurately its corrosive behavior in laboratory tests.^{[5], [6]} Therefore, it is more feasible to investigate the corrosion processes on a lab scale by using model sulfur compounds, and model naphthenic acids, dissolved in model oils that can mimic the main characteristic of crude oils and then try to extend the applicability of these results to real crudes. In this project, a model sulfide compound and a commercial naphthenic acid mixture were mixed together in a model inert mineral oil and then they were used to pretreat steel specimens in a stirred autoclave reactor. The corrosion product scale generated in these experiments was subsequently challenged with a naphthenic acid mixture in a rotating cylinder autoclave reactor to examine their protectiveness under high temperature and high velocity conditions.

EXPERIMENTAL PROCEDURE

Experimental Materials

To assess the corrosion of the materials used in the field, two of the most commonly utilized steels in refineries were selected for experimentation, i.e., the A106 carbon steel (CS) and A182-F5 chrome steel (5Cr). Steel specimens were in the shape of rings with inner diameter 70.43 mm, outer diameter 81.76 mm, and thickness 5 mm. Before experiments, each specimen was polished with 400 and 600-grit silicon-carbide paper (SiC) in succession. Isopropanol was used to flush specimens during polishing to prevent oxidation and overheating. After polishing, specimens were wiped with a paper towel, rinsed with toluene and acetone, and dried with nitrogen flow. Weights of fresh clean specimens were taken with an analytical balance.

After each experiment, specimens were rinsed with toluene and acetone, gently rubbed with a soft plastic brush, treated with “Clarke” solution (ASTM G1 - 03),^{[7], [8]} and reweighed. Based on the weight difference of specimens before and after the experiment and the exposed surface area, the corrosion rate was calculated.

Experimental Solutions

A commercially available n-dodecyl sulfide or DDS (Fisher Chemical) and a commercial naphthenic acid mixture, denoted as NAP in the text below, were selected to mimic natural sulfur compounds and naphthenic acids found in real crudes. They were dissolved in an inert mineral oil to prepare experimental solutions that were later used to pretreat steel specimens. Three different solutions were prepared:

- "NAP only" consisting of NAP dissolved in mineral oil (TAN = 1.75, S = 0%wt),
- "DDS only" prepared of DDS dissolved in mineral oil (TAN = 0, S = 0.25%wt), and
- "DDS + NAP" where both DDS and NAP were dissolved in mineral oil (TAN = 1.75, S = 0.25%wt).

Experimental Equipment

Two different experimental setups were used in this research work. The first experimental setup was a closed stirred autoclave where metal samples were pretreated with the test solutions at high temperature under continuous stirring where they were allowed to develop a protective scale. The second experimental setup was a flow-through rotating cylinder autoclave called the High Velocity Rig (HVR). The HVR was used to investigate the scale tenacity against NAP attack (Figure 1) under high temperature and high velocity conditions. Specimens pretreated with each of the three different experimental solutions in the stirred autoclave were transferred into the HVR where they were exposed to the mineral model oil containing the model NAP at TAN 3.5. The HVR was designed to create a high flow velocity and associated turbulence and shear stress. The core of the HVR system was the reactor, or autoclave with a rotating cylinder setup that enabled flow through of the NAP solution.

Experimental Procedures

The experimental procedure consisted of two consecutive steps:

- 1) *"Pretreatment" - generation of scale in the stirred autoclave.* CS and 5Cr specimens were pretreated in the static autoclave with one of the three experimental solutions that generated corrosion scales on the specimen surface. The pretreatment temperature was 600°F (316°C) and the duration was 24 hours.
- 2) *"Challenge" - evaluation of scale protectiveness in the HVR.* After pretreatment in the static autoclave, the specimens were transferred into the HVR, which was fed with the challenge solution of NAP acid in mineral oil (TAN = 3.5, S = 0%wt). The challenge temperature was 650°F (343°C) and the duration was 24 hours. During the challenge, the speed of the rotating cylinder was set to 2000 rpm (translating to a peripheral velocity of 8.5 m/s, Reynolds number of 1771 and wall shear stress of 74 Pa). A back-pressure of 150 psig was applied to suppress breakout of gas; flow through rate of the oil containing fresh NAP was set to 7.5 cm³/min. In addition to the high TAN value of the challenge solution, the high peripheral velocity helped to create a corrosive condition and to investigate the scale protectiveness.

Further specimen investigation focused on analyzing the structure and chemical composition of the scales using a Scanning Electron Microscope - SEM and Focused Ion Beam / Transmittance Electron Microscope – FIB/TEM combined with energy dispersive X-ray spectroscopy (EDS) as well as Convergent Beam Electron Diffraction (CBED).

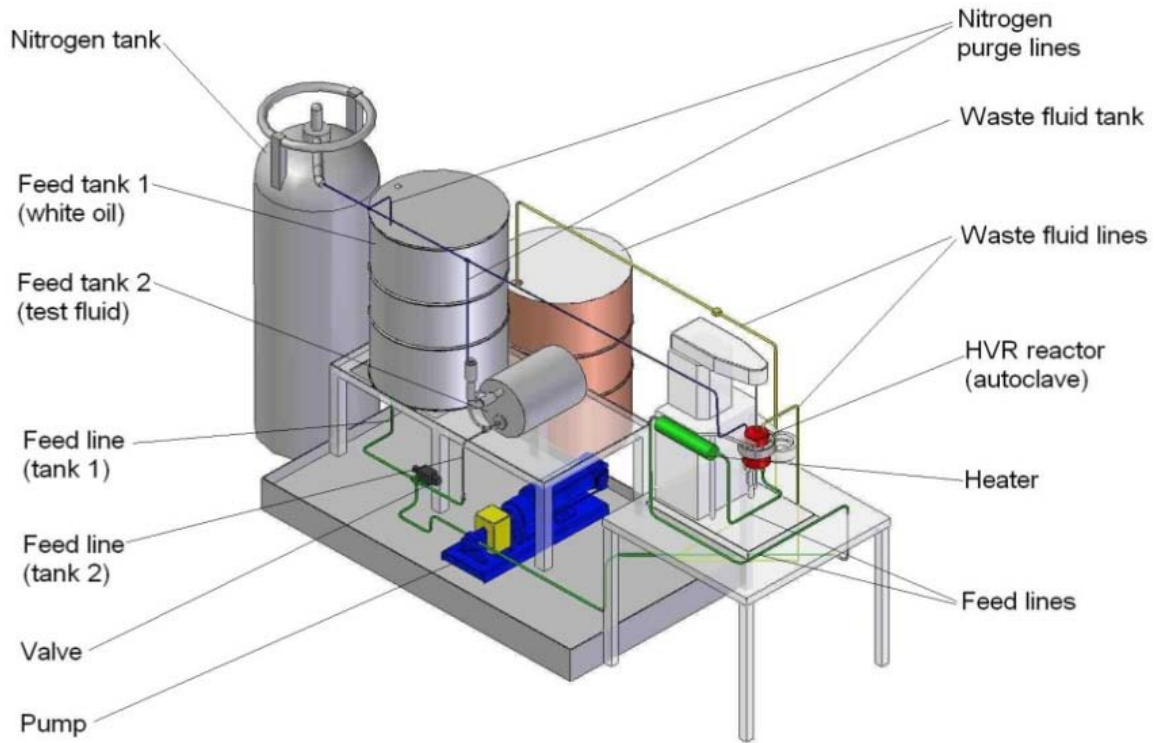


Figure 1: Schematic rendering of the High Velocity Rig (HVR) used in the “challenge” experiment.

Evaluation of Corrosion Rates

Corrosion rates of specimens were calculated based on their weight loss during the experiment. For the pretreatment experiment conducted in the autoclave, the corrosion rate was calculated using Equation (1).

$$CR_{Pretreatment} = \frac{(IW - FW)}{\rho_{steel} \times A_{s,Pretreatment} \times t_{Pretreatment}} \times 10 \times 24 \times 365 \quad (1)$$

where:

$CR_{Pretreatment}$ – Pretreatment corrosion rate, [mm/y]

IW – Initial weight of fresh polished steel specimen, [g]

FW – Final weight of steel specimen after treated with Clarke solution, [g]

ρ_{steel} – Density of steel specimen, [g/cm³]

$A_{s, Pretreatment}$ – Area of steel specimen exposed to corrosive fluid during pretreatment, [cm²]

$t_{Pretreatment}$ – Duration of experimentation in the stirred autoclave, [h]

In a combined pretreatment-challenge experiment, fresh polished specimens were pretreated in the autoclave followed by challenging in the HVR. While the corrosion rate in the pretreatment step could be calculated according to Equation (1), the challenge corrosion was assessed by using the following equation.

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$$CR_{Challenge} = \frac{(IW - FW - WL_{Pretreatment})}{\rho_{steel} \times A_{s,Challenge} \times t_{Challenge}} \times 10 \times 24 \times 365 \quad (2)$$

where:

$CR_{Challenge}$ – Net Corrosion rate from the challenge phase (excluding the autoclave phase), [mm/y]

IW – Initial weight of fresh polished steel specimen, [g]

FW – Final weight of steel specimen after treated with Clarke solution, [g]

$WL_{Pretreatment}$ – Weight loss of specimen in the pretreatment phase, [g]

ρ_{steel} – Density of steel specimen, [g/cm³]

$A_{s, Challenge}$ – Area of steel specimen exposed to corrosive fluid during challenge, [cm²]

$t_{Challenge}$ – Duration of experimentation in the HVR, [h]

RESULTS

The following paragraphs present and discuss the experimental data for the "pretreatment experiments" (where scales were generated in the stirred autoclave) and the "pretreatment - challenge" experiments (where scales generated in the stirred autoclave were subsequently challenged in the HVR).

Pretreatment Experiment Results

Scales were formed in pretreatment experiment on CS and 5Cr specimens using one of the experimental solutions described in previous paragraphs. Figure 2 compares the corrosion rates for CS and 5Cr specimens pretreated at 600°F (316°C) with the three different experimental solutions prepared by using the model compounds. The two types of steel showed similar pretreatment corrosion rates in each of the solutions. Generally, the presence of 5% chromium in the steel did not lower the pretreatment corrosion rates significantly. More interestingly, adding NAP into a "DDS only" solution (last set of data in Figure 2) did not increase the corrosion rate significantly compared to the "NAP only" data.

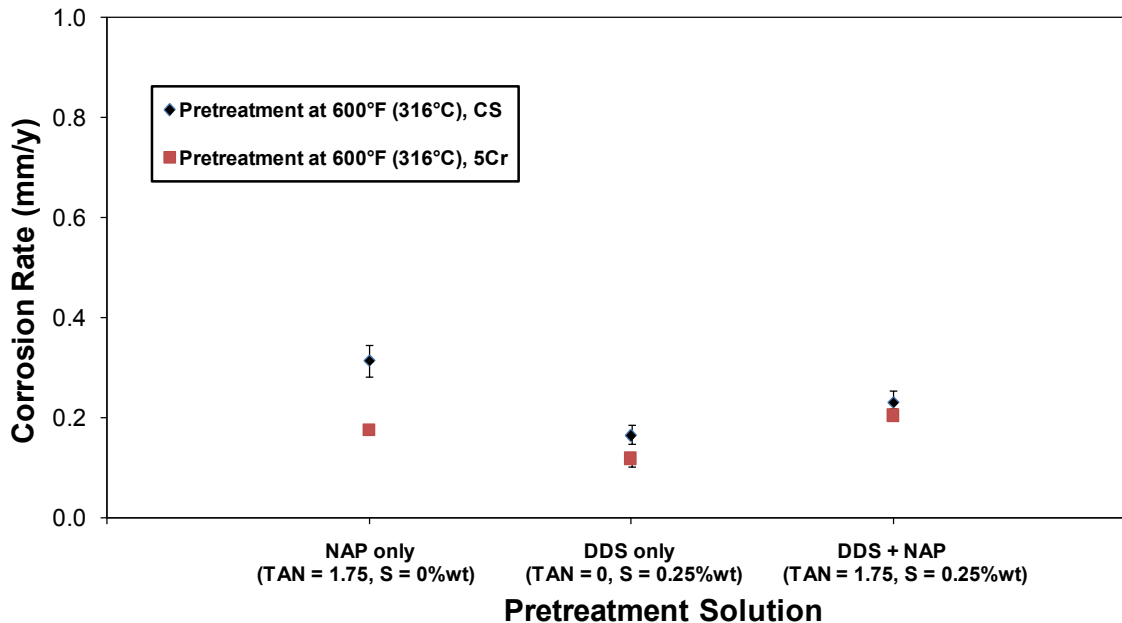


Figure 2: Pretreatment corrosion rates for CS and 5Cr at 600°F (316°C).

Challenge Experiment Results

In the next step, a new set of specimens that was pretreated in the autoclave with each of the three experimental solutions was subsequently transferred into the HVR. The HVR was fed with the "challenge" solution of naphthenic acids dissolved in mineral oil (at TAN 3.5). The challenge corrosion rates for CS and 5Cr are shown in Figure 3. For CS specimens pretreated in "NAP only" solution, the challenge corrosion rates were high and close to CS "pure TAN 3.5 corrosion rate". "Pure TAN 3.5 corrosion rate" refers to the baseline corrosion rate of fresh polished specimens with no surface scale that were installed in the HVR and were corroded by the TAN 3.5 solution. Also, the scale formed in "DDS only" solution on CS showed little protection against NAP challenge. The most protective scale for CS was generated in the "DDS + NAP" solution and its challenge corrosion rate was reduced to one fourth of the "pure TAN 3.5 corrosion rate".

Generally, the 5Cr specimens showed lower challenge corrosion rates than those of CS. Similarly, the scale formed in "DDS only" solution on 5Cr was not protective unless NAP was added to the solution. However, the most striking finding was that 5Cr specimens pretreated in "NAP only" solution gave an almost zero challenge corrosion rate, which contradicted the traditional theory on NAP corrosion. This experiment was repeated four times and the same challenge corrosion rate was confirmed each time. It seemed that there was "something" formed on the steel surface protecting the steel from attack by NAP which was not expected in the absence of DDS and therefore, microscopy analysis on the metal surface was performed to explain the unexpected protection of scale.

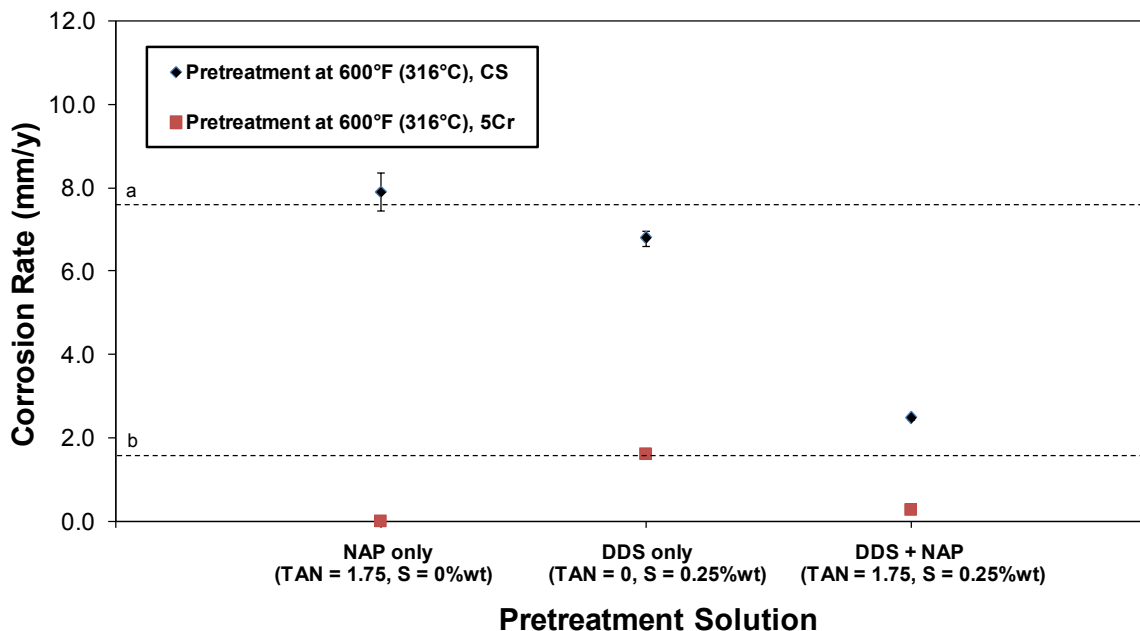


Figure 3: Challenge corrosion rates for CS and 5Cr pretreated with three solutions. Dotted lines "a" and "b" indicate pure TAN 3.5 corrosion rates for CS and 5Cr, respectively.

SEM/EDS Analysis

The scales formed on steel specimens were analyzed first using the Scanning Electron Microscopy (SEM) combined with Energy Dispersive Spectroscopy (EDS). Low corrosion rates of 5Cr specimens obtained during the challenge experiments suggested that the scales formed on this type of steel were protective against NAP attack even in the absence of sulfur containing compounds (DDS). Therefore the following paragraphs will focus mainly on analysis of the unexpected results generated using the 5Cr specimens. Figure 4 shows the surface of 5Cr specimens after pretreatment in the three solutions

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described previously. By visual examination, the "NAP only" solution seemed to have left nothing detectable on the steel surface, which was confirmed by EDS analysis. However, the challenge experimentation indicated that the 5Cr specimen seen in image in Figure 4a was most resilient in the harsh condition of the TAN3.5 challenge (see Figure 3). Therefore it was concluded that the SEM/EDS surface analysis was not helpful in explaining the low challenge corrosion rate of the 5Cr specimen. On the other hand, multiple layers were formed in "DDS only" solution and chromium was found in the inner layer which was covered by an iron sulfide layer (see Figure 4b). In the "DDS+NAP" solution, the layer of iron sulfide was still observed on the specimen surface as shown by image in Figure 4c, however the corresponding challenge corrosion rate was lower (see Figure 3). For both specimen seen in images Figure 4b and Figure 4c, about 5% of chromium was found in the inner scale layer.

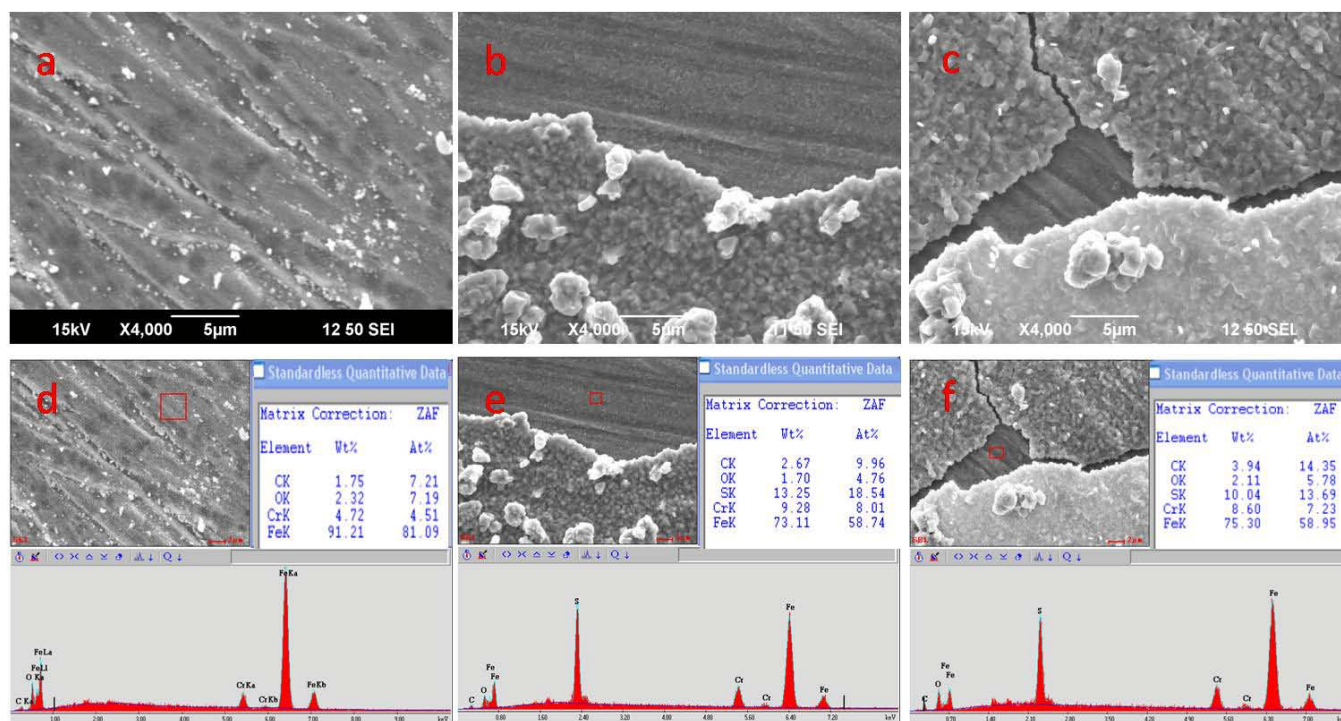


Figure 4: SEM images of 5Cr steel specimens pretreated with (a) "NAP only" solution, (b) "DDS only" solution, and (c) "DDS + NAP" solution, at 600°F (316°C). Images (d), (e), and (f) show corresponding EDS analyses.

Cross-section analysis of the layers for 5Cr revealed consistent information with the surface analysis (see Figure 5). No obvious layer could be seen in image Figure 5a obtained from the "NAP only" solution which had a very low challenge corrosion rate. Image in Figure 5b shows the delaminated scale layer formed in "DDS only" solution. The cross section of the 5Cr specimen from the "DDS+NAP" solution, seen in Figure 5c displays a thicker layer with some materials seen between the outer iron sulfide layer and the bare metal surface. The resolution of the images was not high enough to reveal a detailed layer morphology or profile of chemical composition. Moreover, EDS analysis in image "f" showed peaks of oxygen in the inner layer, which deserved further investigation.

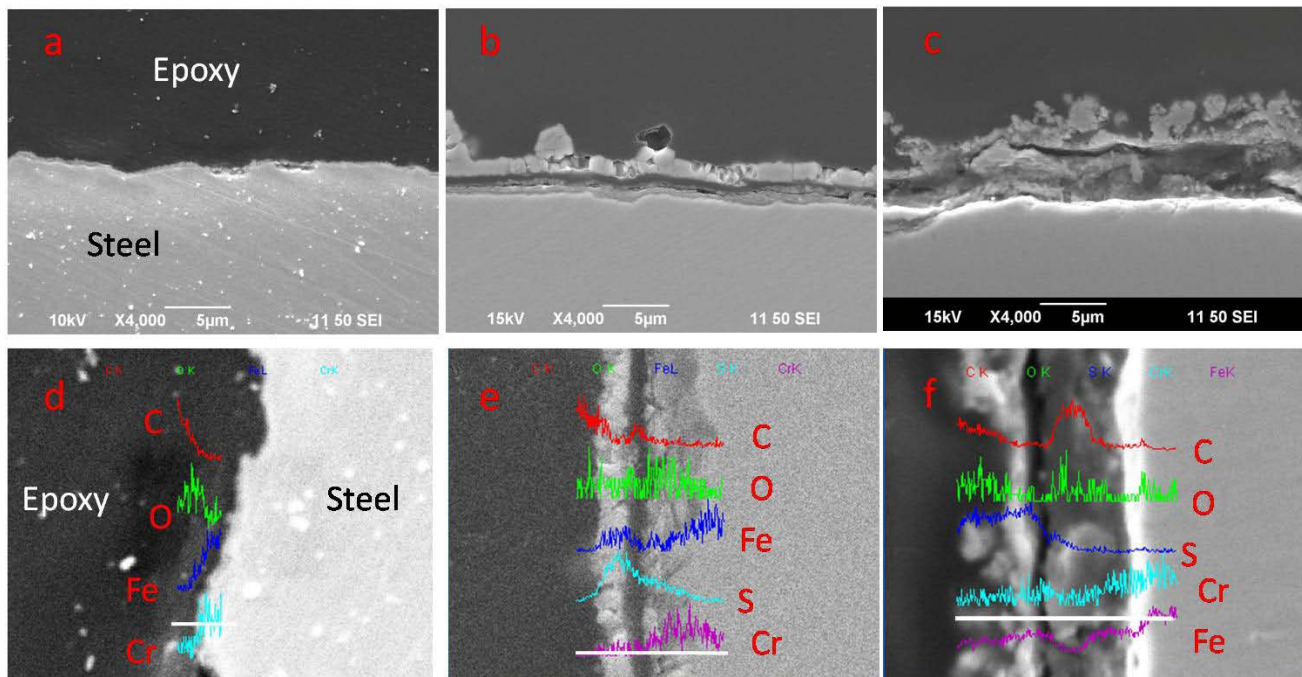


Figure 5: Cross-section SEM images of 5Cr specimens pretreated with (a) "NAP only" solution, (b) "DDS only" solution, and (c) "DDS + NAP" solution, at 600°F (316°C). Bottom images (d), (e), and (f) show corresponding EDS analyses of the scales. The EDS analysis was performed along the white line shown on the bottom of the image.

The 5Cr specimen surface after "challenge" is shown in Figure 6. The 5Cr specimen pretreated with "NAP only" solution gave a zero challenge corrosion rate (Figure 3), but no obvious layer was found through SEM analysis (see Figure 4). After "challenge", a continuous layer was still not visible; only some isolated crystals were observed. However, EDS analysis showed a peak of oxygen in image (Figure 6d) and suggested that there might be a thin oxide layer, and further analysis was necessary for verification. The unprotective layer formed in "DDS only" solution was characterized by delaminated layers and flakes of iron sulfide as shown in images in Figure 6b and Figure 6e. For the scale formed in "DDS + NAP" solution, seen in images in Figure 6c and Figure 6f the layer of iron sulfide was also observed after challenge, but the "challenge" corrosion rate was only one fourth of "pure TAN 3.5 corrosion rate" for 5Cr.

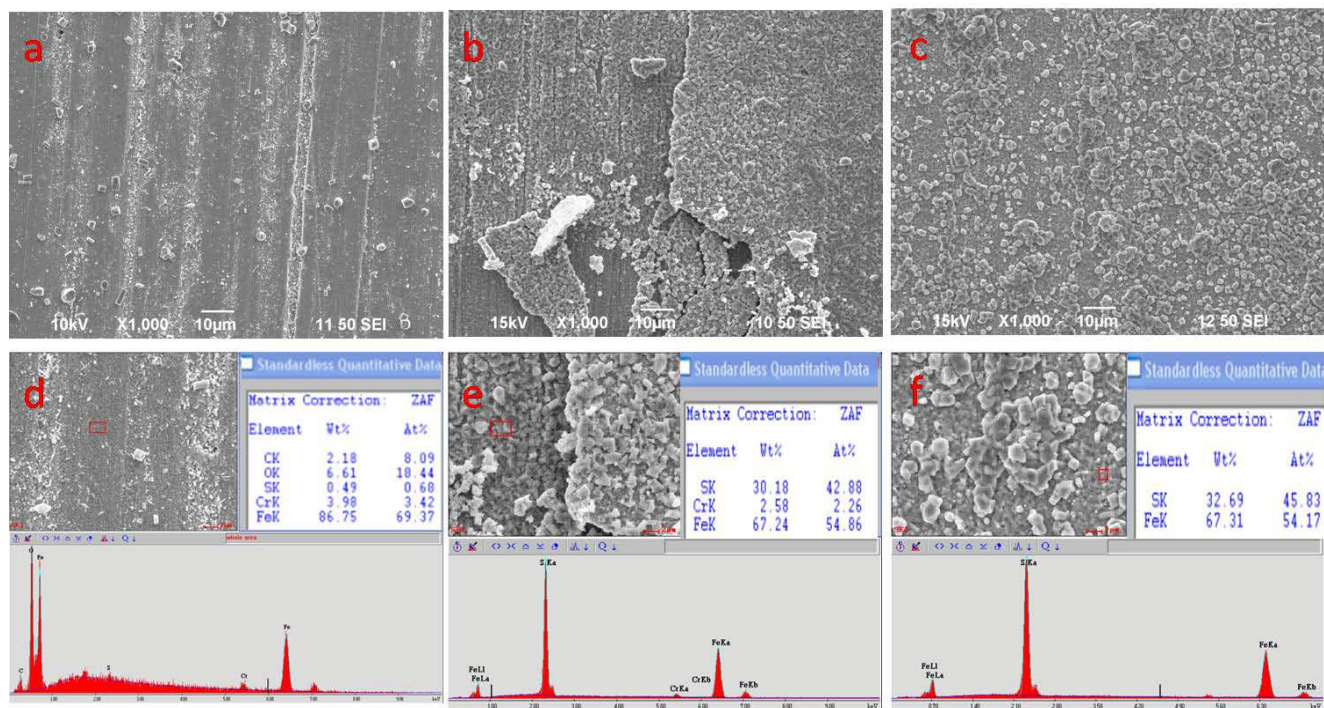


Figure 6: SEM images of 5Cr specimens pretreated with (a) "NAP only" solution, (b) "DDS only" solution, and (c) "DDS + NAP" solution, at 600°F (316°C); challenged with NAP solution (TAN 3.5) at 650°F (343°C). Images (d), (e), and (f) show corresponding EDS analyses.

The cross-section SEM/EDS analysis on the specimen pretreated with "NAP only" solution and challenged with NAP solution (TAN 3.5) revealed more information on the scale layer (see Figure 7). The magnification used was 8,000x and a very thin surface layer was visible but blurry. In addition to the peak of sulfur, EDS analysis showed the peak of oxygen in image seen in Figure 7 d, which was unexpected and deserved further investigation with a more advanced instrument. Again, a delaminated layer was observed in images Figure 7b and Figure 7e and which agrees with the observation that the layer totally failed in the HVR "challenge" (see Figure 3). Adherent and more compact layer formed in "DDS + NAP" solution survived the "challenge" (see image Figure 7c and Figure 7f) and decreased the corrosion rate as shown in Figure 3.

It is noteworthy that the most intensive peak of oxygen appeared in the EDS analyses for the two specimen which had the more protective properties of the surface scale layer. However, the SEM/EDS analysis was not sufficiently powerful to provide submicron resolution and fully reveal the structure of thin surface layer which seemed to be the key to the corrosion protection. An analytical technique offering a higher resolution was needed, and in this case the FIB/TEM/EDS and CBED were used for more in-depth analyses.

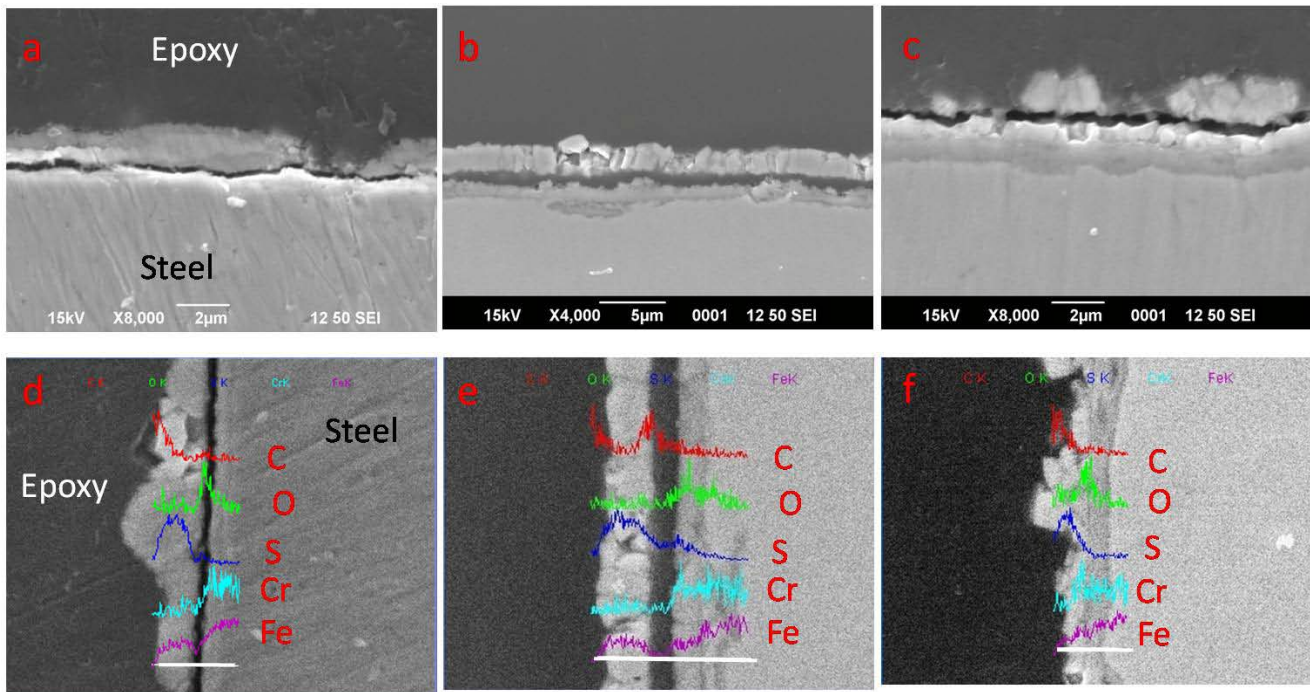


Figure 7: Cross-section SEM images of 5Cr specimens pretreated with (a) "NAP only" solution, (b) "DDS only" solution, and (c) "DDS + NAP" solution, at 600°F (316°C); challenged with NAP solution (TAN 3.5) at 650°F (343°C). Bottom images (d), (e), and (f) show corresponding EDS analyses. The EDS analysis was performed along the white line on the bottom of the images.

TEM/EDS Analysis

FIB/TEM combined with EDS as well as CBED are powerful analytical techniques that reveals the structure and chemical composition of materials on a nanometer scale.^[9] To find the explanation for the protectiveness of scales formed in different solutions, combined FIB/TEM/EDS analyses were conducted on 5Cr specimens pretreated in "DDS only" solution, "DDS + NAP" solution, and "NAP only" solutions. The scale formed in "DDS only" solution is shown in Figure 8 (cross-section TEM image). Two layers were observed and the EDS analysis indicated that the top layer was composed of iron sulfide (Figure 9). According to the analysis on the inner layer shown in Figure 10, iron sulfide was the major component, although there was a minor amount of oxygen which may be due to sample oxidation or contamination. About 5% of chromium showed up in the substrate steel, which was consistent with the chromium content in 5Cr steel.

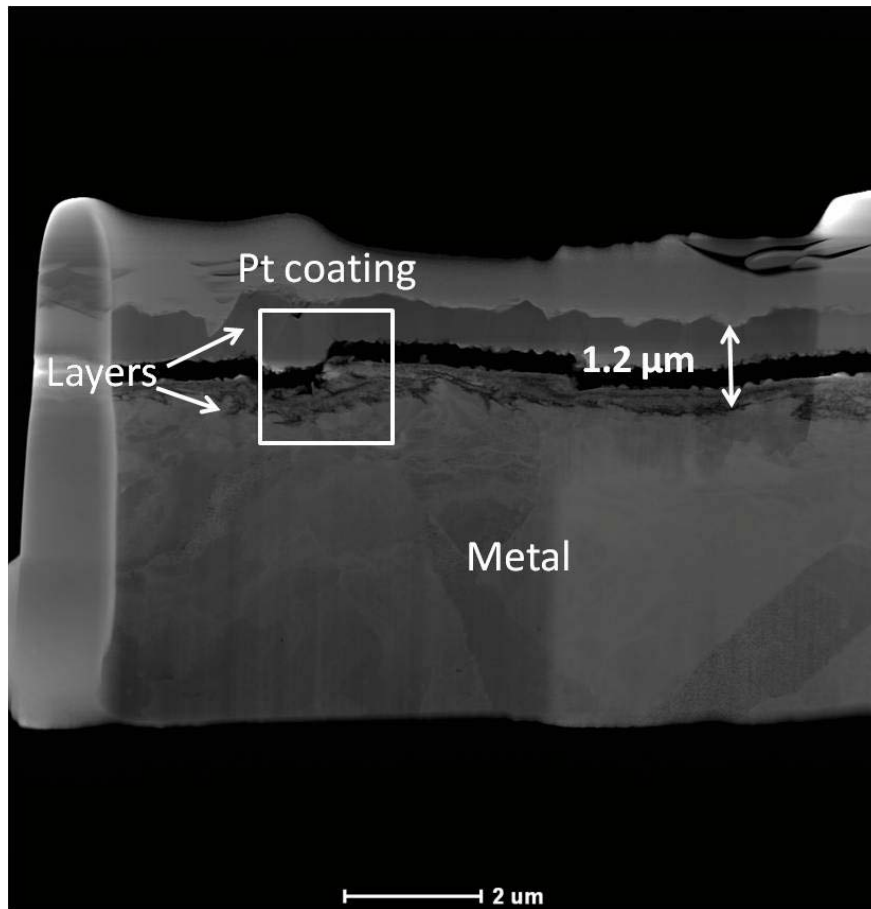


Figure 8: TEM image of 5Cr specimen pretreated with "DDS only" solution at 600°F (316°C). Area in the white square is enlarged in Figure 10.

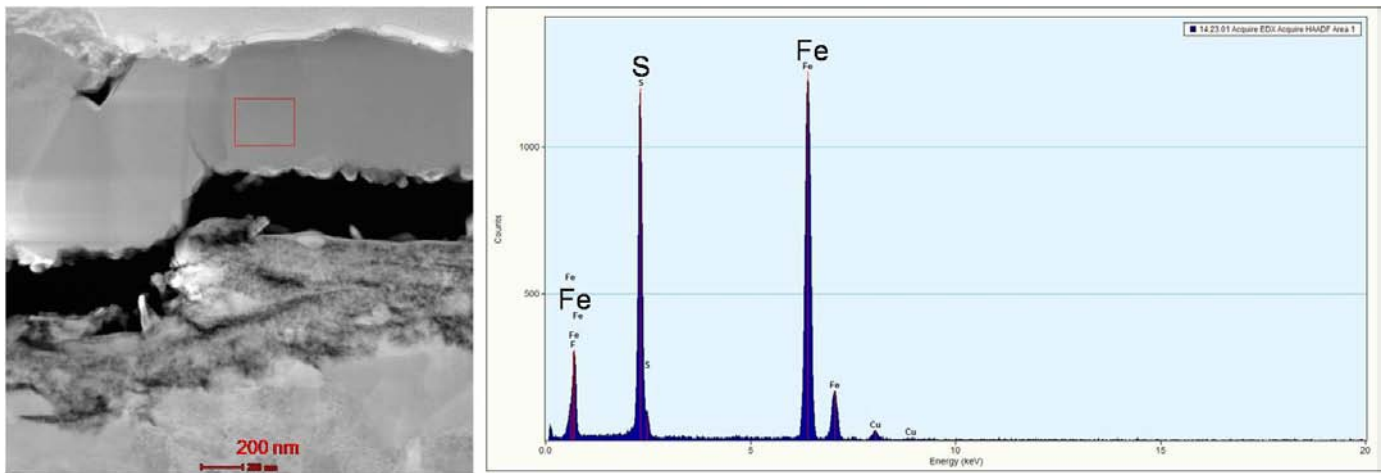


Figure 9: EDS analysis on the outer layer shown in the square of Figure 8. The elemental data were collected in the red square shown on the TEM image.

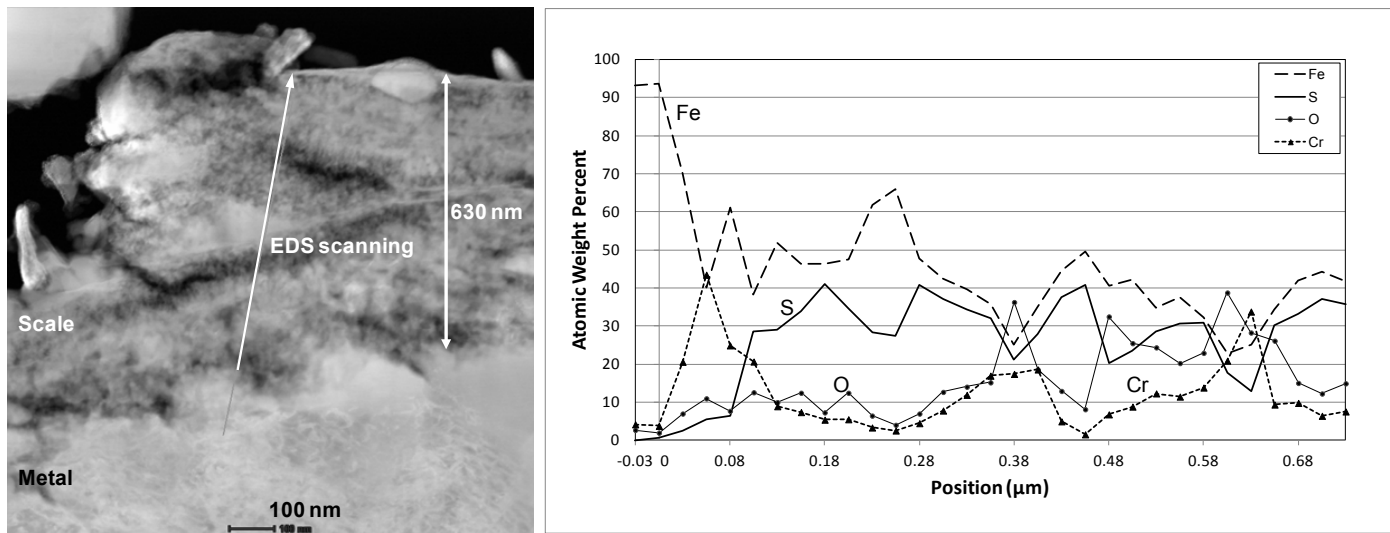


Figure 10: TEM image and EDS analysis on the inner layer of 5Cr specimen pretreated with "DDS only" solution at 600°F (316°C). The elemental data were collected along the white line (from the bottom to the top) indicated on the TEM image.

The scale formed in "DDS + NAP" solution is shown in Figure 11. Comparing the structure of this scale (Figure 11) with that of the scale formed on 5Cr pretreated in "DDS only" solution (Figure 8), the outer layer formed in "DDS + NAP" solution was more intimately attached to the inner layer. The total layer thickness was about 1 μm while the inner layer accounted for less than half of that (Figure 11). The EDS analysis of the scale formed in "DDS + NAP" solution on 5Cr indicated that the chemical composition of the scale inner layer changed (Figure 12). The primary difference in chemical composition of the scales seen in Figure 10 with Figure 12 is that a considerable amount of sulfur in Figure 10 is replaced by oxygen in Figure 12. In Figure 12, the oxygen content is over 40% while the sulfur amount decreases to values lower than 5%. Similar to Figure 10, the chromium concentration in Figure 12 increases from 5% in the steel substrate to about 10% in the inner scale layer (enrichment). Given that the outer layer was composed of iron sulfide in both cases (for "DDS only" and the "NAP + DDS" pretreatments), the difference in the protective properties of scale is most likely related to the oxygen content found in the inner layer.

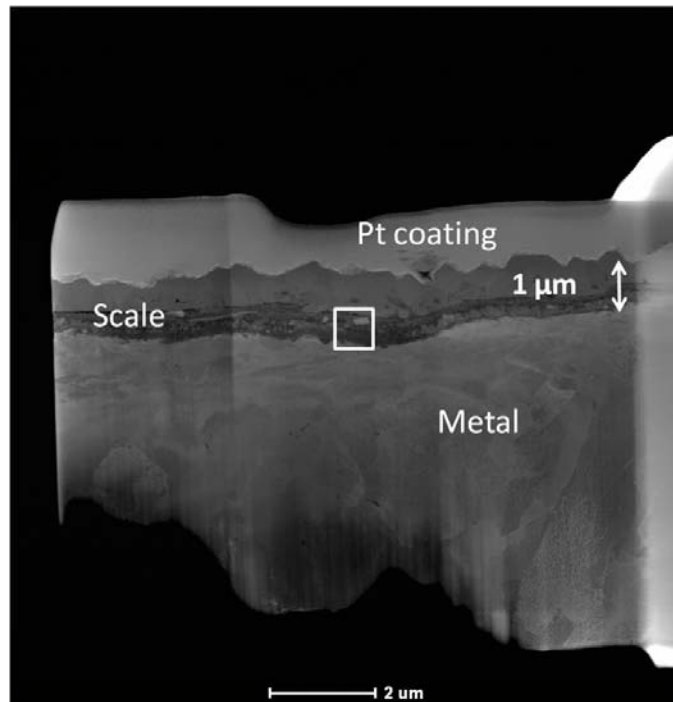


Figure 11: TEM image of 5Cr specimen pretreated with "DDS + NAP" solution at 600°F (316°C). Area in the white square is enlarged in Figure 12.

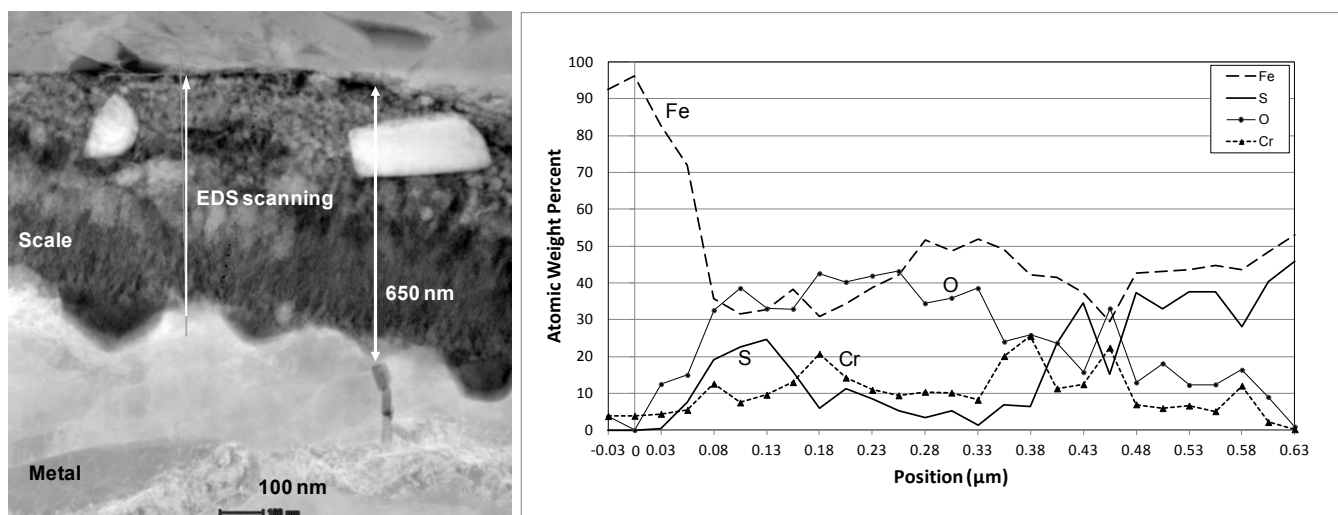


Figure 12: TEM image and EDS analysis on the inner layer of 5Cr specimen pretreated with "DDS + NAP" solution at 600°F (316°C). The elemental data were collected along the white line from the bottom to the top.

Figure 13 shows TEM/EDS analysis on the most protective scale formed in the "NAP only" solution on 5Cr. A thin scale with a thickness of 165 nm was formed on the specimen. Compared with the scale formed in "DDS only" and "DDS + NAP" solutions, it seemed that the scale was composed of only one layer. The EDS analysis reveals that the scale was composed of iron and oxygen, though trace amounts of chromium and sulfur were found. The chromium could be traced back to the 5Cr and sulfur could either be from the trace amounts contained in the commercial naphthenic acid blend used and/or from the slight contamination of the autoclave. Convergent Beam Electron Diffraction (CBED) analysis was performed and it was found that magnetite (Fe_3O_4) was the major component of the oxide layer (see Figure 14).

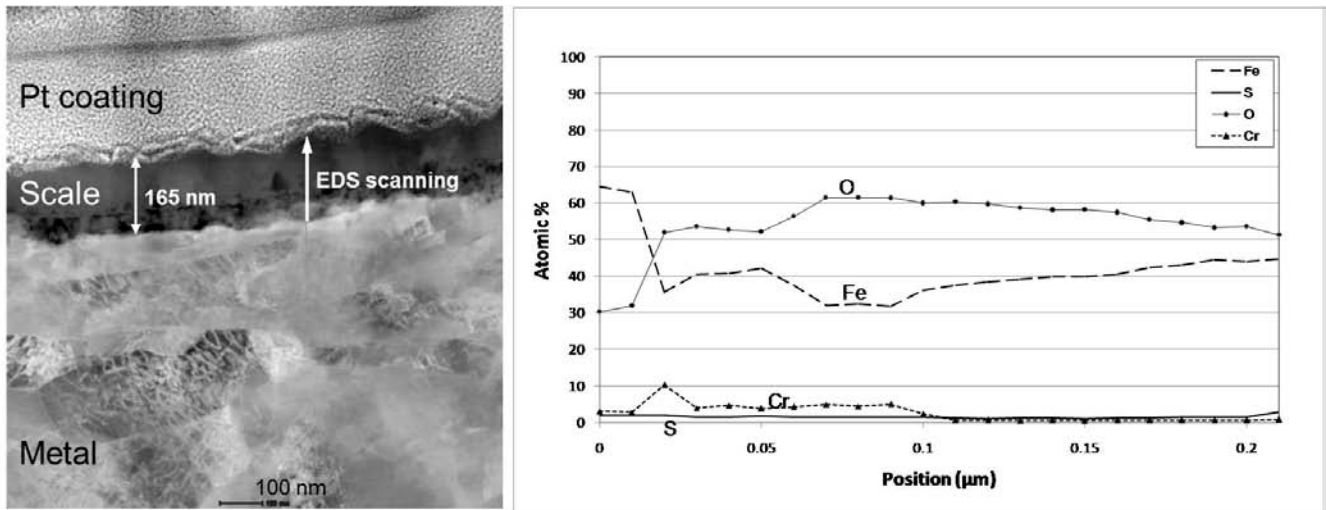


Figure 13: TEM image and EDS analysis on the scale formed on 5Cr specimen pretreated with "NAP only" solution at 600°F (316°C). The elemental data were collected along the white line from the bottom to the top.

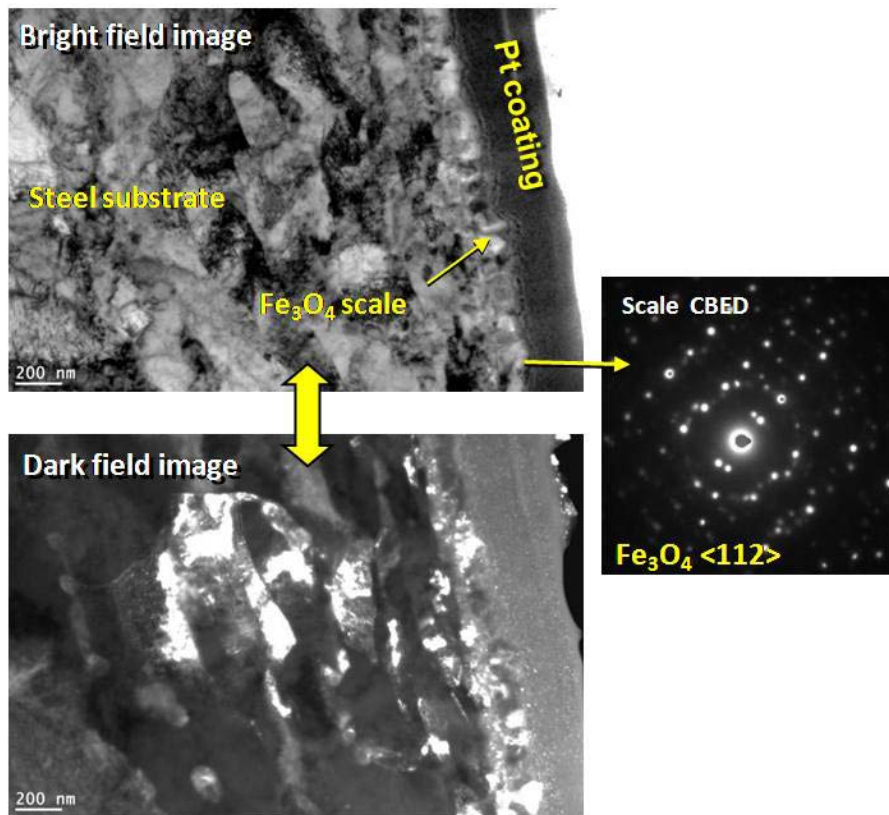


Figure 14: TEM images and CBED pattern of layer formed in "NAP only" solution at 600°F (316°C) for 5Cr specimen.

Following the challenge step by naphthenic acid, the morphology and chemical composition of the oxide layer formed on 5Cr specimens did not change significantly (see Figure 15). Oxygen is still the major element and magnetite is found again (see Figure 16). It is concluded that the magnetite formed in the "NAP only" solution was protecting the steel from the challenge attack by the naphthenic acid.

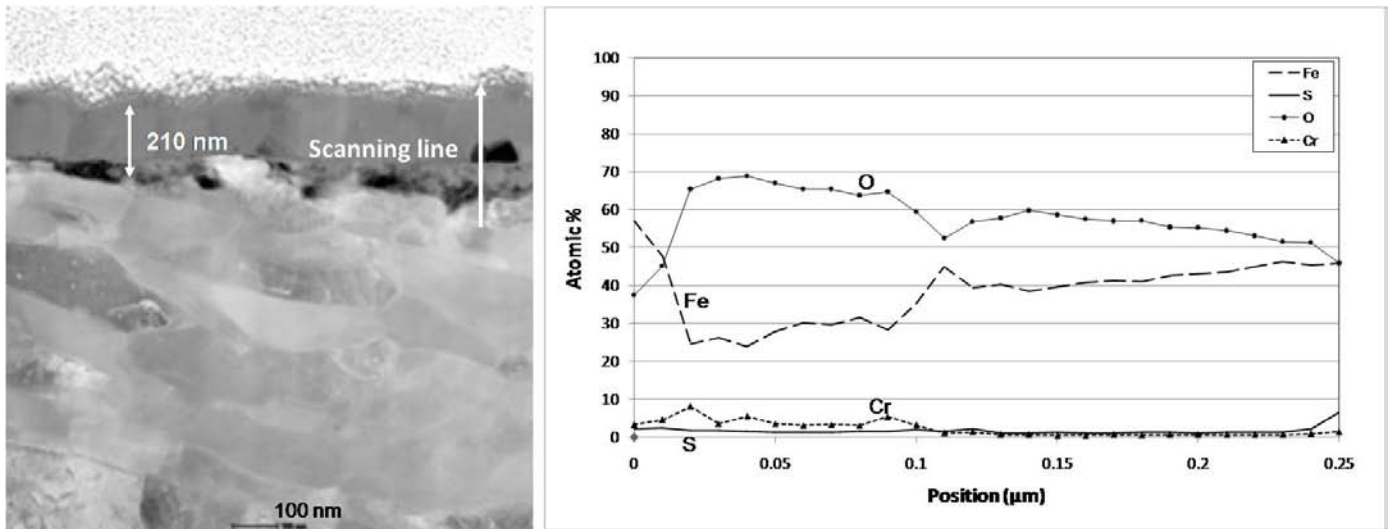


Figure 15: TEM image and EDS analysis on the scale formed on 5Cr specimen pretreated with "NAP only" solution at 600°F (316°C); challenged with NAP solution (TAN 3.5) at 650°F (343°C). The elemental data were collected along the white line from the bottom to the top.

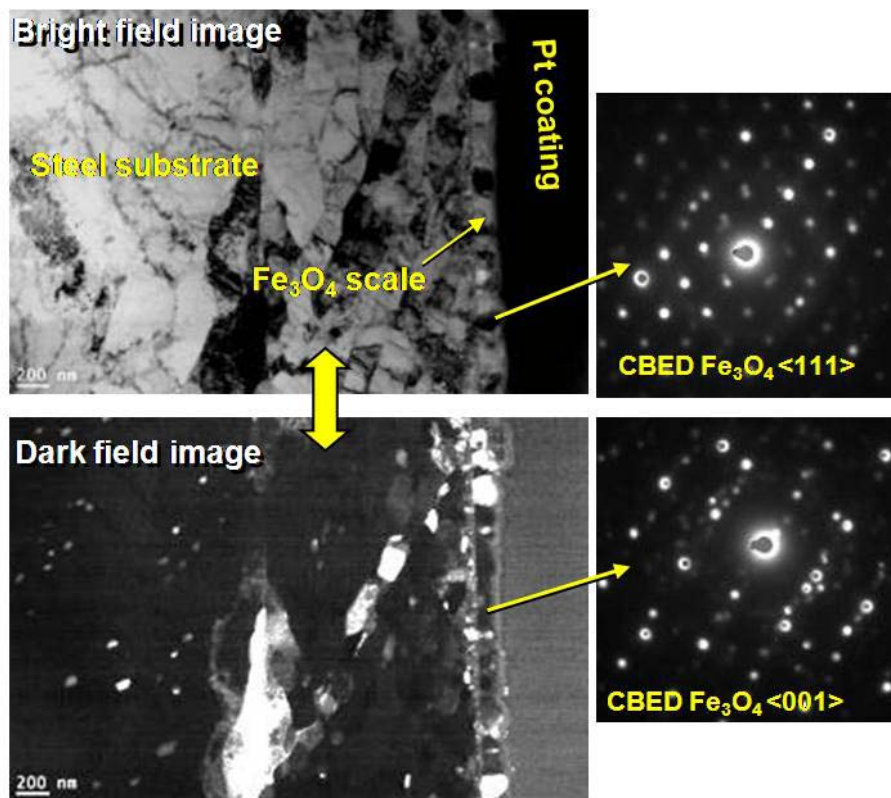


Figure 16: TEM images and CBED patterns of layers formed after pretreatment in "NAP only" solution at 600°F (316°C) and challenged with NAP solution (TAN 3.5) at 650°F (343°C) (5Cr specimen).

Discussion

The formation of an iron oxide or magnetite layer relating to NAP corrosion was reported previously in the literature. Kamel, *et al.*, noted that an iron oxide layer was revealed by XRD and XPS analysis on steel specimens corroded by crude fractions in the autoclave.^[10] However, it was postulated that iron oxide existed in the outermost layer and resulted from sample oxidation after the test. Smart, *et al.*, found the existence of magnetite and minor amount of hematite ($\alpha\text{-Fe}_2\text{O}_3$) and pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$) on carbon steel surface after testing with a high-TAN crude.^[11] The layer of magnetite was suspected to be protective, but the role of naphthenic acid in the formation of iron oxide layer was not considered. Magnetite was also found in experiments by Huang *et al.*^[12] by using model sulfur compound (dimethyl disulfide) and NAP. Again, the appearance of magnetite was considered to be the result of contamination and sulfide layer oxidation.

However, our current research clearly suggested that presence of NAP was necessary to form the oxide layer which was protective against NAP corrosion. Contrary to the commonly accepted point of view, the iron sulfide scale formed in the sulfur-only containing solution (in the form of DDS), was not protective.

It is here further postulated that the formation of the oxide scale is due to the decomposition of iron naphthenates, $\text{Fe}(\text{RCOO})_2$. In fact, the decomposition of iron naphthenates between 200°C to 800°C was reported first in 1976 and magnetite was one of products.^[13] Moreover, decomposition of ferrous carboxylates is widely used in the preparation of nano-scale magnetite.^[14] Investigation of the reaction mechanism suggested that wüstite (FeO) was the initial product and would disproportionate to magnetite.^[14] Therefore, the following reaction sequence might explain the formation of the magnetite layer during the process of NAP corrosion of steel.^{[14], [15]}



The very thin layer of magnetite is of crucial importance when considering the protectiveness of corrosion product scales found in high temperature corrosion of steel in refinery conditions.

CONCLUSIONS

- 1) The iron sulfide scale, formed due to the sulfur content in the oil, was not directly correlated to the reduction of naphthenic acid corrosion.
- 2) Having naphthenic acids in the oil improved the protectiveness of the surface scales, especially for 5Cr steel.
- 3) A thin submicron oxide layer, which was protective against NAP corrosion, was found by using Focused Ion Beam / Transmittance Electron Microscope – FIB/TEM combined with energy dispersive X-ray spectroscopy (EDS) analysis. Its formation was clearly related to the presence of NAP in the oil. By using Convergent Beam Electron Diffraction (CBED) it was found that the oxide layer was composed of magnetite.
- 4) It is hypothesized that decomposition of iron naphthenates resulted in the formation of the magnetite layer. Further experimental and analytical work should focus on the verification of this mechanism.

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REFERENCES

1. S.D. Kapusta, A. Ooms, A. Smith, F. Van den Berg, W. Fort, "Safe Processing of Acid Crudes," CORROSION/2004, paper no. 04637 (Houston, TX: NACE, 2004), p. 1.
2. E. Slavcheva, B. Shone, A. "Turnbull, Review of Naphthenic Acid Corrosion in Oil Refining," *Brit. Corros. J.* 34, 2(1999): p. 125.
3. I. Dzidic, A.C. Somerville, J.C. Raia, H.V. Hart, "Determination of Naphthenic Acids in California Crudes and Refinery Waste Waters by Fluoride Ion Chemical Ionization Mass Spectrometry," *Anal. Chem.* 60, 13(1988): p. 1318.
4. R.D. Kane, M.S. Cayard, "Understanding Critical Factors that Influence Refinery Crude Corrosiveness," *MP* 38, 7 (1999): p. 48.
5. G.M. Bota, D. Qu, S. Nestic, H.A. Wolf, "Naphthenic Acid Corrosion of Mild Steel in the Presence of Sulfide Scales Formed in Crude Oil Fractions at High Temperature," CORROSION/2010, paper no. 10353 (San Antonio, TX: NACE 2010), p. 1.
6. G.M. Bota, S. Nestic, "Naphthenic Acid Challenges of Iron Sulfide Scales from Model Oil on Mild Steel at High Temperature," CORROSION/2013, paper no. 2512 (Orlando, FL: NACE 2013), p. 1.
7. ASTM G1 - 03 (2011), "Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens" (West Conshohocken, PA: ASTM).
8. S.G. Clarke, "The Use of Inhibitors (with Special Reference to Antimony) in the Selective Removal of Metallic Coatings and Rust," *Trans. Electrochem. Soc.* 69, 1 (1936): p. 131.
9. D.G. Stroppa, L.F. Zagonel, L.A. Montoro, E.R. Leite, A.J. Ramirez, "High-Resolution Scanning Transmission Electron Microscopy (HRSTEM) Techniques: High-Resolution Imaging and Spectroscopy Side by Side," *Chemphyschem* 13, 2 (2012): p. 437.
10. M. El Kamel, A. Galtayries, P. Vermaut, B. Albinet, G. Foulonneau, X. Roumeau, B. Roncin, P. Marcus, "Sulfidation Kinetics of Industrial Steels in a Refinery Crude Oil at 300 °C: Reactivity at the Nanometer Scale," *Surf. Interface Anal.* 42, 6-7(2010): p. 605.
11. N.R. Smart, A.P. Rance, A.M. Pritchard, "Laboratory Investigation of Naphthenic Acid Corrosion Under Flowing Conditions," CORROSION/2002, paper no. 02484 (Denver, CO: NACE 2002), p. 1.
12. B.S. Huang, W.F. Yin, D.H. Sang, Z.Y. Jiang, "Synergy Effect of Naphthenic Acid Corrosion and Sulfur Corrosion in Crude Oil Distillation Unit," *Appl. Surf. Sci.* 259 (2012): p. 664.
13. J. Fukushima, K. Kodaira, T. Matsushita, "Preparation and Formation Process of Various Iron Oxide Films by Thermal Decomposition of Iron Naphthenate," *J. Ceram. Soc. Jpn.* 84, 11 (1976): p. 529.
14. F.X. Redl, C.T. Black, G.C. Papaefthymiou, R.L. Sandstrom, M. Yin, H. Zeng, C.B. Murray, S.P. O'Brien, "Magnetic, Electronic, and Structural Characterization of Nonstoichiometric Iron Oxides at the Nanolayer," *JACS* 126, 44 (2004): p. 14583.
15. S. Stolen, R. Gloeckner, F. Gronvold, "Nearly Stoichiometric Iron Monoxide Formed as a Metastable Intermediate in a Two-Stage Disproportionation of Quenched Wüstite. Thermodynamic and Kinetic Aspects," *Thermochim. Acta* 256 (1995): p. 91.