FORMATION OF SULFIDE SCALES AND THEIR ROLE IN NAPHTHENIC ACID CORROSION OF STEELS

A thesis presented to
the faculty of
the Russ College of Engineering and Technology of Ohio University

In partial fulfillment
of the requirements for the degree
Master of Science

Vijaya Kanukuntla
March 2008
This thesis titled
FORMATION OF SULFIDE SCALES AND THEIR ROLE IN NAPHTHENIC ACID CORROSION OF STEELS

by

VIJAYA KANUKUNTLA

has been approved for
the Department of Chemical and Biomolecular Engineering
and the Russ College of Engineering and Technology by

________________________________________________________
Srdjan Nesic
Professor of Chemical and Biomolecular Engineering

________________________________________________________
Dennis Irwin
Dean, Russ College of Engineering and Technology
ABSTRACT

KANUKUNTLA, VIJAYA, M.S., March 2008, Chemical Engineering

FORMATION OF SULFIDE SCALES AND THEIR ROLE IN NAPHTHNIC ACID CORROSION OF STEELS (186 pp.)

Director of Thesis: Srdjan Nesic

The present study has been conducted to investigate the corrosion and scale formation rates of CS-A106 and 5Cr-A182 exposed to different acid concentrations and varying amounts of sulfur compounds. The experiments were designed to determine the effect of time, temperature and acid concentration on the formation and retention of sulfide films formed on the steel surface. A hot oil flow loop “Flow Through Mini Autoclave” was used to conduct experiments forming sulfide scales at different acid concentrations varying from 0.04 to 4. Temperature of these experiments was varied from a low temperature (450°F) to a high temperature (700°F). Tests were conducted for a short period of 3 hr to a long period of 96 hr.

It was observed that sulfide scales protect steel surface from being corroded once they formed on the steel. Amount of scale accumulated on the steel increased with time but the protectiveness of the scale was highly reliant on the time of exposure, acid concentration and temperature. Sulfide scales were subjected to cracking and it reduced the adherence of scale to steel surface. Sulfide scales were not 100% dense and SEM pictures showed porous scales formed in all experiments.

Approved: ________________________________

Srdjan Nesic

Professor of Chemical and Biomolecular Engineering
DEDICATION

To

Thirupathi and Vasantha Kanukunlta (my parents)

and

Rakesh Kumar Gudla (my husband)

and

Kishore and Kiran Kanukuntla (my brothers)

and

Shireesha Kanukunta (my sister)

and

Kiranmai Sreeramoju (my dearest pal)

Whose mental support made this work a success
ACKNOWLEDGEMENTS

I would like to express my gratitude to Dr. Srdjan Nesic for his continuous academic and moral support. His punctuality and sincerity towards work greatly inspired and motivated me throughout my career at Ohio University. His deep knowledge of fundamental concepts of chemical engineering showed me new ways of learning and understanding a subject. His immense moral support and patience when things went wrong encouraged and enabled me to accomplish my duties on time. This thesis is an honor to his dedication towards work and his outstanding guidance and support during my entire stay at Ohio University.

I would like to acknowledge my indebtedness to Mr. Alan Wolf for his support and priceless suggestions during the entire research. I was greatly influenced by his enthusiasm and zeal towards unfolding the secrets of refinery corrosion.

I would also like to thank the technical staff at the Institute for Corrosion and Multiphase Technology, including Mr. Al Schubert, Mr. John Goettge and Mr. Danny Cain for their assistance in technical matters and my colleagues Ghoerghe Bota and Ding Rong Qu for providing a wonderful, competitive and healthy research environment.

I would also like to acknowledge the continuous financial and technical support of the company ExxonMobil Research and Engineering that granted this research project to Institute for Corrosion and Multiphase Technology at Ohio University.
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1 INTRODUCTION

Refinery corrosion continues to be a substantial problem despite efforts to mitigate it over the past eighty years. It is well known that naphthenic (NAP) acids present in oils are the main agents of corrosion [1-6] NAP acid corrosion is complex and very little is known about it as there are many factors affecting it such as sulfur compounds, type of acids, temperature and velocity. Also, most of the literature available deals only with case studies [2] which can contribute very little to understand NAP acid corrosion. Inclination to process the refineries with “opportunity crude” (low cost) with high acid concentrations has made NAP acid corrosion an important contemporary [10].

The general formula of NAP acid is \( R[CH_2]_nCOOH \), where \( R \) can be pentane or hexane ring that can be monocyclic, bicyclic or polycyclic and \( n \) is greater than 12. NAP acids are very large molecules and are heavy; e.g.: the molecular weight of NAP acid found in Californian crude varied from 200 to 700 [2].

NAP acid attack becomes more complex when the effect of sulfur containing compounds in crude oils is also considered. The extent to which these sulfuric compounds accelerate or inhibit NAP acid corrosion is still an unknown factor. The competition between these two processes in aqueous media is described by the chemical reactions shown in equations – 1.1 to 1.3 [6, 12].
Fe + 2R(COOH) → Fe(RCOO)$_2$ + $H_2$  \hspace{1cm} (1.1)

Fe + $H_2S$ → FeS + $H_2$  \hspace{1cm} (1.2)

$Fe(RCOO)_2$ + $H_2S$ → FeS + 2RCOOH  \hspace{1cm} (1.3)

According to equations 1.1-1.3 NAP acids attack the metal surface and react with Fe generating soluble iron naphthenate. At the same time, hydrogen sulfide ($H_2S$) can react with Fe forming an insoluble iron sulfide (FeS) film on the steel surface. According to Piehl [2] these two reactions compete with each other and one reaction can take place retarding the other. $H_2S$ can also react with iron naphthenate regenerating NAP acids.

NAP acid corrosion is mainly influenced by NAP acid concentration, sulfur content, temperature and velocity of the crude as well as materials of construction [2, 4, 6, 9, 10]. Blanco et al [4] stated that NAP acid corrosion also depends on turbulence and physical state of crude oil (liquid or vapor). According to Piehl [2] the type of crude oil can also affect corrosion. Nugent [15] claimed that specific types of acids and their activity can also produce a different rate of corrosion.

\section*{1.1 Effect of Total Acid Number (TAN)}

Piehl [2] stated one of the important variables affecting NAP acid corrosion other than temperature is total acid number (TAN or neutralization number). TAN is defined as the amount of KOH in milligrams required to neutralize all the acids present in one gram of oil, TAN has the units of mg KOH/g Oil [2, 6, 12]. Two standard tests are used to measure TAN namely ASTM D 974 and ASTM D 664. ASTM D 974 is a colorimetric method based on color change of indicator with addition of KOH. ASTM D 664 is a
potentiometric method based on change in electrical conductivity of the sample by addition of KOH. This method is mostly used for oils that are too dark to be determined by the ASTM D974 color change method. These two methods are not entirely accurate, as the TAN determined accounts for not only the presence of NAP acids but also inorganic acids, phenolic compounds, mercaptans and salts [10]. Piehl suggested that ASTM D974 is more accurate as it is less affected by extremely weak acids. However, ASTM D664 is the widely used method in industry today [6].

Piehl analyzed corrosion data from several plants and related corrosion rates to TAN. Corrosion rates increased with increasing TAN at different temperatures ranging from 400 to 700°F [2]. It should be noticed that the data used in these correlations was obtained from low velocity regions of flow such as distillation columns and liquid-packed heat exchangers. Even though no laboratory experiments were conducted, Piehl stated that the threshold acid number range above which only naphthenic acid corrosion can occur is 1.5 to 2 [2]. Later it was demonstrated that crude oils with TAN values greater than 0.5 exhibit significant NAP acid corrosion [13]. However, light Indonesian crude with a TAN value below 0.5 and Nigerian crude with a TAN slightly higher than 0.3 both showed severe corrosion problems [14].

According to Gutzeit [3] at a given temperature increase in TAN value can increase corrosion. He also stated that some NAP acids can be lost due to vaporization at a given temperature and corrosion can be related directly to temperature if this loss can be prevented. Experiments by Slavcheva et al [5] and Craig [8] confirmed that NAP acids do decompose and TAN value falls off exponentially with time.
TAN is not a good measure of NAP acid corrosion as crude oils with same the TAN value were found to respond differently to corrosion [12]. This is because TAN indicates not only the presence of NAP acids but also some other inorganic acids, and it is highly probable that crude oils with the same TAN value can have different amounts of NAP acids[10]. Consequently, the amount (wt %) of NAP acid in the oil was considered to evaluate NAP acid corrosion. Liquid phase chromatography was used to determine wt% of acids by comparing IR absorption of NAP acids in the test sample to that of standard NAP acids [12]. This method was also observed to not be as accurate, as NAP acids in the test sample were prone to show different compositions and molecular weight as those of standard NAP acids. As a result, efforts were unsuccessful in establishing a good correlation between wt% of NAP acid and corrosion rate. Both TAN and wt% of acids turned out to be ineffective measures in assessing NAP acid corrosion.

### 1.2 Effect of time

To determine optimum exposure time, Slavcheva et al [5] conducted experiments at two characteristic temperatures, 410°F and 527°F, for different time periods of exposure to paraffin oil (Fluka), mineral oil (MO) and heavy vacuum gas oil (HVGO). They were enriched with commercially available NAP acids and tested in a glass cell. Carbon steel (C-S) and 5Chrome steel (5Cr-S) were immersed in the oil after it was preheated to the operating temperature. Argon was blown into the cell throughout the experiment to prevent oxidation. After the coupons were allowed to corrode for the desired time period, they were removed from the test system, and the corrosion rate was
measured using the weight loss method. Experiments with different time periods (1.5, 3, 6, 16, 24, 48, 72 hr) revealed that at a lower temperature (410°F) the corrosion rate did not change significantly; at a higher temperature (527°F), the corrosion rate was initially high, then slowly decreased for the first 16 hr exposure while remaining unchanged in further longer exposures. It was concluded that for a better assessment of how NAP acid corrosion is affected by temperature, velocity, sulfur content, and type of acid coupons should be exposed to a minimum of 24 hr exposure time.

### 1.3 Effect of temperature

Temperature plays an important role in NAP acid corrosion. It was reported that NAP acid corrosion can occur in the temperature range of about 430-750°F [1-5, 8, 9, 12]. An increase in temperature is expected to raise high corrosion rates through improving kinetics of the reaction, but at temperatures above 750°F no corrosion can be noticed as the NAP acid concentration diminishes with their decomposition or steel surface being protected by coking [9, 10].

Craig’s [8] laboratory experiments demonstrated low corrosion rates, even at high TAN values (TAN=11), for C-S exposed to low temperatures (450°F). Neither acids decomposed nor TAN value changed in these experiments. According to Craig light activation of acids at low temperatures resulted in low corrosion rates. Experiments at high temperatures (700°F) with C-S and low TAN (TAN =0.8) exhibited high corrosion rates (172 mpy) and demonstrated that a high temperature can activate even small amounts of acids resulting in high corrosion rates. Both Craig’s [8] and Slavcheva et al
experiments at high temperatures revealed that the TAN value of the acid decreases exponentially, though the corrosion rate is initially high.

NAP acids in the liquid phase will decompose and vaporize when they are heated to their boiling point. When these vapors condense and form a condensate film, the film can have a different TAN from that of original bulk liquid. According to Gutzeit [3], corrosion is controlled by the rate at which NAP acids in vapor condense and by the modified TAN value of the condensate film; he also stated that NAP acid corrosion can occur in liquid phase only while acids in vapor phase have no significant effect on corrosion. Several experiments were conducted at two temperatures (480°F and 580°F) in both liquid and vapor phase with different TANs. Corrosion rates at 480°F were observed to be higher in liquid phase than in vapor phase and according to Gutzeit, slow condensation and low TAN value of condensate film resulted in low corrosion rates in vapor. Conversely, experiments at 580°F illustrated high corrosion rates in the vapor phase and corrosion rates were averaged from 150 to 350% to those of liquid phase. He further explained that rapid condensation and increased TAN value of condensate film caused to observe high corrosion rates, e.g.: liquid with a TAN value 20 formed a condensate film with TAN value 36. According to him NAP acids present in vapor phase did not play any role in corrosion.
Gutzeit also stated that the corrosion rate can increase with temperature if TAN remains unchanged, in fact tripling with a ~131°F raise in temperature. According to Gutzeit, corrosion kinetics can be represented by an Arrhenius equation at temperatures above 550°F with the activation energy of C-S being 68.5 kJ/mol. Laboratory experimental data from Slavcheva et al [5] supported Gutzeit’s statements, but their calculated activation energies (31.8 kJ/mol and 23.8 kJ/mol for cyclohexane carboxylic acid and NAP acid) were lower than those reported by Gutzeit.

1.4 Effect of acid type

It was already reported that crude oils with the same TAN value may differ in NAP acid concentration and behave differently towards corrosion. Slavcheva et al [5] conducted experiments with a group of NAP acids with different carbon numbers, boiling points and the same TAN value. The composition of these oils was analyzed by using fast atom bombardment mass spectroscopy (FABMS). It was observed that the number of \((\text{CH}_2)_n\) groups present in the oil plays a key role in NAP acid corrosion. The corrosion rate by NAP acids increased with an increase of \((\text{CH}_2)_n\) groups up to \(n = 3\). Slavcheva et al suggested that at higher values of \(n\), adsorption of acid molecules was retarded by the steric hindrance between the long carbon chains, and thus the corrosion rate decreased.
1.5 Effect of sulfur

When the total sulfur level in the crude is less than or equal to 1 wt% the oil is called sweet and when it is greater than 1 wt% it is called sour [6]. Sulfur content in crude can be determined by the ASTM D4294 method and has been found to be an inaccurate method as it could be influenced by the presence of halides and heavy metals [11]. Sulfur appears in many forms in crude, such as polysulfides, mercaptans, aliphatic sulfides, disulfides and thiophenes [6, 10]; these sulfur compounds react with the metal surface to form metallic sulfides, organic complexes, and H₂S [6]. Among all these products H₂S is considered to be the most corrosive component [9]; H₂S is produced at temperatures above 500°F by the decomposition of certain sulfur compounds [6]. It was assumed that the ability of sulfur compounds to form H₂S determines the severity of corrosion, not the sulfur content in crude [2, 9, 10]. Until now, no correlation was established between H₂S evolution and temperature.

When H₂S reacts with a steel surface, it produces insoluble FeS whereas NAP acid produces soluble iron naphthenate [2, 6]. According to Piehl [2], when both NAP acid and H₂S are present in oil, there will be a competition between the two processes, with one reaction taking place at the expense of other reaction; he also stated that the insoluble iron sulfide film protects the steel surface from being corroded. Slavcheva et al and Craig’s [8] laboratory experiments confirmed the inhibitive effect of the FeS film toward corrosion. The strength of the FeS layer to provide protection to steel surface is determined by test conditions such as TAN, temperature, velocity, and time of exposure.
Piehl’s [2] field data analysis and Craig’s [8] experiments with high acid concentrations demonstrated that TAN can reduce adhesive force between metal and FeS layer and enhance scale damage promoting more corrosion.

Craig [8] differentiated NAP acid corrosion into three types based on sulfur compounds activity namely pure NAP acid corrosion, sulfidation corrosion and NAP acid corrosion.

**Pure NAP acid corrosion:** As the name suggests corrosion is mainly by NAP acids, and effect of sulfur compounds is very small even if they are present. Corrosion product is mainly soluble iron naphthenate and no film is formed on the surface. High corrosion rates would result with TAN increase as no protection is provided to the steel.

**Sulfidation corrosion:** Sulfur compounds form protective layers by corroding the steel surface first. Corrosion in this phase is termed as sulfidation corrosion. Scale offers good protection and begins to separate from the surface. This type of corrosion is aggravated by the presence of acids.

**NAP acid corrosion:** It represents the corrosion when the film breaks down and offers partial protection. Corrosion increases with acid concentration but at slower rate probably “by the suppression of ionization by stronger acids”.

A new measure called “Naphthenic acid corrosion index (NACI)” has been established that could differentiate the above three mechanisms. NACI is defined as the “ratio of corrosion rate in mpy to the weight of adherent corrosion film in milligrams per square centimeter” [8]. It was described that values below 10 indicate sulfidation attack while values above 10 would suggest NAP acid attack.
The relationship between TAN, sulfur content and corrosion rate is not yet understood clearly. However, McConomy curves are still in use to predict the relative corrosivity of crude oils at different temperatures based on sulfur content [9, 10]. These curves can be useful when sulfur is the only contaminant, but are not very reliable as they lack in demonstrating the effect of velocity [9].

1.6 Effect of velocity

Blanco et al [4] stated that velocity and turbulence play an important role in NAP acid corrosion and proposed that corrosion rate is directly proportional to velocity. High velocity regions such as transfer lines, valves, bubble tops, furnace tubes and atmospheric/vacuum columns are severely affected by NAP acid [6] whereas distillation columns, piping and exchangers are least affected [2].

Gutzeit’s [3] experiments with white oil-NAP acid mixtures in the liquid phase at 536°F with velocities up to 4m/s showed a small effect of velocity on corrosion rate. In contrast to this effect, these acid blends in the vapor phase showed higher corrosion rates with a small increase in velocity from 0 to 0.12 m/s. He explained that rapid evaporation of liquid and condensation of vapor onto the metal resulted in high corrosion. A further increase in velocity up to 4 m/s in vapor showed a decrease in corrosion rate with velocity. Gutzeit assumed that at these velocities, centrifugal forces in the system prevented the formation of a condensate layer resulting in reduced corrosion rates.

Recently, experiments were done using “jet impingement installation” to investigate the NAP acid erosion-corrosion resistance of C-S, pack-aluminized carbon steel and
molybdenum-bearing stainless steels [18]. This equipment was operated at high temperatures and fast flow conditions. Greater resistance to corrosion was observed by both pack-aluminized carbon steel and molybdenum-bearing stainless steels when compared to C-S. NAP acid erosion-corrosion was directly proportional to both experimental temperatures and high fluid velocities. The increase in NAP erosion-corrosion with temperatures and flow velocity “enhanced mass transfer and accelerated corrosion reactions at the surface and as well as the rapid spallation of corrosion products from the metal surface.” It should be noticed that the jet impingement method did not succeed in reproducing real refinery conditions.

Tebbal and Kane [10] stated that wall shear stress has a greater impact on corrosion than velocity. Degree of vaporization, liquid density, liquid viscosity, vapor density, vapor viscosity and pipe diameter would determine the severity of corrosion by wall shear stress. Their laboratory experiments proved the effect of shear stress on corrosion, but corrosion rates were no way comparable to those from field data.
1.7 Materials of construction

Piehl’s [2] data showed good resistance offered by C-S, 5Cr-S and AISI 304SS when processed by crude with TAN varying from 1.3 to 2.2 at temperatures above 725°F (385°C) in vacuum and atmospheric columns. However there were many incidents where C-S, 5Cr-S, 9Cr-S, AISI 347SS, AISI 304SS failed to withstand high corrosion. Gutzeit’s [3] experiments at low temperatures and TAN showed AISI 410 SS was more affected by corrosion than C-S, 7Cr-0.5Mo steel and 9Cr-1Mo. He assumed that the attack on AISI 410 was mainly localized, but he was unable to derive this conclusion. He suggested AISI 410 was still preferable to C-S and chrome steels at high temperatures and TAN as it offers some advantages even after the passive surface film breaking.

Gutzeit [3] analyzed various austenitic (18/8) stainless steels that had undergone heat treatment and preactivation. Among the steels that were heat treated, AISI 304 was more susceptible to corrosion with increase in TAN and temperature whereas AISI 316 and 317 exhibited greater resistance to corrosion. Experiments with TAN=29 at 560°F revealed that AISI 316 provides better resistance in a solution annealed condition than in a stabilized condition. According to him, steels cannot with stand to NAP acid attack if they are sensitized and stabilized. Among the preactivated steels, AISI 410, AISI 304 and AISI 304L were only steels which showed increase in corrosion with temperature.

Piehl’s field data using a Californian crude with TAN =3.9 at 520°F processed with different materials showed that C-S experienced severe corrosion while AISI 316SS and AISI 317SS offered high quality resistance to corrosion. Molybdenum (Mo) present
in these stainless steels was found to show discernable resistance towards corrosion. Craig’s [8] experiments with high TAN, temperature and velocities using AISI 316L (2.4% Mo) and AISI 317LS (3.7% Mo) demonstrated that as Mo content increased the steel offers greater resistance towards corrosion. However, AISI 316SS would corrode significantly when Mo content falls below 2.3wt % [23]; this was proven to be correct when AISI 316SS thermo wells with Mo content of slightly less than 2.3wt% exhibited corrosion [2]. AISI 316SS was deduced to be the best material to resist against NAP acid corrosion, although it is susceptible to polythionic cracking [2]. Ultimately process conditions would determine the critical level of Mo content in steels, above which the steels withstand high corrosive environments [2].
2 RESEARCH OBJECTIVES

Though considerable work has been done to evaluate NAP acid corrosion in refineries, it turned out to be unsuccessful when the interdependence of NAP acid and sulfide compounds on corrosion is considered. According to Craig, sulfur compounds respond differently and inhibit or accelerate NAP acid corrosion depending on operating conditions [8]. So far, research has been focused on understanding how NAP acid corrosion is affected by acid concentration, while very little has been contributed to assess sulfide scale formation, retention, adherence and ability to protect metal surface.

The objective of the proposed work is to understand the relationship of key parameters like TAN, temperature, sulfur content and time period with corrosion. This includes

- Identifying the role of sulfur containing species in NAP acid corrosion at different TANs, temperatures and time periods
- Evaluating the factors affecting the protectiveness of iron sulfide scales formed on steels at different operating conditions

In the past, static autoclaves had been used to conduct experiments where samples were immersed in test oil and tested at required temperature for desired period. The autoclave is sealed and the contents in it are rotated throughout the experiment so that uniform distribution of temperature is attained. These experiments had the very important disadvantage of build up of H₂S which created high pressures leading to unwanted secondary reactions like coking, sulfide decomposition or NAP acid decomposition.
Accumulation of corrosion products in the autoclave and the thermal destruction of corrodants strongly affect the test results by reducing the test sensitivity and making it difficult to relate the test data to refinery conditions.

This problem is addressed in “Flow Through Mini Autoclave (FTMA)” where there is a continuous flow of test oil to the sample chamber which prevents the accumulation of corrosion products and H₂S build up. Most of the aforementioned experimental efforts were performed in the range of ~400-600°F and different flow conditions while FTMA experiments will cover a different larger temperature range 450-700°F under very low flow conditions. C-S and 5Cr-S samples will be tested in FTMA described below with test oils having different TAN values.
3 TEST MATRIX

The following test matrix was planned to achieve the above objectives.

Table 1. Experimental parameters

<table>
<thead>
<tr>
<th>Series</th>
<th>TAN (mg KOH/g Oil)</th>
<th>Total Sulfur(TS) (wt% Oil)</th>
<th>Temperature (°F)</th>
<th>Test period (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.25</td>
<td>620</td>
<td>3, 6, 24, 48, 96</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0.25</td>
<td>620</td>
<td>3, 6, 24, 48</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>0.25</td>
<td>620</td>
<td>3, 6, 24, 48</td>
</tr>
<tr>
<td>4</td>
<td>0.1</td>
<td>0.25</td>
<td>650</td>
<td>3, 6, 24, 48, 96</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>0.25</td>
<td>650</td>
<td>3, 6, 24, 48</td>
</tr>
<tr>
<td>6</td>
<td>0.1, 1, 4</td>
<td>0.25</td>
<td>620</td>
<td>24</td>
</tr>
<tr>
<td>7</td>
<td>0.1, 1, 2, 4</td>
<td>0.25</td>
<td>650</td>
<td>24</td>
</tr>
<tr>
<td>8</td>
<td>0.04, 0.4, 0.8, 1.6, 2, 4</td>
<td>0.1</td>
<td>650</td>
<td>24</td>
</tr>
<tr>
<td>9</td>
<td>0.1</td>
<td>0.25</td>
<td>450, 550, 600, 620, 650, 700</td>
<td>24</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>0.25</td>
<td>550, 650, 700</td>
<td>24</td>
</tr>
<tr>
<td>11</td>
<td>0.8</td>
<td>0.1</td>
<td>550, 650, 700</td>
<td>24</td>
</tr>
</tbody>
</table>
Series 1 to series 5 explain the effect of time under different conditions of TAN, TS and temperature. Series 1 set of experiments are conducted at TAN=0.1 (low), TS=0.25 and temperature of 620°F. In series 2 and 3 the TAN value is changed to 1 and 4 respectively. In the next two series 4 and 5 the temperature is set at 650°F. A very low TAN value (series 1) is selected in the beginning so that sulfide scales are allowed to form and TAN value is gradually increased to observe NAP acid effect (series 2 and series 3).

Series 6 to series 8 explain the effect of TAN at different TS and temperature. Series 6 set of experiments are conducted at TS=0.25, 620°F temperature and for a time period of 24 hr. In series 7 temperatures is increased to 650°F and in the next series TS is decreased from 0.25 to 0.1 to observe the effect of TS at lower value.

Series 9 to series 11 explain the effect of temperature at different TAN and TS. Series 9 set of experiments are conducted to at TAN=0.1, TS=0.25 and for a time period of 24 hr. In series 10 TAN values is increased from 0.1 to 2 to observe the effect of temperature at higher TAN and in the final series 11 both TAN and TS are decreased to 0.8 and 0, 1 respectively to observe how temperature can influence corrosion at a lower TAN and TS value.
4 EXPERIMENTAL SET UP AND PROCEDURE

4.1 Flow Through Mini Autoclave (FTMA)

The flow through mini autoclave (FTMA) is a hot oil flow loop where oil from a feed tank is continuously allowed to flow through samples in test tube. Oil enters and leaves the test tube with a relatively shorter residence time (~5 min) while reducing the problem of H₂S and corrosion product build up and acid decomposition. The FTMA (Figure 1) is made of two identical experimental units that are designed for experiments with low flow rates under high temperature. Each unit has a feeding tank, test fluid tank, small peristaltic pump, metering pump, reactor and waste container. The system is heated with heating tape and external resistive heaters; temperature is controlled from a control panel situated outside the experimental room. The system operates in the temperature range 50 – 750°F. Pressure inside the FTMA reactor is dependent on fluid flow rate and viscosity; regulation of pressure is achieved by a back-pressure valve. The entire system is purged with nitrogen provided from an auxiliary tank.

The pipe/coupon assembly (Figure 3) is the heart of the FTMA. It is a 20 inch long tube that contains several inserts shown in Figure 4. The back end of the tube has a provision for inserting a thermo couple. The thermo couple extends to the sample chambers. Two sample chambers made of ¾”ID, ¾” long hollow cylinders are located in the middle of the tube (Figure 4.). Coupons (C-S and 5Cr-S) are mounted in the sample chambers and the dimensions of the coupons are 5/8” x 5/8” x 1/16”.

A FTMA test run starts with a warm up achieved when the system is continuously flushed with “white”, i.e., pure non-corrosive oil (called “Tufflo” in the text below) and warmed up to experimental temperature. A peristaltic pump is used to pump this oil from the oil tank to the FTMA reactor. In the FTMA tube, Tufflo flows through the front end insert, distribution disc sample chambers and back end insert, and then exits the tube. This warm up procedure continues until the preset temperature is reached. Once the preset temperature is reached, the inlet feed to the system is manually switched from Tufflo to the experimental fluid feed using a switch valve. The experimental fluid then flows across the samples for the desired test period at the required temperature. The temperature during the experiment is monitored by a thermocouple inserted in the FTMA reactor. After the experiment, the feed is switched back again manually to Tufflo for 45 minutes in order to flush the samples with the purpose of cleaning the system for future experiment.
4.2 Materials

4.2.1 Test samples

Two types of steel coupons have been used in FTMA experiments: C-S and -Cr-S. The coupons have a square shape with a central hole. Coupon sizes are $5/8'' \times 5/8'' \times 1/16''$ and hole diameter is 1/8''. These dimensions have ± 0.03'' tolerances, therefore each coupon is measured and total surface area is calculated before experiments.

4.2.2 Test oils

Tufflo is a clear petroleum distillate with light paraffin content and is considered as a chemically inert fluid; it is used while preheating the test oil and in flushing the system. The test oil is “yellow” oil that is commercially available base stock with a total sulfur (TS) = 0.25wt% oil. This yellow oil is spiked with commercially available NAP acids and brought to requested NAP acid concentration TAN = 0.1 – 4, while in some of the experiments yellow oil is diluted with Tufflo to lower the sulfur concentration.

4.2.3 Sample preparation

Three coupons of each type of steel are used in every test and coupon dimensions are measured and recorded to calculate total surface area being exposed. Both types of coupons are polished with 400 and 600 grit papers under isopropanol flow. Isopropanol prevents oxygen contamination of coupons and prevents heat generation when rubbing the coupons. Then coupons are rinsed with toluene and acetone and dried under a nitrogen stream. Finally, coupons are weighed using a Mettler Toledo AT 201 analytical
balance and the values are documented in the notebook with a name “Initial weight”. Coupons are then inserted in the FTMA test section as described in (Figure 4).

4.2.4 Scale removal

Scale is removed from coupons using a Clarke solution (ASTM G1-90) which is prepared from 42 ml hydrochloric acid (HCl 12.1 N, analytical purity, Fisher A 144c-212), 2.5 g stannous chloride (SnCl₂·2H₂O, 99.99%, Fluka 98529) and 1 g antimony (III) oxide (Sb₂O₃).

After the experiment, each unit is disassembled. Also coupons are removed, rinsed with toluene and acetone, dried under nitrogen flow and weighted while the values are noted as “Rinse weight.” Next coupons are rubbed, dried and weighed and noted down under the name “Rub weight”. Later, each coupon is dipped in Clarke solution for 20 seconds and then rinsed with deionized water and acetone; this is repeated several times to remove the scale that was chemically attached to the surface. Coupons are dried with nitrogen and weighted. This procedure is repeated ~5-6 times until no significant weight change between successive rinsing is noticed. At this point it is considered that all the FeS scale on the surface has been removed and weight of the sample is noted as “Final weight”.
4.2.5 Corrosion and scale formation rate measurements

In a given test Fe can be lost either as iron naphthenate or as FeS. Iron naphthenate is soluble in the test oil while FeS is an insoluble product. Depending on TAN, temperature, time period and sulfur contents, fraction of iron conversion to iron naphthenate and FeS varies. FeS scale can be subjected to internal stresses where dense, attached and thin film formed initially can become thick, loose, porous detached film by the end of a test. Four types of weights are measured to account for the changes in adherence and strength of FeS scale, namely initial weight, rinse weight, rub weight and final weight.

The difference between initial and final weights represents the amount of Fe lost in a given experiment which is used to measure corrosion rate.

Corrosion rate in \( \text{mm/y} \) is defined as

\[
CR = \frac{(IW - FW)}{\rho_{Fe} \cdot A_c \cdot t} \cdot 24 \cdot 365 \cdot 10
\]  

(4-1)

Corrosion rate in \( \text{mpy} \) is defined as

\[
CR = \frac{(IW - FW)}{\rho_{Fe} \cdot A_c \cdot t} \cdot \frac{24 \cdot 365 \cdot 10000}{2.54}
\]  

(4-2)
Where

\[ CR \] - Corrosion rate in mm/y
  - Corrosion rate in mpy

\[ IW \] - Initial weight of coupon in grams,

\[ FW \] - Final weight of coupon in grams,

\[ \rho_{Fe} \] - Density of iron (7.87 g/cm\(^3\))

\[ A_e \] - Total surface area of coupon in cm\(^2\),

\[ t \] - Time period of experiment in hours

The difference between rinse and final weight represents the amount of total scale retained on steel after the experiment that includes loose and adherent scales and is described as “retained scale.”

Retained scale thickness in µm is defined as

\[
RST = \frac{(R_{iW} - FW)}{\rho_{FeS} \cdot A_e \cdot 10000}
\]

(4-3)

Where

\[ RST \] - Retained scale thickness in µm FeS

\[ R_{iW} \] - Rinse weight of coupon in grams

\[ \rho_{FeS} \] - Density of iron sulfide (87.91 g/cm\(^3\))
The difference between rub and final weight represents the amount of scale that is strongly adherent to the surface and is denoted as “adherent scale”.

Adherent scale thickness in μm is defined as

\[
AST = \frac{(R_2W - FW)}{\rho_{FeS} \cdot A_c} \cdot 10000
\]  

(4-4)

Where

\(AST\) - Adherent scale thickness in μm FeS

\(R_2W\) - Rub weight of coupon in grams

A better characterization of scale formation and the whole corrosion process is given by the estimation of numbers of moles of iron lost from the steel and the number of iron moles used for iron sulfide film growth.

Moles of Fe lost in moles/m\(^2\)/y is defined as

\[
{n_{Fe}} = \frac{(IW - FW)}{M_{Fe} \cdot A_c \cdot t} \cdot 24 \cdot 365 \cdot 10000
\]

(4-5)

Where

\(n_{Fe}\) - Fe lost rate in moles/m\(^2\)/y

\(M_{Fe}\) - Molecular weight of iron in gm/gm mole (55.8 g/g mole)
Total moles of FeS retained on steel surface in moles/m²/y is defined as

\[ n_{FeS,R} = \frac{(R,W - FW)}{M_{FeS} \cdot A_c \cdot t} \cdot 24 \cdot 365 \cdot 10000 \]  

(4-6)

\( n_{FeS,R} \) - Retained scale formation rate in moles/m²/y

\( M_{FeS} \) - Molecular weight of iron sulfide (87.85 g/g mole)

Moles of FeS adherent to steel surface in moles/m²/y is defined as

\[ n_{FeS,A} = \frac{(R,W - FW)}{M_{FeS} \cdot A_c \cdot t} \cdot 24 \cdot 365 \cdot 10000 \]  

(4-7)

\( n_{FeS,A} \) - Adherent scale formation rate in moles/m²/y

The difference between initial and rinse weight represents the fraction of Fe converted as iron naphthenate and very loose FeS scale that is suspended on the steel surface and lost during the experiment.

The difference between rinse and rub weight is equivalent to the FeS scale that is slightly adherent to the steel surface which can be removed off by mechanical means.

The difference between rub and final weight gives the amount of FeS that is chemically attached to the steel surface which can be removed off only by chemical means.
Porosity of the scale represents void spaces in the scale, and is measured as a percent between 0-100.

It can be calculated as

$$Porosity_{res} = \left[1 - \left( \frac{Scale\ thickness_{wt,loss}}{Scale\ thickness_{SEM}} \right) \right] \times 100 \quad (4-8)$$
5 RESULTS AND DISCUSSIONS

5.1 Time dependency

5.1.1 620°F time series

5.1.1.1 $TAN=0.1$

All the corrosion and scale formation rates expressed below are divided with a single value and thus normalized. TAN in mg KOH/g Oil and TS in wt% Oil are expressed without units for convenience. All the surface analysis and cross sectional images with different magnifications are presented in Appendix A.

For TAN=0.1 and TS=0.25 a series of experiments were conducted at varying time intervals (3 – 96 hr) with both C-S and 5Cr-S. It was observed that for C-S the corrosion rate started out higher and then rapidly decreased in the first 24 hr, as shown in Figure 5. The reduction of the corrosion rate could be ascribed to the growth of the protective sulfide scale layer. The corrosion rate remained stable beyond 24 hr even in the longest tests which lasted 96 hr.

Figure 6 shows the amount of scale accumulated on the steel surface vs. time, or more precisely, the scale retained on the steel surface after the experiments, expressed in terms of a hypothetical scale thickness calculated by assuming 100% dense pure FeS with no pores. A portion of the scale was rather loose and was easily removed mechanically by rinsing and gentle rubbing. The adherent scale was the one that needed to be removed by using a Clarke solution. The total amount of scale retained on steel was obtained by summing the loose amount of scale and adherent amount of scale. It is hypothesized that
the loose scale was not very protective while the adherent scale offered most of the protection from corrosion seen in the experiments as it can be observed that the amount of scale increased steadily with time, however beyond the 24 h it did not offer much additional protection. In short exposures (3 and 6 hr) all the scale retained on the surface was rather adherent while in longer exposures a significant amount of the scale was loose.

Figure 7 shows the “molar balance,” i.e. the comparison of the number of moles of Fe lost through corrosion and the number of moles of FeS scale retained on the steel surface during the course of the experiment. The two numbers should theoretically be the same if sulfidation was the only type of corrosion and also if none of the scale spalled off during the experiments. It is possible that some of the steel or scale were lost to NAP acid attack (however this cannot be significant at such a low TAN=0.1). More likely, some of the loose scale spontaneously spalled off during the course of the experiment and was never recovered.

SEM surface images for C-S show that scale surface displayed the polishing lines of the metal surface even after long exposures (Figure 12 and Figure 14). In longer tests, it appears that more scale was cracked and partially spalled (Figure 12). These SEM observations corroborate what was observed in Figure 6, where total and adherent scales were almost identical in short time tests and with significant differences in long tests. Most of the images suggest a layered (laminar) structure of the scale with the outer layers progressively cracking and spalling with time.
Porosity of scale represents void spaces in the scale. Scale thickness is calculated in two ways. One is calculated from weight loss measurements, where it was assumed that the scale is 100% dense and the other is computed from the SEM cross sectional view, where height of scale is measured as thickness. Theoretically, these two measures should be the same if the scale was 100% dense. However it is possible scale becomes loose and porous due to cracks that were developed during the course of the test. As a result, it is very likely that porosity is a positive number in these experiments. For C-S it was observed that porosity of scale was very high for short periods of exposure;

Porosity began at approximately 90%, then decreased with time and at the end of 96 hr porosity was only about 10%. Probably the loose scale spalled off continuously with time leaving only adherent scale attached to the steel surface.

Similarly as for C-S steel, it was observed that the corrosion rate of 5Cr-S started out at a high and then decreased over the first 24 hr, as shown in Figure 16. The scale thickness increased with time for 5Cr-S (Figure 17) just as it did for C-S; however, most of the retained scale on 5Cr-S appeared to be firmly adherent to the steel surface. Some spalling was observed at exposures of 24 hr or longer what was confirmed by SEM images (Figure 21 and Figure 23). Porosity of the scale was high for short periods of exposure like in C-S decreased with time. After 3 hr exposure porosity was about 80% and at the end of 96 hr scale was 40% porous.
Table 2. List of figures used in section 5.1.1.1

<table>
<thead>
<tr>
<th>Caption</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 5</td>
<td>Effect of time on corrosion rate of C-S samples exposed to TAN=0.1, TS=0.25 at 620°F temperature.</td>
</tr>
<tr>
<td>Figure 6</td>
<td>Effect of time on scale thickness of C-S samples exposed to TAN=0.1, TS=0.25 at 620°F temperature.</td>
</tr>
<tr>
<td>Figure 7</td>
<td>Comparison of moles of Fe lost and FeS retained with variation in time on C-S exposed to TAN=0.1, TS=0.25 at 620°F temperature.</td>
</tr>
<tr>
<td>Figure 12</td>
<td>Surface morphology of C-S sample exposed to TAN=0.1, TS=0.25 at 620°F temperature and 48hr test period.</td>
</tr>
<tr>
<td>Figure 14</td>
<td>Surface morphology of C-S sample exposed to TAN=0.1, TS=0.25 at 620°F temperature and 96 hr test period.</td>
</tr>
<tr>
<td>Figure 16</td>
<td>Effect of time on corrosion rate of 5Cr-S samples exposed to TAN=0.1, TS=0.25 at 620°F temperature.</td>
</tr>
<tr>
<td>Figure 17</td>
<td>Effect of time on scale thickness of 5Cr-S samples exposed to TAN=0.1, TS=0.25 at 620°F temperature.</td>
</tr>
<tr>
<td>Figure 21</td>
<td>Surface morphology of 5Cr-S sample exposed to TAN=0.1, TS=0.25 at 620°F temperature and 24 hr test period.</td>
</tr>
<tr>
<td>Figure 23</td>
<td>Surface morphology of 5Cr-S sample exposed to TAN=0.1, TS=0.25 at 620°F temperature and 48 hr test period.</td>
</tr>
</tbody>
</table>
5.1.1.2 $TAN=1$

A similar series of experiments as described above was conducted at $TAN=1$, with other conditions remaining the same: $TS=0.25$ and at $620^\circ F$. For C-S, the trends were generally similar to those obtained at $TAN=0.1$. The corrosion rate was higher for short exposures (3 and 6hr) but decreased after that and reached a steady state after 24 hr (Figure 27). The magnitude of the corrosion rates observed at $TAN=1$ was very similar to those observed at $TAN=0.1$; this suggests that the main corrodents in both series of experiments were the sulfur containing species, rather than NAP acids.

The amount of scale retained on the steel surface for C-S is shown in Figure 28; scale steadily increased with an increase of time of exposure. After short tests, almost all the scale that was retained was adherent (approximately 95 to 100%), while an increase in the spalling was observed at long exposures (48hr), e.g. after a 48 hr test only 70% of the retained scale was adherent.

Figure 29 shows that the difference between the number of moles of Fe lost to corrosion and the number of FeS moles retained on the surface for C-S was significant, even in short periods, which is different from $TAN=0.1$ experiments. Most likely a part of the Fe was attacked by NAP acid and was converted to soluble iron naphthenate.

For 5Cr-S, the corrosion rate (Figure 30) and the scale retention (Figure 31) were similar as for C-S. However, for 5Cr-S there was no difference in the molar balance for the $TAN=1$ and $TAN=0.1$ (Figure 32) which is contrast with the C-S. It seems that most
of the Fe lost to the 5Cr-S was due to sulfidation and ended up as FeS at either TAN value.

**Table 3.** List of figures used in section 5.1.1.2

<table>
<thead>
<tr>
<th>Caption</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 27</td>
<td>Effect of time on corrosion rate of C-S samples exposed to TAN=1, TS=0.25 at 620°F temperature.</td>
</tr>
<tr>
<td>Figure 28</td>
<td>Effect of time on scale thickness of C-S samples exposed to TAN=1, TS=0.25 at 620°F temperature.</td>
</tr>
<tr>
<td>Figure 29</td>
<td>Comparison of moles of Fe lost and FeS retained with variation in time on C-S exposed to TAN=1, TS=0.25 at 620°F temperature.</td>
</tr>
<tr>
<td>Figure 30</td>
<td>Effect of time on corrosion rate of 5Cr-S samples exposed to TAN=1, TS=0.25, 620°F temperature.</td>
</tr>
<tr>
<td>Figure 31</td>
<td>Effect of time on scale thickness of 5Cr-S samples exposed to TAN=1, TS=0.25, 620°F temperature.</td>
</tr>
<tr>
<td>Figure 32</td>
<td>Comparison of moles of Fe lost and FeS retained with variation in time on 5Cr-S exposed to TAN=1, TS=0.25 at 620°F temperature.</td>
</tr>
</tbody>
</table>
5.1.1.3 $\text{TAN}=4$

A set of experiments were conducted with high acid concentrations ($\text{TAN}=4$), with other conditions being the same: $\text{TS}=0.25$, 620°F. A similar trend in the corrosion rate was seen: high values in the beginning and then decreasing (Figure 33); however, the magnitude of the corrosion rates at $\text{TAN}=4$ was 5 times higher than those observed at $\text{TAN}=0.1$ and $\text{TAN}=1$. This suggests that the main corrosive species in $\text{TAN}=4$ experiments were NAP acids, and not the sulfur containing species which were dominant at $\text{TAN}=0.1$ and $\text{TAN}=1$.

In Figure 34 it can be seen that the amount of scale retained on the C-S surface was not really changing during the course of the experiments, with most of it being non-adherent. Figure 35 which shows the molar balance which indicates that most of the Fe lost was due to NAP attack and was converted to iron naphtenate and possibly to loose scale which was never recovered. Only about 20 to 30% of the Fe lost was recovered as FeS scale after short exposures, down to 2% after long exposures.

The data for 5Cr-S are similar as shown in Figure 36 - Figure 38 with the main difference being a somewhat lower fraction of scale retained on the surface but higher fraction of adherent scale surviving the experiments on the 5Cr-S when compared with the C-S. However, this did not have any effect on the corrosion rate, probably due to the fact that most of the attack was due to NAP acids.
### Table 4. List of figures used in section 5.1.1.3

<table>
<thead>
<tr>
<th>Caption</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>Figure 33</td>
<td>Effect of time on corrosion rate of C-S samples exposed to TAN=4, TS=0.25, 620°F temperature.</td>
</tr>
<tr>
<td>Figure 34</td>
<td>Effect of time on scale thickness of C-S samples exposed to TAN=4, TS=0.25, 620°F temperature.</td>
</tr>
<tr>
<td>Figure 35</td>
<td>Comparison of moles of Fe lost and FeS retained with variation in time on C-S exposed to TAN=4, TS=0.25 at 620°F temperature.</td>
</tr>
<tr>
<td>Figure 36</td>
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<td>Comparison of moles of Fe lost and FeS retained with variation in time on 5Cr-S exposed to TAN=4, TS=0.25 at 620°F temperature.</td>
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5.1.2 650°F time series

5.1.2.1 $TAN=0.1$

For $TAN=0.1$ the same set of experiments (3-96 hr) was conducted at 650°F as described for 620°F above, with the same TS=0.25. Corrosion rates for C-S showed a similar trend to that obtained at 620°F. Corrosion rate was high initially, then decreased for the first 24 hr of exposure and remained relatively unchanged beyond 24 hr exposure (Figure 39). However the corrosion rates were slightly higher at 650°F compared than those obtained at 620°F. This could be ascribed to increase in the kinetics of reactions with temperature.

Figure 40 shows scale accumulated on the steel surface during the course of the experiment. The scale steadily increased with time, but was not protective beyond 24 hr was not protective. Most of the scale that was retained was adherent in short exposure s (approximately 90%) while the scale adherence decreased with time and only 70% scale was adherent after 96 hr exposure.

A comparison for the number of moles of Fe lost and moles of FeS retained on the steel surface is shown in Figure 41. It was observed that after short exposures most of Fe lost was recovered as FeS (approximately 90%) and this recovery steadily decreased with time, resulting in only 30% of FeS retaining on the steel surface after 96 hr exposure. It suggests that the scale became less attached to the surface, probably due to cracks and internal stresses and spalled off from the surface which could not be recovered.
Surface analysis of C-S displayed polishing lines generated during sample preparation Figure 42. Inter-connected cracks were observed when exposed for 24 hr which might have initiated scale spalling (Figure 44). More scale detachment was observed in Figure 46 when exposed to longer durations of exposure (48hr) which explains more cracks developed during the course of experiment which aggravated scale detachment. This analysis can corroborate to the observation of Figure 41, which shows a large difference in the moles of Fe lost and FeS recovered. The porosity of the scale decreased from 85% to 55% when exposed from 3 to 96 hr.

For 5Cr-S corrosion rates and scale thickness were very similar to those of C-S. The corrosion rate decreased with time and reached steady state after 24 hr exposure (Figure 50). Scale thickness increased with time, with most of the retained scale adherent to the steel surface: 95% of the retained scale was adherent to the steel (Figure 51). However, scale adherence was reduced with time, as at the end of 96 hr exposure, only 70% of retained scale was recovered as adherent scale. Comparison of moles shows that most Fe was recovered as FeS after short exposures and decreased with long exposures (Figure 52). Porosity of the scale did not show any trend while changing from 40 to 80%.

SEM images for 5Cr-S steel are similar to what was observed on C-S. Cracks that were observed at 24 hr (Figure 55) intensified during the next couple of hours resulting in more scale loss at the end (Figure 57). When exposed to 96 hr the scale was composed of very tiny grains (Figure 59).
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5.1.2.2 $TAN=1$

For $TAN = 1$ a similar set of experiments was conducted with other conditions being the same: $TS=0.25$ and at $650^\circ F$. The same trend was observed as in tests at $TAN=0.1$: Initial high corrosion rates followed by steady state corrosion after 24 hr (Figure 61). Corrosion rates at $650^\circ F$ were slightly higher than at $620^\circ F$ which confirms that high temperatures can accelerate the kinetics of the corrosion reactions. The magnitude of corrosion rate at $TAN=1$ was not very different to that with $TAN=0.1$ at $650^\circ F$, where a similar type of trend that was also observed at $620^\circ F$. Thus the main corroding species are still sulfur containing species.

Figure 62 shows the amount of the scale retained on the surface after experiments. Scale thickness increased steadily with time, and unlike with $TAN=0.1$, here almost all the scale retained was adherent even in long exposures.

Figure 63 gives the comparison of moles of Fe lost to the moles of FeS retained on the steel surface. Fraction of retained FeS on the steel surface decreased with time of exposure, which showed again that a good proportion of scale in long exposures became loose and less attached and thereby spalled off from the surface.

SEM surface images for C-S displayed polishing lines generated on the steel surface even after 24 hr exposure (Figure 68). For 24 hr exposure scale showed distinct channels that were generated from metal loss and extended along the polishing lines (Figure 68). Surface was damaged by cracks which enhanced scale spalling. This can corroborate the observation in Figure 63 where FeS recovery was only 40%. For 48 hr
exposure a layered structure was not visible and the scale appeared to be more granular with deep cracks (Figure 70). Scale was highly porous in almost all exposures. Porosity decreased with time of exposure but not significantly. Porosity was ~90% when exposed to 3hr and was about 70% after 48 hr exposure.

For 5Cr-S corrosion rate and scale retention were similar to that of C-S. Corrosion rate for 48 hr was slightly than for 24 hr but was not significantly (Figure 72). Scale showed an increase in thickness with time and most of the retained scale was adherent even in long exposures similar to C-S (Figure 73). However the fraction of scale adherent to the surface was slightly higher than on C-S which might explain that the scale was more tenacious on 5Cr-S, (e.g.: when exposed for 24 hr, 37% of Fe was recovered as adherent FeS on C-S and whereas 50% of Fe was recovered as adherent FeS on 5Cr-S). However, the amount of the adherent scale was identical when exposed to 48 hr for both C-S and 5Cr-S.

SEM surface images of 5Cr-S for 6 hr exposure show part of the scale that was detached from the steel surface, exposing the inner surface (Figure 75). Cracks developed through the scale probably made it less well attached and caused scale spalling. When exposed for 24 hr, the layered structure was not observed (Figure 77). When further exposed (48 hr) the surface of the scale became more granular (Figure 79). Scale was very porous in the case of 5Cr-S just like was the case with C-S. After a 6hr exposure porosity was about 83% and decreased to approximately 75% after a 48 hr exposure.
### Table 6. List of figures used in section 5.1.2.2

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5.2 TAN dependency

5.2.1 620°F TAN series

A series of experiments were conducted with different TAN concentrations varying from 0.1 to 4 and constant TS=0.25 at 650°F and for 24hr with both C-S and 5Cr-S. For C-S the corrosion rates were not greatly altered when TAN changed from 0.1 to 1 but it increased ~ 7 fold when TAN was set to 4 (Figure 81).

Figure 82 shows the amount of scale accumulated vs. TAN. No difference was seen from TAN=0.1 to 1. However, no adherent scale thickness was observed at TAN=4 suggesting a domination of NAP attack over sulfidation. It is not clear from these data whether NAP acid was the primary corrodent or acted to help loosen up and remove the scale from the surface, or both. Figure 83 gives comparison of moles of Fe lost and FeS retained on the steel surface with variation in TAN showing a large difference at TAN=4.

5Cr-S showed the same characteristic trends for corrosion rate and scale as abovementioned for C-S (Figure 84 and Figure 85). Very high corrosion rates were observed with virtually no scale and protection at TAN=4 (Figure 86).
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5.2.2 650°F TAN series

5.2.2.1 \( TS=0.25 \)

A series of experiments were conducted with different TAN concentrations varying from 0.1 to 4 at constant test period 24 hr with other conditions being the same as above: \( TS=0.25 \) and 650°F for both C-S and 5Cr-S. It was observed that corrosion rate did not change much until TAN=2, but increased 5 fold at TAN=4 (Figure 87). Clearly the NAP acids was the main corrodents at TAN=4 as steel corrosion shifted from sulfidation to NAP acid controlled attack.

Figure 88 shows amount of scale accumulated vs. TAN. Retained and adherent scales did not change much until TAN=1 but a decrease in scale thickness was observed from TAN=2; this musk likely occurred due to of reduction in adherence between the steel surface and the scale with increase in NAP acid concentration. Only 2% of Fe was recovered as adherent scale at TAN=4 show that the steel surface was covered by very thin layer of FeS and thus barely protected.

A comparison between the number of moles of Fe lost and moles of FeS formed during the experiment is presented in (Figure 89). A large difference between moles of Fe lost and the FeS recovered was observed at TAN=4, which is consistent with previous observations.

SEM pictures for C-S showed that the scale displayed polishing lines on the metal surface for TANs 0.1, 1 and 2. Cracks were observed when exposed to TAN=0.1, 1 and 2. At TAN=2, scale was affected severely and chunks of scale spalled off from the
surface exposing new surface (Figure 90). This can explain the decrease in scale thickness from TAN=2 when compared to low TANs. At TAN=4 layered structure of the scale was not observed (Figure 92).

Porosity of scale showed an increasing trend with increasing TAN. Porosity increased from ~75% to ~98% with TAN varying from 0.1 to 4. It could be understood that at TAN=4 no scale was left and whatever the scale that was left was completely void.

5Cr-S showed a similar trend when exposed to different TANs. Corrosion rates were more or less equal when TAN changed from 0.1 to 2 and rose to very high values when TAN increased to 4 (Figure 94). Magnitudes of corrosion rate and scale thickness were similar to those of C-S. Scale on 5Cr-S was susceptible to NAP acid attack and only 1% of Fe lost was left, as scale which was extremely unprotective (Figure 95).

SEM picture at TAN=0.1 showed scale that was soft and it is not severely damaged (Figure 55). At TAN=1 cracks were noticeable and scale was filled with bubbles (Figure 77). At TAN=2 scale was damaged and scale broken into pieces with some of them still left on the surface (Figure 97). This can corroborate the observation in Figure 95, where a decrease in scale thickness was observed.

At TAN=4, 5Cr-S too showed the same increasing trend in porosity with TAN. It increased from ~55% to ~80% when TAN increased from 0.1 to 4. It could be observed that the scale porosity in 5Cr-S was little less at TAN=4 when compared to that in C-S. It might suggest that 5Cr-S did not lose all of its scale and scale might little tenacious on 5Cr-S.
Table 8. List of figures used in section 5.2.2.1

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5.2.2.2 **TS=0.1**

The Effect of TAN was also observed at lower TS (TS=0.1) value with same set of parameters: 24hr exposure, 650°F, C-S and 5Cr-S. Here TAN was varied from a low value of 0.04 to a high value of 4. Similar trend in corrosion rate was observed with corrosion rate being more or less equal until TAN=1 and suddenly increased to ~ 7 fold when TAN=4 was used (Figure 101). Corrosion rates were not very different at two TS values until TAN=2. However for TAN=2 and 4, low TS corrosion rates were little higher than high TS. This can be ascribed to less protection offered to the steel surface with less sulfur content.

Retained scale thickness and adherent scale remained constant on average for TANs from 0.4 to 1, but for higher TANs (TAN=2 and 4), adherent scale thickness decreased and only 5% of scale was adherent at high TAN (Figure 102).

A comparison of number of moles of Fe lost and moles of FeS retained during the experiment is presented in Figure 103. At low TAN most of Fe lost appeared as FeS, which shows corrosion is mainly by sulfdation. Significant difference between moles of Fe lost and FeS recovered was observed at high TANs (TAN=2 and TAN=4) which shows that a major fraction of Fe was attacked by NAP acid and lost as iron naphthenate.

SEM pictures for C-S show that the scale surface displayed polishing lines at TAN=2 and TAN=4. At TAN=2 long interconnected cracks were observed, with some proportion of scale being peeled off at edges (Figure 104). This cracking was enhanced with TAN and large chunks of scale peeled off from the surface (Figure 106). This SEM
observation can be corroborated to what was observed in Figure 103 where high corrosion rates with very small scale were observed at TAN=4.

For 5Cr-S corrosion rate increased with TAN, similar to C-S. But effect of TAN was visible only when TAN value was above 2 (Figure 108). Scale thickness showed a decreased trend with TAN (Figure 109). Comparison of moles of Fe lost and FeS retained is shown in Figure 110. It was observed that at low TAN most of Fe appeared as FeS which illustrates that corrosion was mainly by sulfidation. A significant difference between Fe and FeS was observed from TAN=2, implying most of Fe was lost as iron naphthenate. At TAN=4 attack of NAP acid was very severe and only ~5% of scale was left on the surface.

Surface analysis of 5Cr-S at TAN=2 show that the steel surface was severely damaged by NAP acid effect. A thin FeS layer was loosely attached to surface while major proportion of it was non adherent exposing the inner surface. Polishing lines were visible even on the thin layer (Figure 111). At TAN=4 surface was covered with FeS layers with cracks separating them (Figure 113).
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5.3 Sulfur dependency

Experiments were conducted at 650°F for TANs ranging from 0.1 to 4 in order to compare the results for TS values from 0.25 to 0.1 for both C-S and 5Cr-S. The same characteristic trend for corrosion rate was followed by C-S at two different sulfur concentrations and 5Cr-S also showed the same features: however 5Cr-S was more attacked by NAP acid when compared to C-S. An increase in the corrosion rate was observed at TAN=4 when TS=0.25 used which for TS=0.1 was observed at TAN=2 for both C-S and 5Cr-S (Figure 115 and Figure 117). This can suggest that NAP acid attack on steel is dependent on sulfur concentration: more the sulfur lesser the NAP acid attack and greater the protection to steel. Amount of scale retained on the steel surface was also found to be greater when higher TS was used: more protection was offered at high TS at least with in the range of sulfur and acid concentrations tested. Adherent scale thickness showed a decrease with increase in TAN for both C-S and 5Cr-S at both the sulfur concentrations (Figure 116 and Figure 118).
Table 10. List of figures used in section 5.3

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5.4 Temperature dependency

5.4.1 TAN=0.1 and TS=0.25 temperature series

A series of experiments were conducted at TAN=0.1 and TS=0.25 for different temperatures (450 - 700°F) with both C-S and 5Cr-S at 24hr test duration. Figure 119 shows effect of temperature on corrosion rates of C-S. This increase can be ascribed to an increase in the kinetics of the reaction with increasing temperature.

Figure 120 shows accumulated scale thickness variation with temperature. It was observed that scale thickness increased with temperature, with most of the scale being adherent to the steel surface.

Figure 121 gives comparison of moles of Fe lost to moles of FeS retained on the steel surface. It was observed that all of the Fe was appeared as FeS at low temperatures, but the conversion rate decreased with temperature; at 700°F, only 40% of Fe was converted into FeS.

For 5Cr-S, corrosion rate increased with temperature similar to C-S (Figure 122). Scale thickness increased with temperature with most of the scale being adherent to the steel surface at all temperatures (Figure 123). At low temperatures, most of the lost Fe converted into FeS similar to C-S. At high temperature, the difference between Fe lost and FeS scale found was significant, which shows that a major fraction of scale was loose and unprotective (Figure 124).
Table 11. List of figures used in section 5.4.1

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5.4.2 TAN= 2 and TS= 0.25 temperature series

A series of experiments were conducted at TAN=2 and TS=0.25 at different temperatures (550 - 700°F) for both C-S and 5Cr-S for 24 hr test duration. It was observed that for C-S corrosion rate decreased slightly between 550°F and 650°F and then increased between 650°F and 700°F (Figure 125).

Figure 126 shows scale accumulated on the steel surface with temperature. It was observed that scale thickness increased with time; the same trend was observed with TAN=0.1. Most of the retained scale was adherent at high temperatures of 650 and 700°F, while scale adherence was less at low temperature 550°F.

Figure 127 gives comparison of moles Fe lost to moles of FeS retained on the steel surface during the course of the experiment. It can be observed that the difference between moles Fe lost to retained FeS was significant at high temperatures 650 and 700°F and only 30% of Fe lost was appeared as retained FeS. The same characteristic trend was observed with TAN=0.1, which suggests that increase in temperature caused more scale spallation.

Surface morphology of C-S showed that the steel surface is severely attacked by NAP acid where chunks of FeS scale spalled off from the surface at 650°F (Figure 90). At 700°F the scale was more crystalline and deep cracks were observed (Figure 130). Cross sectional analysis of scale showed that scale was deeply damaged with vertical and horizontal cracks through it at 650°F (Figure 91). Scale porosity showed a decreasing
trend with temperature. Porosity decreased from ~90% to ~70% when temperature increased from 550 to 700°F.

5Cr-S too showed a similar characteristic trend for corrosion and scale formation rates as for C-S. Corrosion rates and scale formation rates at TAN=0.1 were not very different from those at TAN=2 as shown in Figure 132 and Figure 133. Surface morphology of 5Cr-S shows that scale surface displayed polishing lines even at high temperatures. At 700°F the scale is more crystalline (Figure 137). Scale porosity was about ~98% at 550°F and decreased to ~80% at 700°F.
Table 12. List of figures used in section 5.4.2

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5.4.3 TAN=0.8 and TS=0.1 temperature series

A series of experiments were conducted for TAN=0.8, but at a lower TS value 0.1 with all other conditions remaining the same: 550-700°F and 24 hr exposure. It was observed that the corrosion rate increased steadily with temperature (Figure 139).

Figure 140 shows the amount of scale retained on steel surface as a function of temperature. It was observed that the retained scale thickness increased with temperature whereas adherent scale thickness decreased with increasing temperature from 650 to 700°F.

Figure 141 gives a comparison of the moles of Fe lost and moles of FeS retained during the experiment. It was observed that around 40 – 50% of Fe lost appeared as retained FeS in each test. At low temperatures all scale retained on the surface was adherent, while at high temperature only 25% of Fe appeared as adherent FeS showing that significant proportion of the scale was lost and unprotective.

SEM pictures of C-S show cracks were generated even at low temperature (Figure 142). At high temperature (700°F), the surface was covered by “blooms” under which it was believed that corrosion happened at a faster rate (Figure 146). This observation corroborates what was observed in (Figure 139) where corrosion rate was high at high temperature. At 500°F cross sectional analysis showed the bulky scale that was segregated into pieces. At 650 and 700°F scale was cracked both vertically and horizontally (Figure 145 and Figure 147). Porosity of the scale was about 70 – 80% at all temperatures. Scale porosity showed an increased trend with temperature unlike with
TAN=2 and TS=0.25. It increased ~80 to ~85% when temperature increased from 500 to 700°F.

For 5Cr-S it was observed that corrosion rate increased steadily with temperature (Figure 148). Scale thickness increased with temperature but unlike C-S all the retained scale was adherent even at high temperatures (Figure 149). Approximately 80% of Fe lost appeared as adherent FeS, even at high temperatures, proving that scale is more tenacious on 5Cr-S (Figure 150).

SEM pictures of 5Cr-S at high temperature (700°F) show that the scale was composed of crystals (Figure 155). Scale was not damaged as on C-S and scale porosity decreased from 95% to 65% with temperature change from 550 to 700°F.
### Table 13. List of figures used in section 5.4.3

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<th>Caption</th>
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5.5 Comparison of Steels

5.5.1 Time dependency

At 620°F corrosion rate and scale thickness of C-S and 5Cr-S were compared for different time intervals (3-96 hr) at different TAN concentrations (TAN=0.1 to 4) keeping constant TS=0.25. Both C-S and 5Cr-S followed the same trend for corrosion rate and scale thickness for all TANs. Corrosion rate was high initially and dropped down and reached a steady state after 24 hr exposure. Scale thickness increased steadily with time. At TAN=0.1 corrosion rates of C-S and 5Cr-S were very close and at 96 hr they were almost equal (Figure 157). At TAN=1 corrosion rate of C-S was slightly higher than 5Cr-S, but the scale thickness was equal in all exposure (Figure 159 and Figure 160). At TAN=4 corrosion rate and scale thickness were similar while 5Cr-S showed higher corrosion rate at TAN=4 for long exposures (Figure 161 and Figure 162).

The same set of results was compared at 650°F for both C-S and 5Cr-S with all other conditions being same: TAN= 0.1 to 1, TS=0.25, 3-96 hr. At TAN=0.1 corrosion rates were very similar to C-S and 5Cr-S; at the end of 96 hr, 5Cr-S showed a higher corrosion rate and scale thickness than C-S (Figure 163). At TAN=1 both corrosion rate and scale thickness coincided in almost all the cases (Figure 165 and Figure 166).
Table 14. List of figures used in section 5.5.1

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<th>Caption</th>
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<td>Figure 166</td>
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5.5.2 TAN dependency

Corrosion rate and scale thickness for both C-S and 5Cr-S were compared at different TAN concentrations (0.1 to 4) at constant TS=0.25 and 650°F. Corrosion rate of both C-S and 5Cr-S and did not vary much until TAN=2, and then increased 5 fold at TAN=4. Both C-S and 5Cr-S were covered with only ~1% of scale when exposed to TAN=4. At TAN=4 corrosion rate and scale thickness of 5Cr-S were little higher than C-S (Figure 169 and Figure 170).

Effect of TAN was also compared at a different TS value of 0.1. Here TAN was varied from a variety of low value TAN=0.04 to high value TAN=4. Corrosion rate was unchanged up to TAN=1 and an increase in corrosion rate was observed from TAN=2 unlike to what happened at TS=0.25 where only TAN=4 showed higher corrosion rate. At TAN=4 5Cr-S showed a slightly higher corrosion rate and scale thickness than C-S similar trend observed at TS=0.25 (Figure 171 and Figure 172).
Table 15. List of figures used in section 5.5.2

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<thead>
<tr>
<th>Caption</th>
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<td>Comparison of corrosion rate of C-S and 5Cr-S at different TAN concentrations exposed to TS=0.25, 24 hr test period and 650°F temperature.</td>
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<td>Figure 170</td>
<td>Comparison of scale thickness of C-S and 5Cr-S at different TAN concentrations exposed to TS=0.25, 24 hr test period and 650°F temperature.</td>
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<td>Figure 171</td>
<td>Comparison of corrosion of C-S and 5Cr-S at different TAN concentrations exposed to TS=0.1, 24 hr test period and 650°F temperature.</td>
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<td>Figure 172</td>
<td>Comparison of scale thickness of C-S and 5Cr-S at different TAN concentrations exposed to TS=0.1, 24 hr test period and 650°F temperature.</td>
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5.5.3 Temperature dependency

Effect of temperature was compared for C-S and 5Cr-S at low acid concentration TAN=0.1 and TS=0.25. Both C-S and 5Cr-S showed an increase in corrosion rate and scale thickness with temperature. Corrosion rate was similar at each temperature, while at 700°F 5Cr-S showed higher corrosion rate and scale thickness (Figure 173 and Figure 174). At TAN=2 corrosion rates of C-S and 5Cr-S were not greatly different but scale on 5Cr-S was observed to be more adherent than on C-S (Figure 175 and Figure 176). A set of experiments conducted at low TS value 0.1 with TAN=0.8 were compared for C-S and 5Cr-S. Corrosion rates were not greatly varied, but scale thickness of C-S was very less when compared to 5Cr-S at 700°F (Figure 177 and Figure 178); this may suggest that scale on 5Cr-S more tenacious than C-S under these conditions.
Table 16. List of figures used in section 5.5.3

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<th>Caption</th>
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<td>Figure 173</td>
<td>Comparison of corrosion of C-S and 5Cr-S at different temperatures exposed to TAN=0.1, TS=0.25, 24 hr test period.</td>
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<td>Figure 174</td>
<td>Comparison of scale thickness of C-S and 5Cr-S at different temperatures exposed to TAN=0.1, TS=0.25, 24 hr test period.</td>
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<td>Figure 175</td>
<td>Comparison of corrosion rate of C-S and 5Cr-S at different temperatures exposed to TAN=2, TS=0.25, 24 hr test period.</td>
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<td>Figure 176</td>
<td>Comparison of corrosion rate of C-S and 5Cr-S at different temperatures exposed to TAN=2, TS=0.25, 24 hr test period.</td>
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<td>Figure 178</td>
<td>Comparison of scale thickness of C-S and 5Cr-S at different temperatures exposed to TAN=0.8, TS=0.1, 24 hr test period.</td>
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6 CONCLUSIONS

Both C-S and 5Cr-S showed the same characteristic trends of corrosion and scale formation rates in all the experiments. Conclusions about the effect of time, TAN, temperature and sulfur content are summarized below.

6.1 Effect of time

- Time has the same effect on the corrosion of steels at different TANs. Corrosion rate started out to be high initially, decreased with time and remained unchanged beyond 24 hr of exposure in the presence of sulfur.
- To better understand the effect of TAN, temperature and total sulfur on corrosion of steels they should be exposed to minimum of 24 hr.
- Scale thickness increased with time when exposed to low TAN. However the scale formed in longer exposures could not offer much protection to steel. At high TANs scale thickness appeared to decrease with time unlike to low TANs.
- Most of Fe was recovered as FeS for short exposure period at low TANs and the recovery reduced with time which illustrated that FeS scale formed became poorly attached to the steel surface and spalled off during the course of the experiment. At high TANs major part of Fe was recovered as iron naphthenate.
- At low TANs significant proportion of the retained scale was adherent to the steel even after long exposures (~ 70%), where as at high TANs only 2% of the scale was adherent which could barely protect the steel.
• At low TANs corrosion was mainly by sulfur compounds and at high TANs corrosion was greatly affected by NAP acids.

6.2 Effect of TAN

• Increase in TAN appeared to increase the corrosion rate but it needed to reach a threshold value above which the effect of TAN was clearly observed. The threshold value of TAN depended on the sulfur content in the oil. Under 0.25 wt% TS and 620 -650°F temperature range, threshold value of TAN above which NAP acids were highly reactive lied between 2 and 4 which is consistent with NACE paper 02555. 25

• At high TAN most of Fe was converted as iron naphthenate and very small proportion appeared as FeS

• Scale adherence to the steel surface was dependent on TAN and scale could withstand to NAP acid attack until TAN reached its threshold value.

6.3 Effect of temperature

• Temperature influenced corrosion of both the steels greatly. High corrosion was observed at high temperatures. Scale thickness increased with temperature however scale at high temperatures could not offer much protection to both the steels.

• A good proportion of scale retained on 5Cr-S even at high temperatures suggests that scale is more tenacious on 5Cr-S than on C-S. However 5Cr-S showed
greater corrosion rates compared to C-S when exposed to TS=0.25 and different TANs=0.1 and 2.

6.4 Scale formation

- Better protection was offered to the steel when the oil exposed to it was rich in sulfur.

- Not all the scale formed in test could be recovered. Depending on the operating conditions scale was observed to be
  - Very loose scale that was lost during the experiment and did not offer any protection
  - Loose scale that was just retained on the steel surface even after the experiment, offering some protection
  - Adherent scale that was strongly adherent to the steel surface and offered most protection

- FeS scale showed multi layered structure and is subjected to internal stresses and cracking. Cracking leads to poorer adherences and ultimately detachment of the scale from the surface. Damage of the scale is greatly dependant on time of exposure and TAN. Scales were severely damaged when exposed to high TANs

- FeS scales are not 100% dense and SEM pictures compared to weight loss showed on average very porous scales formed in all the experiments. Time influenced porosity of the scale and it showed a decreased trend with increase of
time. Porosity of the scale increased with increase of TAN value. Porosity did not show any characteristic change with temperature.
7 FUTURE WORK

So far experiments were conducted with a model (yellow) oil to understand the corrosion dependence of steels on TAN, TS and temperature. Future works will include tests using real crude fractions with similar characteristics (same TAN and TS) under same experimental conditions. The results of these experiments will be compared to model oil test results to investigate whether there are differences in behavior in the case of NAP corrosion.

If the results are found to be similar then next step could be building a model for NAP corrosion. If the results are observed to be significantly different then some more experiments with model oils will be conducted with different model oil which reproduce better real crude fractions characteristics.
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4. Blanco, F. E.; Hopkinson, B.; Ramirez, I.; Corrosion by naphthenic Organic Acids in the Processing of some Venezuela crudes, APREL Meeting ,Mexico City, Mexico, August **1957**.


22. ASTM G 31-72, Standard Practice for Laboratory Immersion Corrosion testing, 1995, 03 (02), p.89.


Figure 1. The two FTMA units (Left and Right)
Figure 2. FTMA unit
Figure 3. Exploded view of the FTMA reactor
Figure 4. FTMA reactor – detail of the coupons set-up

Figure 5. Effect of time on corrosion rate of C-S samples exposed to TAN=0.1, TS=0.25 at 620°F temperature. Corresponding surface analysis and cross sectional Images can be viewed from Figure 8 to Figure 13.
Figure 6. Effect of time on scale thickness of C-S samples exposed to TAN=0.1, TS=0.25 at 620°F temperature. Corresponding surface analysis and cross sectional Images can be viewed from Figure 8 to Figure 13.

Figure 7. Comparison of moles of Fe lost and FeS retained with variation in time on C-S exposed to TAN=0.1, TS=0.25 at 620°F temperature. Corresponding surface analysis and cross sectional Images can be viewed from Figure 8 to Figure 13.
Figure 8. Surface morphology of C-S sample exposed to TAN=0.1, TS=0.25 in 620°F temperature and 6hr test period. Corresponding corrosion rate, scale formation rate and mole balance can be viewed at Figure 5, Figure 6 and Figure 7 respectively.

Figure 9. X-Sectional view of C-S sample exposed to TAN=0.1, TS=0.25 at 620°F temperature and 6hr test period. Corresponding corrosion rate, scale formation rate and mole balance can be viewed at Figure 5, Figure 6 and Figure 7 respectively.

Figure 10. Surface morphology of C-S sample exposed to TAN=0.1, TS=0.25 at 620°F temperature and 24hr test period. Corresponding corrosion rate, scale formation rate and mole balance can be viewed at Figure 5, Figure 6 and Figure 7 respectively.

Figure 11. X-Sectional view of C-S sample exposed to TAN=0.1, TS=0.25 at 620°F temperature and 24 hr test period. Corresponding corrosion rate, scale formation rate and mole balance can be viewed at Figure 5, Figure 6 and Figure 7 respectively.
Figure 12. Surface morphology of C-S sample exposed to TAN=0.1, TS=0.25 at 620°F temperature and 48hr test period. Corresponding corrosion rate, scale formation rate and mole balance can be viewed at Figure 5, Figure 6 and Figure 7 respectively.

Figure 13. X-Sectional view of C-S sample exposed to TAN=0.1, TS=0.25 at 620°F temperature and 48 hr test period. Corresponding corrosion rate, scale formation rate and mole balance can be viewed at Figure 5, Figure 6 and Figure 7 respectively.

Figure 14. Surface morphology of C-S sample exposed to TAN=0.1, TS=0.25 at 620°F temperature and 96 hr test period. Corresponding corrosion rate, scale formation rate and mole balance can be viewed at Figure 5, Figure 6 and Figure 7 respectively.

Figure 15. X-Sectional view of C-S sample exposed to TAN=0.1, TS=0.25 at 620°F temperature and 96 hr test period. Corresponding corrosion rate, scale formation rate and mole balance can be viewed at Figure 5, Figure 6 and Figure 7 respectively.
Figure 16. Effect of time on corrosion rate of 5Cr-S samples exposed to TAN=0.1, TS=0.25 at 620°F temperature. Corresponding surface analysis and cross sectional pictures can be viewed from Figure 19 and Figure 26.

Figure 17. Effect of time on scale thickness of 5Cr-S samples exposed to TAN=0.1, TS=0.25 at 620°F temperature. Corresponding surface analysis and cross sectional pictures can be viewed from Figure 19 and Figure 26.
Figure 18. Comparison of moles of Fe lost and FeS retained with variation in time on C-S exposed to TAN=0.1, TS=0.25 at 620°F temperature. Corresponding surface analysis and cross sectional pictures can be viewed from Figure 19 and Figure 26.
Figure 19. Surface morphology of 5Cr-S sample exposed to TAN=0.1, TS=0.25 at 620°F temperature and 6hr test period. Corresponding corrosion rate, scale formation rate and mol balance can be viewed at Figure 16, Figure 17 and Figure 18 respectively.

Figure 20. X-Sectional view of 5Cr-S sample exposed to TAN=0.1, TS=0.25 at 620°F temperature and 6 hr test period. Corresponding corrosion rate, scale formation rate and mol balance can be viewed at Figure 16, Figure 17 and Figure 18 respectively.

Figure 21. Surface morphology of 5Cr-S sample exposed to TAN=0.1, TS=0.25 at 620°F temperature and 24 hr test period. Corresponding corrosion rate, scale formation rate and mol balance can be viewed at Figure 16, Figure 17 and Figure 18 respectively.

Figure 22. X-Sectional view of 5Cr-S sample exposed to TAN=0.1, TS=0.25 at 620°F temperature and 24 hr test period. Corresponding corrosion rate, scale formation rate and mol balance can be viewed at Figure 16, Figure 17 and Figure 18 respectively.
Figure 23. Surface morphology of 5Cr-S sample exposed to TAN=0.1, TS=0.25 at 620°F temperature and 48 hr test period. Corresponding corrosion rate, scale formation rate and mol balance can be viewed at Figure 16, Figure 17 and Figure 18 respectively.

Figure 24. X-Sectional view of 5Cr-S sample exposed to TAN=0.1, TS=0.25 at 620°F temperature and 48 hr test period. Corresponding corrosion rate, scale formation rate and mol balance can be viewed at Figure 16, Figure 17 and Figure 18 respectively.

Figure 25. Surface morphology of 5Cr-S sample exposed to TAN=0.1, TS=0.25 at 620°F temperature and 96 hr test period. Corresponding corrosion rate, scale formation rate and mol balance can be viewed at Figure 16, Figure 17 and Figure 18 respectively.

Figure 26. X-Sectional view of 5Cr-S sample exposed to TAN=0.1, TS=0.25 at 620°F temperature and 96 hr test period. Corresponding corrosion rate, scale formation rate and mol balance can be viewed at Figure 16, Figure 17 and Figure 18 respectively.
Figure 27. Effect of time on corrosion rate of C-S samples exposed to TAN=1, TS=0.25 at 620°F temperature.

Figure 28. Effect of time on scale thickness of C-S samples exposed to TAN=1, TS=0.25 at 620°F temperature.
Figure 29. Comparison of moles of Fe lost and FeS retained with variation in time on C-S exposed to TAN=1, TS=0.25 at 620°F temperature.

Figure 30. Effect of time on corrosion rate of 5Cr-S samples exposed to TAN=1, TS=0.25, 620°F temperature.
Figure 31. Effect of time on scale thickness of 5Cr-S samples exposed to TAN=1, TS=0.25, 620°F temperature.

Figure 32. Comparison of moles of Fe lost and FeS retained with variation in time on 5Cr-S exposed to TAN=1, TS=0.25 at 620°F temperature.
Figure 33. Effect of time on corrosion rate of C-S samples exposed to TAN=4, TS=0.25, 620°F temperature.

Figure 34. Effect of time on scale thickness of C-S samples exposed to TAN=4, TS=0.25, 620°F temperature.
Figure 35. Comparison of moles of Fe lost and FeS retained with variation in time on C-S exposed to TAN=4, TS=0.25 at 620°F temperature.

Figure 36. Effect of time on corrosion rate of 5Cr-S samples exposed to TAN=4, TS=0.25, 620°F temperature.
Figure 37. Effect of time on scale thickness of 5Cr-S samples exposed to TAN=4, TS=0.25, 620°F temperature.

Figure 38. Comparison of moles of Fe lost and FeS retained with variation in time on 5Cr-S exposed to TAN=4, TS=0.25 at 620°F temperature.
Figure 39. Effect of time on corrosion rate of C-S samples exposed to TAN=0.1, TS=0.25, 650°F temperature. Corresponding surface analysis and cross sectional images can be viewed from Figure 42 to Figure 49.

Figure 40. Effect of time on scale thickness of C-S samples exposed to TAN=0.1, TS=0.25, 650°F temperature. Corresponding surface analysis and cross sectional images can be viewed from Figure 42 to Figure 49.
Figure 41. Comparison of moles of Fe lost and FeS retained with variation in time on C-S exposed to TAN=0.1, TS=0.25 at 650°F temperature. Corresponding surface analysis and cross sectional images can be viewed from Figure 42 to Figure 49.

Figure 42. Surface morphology of C-S sample exposed to TAN=0.1, TS=0.25 at 650°F temperature and 6hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 39, Figure 40 and Figure 41 respectively.

Figure 43. X-Sectional view of C-S sample exposed to TAN=0.1, TS=0.25 at 650°F temperature and 6 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 39, Figure 40 and Figure 41 respectively.
Figure 44. Surface morphology of C-S sample exposed to TAN=0.1, TS=0.25 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 39, Figure 40 and Figure 41 respectively.

Figure 45. X-Sectional view of C-S sample exposed to TAN=0.1, TS=0.25 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 39, Figure 40 and Figure 41 respectively.

Figure 46. Surface morphology of C-S sample exposed to TAN=0.1, TS=0.25 at 650°F temperature and 48 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 39, Figure 40 and Figure 41 respectively.

Figure 47. X-Sectional view of C-S sample exposed to TAN=0.1, TS=0.25 at 650°F temperature and 48 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 39, Figure 40 and Figure 41 respectively.
Figure 48. Surface morphology of C-S sample exposed to TAN=0.1, TS=0.25 at 650°F temperature and 96 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 39, Figure 40 and Figure 41 respectively.

Figure 49. X-Sectional view of C-S sample exposed to TAN=0.1, TS=0.25 at 650°F temperature and 96 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 39, Figure 40 and Figure 41 respectively.

Figure 50. Effect of time on corrosion rate of 5Cr-S samples exposed to TAN=0.1, TS=0.25 and 650°F temperature. Corresponding surface analysis and cross sectional images can be viewed from Figure 53 to Figure 60.
Figure 51. Effect of time on scale thickness of 5Cr-S samples exposed to TAN=0.1, TS=0.25 and 650°F temperature. Corresponding surface analysis and cross sectional images can be viewed from Figure 53 to Figure 60.

Figure 52. Comparison of moles of Fe lost and FeS retained with variation in time on 5Cr-S exposed to TAN=0.1, TS=0.25 at 650°F temperature. Corresponding surface analysis and cross sectional images can be viewed from Figure 53 to Figure 60.
Figure 53. Surface morphology of 5Cr-S sample exposed to TAN=0.1, TS=0.25 at 650°F temperature and 6 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 50, Figure 51 and Figure 52 respectively.

Figure 54. X-Sectional view of 5Cr-S sample exposed to TAN=0.1, TS=0.25 at 650°F temperature and 6 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 50, Figure 51 and Figure 52 respectively.

Figure 55. Surface morphology of 5Cr-S sample exposed to TAN=0.1, TS=0.25 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 50, Figure 51 and Figure 52 respectively.

Figure 56. X-Sectional view of 5Cr-S sample exposed to TAN=0.1, TS=0.25 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 50, Figure 51 and Figure 52 respectively.
Figure 57. Surface morphology of 5Cr-S sample exposed to TAN=0.1, TS=0.25 at 650°F temperature and 48 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 50, Figure 51 and Figure 52 respectively.

Figure 58. X-Sectional view of 5Cr-S sample exposed to TAN=0.1, TS=0.25 at 650°F temperature and 48 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 50, Figure 51 and Figure 52 respectively.

Figure 59. Surface morphology of 5Cr-S sample exposed to TAN=0.1, TS=0.25 at 650°F temperature and 96 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 50, Figure 51 and Figure 52 respectively.

Figure 60. X-Sectional view of 5Cr-S sample exposed to TAN=0.1, TS=0.25 at 650°F temperature and 96 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 50, Figure 51 and Figure 52 respectively.
Figure 61. Effect of time on corrosion rate of C-S samples exposed to TAN=1, TS=0.25, 650°F temperature. Corresponding surface analysis and cross sectional images can be viewed from Figure 64 to Figure 71.

Figure 62. Effect of time on scale thickness of C-S samples exposed to TAN=1, TS=0.25, 650°F temperature. Corresponding surface analysis and cross sectional images can be viewed from Figure 64 to Figure 71.
Figure 63. Comparison of moles of Fe lost and FeS retained with variation in time on C-S exposed to TAN=1, TS=0.25 at 650°F temperature. Corresponding surface analysis and cross sectional images can be viewed from Figure 64 to Figure 71.

Figure 64. Surface morphology of C-S sample exposed to TAN=1, TS=0.25 at 650°F temperature and 3 hr test period. Corresponding corrosion rate, scale formation rate and scale thickness can be viewed at Figure 61, Figure 62 and Figure 63 respectively.

Figure 65. X-Sectional view of C-S sample exposed to TAN=1, TS=0.25 at 650°F temperature and 3 hr test period. Corresponding corrosion rate, scale formation rate and scale thickness can be viewed at Figure 61, Figure 62 and Figure 63 respectively.
Figure 66. Surface morphology of C-S sample exposed to TAN=1, TS=0.25 at 650°F temperature and 6 hr test period. Corresponding corrosion rate, scale formation rate and scale thickness can be viewed at Figure 61, Figure 62 and Figure 63 respectively.

Figure 67. X-Sectional view of C-S sample exposed to TAN=1, TS=0.25 at 650°F temperature and 6 hr test period. Corresponding corrosion rate, scale formation rate and scale thickness can be viewed at Figure 61, Figure 62 and Figure 63 respectively.

Figure 68. Surface morphology of C-S sample exposed to TAN=1, TS=0.25 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale formation rate and scale thickness can be viewed at Figure 61, Figure 62 and Figure 63 respectively.

Figure 69. X-Sectional view of C-S sample exposed to TAN=1, TS=0.25 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale formation rate and scale thickness can be viewed at Figure 61, Figure 62 and Figure 63 respectively.
Figure 70. Surface morphology of C-S sample exposed to TAN=1, TS=0.25 at 650°F temperature and 48 hr test period. Corresponding corrosion rate, scale formation rate and scale thickness can be viewed at Figure 61, Figure 62 and Figure 63 respectively.

Figure 71. X-Sectional view of C-S sample exposed to TAN=1, TS=0.25 at 650°F temperature and 48 hr test period. Corresponding corrosion rate, scale formation rate and scale thickness can be viewed at Figure 61, Figure 62 and Figure 63 respectively.

Figure 72. Effect of time on corrosion rate of 5Cr-S samples exposed to TAN=1, TS=0.25, 650°F temperature. Corresponding surface analysis and cross sectional images can be viewed from Figure 75 to Figure 80.
Figure 73. Effect of time on scale thickness of 5Cr-S samples exposed to TAN=1, TS=0.25, 650°F temperature. Corresponding surface analysis and cross sectional images can be viewed from Figure 75 to Figure 80.

Figure 74. Comparison of moles of Fe lost and moles FeS retained with variation in time on 5Cr-S exposed to TAN=1, TS=0.25, 650°F. Corresponding surface analysis and cross sectional images can be viewed from Figure 75 to Figure 80.
Figure 75. Surface morphology of 5Cr-S sample exposed to TAN=1, TS=0.25 at 650°F temperature and 6 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 72, Figure 73 and Figure 74 respectively.

Figure 76. X-Sectional view of 5Cr-S sample exposed to TAN=1, TS=0.25 at 650°F temperature and 6 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 72, Figure 73 and Figure 74 respectively.

Figure 77. Surface morphology of 5Cr-S sample exposed to TAN=1, TS=0.25 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 72, Figure 73 and Figure 74 respectively.

Figure 78. X-Sectional view of 5Cr-S sample exposed to TAN=1, TS=0.25 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 72, Figure 73 and Figure 74 respectively.
Figure 79. Surface morphology of 5Cr-S sample exposed to TAN=1, TS=0.25 at 650°F temperature and 48 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 72, Figure 73 and Figure 74 respectively.

Figure 80. X-Sectional view of 5Cr-S sample exposed to TAN=1, TS=0.25 at 650°F temperature and 48 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 72, Figure 73 and Figure 74 respectively.

Figure 81. Effect of TAN on corrosion rate of C-S samples exposed to TS=0.25, 620°F temperature and 24hr test period.
Figure 82. Effect of TAN on scale thickness of C-S samples exposed to TS=0.25, 620°F temperature and 24hr test period.

Figure 83. Comparison of moles of Fe lost and moles FeS retained with variation in TAN on C-S exposed to TS=0.25, 620°F temperature and 24hr test period.
Figure 84. Effect of TAN on corrosion rate of 5Cr-S samples exposed to TS=0.25, 620°F temperature and 24hr test period.

Figure 85. Effect of TAN on scale thickness of 5Cr-S samples exposed to TS=0.25, 620°F temperature and 24hr test period.
Figure 86. Comparison of change of moles of Fe lost and moles FeS retained with variation in TAN on 5Cr-S exposed to TS=0.25, 620°F temperature and 24hr test period.

Figure 87. Effect of TAN on corrosion rate of C-S samples exposed to TS=0.25, 650°F temperature and 24hr test period. Corresponding surface analysis images at TAN=0.1, 1, 2 and 4 can be viewed at Figure 44, Figure 68, Figure 90 and Figure 92 and cross sectional images can be viewed at Figure 45, Figure 69, Figure 91 and Figure 93 respectively.
Figure 88. Effect of TAN on scale thickness of C-S samples exposed to TS=0.25, 650°F temperature and 24hr test period. Corresponding surface analysis images at TAN=0.1, 1, 2 and 4 can be viewed at Figure 44, Figure 68, Figure 90 and Figure 92 and cross sectional images can be viewed at Figure 45, Figure 69, Figure 91 and Figure 93 respectively.

Figure 89. Comparison of moles of Fe lost and moles FeS retained with variation in TAN on C-S exposed to TS=0.25, 650°F temperature and 24hr test period. Corresponding surface analysis images at TAN=0.1, 1, 2 and 4 can be viewed at Figure 44, Figure 68, Figure 90 and Figure 92 and cross sectional images can be viewed at Figure 45, Figure 69, Figure 91 and Figure 93.
Figure 90. Surface morphology of C-S sample exposed to TAN=2, TS=0.25 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 87, Figure 88 and Figure 89 respectively.

Figure 91. X-Sectional view of C-S sample exposed to TAN=2, TS=0.25 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 87, Figure 88 and Figure 89 respectively.

Figure 92. Surface morphology of C-S sample exposed to TAN=4, TS=0.25 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 87, Figure 88 and Figure 89 respectively.

Figure 93. X-Sectional view of C-S sample exposed to TAN=4, TS=0.25 at 50°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 87, Figure 88 and Figure 89 respectively.
Figure 94. Effect of TAN on corrosion rate of 5Cr-S samples exposed to TS=0.25, 650°F temperature and 24hr test period. Corresponding surface analysis images at TAN=0.1, 1, 2 and 4 can be viewed at Figure 55, Figure 77, Figure 97 and Figure 99 and cross sectional images can be viewed at Figure 56, Figure 78, Figure 98 and Figure 100 respectively.

Figure 95. Effect of TAN on scale thickness of 5Cr-S samples exposed to TS=0.25, 650°F temperature and 24hr test period. Corresponding surface analysis images at TAN=0.1, 1, 2 and 4 can be viewed at Figure 55, Figure 77, Figure 97 and Figure 99 and cross sectional images can be viewed at Figure 56, Figure 78, Figure 98 and Figure 100 respectively.
Figure 96. Comparison of moles of Fe lost and moles FeS retained with variation in TAN on 5Cr-S exposed to TS=0.25, 650°F temperature and 24hr test period. Corresponding surface analysis images at TAN=0.1, 1, 2 and 4 can be viewed at Figure 55, Figure 77, Figure 97 and Figure 99 and cross sectional images can be viewed at Figure 56, Figure 78, Figure 98 and Figure 100 respectively.

Figure 97. Surface morphology of 5Cr-S sample exposed to TAN=2, TS=0.25 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 94, Figure 95 and Figure 96 respectively.

Figure 98. X-Sectional view of 5Cr-S sample exposed to TAN=2, TS=0.25 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 94, Figure 95 and Figure 96 respectively.
Figure 99. Surface morphology of 5Cr-S sample exposed to TAN=4, TS=0.25 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 94, Figure 95 and Figure 96 respectively.

Figure 100. X-Sectional view of 5Cr-S sample exposed to TAN=4, TS=0.25 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 94, Figure 95 and Figure 96 respectively.

Figure 101. Effect of TAN on corrosion rate of C-S samples exposed to TS=0.1, 650°F temperature and 24hr test period. Corresponding surface analysis and cross sectional images can be viewed from Figure 104 to Figure 107.
Figure 102. Effect of TAN on scale thickness of C-S samples exposed to TS=0.1, 650°F temperature and 24hr test period. Corresponding surface analysis and cross sectional images can be viewed from Figure 104 to Figure 107.

Figure 103. Comparison of moles of Fe lost and moles FeS retained with variation in TAN on C-S exposed to TS=0.1, 650°F temperature and 24hr test period. Corresponding surface analysis and cross sectional images can be viewed from Figure 104 to Figure 107.
Figure 104. Surface morphology of C-S sample exposed to TAN=2, TS=0.25 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 101, Figure 102 and Figure 103 respectively.

Figure 105. X-Sectional view of C-S sample exposed to TAN=2, TS=0.25 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 101, Figure 102 and Figure 103 respectively.

Figure 106. Surface morphology of C-S sample exposed to TAN=4, TS=0.1 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 101, Figure 102 and Figure 103 respectively.

Figure 107. X-Sectional view of C-S sample exposed to TAN=4, TS=0.1 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 101, Figure 102 and Figure 103 respectively.
Figure 108. Effect of TAN on corrosion rate of 5Cr-S samples exposed to TS=0.1, 650°F temperature and 24hr test period. Corresponding surface analysis and cross sectional images can be viewed from Figure 111 to Figure 114.

Figure 109. Effect of TAN on scale thickness of 5Cr-S samples exposed to TS=0.1, 650°F temperature and 24hr test period. Corresponding surface analysis and cross sectional images can be viewed from Figure 111 to Figure 114.
Figure 110. Comparison of moles of Fe lost and moles FeS retained with variation in TAN on 5Cr-S exposed to TS=0.1, 650°F temperature and 24hr test period. Corresponding surface analysis and cross sectional images can be viewed from Figure 111 to Figure 114.

Figure 111. Surface morphology of 5Cr-S sample exposed to TAN=2, TS=0.1 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 108, Figure 109 and Figure 110 respectively.

Figure 112. X-Sectional view of 5Cr-S sample exposed to TAN=2, TS=0.1 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 108, Figure 109 and Figure 110 respectively.
Figure 113. Surface morphology of 5Cr-S sample exposed to TAN=4, TS=0.1 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 108, Figure 109 and Figure 110 respectively.

Figure 114. X-Sectional view of 5Cr-S sample exposed to TAN=4, TS=0.1 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 108, Figure 109 and Figure 110 respectively.

Figure 115. Comparison of effect of TAN and TS on corrosion rate of C-S samples exposed 650°F temperature and 24 hr test period.
Figure 116. Comparison of effect of TAN and TS on scale thickness of C-S samples 650°F temperature and 24 hr test period.

Figure 117. Comparison of effect of TAN and TS on corrosion rate of 5Cr-S samples exposed 650°F temperature and 24 hr test period.
Figure 118. Comparison of effect of TAN and TS on scale thickness of 5Cr-S samples exposed to 650°F temperature and 24 hr test period.

Figure 119. Effect of temperature on corrosion rate of C-S samples exposed to TAN=0.1, TS=0.25 and 24 hr test period.
Figure 120. Effect of temperature on scale thickness of C-S samples exposed to TAN=0.1, TS=0.25 and 24 hr test period.

Figure 121. Comparison of moles of Fe lost and moles FeS retained with variation in temperature on C-S exposed to TAN=0.1, TS=0.25 and 24 hr test period.
Figure 122. Effect of temperature on corrosion rate of 5Cr-S samples exposed to TAN=0.1, TS=0.25 and 24 hr test period.

Figure 123. Effect of temperature on scale thickness of 5Cr-S samples exposed to TAN=0.1, TS=0.25 and 24 hr test period.
Figure 124. Comparison of moles of Fe lost and moles FeS retained with variation in temperature on C-S exposed to TAN=0.1, TS=0.25 and 24 hr test period.

Figure 125. Effect of temperature on corrosion rate of C-S samples exposed to TAN=2, TS=0.25 and 24 hr test period. Corresponding surface analysis images at 550, 650 and 700°F can be viewed at Figure 128, Figure 90 and Figure 130 respectively and cross sectional images can be viewed at Figure 129, Figure 91 and Figure 131 respectively.
Figure 126. Effect of temperature on scale thickness of C-S samples exposed to TAN=2, TS=0.25 and 24 hr test period. Corresponding surface analysis images at 550, 650 and 700°F can be viewed at Figure 128, Figure 90 and Figure 130 respectively and cross sectional images can be viewed at Figure 129, Figure 91 and Figure 131 respectively.

Figure 127. Comparison of moles of Fe lost and moles FeS retained with variation in temperature on C-S exposed to TAN=2, TS=0.25 and 24 hr test period. Corresponding surface analysis images at 550, 650 and 700°F can be viewed at Figure 128, Figure 90 and Figure 130 respectively and cross sectional images can be viewed at Figure 129, Figure 91 and Figure 131 respectively.
Figure 128. Surface morphology of C-S sample exposed to TAN=2, TS=0.25 at 550°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 125, Figure 126 and Figure 127 respectively.

Figure 129. X-Sectional view of C-S sample exposed to TAN=2, TS=0.25 at 550°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 125, Figure 126 and Figure 127 respectively.

Figure 130. Surface morphology of C-S sample exposed to TAN=2, TS=0.25 at 700°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 125, Figure 126 and Figure 127 respectively.

Figure 131. X-Sectional view of C-S sample exposed to TAN=2, TS=0.25 at 700°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 125, Figure 126 and Figure 127 respectively.
Figure 132. Effect of temperature on corrosion rate of 5Cr-S samples exposed to TAN=2, TS=0.25 and 24 hr test period. Corresponding surface analysis images at 550, 650 and 700°F can be viewed at Figure 135, Figure 97 and Figure 137 respectively and cross sectional images can be viewed at Figure 136 Figure 98 and Figure 138 respectively.

Figure 133. Effect of temperature on scale thickness of 5Cr-S samples exposed to TAN=2, TS=0.25 and 24 hr test period. Corresponding surface analysis images at 550, 650 and 700°F can be viewed at Figure 135, Figure 97 and Figure 137 respectively and cross sectional images can be viewed at Figure 136 Figure 98 and Figure 138 respectively.
Figure 134. Comparison of moles of Fe lost and moles FeS retained with variation in temperature on 5Cr-S exposed to TAN=2, TS=0.25 and 24 hr test period. Corresponding surface analysis images at 550, 650 and 700°F can be viewed at Figure 135, Figure 97 and Figure 137 respectively and cross sectional images can be viewed at Figure 136 Figure 98 and Figure 138 respectively.

Figure 135. Surface morphology of 5Cr-S sample exposed to TAN=2, TS=0.25 at 550°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 132, Figure 133 and Figure 134 respectively.

Figure 136. X-Sectional view of 5Cr-S sample exposed to TAN=2, TS=0.25 at 550°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 132, Figure 133 and Figure 134 respectively.
Figure 137. Surface morphology of 5Cr-sample exposed to TAN=2, TS=0.25 at 700°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 132, Figure 133 and Figure 134 respectively.

Figure 138. X-Sectional view of 5Cr-S sample exposed to TAN=2, TS=0.25 at 700°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 132, Figure 133 and Figure 134 respectively.

Figure 139. Effect of temperature on corrosion rate of C-S samples exposed to TAN=0.8, TS=0.1 and 24 hr test period. Corresponding surface analysis and cross sectional images can be viewed from Figure 142 to Figure 147.
Figure 140. Effect of temperature on scale thickness of C-S samples exposed to TAN=0.8, TS=0.1 and 24 hr test period. Corresponding surface analysis and cross sectional images can be viewed from Figure 142 to Figure 147.

Figure 141. Comparison of moles of Fe lost and moles FeS retained with variation in temperature on C-S exposed to TAN=0.8, TS=0.1 and 24 hr test period. Corresponding surface analysis and cross sectional images can be viewed from Figure 142 to Figure 147.
Figure 142. Surface morphology of C-S sample exposed to TAN=0.8, TS=0.1 at 550°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 139, Figure 140 and Figure 141 respectively.

Figure 143. X-Sectional view of C-S sample exposed to TAN=0.8, TS=0.1 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 139, Figure 140 and Figure 141 respectively.

Figure 144. Surface morphology of C-S sample exposed to TAN=0.8, TS=0.1 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 139, Figure 140 and Figure 141 respectively.

Figure 145. X-Sectional view of C-S sample exposed to TAN=0.8, TS=0.1 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 139, Figure 140 and Figure 141 respectively.
Figure 146. Surface morphology of C-S sample exposed to TAN=0.8, TS=0.1 at 700°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 139, Figure 140 and Figure 141 respectively.

Figure 147. X-Sectional view of C-S sample exposed to TAN=0.8, TS=0.1 at 700°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 139, Figure 140 and Figure 141 respectively.

Figure 148. Effect of temperature on corrosion rate of 5Cr-S samples exposed to TAN=0.8, TS=0.1 and 24 hr test period. Corresponding surface analysis and cross sectional images can be viewed from Figure 151 to Figure 156.
Figure 149. Effect of temperature on scale thickness of 5Cr-S samples exposed to TAN=0.8, TS=0.1 and 24 hr test period. Corresponding surface analysis and cross sectional images can be viewed from Figure 151 to Figure 156.

Figure 150. Comparison of moles of Fe lost and moles FeS retained with variation in temperature on 5Cr-S exposed to TAN=0.8, TS=0.1 and 24 hr test period. Corresponding surface analysis and cross sectional images can be viewed from Figure 151 to Figure 156.
Figure 151. Surface morphology of 5Cr-S sample exposed to TAN=0.8, TS=0.1 at 550°F temperature and 24 hr test period. Corrosion rate, scale thickness and mole balance can be viewed at Figure 148, Figure 149 and Figure 150 respectively.

Figure 152. X-Sectional view of 5Cr-S sample exposed to TAN=0.8, TS=0.1 at 550°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 148, Figure 149 and Figure 150 respectively.

Figure 153. Surface morphology of 5Cr-S sample exposed to TAN=0.8, TS=0.1 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 148, Figure 149 and Figure 150 respectively.

Figure 154. X-Sectional view of 5Cr-S sample exposed to TAN=0.8, TS=0.1 at 650°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 148, Figure 149 and Figure 150 respectively.
Figure 155. Surface morphology of 5Cr-S sample exposed to TAN=0.8, TS=0.1 at 700°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 148, Figure 149 and Figure 150 respectively.

Figure 156. X-Sectional view of 5Cr-S sample exposed to TAN=0.8, TS=0.1 at 700°F temperature and 24 hr test period. Corresponding corrosion rate, scale thickness and mole balance can be viewed at Figure 148, Figure 149 and Figure 150 respectively.

Figure 157. Comparison of corrosion rate of C-S and 5Cr-S at different time periods exposed to TAN=0.1, TS=0.25 and 620°F temperature.
Figure 158. Comparison of scale thickness of C-S and 5Cr-S at different time periods exposed to TAN=0.1, TS=0.25 and 620°F temperature.

Figure 159. Comparison of corrosion rate of C-S and 5Cr-S at different time periods exposed to TAN=1, TS=0.25 and 620°F temperature.
Figure 160. Comparison of scale thickness of C-S and 5Cr-S at different time periods exposed to TAN=1, TS=0.25 and 620°F temperature.

Figure 161. Comparison of corrosion rate of C-S and 5Cr-S at different time periods exposed to TAN=4, TS=0.25 and 620°F temperature.
Figure 162. Comparison of scale thickness of C-S and 5Cr-S at different time periods exposed to TAN=4, TS=0.25 and 620°F temperature.

Figure 163. Comparison of corrosion rate of C-S and 5Cr-S at different time periods exposed to TAN=0.1, TS=0.25 and 650°F temperature.
Figure 164. Comparison of scale thickness of C-S and 5Cr-S at different time periods exposed to TAN=0.1, TS=0.25 and 650°F temperature.

Figure 165. Comparison of corrosion rate of C-S and 5Cr-S at different time periods exposed to TAN=1, TS=0.25 and 650°F temperature.
Figure 166. Comparison of scale thickness of C-S and 5Cr-S at different time periods exposed to TAN=1, TS=0.25 and 650°F temperature.

Figure 167. Comparison of corrosion rate of C-S and 5Cr-S at different TAN concentrations exposed to TS=0.25, 24 hr test period and 620°F temperature.
Figure 168. Comparison of scale thickness of C-S and 5Cr-S at different TAN concentrations exposed to TS=0.25, 24 hr test period and 620°F temperature.

Figure 169. Comparison of corrosion rate of C-S and 5Cr-S at different TAN concentrations exposed to TS=0.25, 24 hr test period and 650°F temperature.
Figure 170. Comparison of scale thickness of C-S and 5Cr-S at different TAN concentrations exposed to TS=0.25, 24 hr test period and 650°F temperature.

Figure 171. Comparison of corrosion of C-S and 5Cr-S at different TAN concentrations exposed to TS=0.1, 24 hr test period and 650°F temperature.
Figure 172. Comparison of scale thickness of C-S and 5Cr-S at different TAN concentrations exposed to TS=0.1, 24 hr test period and 650°F temperature.

Figure 173. Comparison of corrosion of C-S and 5Cr-S at different temperatures exposed to TAN=0.1, TS=0.25, 24 hr test period.
Figure 174. Comparison of scale thickness of C-S and 5Cr-S at different temperatures exposed to TAN=0.1, TS=0.25, 24 hr test period.

Figure 175. Comparison of corrosion rate of C-S and 5Cr-S at different temperatures exposed to TAN=2, TS=0.25, 24 hr test period.
Figure 176. Comparison of corrosion rate of C-S and 5Cr-S at different temperatures exposed to TAN=2, TS=0.25, 24 hr test period.

Figure 177. Comparison of scale thickness of C-S and 5Cr-S at different temperatures exposed to TAN=0.8, TS=0.1, 24 hr test period.
Figure 178. Comparison of scale thickness of C-S and 5Cr-S at different temperatures exposed to TAN=0.8, TS=0.1, 24 hr test period.
APPENDIX A: Surface and cross sectional pictures of C-S and 5Cr-S

Figure A 1. Surface morphology of C-S exposed to TAN=0.1, TS=0.25, 620 °F temperature and 3 hr test period.

Figure A 2. Cross sectional view of C-S exposed to TAN=0.1, TS=0.25, 620 °F temperature and 3 hr test period (5KX).

Figure A 3. Cross sectional view of C-S exposed to TAN=0.1, TS=0.25, 620 °F temperature and 3 hr test period (10KX).

Figure A 4. Line analysis of C-S exposed to TAN=0.1, TS=0.25, 620 °F temperature and 3 hr test period.
Figure A 5. Compositional analysis of C-S exposed to TAN=0.1, TS=0.25, 620 °F temperature and 3 hr test period.

Figure A 6. Surface morphology of C-S exposed to TAN=0.1, TS=0.25, 620 °F temperature and 6 hr test period.

Figure A 7. Cross sectional view of C-S exposed to TAN=0.1, TS=0.25, 620 °F temperature and 6 hr test period (5KX).
Figure A 8. Surface morphology of C-S exposed to TAN=0.1, TS=0.25, 620 °F temperature and 24 hr test period.

Figure A 9. Cross sectional view of C-S exposed to TAN=0.1, TS=0.25, 620 °F temperature and 24 hr test period (5KX).

Figure A 10. Surface morphology of C-S exposed to TAN=0.1, TS=0.25, 620 °F temperature and 48 hr test period.

Figure A 11. Cross sectional view of C-S exposed to TAN=0.1, TS=0.25, 620 °F temperature and 48 hr test period (2.5KX).
Figure A 12. Cross sectional view of C-S exposed to TAN=0.1, TS=0.25, 620 °F temperature and 48 hr test period (10KX).

Figure A 13. Line analysis of C-S exposed to TAN=0.1, TS=0.25, 620 °F temperature and 48 hr test period (10KX).

Figure A 14. Surface morphology of C-S exposed to TAN=0.1, TS=0.25, 620 °F temperature and 96 hr test period.

Figure A 15. Back scatter image of C-S exposed to TAN=0.1, TS=0.25, 620 °F temperature and 96 hr test period.
Figure A 16. Cross sectional view of C-S exposed to TAN=0.1, TS=0.25, 620 °F temperature and 96 hr test period (5KX).

Figure A 17. Line analysis of C-S exposed to TAN=0.1, TS=0.25, 620 °F temperature and 48 hr test period (5KX).

Figure A 18. Surface morphology of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 620°F temperature and 3 hr test period.

Figure A 19. Cross sectional view of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 620°F temperature and 3 hr test period.
Figure A 20. Line analysis of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 620°F temperature and 3 hr test period.

Figure A 21. Compositional analysis of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 620°F temperature and 3 hr test period.

Figure A 22. Surface morphology of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 620°F temperature and 6 hr test period.

Figure A 23. Cross sectional view of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 620°F temperature and 6 hr test period.
Figure A 24. Line analysis of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 620°F temperature and 6 hr test period.

Figure A 25. Surface morphology of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 620°F temperature and 24 hr test period (1KX).

Figure A 26. Surface morphology of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 620°F temperature and 24 hr test period (5 KX).

Figure A 27. Cross sectional view of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 620°F temperature and 24 hr test period.
Figure A 28. Line analysis of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 620°F temperature and 24 hr test period.

Figure A 29. Surface morphology of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 620°F temperature and 48 hr test period (100X).

Figure A 30. Cross sectional view of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 620°F temperature and 48 hr test period.

Figure A 31. Line analysis of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 620°F temperature and 48 hr test period.
Figure A 32. Surface morphology of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 620°F temperature and 96 hr test period (100X).

Figure A 33. Cross sectional view of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 620°F temperature and 96 hr test period.

Figure A 34. Line analysis of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 620°F temperature and 96 hr test period.

Figure A 35. Surface morphology of C-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 6 hr test period (500X).
Figure A 36. Surface morphology of C-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 6 hr test period (1KX).

Figure A 37. Cross sectional view of C-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 6 hr test period.

Figure A 38. Cross sectional view (BSE) of C-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 6 hr test period.

Figure A 39. Surface morphology of C-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 24 hr test period (30X).
Figure A 40. Surface morphology of C-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 24 hr test period (100X).

Figure A 41. Surface morphology of C-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 24 hr test period (1KX).

Figure A 42. Surface morphology of C-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 48hr test period (100X).

Figure A 43. Surface morphology of C-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 48hr test period (500X).
Figure A 44. Cross sectional view (BSE) of C-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 48 hr test period.

Figure A 45. Surface morphology of C-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 96 hr test period (100X).

Figure A 46. Surface morphology of C-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 96 hr test period (1KX).

Figure A 47. Cross sectional view of C-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 96 hr test period.
Figure A 48. Surface morphology of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 6 hr test period (100X).

Figure A 49. Surface morphology of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 6 hr test period (1KX).

Figure A 50. Cross sectional view of C-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 6 hr test period (4KX).

Figure A 51. Cross sectional view of C-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 6 hr test period (8KX).
Figure A 52. Surface morphology of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 24 hr test period (100X).

Figure A 53. Surface morphology of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 24 hr test period (500X).

Figure A 54. Surface morphology of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 48 hr test period (100X).

Figure A 55. Cross sectional view of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 48 hr test period (4KX).
Figure A 56. Cross sectional view of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 48 hr test period (10KX).

Figure A 57. Surface morphology of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 96 hr test period (100X).

Figure A 58. Surface morphology of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 96 hr test period (1KX).

Figure A 59. Cross sectional view of 5Cr-S coupon exposed TAN=0.1, TS=0.25, 650°F temperature and 96 hr test period (10KX).
Figure A 60. Surface morphology of C-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 3 hr test period (1KX).

Figure A 61. Cross sectional view of C-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 3 hr test period (5KX).

Figure A 62. Line analysis of C-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 3 hr test period (5KX).

Figure A 63. Surface morphology of C-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 6 hr test period (1KX).
Figure A 64. Cross sectional view of C-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 6 hr test period (5KX).

Figure A 65. Line analysis of view of C-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 6 hr test period (5KX).

Figure A 66. Surface morphology of C-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 24 hr test period (500X).

Figure A 67. Surface morphology of C-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 24 hr test period (5KX).
Figure A 68. Cross sectional view of C-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 24 hr test period (5KX).

Figure A 69. Line analysis of C-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 24 hr test period (5KX).

Figure A 70. Surface morphology of C-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 48 hr test period (250X).

Figure A 71. Surface morphology of C-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 48 hr test period (5KX).
Figure A 72. Cross sectional view of C-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 48 hr test period (5KX).

Figure A 73. Line analysis of C-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 48 hr test period (5KX).

Figure A 74. Surface morphology of 5Cr-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 6 hr test period (250X).

Figure A 75. Surface morphology of 5Cr-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 6 hr test period (1KX).
Figure A 76. Surface morphology of 5Cr-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 6 hr test period (2.5X).

Figure A 77. Cross sectional view of 5Cr-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 6 hr test period (5KX).

Figure A 78. Line analysis of 5Cr-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 6 hr test period (5KX).

Figure A 79. Surface morphology of 5Cr-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 24 hr test period (500X).
Figure A 80. Surface morphology of 5Cr-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 24 hr test period (1.5KX).

Figure A 81. Cross sectional view of 5Cr-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 24 hr test period (5KX).

Figure A 82. Line analysis of 5Cr-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 6 hr test period (5KX).

Figure A 83. Surface morphology of 5Cr-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 48 hr test period (1kX).
Figure A 84. Surface morphology of 5Cr-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 24 hr test period (5KX).

Figure A 85. Cross sectional view of 5Cr-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 48 hr test period (2.5KX).

Figure A 86. Line analysis of 5Cr-S coupon exposed TAN=1, TS=0.25, 650°F temperature and 48 hr test period (2.5KX).