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Effect of Time on High Temperature Naphthenic Acid and Sulfur Corrosion of Carbon Steel under Continuous Oil Flow Conditions

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ABSTRACT

The present research study investigated the effect of time duration on crude fractions corrosivity in high temperature experiments performed in a flow through apparatus with continuous replenishment. The experiments duration varied from 1 to 7 days and assessed the corrosivity as function of time for three different vacuum gas oils (VGO). Along with the metal loss evaluations, naphthenic (NAP) acids and sulfur species concentrations were monitored by potentiometric titrations and X-Ray Fluorescence spectrometry (XRF), respectively. Corrosion damage of the metal surfaces and the scales formed on them were analyzed by Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS). The study provided valuable information on NAP acids and sulfur species corrosivity and their chemical evolution during long time experiments by integrating metal losses with feed and product analyses.

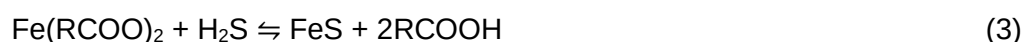
Key words: naphthenic acid corrosion, sulfur corrosion, crude fractions, time effect, high temperature

INTRODUCTION

Naphthenic (NAP) acid and sulfur corrosion is one of the major problems in refinery, especially with the increase in processing of opportunity crudes.¹⁻⁵ These low quality, discounted, heavy crude oils contain high concentrations of NAP acids and sulfur based corrosive species. It is reported that the presence of these species leads to detrimental effect on equipment integrity and process unit reliability.²⁻⁶ Thus, in refineries, special procedures and strategies (for instance, crude blending) have to be adopted when processing these crudes, in order to mitigate the corrosive effects associated with NAP acid and sulfur

components.⁷ Consequently, to be able to make such decisions for mitigation, understanding the corrosion reaction mechanism of NAP acid and sulfur corrosion is imperative.

NAP acids concentration in oil is measured by titration and it is commonly named as Total Acid Number (TAN) expressed as mg of KOH necessary to neutralize 1g of oil. NAP acids are highly corrosive when oil is distilled and reach their highest effect at a temperature range of 220 - 400°C when they attack the metal and form oil soluble iron naphthenates. In the same temperature range of NAP acids, the sulfur compounds in oil are also corrosive with their highest activity peak around 425°C. Sulfur compounds in oil thermally decompose at these high temperatures and form hydrogen sulfide that reacts with metal generating iron sulfide (FeS), a solid crystalline corrosion product that builds up on metal surfaces as multilayered scales. Both of these corrosive species interact synergistically at high temperature and their combined effects are commonly considered to be described by the three reactions mentioned below:^{1-3, 8}



NAP acids attack the metal as in reaction (1) and form oil soluble iron salts, while hydrogen sulfide interacts with the metal too (sulfidation) and generates the solid FeS - reaction (2). The two reactions (1) and (2) occur almost simultaneously and they are followed by reaction (3) when excess H₂S reacts with the iron naphthenates forming more FeS and regenerating the original NAP acids from their salts. Thus, the hydrogen sulfide by regenerating the NAP acids as in reaction (3) reintroduces them into the corrosive cycle of acids and S-compounds.

The corrosion mechanism due to NAP acid and sulfur compounds (NAP acid and sulfidic corrosion) has been intensively studied in the past.²⁻¹¹ Nevertheless, the mechanism associated with these species is still not clearly understood, although the effect of factors such as S/TAN ratio, temperature, molecular weight and structure of the corrosive species present in crude oil, were considered in the effort to understand the interaction between NAP acid and S-compounds.^{6, 9-13} Jin et al. reported that the scale formed in corrosion experiments with real crude fractions consists mainly of iron sulfide (FeS) but it also includes a thin layer of iron oxide.¹⁴ They also developed a mechanistic corrosion model of NAP acid and sulfur corrosion that includes the formation of the iron oxide layer for a fixed duration.

Most of the experimental data published in the literature and related to NAP acid corrosion were generated under static conditions in autoclaves or in glass equipment. This research work had as a main objective to study the NAP acids and sulfur corrosion at high temperature under continuous flow conditions, at different time intervals, and using real crude fractions. Three different vacuum gas oils (VGO) labeled as A1, B1 and C1 were evaluated using a special “flow through” apparatus at 343°C in experiments with durations of 24h to 168h (1 - 7 days). The TAN and total sulfur content of the three selected VGO are presented in Table 1. The metal samples and the scales formed on their surfaces in these experiments were analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).

Table 1: TAN and total S content (wt.%) of fractions selected for this study

VGO Fraction	TAN (mg KOH/g)	S (wt.%)
A1	8.30	0.75
B1	2.77	1.35
C1	1.51	1.92

EXPERIMENTAL PROCEDURE

Experimental Method

All experiments evaluating the corrosive effects of VGO for different time durations were performed in the Flow Through Mini-Autoclave (FTMA) which is a “flow through” apparatus that allows a constant refreshing of the corrosive species on specimens surface during the test. The very low oil flow rate in the FTMA and the specific design of this apparatus creates almost stagnant flow conditions at the specimen surface level. Thus, the FTMA testing conditions are similar to those of the static autoclave; however, the continuous oil flow in the FTMA reactor exposes the specimens to a constant concentration of corrosive species and prevents the accumulation of corrosion products. The effect of time duration on crude fractions corrosivity was assessed in the FTMA tests by measuring the samples corrosion rates, while periodically monitoring the evolution of TAN in every test. In addition, the total sulfur content and iron concentrations were determined periodically for one of the selected VGO. The structure, morphology, and the chemical composition of scales formed in every test on the samples were analyzed using the SEM/EDS.

Experimental Equipment

Figure 1 depicts a schematic representation of the FTMA “flow through” system used to test the carbon steel (CS) specimens under the experimental conditions mentioned in Table 2. The FTMA comprises of three feeding tanks, the reactor, two pumps - HPLC and gear pump, and a waste container where the used fluid is collected. The FTMA system also includes a three-way valve that is utilized for alternating the oil feeds if it is required by specific experimental procedures. In this study, only one vessel was used and filled with a VGO fraction that was pumped continuously from it to the FTMA reactor containing the CS specimens during testing. The temperature during experiments was controlled through a thermocouple inserted into the reactor up to the specimen location. A back-pressure valve was utilized to maintain pressure inside the reactor and to prevent the volatile species from vaporizing into the gaseous phase. Thus, the experiment is carried out only in liquid phase.

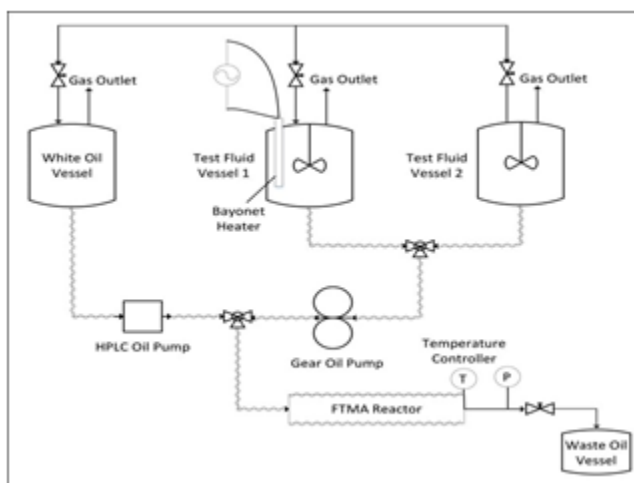


Figure 1: Schematic representation of the Flow Through Mini Autoclave (FTMA), a “flow through” apparatus.

In every experiment, initially, the polished steel specimens were placed inside the FTMA reactor which was then inserted into the apparatus flow system. The reactor with the specimens were heated gradually to 343°C with mineral oil (White Oil Vessel in Figure 1) being pumped through the reactor.

When the FTMA system reached the preset temperature of 343°C, the oil feed was switched from mineral oil to the experimental VGO fraction (Test Fluid Vessel 1 in Figure 1). The oil flow through the FTMA reactor was set to 1.5 cm³/min for the VGO long experiments. At the end of the VGO experimental time phase, the flow was switched back to mineral oil and the FTMA system was flushed to remove completely the VGO from the reactor and the feeding lines. Then the FTMA was turned off and allowed to cool. Each experiment was performed using four steel specimens: two were dedicated for weight loss measurements, and two for SEM and EDS analysis.

The specimens and the corrosion by-product (scales) formed on them during the experiments were analyzed using the scanning electron microscopy JEOL JSM-6390 for the scale surface characterization and scale structure morphology in cross-sections. The EDS detector connected with SEM was employed to ascertain the chemical composition of the scales formed on the specimens.

Iron (Fe) and sulfur (S) concentrations in oil samples were measured using the X-Ray Fluorescence (XRF). The XRF analyzer PetraMax (XOS) is a high definition X-ray fluorescence (HDXRF) instrument that measures the S and Fe concentrations in oil samples according to ASTM D 4294.¹⁵

The acidity of the crude fractions was monitored during the experiments by measuring the TAN on samples collected on different time intervals. The TAN measurements were performed according to ASTM D664 using the Aquamax (GR Scientific) TAN titrator.¹⁶

Table 2: Experimental conditions in the FTMA experiments.

Test Fluid	TAN (mg KOH/g oil)	Total Sulfur (wt.%)	T (°C)	Time (h)	Oil Flow Rate (cm ³ /min)	P (kPa)
Fraction A1	8.30	0.75	343	24, 48, 72, 168	1.5	791
Fraction B1	2.77	1.35	343	24, 48, 72, 168	1.5	791
Fraction C1	1.51	1.92	343	24, 48, 72, 168	1.5	791

Experimental Materials

The three VGO *i.e.* fractions A1, B1, and C1 were selected for this experimental work based on their performance in previous corrosion tests. The total sulfur (S) content (wt.%) and the TAN (mg KOH/g oil) of fractions A1, B1, and C1 are given in Table 2.

The specimens used in these FTMA experiments were made of UNS K03006 carbon steel (CS) and had a rectangular geometry with the specific dimensions; 16 mm X 15.2 mm X 0.6 mm with a central circular hole of 3.84 mm diameter. Table 3 presents the chemical composition of the CS UNS K03006 used to fabricate these specimens.

Prior to each experiment, the CS specimens were polished sequentially with 400 and 600 grit silicon carbide paper under isopropanol flush to prevent heating and oxidation of the specimens. After polishing, the specimens were rinsed with toluene and acetone, and dried under the flow of nitrogen gas. The geometrical dimensions of each specimen were measured with a caliper and recorded. The cleaned specimens were then weighed using an analytical balance and installed within the FTMA reactor. At the end of the experiment, the specimens were taken out of the reactor and processed for corresponding assessments - weight loss evaluation and SEM/EDS analysis. In weight loss evaluations, specimens were rinsed with toluene and acetone, and then the scale formed on their surfaces was removed mechanically by brushing them with a stiff plastic brush. The scale that survived on specimens after brushing was further removed chemically by immersing them into Clarke solution

(ASTM G 1-90) several times.¹⁷ After every immersion in Clarke solution, the specimens were dried under nitrogen flush and weighed on the analytical balance.

Table 3: Chemical composition (wt.%) of carbon steel specimen.

C	Si	P	Mn	S	Cr	Cu	Ni	Mo	V	Fe
0.18	0.41	0.11	0.8	0.06	0.02	0.08	0.04	0.02	0.03	Balance

Corrosion Rates Evaluation

The corrosivity of VGO in FTMA experiments was evaluated by measuring the metal losses of specimens used in these tests. Based on specimen metal losses, the corrosion rates were calculated with equation (4) using the difference between specimen weight before and after the experiment. All corrosion rates are expressed in mm/y.

$$CR = \frac{(IW - FW)}{\rho_{Fe} \cdot A_c \cdot t} \cdot 24 \cdot 365 \cdot 1000 \quad (4)$$

where,

CR - corrosion rate [mm/y],

IW - initial weight (before the experiment) [kg],

FW - final weight (after final “clarking”) [kg],

ρ_{Fe} - iron density [kg/m³],

A_c - coupon area exposed to VGO fraction [m²],

t - time of the experiment [h].

RESULTS AND DISCUSSION

Corrosion Rate Results

Corrosion rates of CS specimens used in these experiments provided a good information regarding the effect of testing duration on crudes corrosivity. Thus, the corrosion rates comparison in Figure 2 suggests that in general, for the three selected fractions their corrosivity decreased with time. However, in case of fractions A1 and B1 in short time testing, the 24h test interval did not influence their corrosivity and the corresponding corrosion rates were similar for the two considered time intervals *i.e.* 24h and 48h. Only when the test duration was increased to 72h and 168h respectively, there was a significant drop in corrosion rate values for the two fractions. In case of fraction C1 after a pronounced drop of corrosion rates on going from 24h to 48h test interval, their values remained the same in the 72h test and decreased further in the 168h test.

The corrosion rates measured in this set of experiments were also compared as a function of the crude fraction original TAN and total sulfur content. Comparison of corrosion rates with total sulfur as reference indicates that the higher was the total sulfur content in the crude fraction, the more corrosive it was regardless of the fraction TAN content or the experimental time duration. Hence, their corrosivity order was $CR_{A1} < CR_{B1} < CR_{C1}$.