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A COMPREHENSIVE STUDY ON NAPHTHENIC ACID CORROSION

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ABSTRACT

This study included stirred autoclave tests to broaden the understanding of the interaction between sulfide films and naphthenic acids, and Hot Oil Flow Loop (HOFL) experiments that provided information on the influence of flow on the corrosion process. A series of parametric tests were conducted in an ultra low sulfur, hydrotreated base oil with additions of high purity reagent grade naphthenic acid. Naphthenic acid corrosion was produced at TAN levels of 1.5 mg KOH/g and higher. The limiting TAN was dependent on magnitude of the mechanical forces produced by the flowing oil (i.e. higher limiting TAN values associated with lower flow velocities). The relative naphthenic acid corrosion resistance of 5Cr-0.5Mo (5Cr) and 9Cr-1Mo (9Cr) steels were only marginally different. The studies also showed that naphthenic acid corrosion could be successfully inhibited on two materials (5Cr and 9Cr steels) by the presence of moderate levels of H_2S. However, this phenomenon was limited by resistance of the material to velocity accelerated sulfidic corrosion at higher levels of H_2S and wall shear stress. Selective studies of the influence of other sulfur species on naphthenic acid corrosion were conducted. It was found that successful inhibition of naphthenic acid corrosion was only achieved when intermediate levels of H_2S were present in the off-gas either from direct H_2S loading or from thermal decomposition of the sulfur species.

Keywords: Naphthenic acid, petroleum, refining, TAN, Total Acid Number, hydrogen sulfide, inhibition, research, test

INTRODUCTION

Predicting crude oil corrosivity is of critical importance and a particularly difficult aspect of refinery operations. Corrosivity is one of many factors that are often incorporated into the purchase price for the refinery feed stock as well as a necessary input when assessing the serviceability of refinery process equipment. At the start of this program in the mid-1990's, there were obvious limitations in:

- the understanding of the interactions between corrosive species commonly found in refinery crude oil feedstocks and process streams,

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- the understanding of the interaction between chemical and mechanical effects in flowing high temperature oil systems, and
- the availability of and confidence in proven corrosivity prediction tools

Such knowledge is important when corrosive species are combined with high velocity flow encountered in certain refinery operations. A major joint industry program (JIP) involving over 20 companies was organized by InterCorr International, Inc. to address this subject. Whereas the originally proposed program concept was to utilize "synthetic" environments (i.e. high purity base oils, reagent grade acids and sulfur compounds), the emphasis of the program was shifted toward "real" environments based on sponsor input. The plan was changed to incorporate readily available "low" sulfur hydrocarbon fraction produced in a refinery to which selected dosages of naphthenic acids were to be added. It was further agreed that the naphthenic acids used in this study would be derived from crude oils and obtained from commercial suppliers. However, as the program progressed, this approach soon complicated the analysis of the data mainly due to interference related to impurities in the base oil and in the crude derived naphthenic acids. However, this effort did lead to the initiation of several focussed studies on naphthenic acid characterizations (boiling point, ring structures), differentiation of corrosivity of naphthenic acids, and protective behavior of sulfide films that may not have been pursued otherwise.

The final portion of the program focussed on using methods consistent with the originally proposed scope which utilized a very low sulfur hydrotreated base oil and reagent grade naphthenic acid to produce test environments which had ultra-low levels of sulfur impurities (<0.1 wt.%). This approach was successful in allowing differentiation in the corrosion behavior based on velocity, acid strength (TAN) and sulfur species for several commonly used materials including: 5Cr, 9Cr and 12Cr steels. This paper describes the results of selected studies of this program, which are of particular importance and relevance to refinery operations.

BACKGROUND - NAPHTHENIC ACID CORROSION

Naphthenic acids are present in many crude oils in varying amounts and provide a class of corrosion-inducing contaminants. Areas especially noted for producing crude oils containing elevated concentrations of naphthenic acid have historically included California, Venezuela, India, China, and Russia. More recently, these areas have also included some regions not historically noted for having high levels of naphthenic acid which include the North Sea, West Africa, Mexico and offshore Brazil.

At the start of this program, little quantitative information was known regarding, variations in molecular weight, boiling point and ring structure and their relationship to corrosivity in petroleum refining systems. As with most organic molecules, these variables can influence both their fractionation characteristics and chemical reactivity. Simplistically, the naphthenic acid content in oils is assessed in terms of total acid number (TAN) which is referred to in terms of milligrams of KOH needed to neutralize a gram of oil sample. Values of TAN in the range of 0.1 to 3.5 [TAN units used herein: mg KOH/g] are common but particularly severe situations have been found for particular hydrocarbon fractions that can have TAN values in excess of 10. The complexity of the situation is evident considering that organic acid components in crude oils can vary considerably with their source. Furthermore, these acidic components can include both

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naphthenic acids (those typically referred to as having two or more cyclopentane rings) and lower molecular weight straight chain organic acids further complicating the picture.

Naphthenic acid corrosion is differentiated from sulfidic corrosion by the corrosion mechanism and the morphology of the attack. Sulfidic corrosion is usually described as being a general mass loss or wastage of the exposed surface with the formation of a sulfide corrosion scale. By comparison, naphthenic acid corrosion is typically characterized as having more localized attack particularly at areas of high velocity and, in some cases, where condensation of concentrated acid vapors can occur in crude distillation units. The attack is oftentimes described as lacking surface corrosion products thereby exposing fresh metal. Consequently, damage is in the form of unexpectedly high corrosion rates and localized attack on alloys that would normally be expected to resist sulfidic corrosion (particularly steels with more than 9% Cr). In some cases, even very highly alloyed materials (i.e., 12Cr, 316SS and 317SS, and in some rare cases even 6Mo stainless alloys) have been reported to exhibit sensitivity to corrosion.

As a rule-of-thumb, crude oils with a TAN greater than 0.3 to 0.5 and refined crude oil fractions with a TAN higher than 1.5 have been generally considered to be potentially corrosive due to the presence of naphthenic acid. [1-4] The difference in these two values comes from the concentration of naphthenic acid in certain hydrocarbon fractions during refining. One problem is that such simple rules do not always indicate which hydrocarbon fractions and in what locations in the process the concentration of the corrosive acids will occur. Areas of work in this program, but not reported herein, were the characterization and differentiation of naphthenic acids based on

- their boiling point range
- TAN versus true boiling point,
- Sulfur specification, and
- Chemical structure using Fast Atom Bombardment - Mass Spectroscopy (FAB-MS)

These techniques showed both the specific types of acids present, and how these acids may concentrate during crude oil distillation. This type of information can potentially result in a better understanding of naphthenic acid corrosivity and help locate potential problem areas in the refinery.

A major controversy in the prediction and control of naphthenic acid corrosion mentioned at the start of this program was that, under certain conditions, the presence of sulfur-containing compounds is believed to inhibit naphthenic acid corrosion. This understanding has come primarily from experiential information obtained from:

- refining high TAN crudes that are also high in sulfur species, and
- blending of high TAN crudes with low TAN crudes of varying sulfur content.

However, the particular forms of sulfur that can participate in this process and the threshold amounts have not been defined. The mechanism by which this effect can be understood may be the one that unifies the understanding of crude oil corrosivity. It involves a realization that both sulfur and acid species are present to a varying degree in all crude oils and fractions. In certain limited amounts, sulfur compounds may provide a limited degree of protection from corrosion with the formation of pseudo-passivity sulfide films on the metal surfaces. However, increases in

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either reactive sulfur species or naphthenic acids to levels beyond their threshold limits for various alloys may accelerate corrosion. The present study has looked into these questions and provides some valuable and practical insights.

There is also growing evidence to indicate that both sulfidic and naphthenic acid corrosion can be accelerated by velocity of the flowing process environment or by local turbulence. The wall shear stress produced by the flowing media contributes an added mechanical means to remove the normally protective sulfide films. The wall shear stress is proportional to velocity but also takes into account the physical properties of the flowing media. These properties include density and viscosity of medium (or media) which is, in turn, affected by the degree of vaporization and temperature. This program placed a strong emphasis on quantifying the mechanical forces produced by the flow in terms of wall shear stress, which can act on the surface of operating equipment.

INFLUENCE OF NAPHTHENIC ACID ON SULFIDE FILMS

A series of tests were conducted for exposure durations of 1 to 30 days. All tests were performed at 345 C (650 F). These tests included the exposures with the base oil without addition of H_2S or naphthenic acid. The data from these tests were compared to operating experience with equipment in service in the refinery processing the Escravos-Cabina (E-C) blend. Tests with H_2S were also conduced and the corrosion versus exposure time evaluated to assess the rate of sulfide film formation and its influence on corrosion rates. Stirred autoclave tests were conducted with additions of low, medium and high boiling point naphthenic acids. However, a special study was conducted using autoclave tests whereby coupons were pre-sulfided in a high H_2S, low TAN environment [i.e. TAN 0.7 and H_2S loading of (0.45 psia)]. Corrosion rates on pre-sulfided corrosion coupons were compared with those on bare coupons. Additionally, pre-sulfided coupons were re-exposed to an environment having high TAN and low H_2S. (i.e. TAN 7 and no H_2S loading). Sulfide film thickness was measured using a metallographic technique on coupons both before and after exposure to this high TAN environment.

Coupons of 0Cr, 5Cr, 12Cr and 18Cr-8Ni steels were treated by pre-exposure to a high H_2S / oil environment with no added naphthenic acid for 30 days. This exposure was intended to produce a sulfide corrosion scale on the surface of the coupons. Control specimens were used to determine the sulfide film thickness and to establish the starting coupon weights for the second part of the test sequence involving exposure to the high TAN environment without H_2S additions. The pre-sulfided 12Cr and 18Cr-8Ni coupons exhibited much higher mass loss corrosion rates than did bare coupons of the same materials in the high TAN environment. The coupons made from 0Cr and 5 Cr steels also showed this behavior, but to a lesser degree, and with greater scatter, than with the higher alloy materials. This behavior suggested that the sulfide film affected the corrosion behavior of the various steels in high TAN environment. These results prompted a more detailed focus study on the behavior of sulfide films in high TAN environments.

Metallographic measurements of sulfide film thickness before and after exposure to a high TAN environment revealed that naphthenic acid had the ability to chemically dissolve sulfide films on the metal surface for all alloys examined. See Table 1.

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TABLE 1
Sulfide Film Thickness Measurements Before and After Exposure to High TAN/Low H2S Environment (0.001 in. = 0.025 mm)

Coupon Material	*Pre-sulfided Film Thickness (inches)*	*Film Thickness after High TAN/Low H_2S Exposure (inches/ percent change)*
0Cr steel (A516-70)	0.0033	0.0017 / -48.5
5Cr steel	0.0054	0.0021 / -61.1
12Cr steel	0.0027	0.0011 / -59.3
18Cr steel	0.0035	0.0009 / -74.3

The sulfide film thickness was measured for 0Cr, 5Cr, 12Cr and 18Cr-8Ni steel coupons after an initial exposure in a highly sulfidizing environment and again after subsequent exposure to an environment with high TAN and low sulfur. The film thicknesses were measured by metallographic sectioning of corrosion coupons. Thickness measurements were made on four different surfaces for each coupon, then averaged for each material.

The reduction in film thickness resulting from the high TAN exposure after 3 days was in the range of 58 to 75 percent with increasing percentage reductions for the higher Cr alloys. These data were consistent with the trends observed in the corrosion experiments on pre-sulfided and bare coupons also examined in this study. This series of tests identified conclusively that naphthenic acids could chemical dissolve sulfide films on metal surfaces. It also provided evidence of one potential mechanism of naphthenic acid corrosion, whereby it can chemically dissolve normally protective sulfide films on the surface of metals thus allowing naphthenic acid to attack the material substrate. These results also indicated that little or no velocity or agitation was needed to obtain this effect since it was basically a chemical dissolution process. However, speculation was that this corrosion mechanism could also be worsened by coupling this chemical attack mechanism with mechanical effects in flowing systems.

ENGINEERING DATA DEVELOPMENT WITH 5 AND 9 CR STEELS

A series of hot oil flow loop (HOFL) tests was initiated (test system shown in Figure 1. It was based on testing in synthetic environments composed of Tufflo 1200 with additions of reagent grade Kodak / Fluka naphthenic acid. Both of these constituents were characterized as having ultra-low levels of sulfur species present in them. These tests had the following boundary conditions:

- Base Oil – Tufflo 1200
- Naphthenic Acid – Kodak / Fluka
- TAN – 0 to 3.5 mg KOH/100 gm
- H_2S loadings – 0, 0.2 and 0.45 psia
- Temperature – 343 C (650 F)
- Velocity – 16 to 97 mps (50 to 350 fps)
- Target coupons – 5Cr and9Cr steels

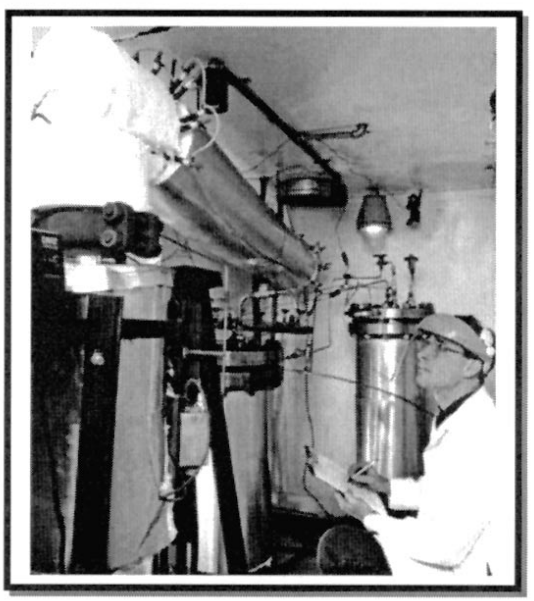

Figure 1 – Photo of Hot Oil Test Loop.

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The test plan was to obtain corrosion data on these materials as a function of flow velocity and TAN in an effort to define the region where naphthenic acid corrosion did and did not occur. Initially, these tests did not contain any H_2S loading. This approach allowed the corrosion behavior of 5Cr and 9Cr steels to be observed in a system without the complicating influence of sulfur species. Once the baseline H_2S-free tests were complete, additional HOFL tests were performed with a variety of H_2S loadings at variable H_2S partial pressures. The results of the HOFL tests conducted in the ultra-low sulfur base oil and naphthenic acid showed consistent data trends with well-defined thresholds for the onset of impingement attack relative to TAN levels and flow velocity. See Figures 2 and 3.

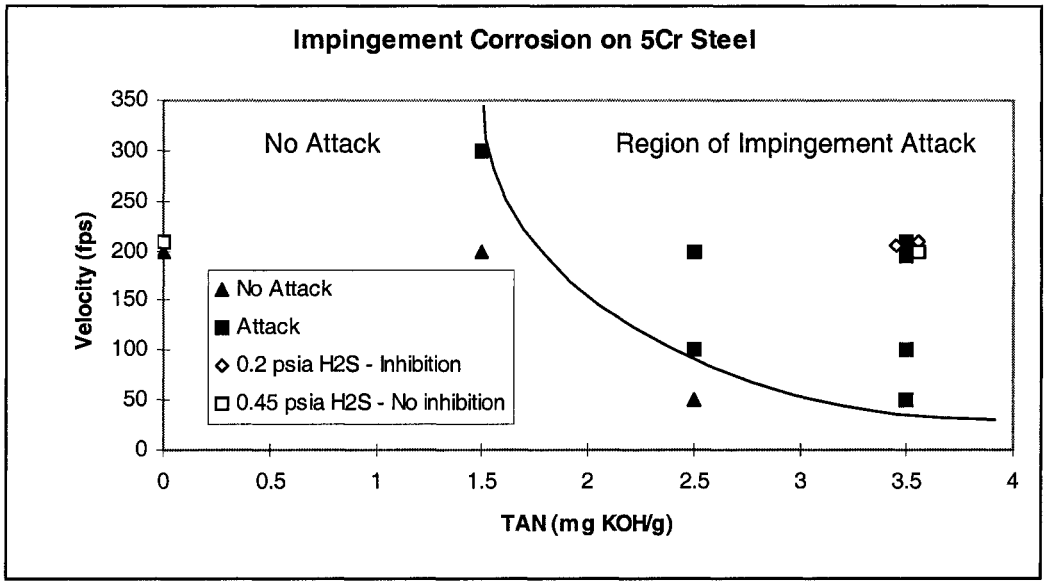

Figure 2 - Impingement attack for 5Cr in HOFL tests at 650 F
as a function of velocity and TAN with influence of H_2S. Note:100 fps = 30.5 mps

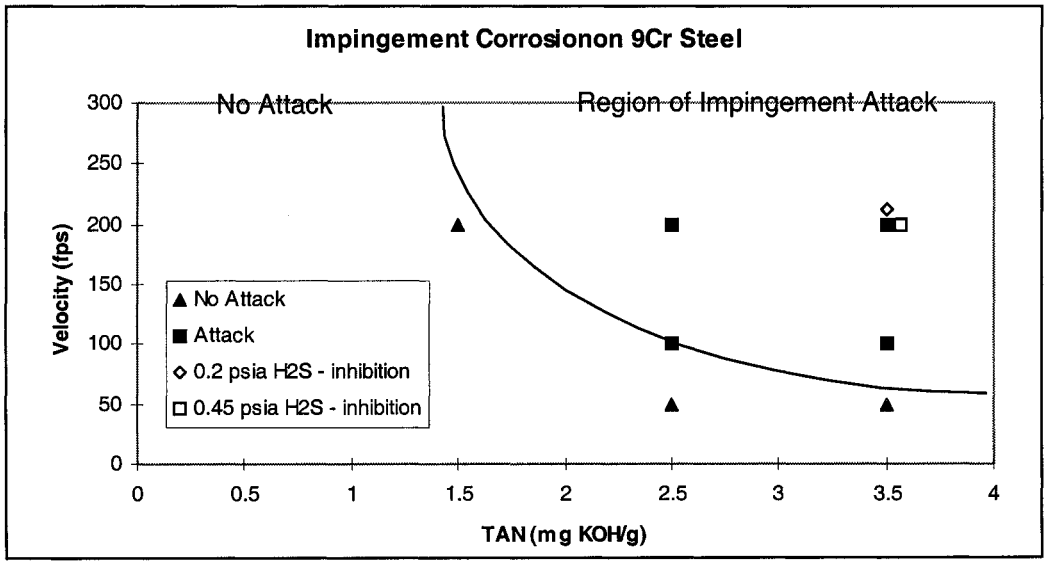

Figure 3 - Impingement attack for 9Cr in HOFL tests at 650 F
as a function of velocity and TAN with influence of H_2S. Note:100 fps = 30.5 mps

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The results of the HOFL tests for 5Cr and 9Cr steels are shown in the indicated figures. Both materials showed a similar trend of increasing impingement attack rate with increasing velocity and TAN. Two well-defined regions (i.e. impingement attack and no impingement attack) were identified defining the naphthenic acid corrosion behavior of these materials. Below specific limits of flow velocity and TAN no naphthenic acid impingement attack was observed.

Comparison of 5 and 9 Cr Steels. The naphthenic acid corrosion behavior of the 5Cr steel and that of the 9Cr steel were similar in nature. Both exhibited the onset of impingement attack at about a TAN value of 1.5 or higher which depended on the flow velocity in the HOFL apparatus. Localized impingement attack was observed to occur at TAN levels of about 1.5 and greater. For high velocities [64 mps (>200 fps)], the onset of impingement attack occurred at TAN 1.5. However, as the TAN levels in the HOFL tests were increased, the threshold flow velocity for attack was reduced. At TAN 3.5, the lowest velocity employed in these tests (50 fps) resulted in impingement attack. The behavior of the 9Cr steel in the HOFL tests was very similar to that noted for the 5Cr steel. Only a slight increase in resistance to impingement attack was observed at TAN 3.5 and a flow velocity of 16 mps (50 fps) was noted. Therefore, increasing the chromium content of the steel from 5 to 9 wt. percent did not appear to have benefits in terms of resistance to naphthenic acid corrosion.

Lower TAN Limits for Naphthenic Acid Corrosion. The lower limit for naphthenic acid corrosion in the HOFL tests was at a TAN value of about 1.5. This finding was in close agreement with refinery experience for the onset of naphthenic acid corrosion of steels with intermediate alloy content. In refinery vacuum distillation, general guidelines are that naphthenic acid corrosion is a concern when the TAN of the hydrocarbon fraction is 1.5 or greater. These HOFL tests provided good correlation with plant experience. However, the data also suggest that this threshold may be variable depending on the flow conditions. It is possible that the results of HOFL tests conducted at TAN 1.5 at velocities greater than 200 fps (e.g. higher wall shear stress) could result in impingement attack of 5Cr and 9Cr steels.

Figure 4 shows the relationship between flow rate and wall shear stress for the HOFL apparatus using the Tufflo 1200 base oil. It indicates that in the range of 200 to 300 fps, the maximum wall shear stress developed by the HOFL was in the range of 600 to 1200 Pa. To ascertain the relationship of this condition to refinery conditions, flow-modeling analyses would have to be conducted on the specific flow conditions present in the plant. These will vary with the geometry of the systems, physical properties of the oil and percentages of the phases present, plant throughput, and flow regime. ***It should be cautioned that direct use of the results presented in Figures 2 and 3 on the basis of linear flow velocity will not usually provide accurate prediction of corrosion behavior.*** Wall shear stress is usually a more relevant parameter when attempting to predict the influence of fluid flow (particularly multiphase flow) on the corrosion behavior.

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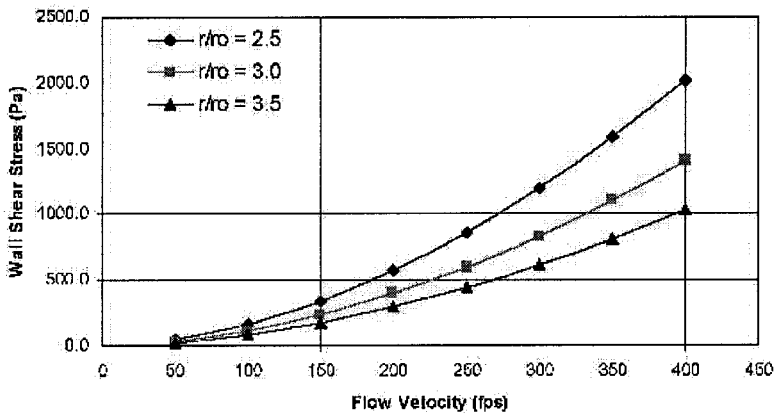

Figure 4 –Wall shear stress versus HOFL flow velocity with Tufflo 1200 oil. [5]
Note:100 fps = 30.5 mps

Influence of H_2S. Additions of H_2S to a test condition that produced severe naphthenic acid impingement attack (TAN 3.5 and 200 fps) significantly influenced the corrosion behavior of both 5Cr and 9Cr steels. Low levels of H_2S loading in the system were found to "inhibit" impingement attack. However, higher levels of H_2S loading provided either inhibition or no inhibition depending on the resistance of the material to sulfidic corrosion. See Figures 2 and 3. For 5Cr steel, addition of 0.2 psia H_2S to the test environment resulted in a complete inhibition of impingement attack on this material. However, when a higher level of H_2S was imposed (0.45 psia H_2S), localized, flow-induced corrosion was initiated. It was suspected that this onset of localized impingement attack at the higher H_2S loading was related to velocity accelerated sulfidic corrosion. This phenomenon could occur from the combined influence of the mechanical forces of the fluid flow with the normal sulfidic corrosion process.

Tests were performed to evaluate the abovementioned theory at a condition that did not produce naphthenic acid corrosion. This condition consisted of the Tufflo 1200 oil with no naphthenic acid addition and a HOFL flow velocity of 200 fps. Tests were conducted on 5Cr steel target coupons both with and without a high H_2S loading (0.45 psia H_2S). The test without H_2S (and with no naphthenic acid addition) did not produce impingement attack. However, at this same condition with an H_2S loading of 0.45 psia, localized impingement corrosion was observed. Due to the lack of naphthenic acid in these test environments, the only chemical species with substantial potential for corrosivity was the sulfur originating from the H_2S loading. Therefore, it appears that flow induced wall shear stress can separately influence the corrosion by naphthenic acid and by sulfur species as well.

For comparison, another series of tests with variable H_2S loading was conducted, this time with 9Cr steel target coupons at TAN 3.5 and 200 fps. In the case without H_2S, extensive naphthenic acid corrosion was observed. This was similar to that observed for the 5Cr steel. However, when tests were conducted with 0.2 psia H_2S and 0.45 psia H_2S, no impingement attack was observed to occur. In these cases, both the lower and higher levels of H_2S were successful in inhibiting naphthenic acid impingement attack on this material. The differences in the corrosion behavior between the 5Cr and 9Cr steel target coupons in the environment with 0.45 psia H_2S is likely the result of the higher sulfidic corrosion resistance of the 9Cr steel. This material maintained its corrosion resistance even under the worse case examined in this study containing both high

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levels of naphthenic acid and H_2S at 200 fps in the HOFL test. While, the actual corrosion behavior of these materials in service may vary, the behavior of the 9Cr steel could be expected to be better than that of the 5Cr steel with respect to naphthenic acid corrosion resistance. This would be on the basis that it might have a broader range of protection from reactive sulfur species such as H_2S in environments containing naphthenic acid.

Corrosion Mechanisms. Visual examination of 5Cr and 9Cr steel target specimens indicated that the mechanism of naphthenic acid corrosion was related to loss of the protective sulfide film on the metal surface. This loss of protection could arise from either chemical dissolution or mechanical action of the flowing fluid, or some combination of these phenomena. See Figures 5 through 7.

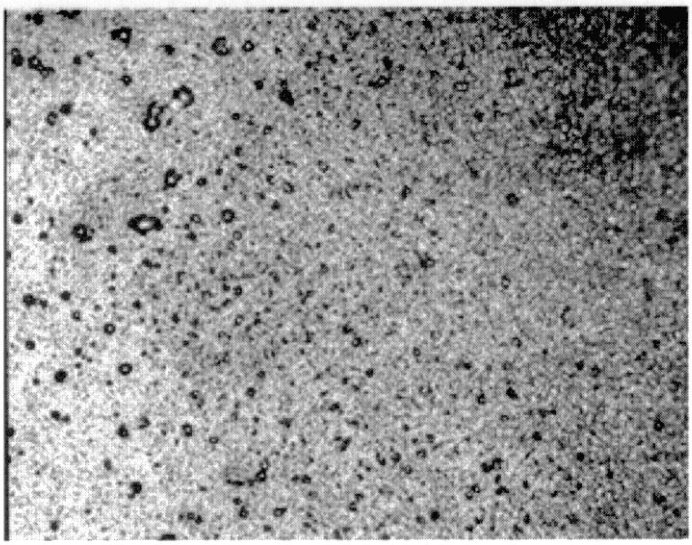

Figure 5 - Local chemical dissolution of sulfide film by high TAN environment.

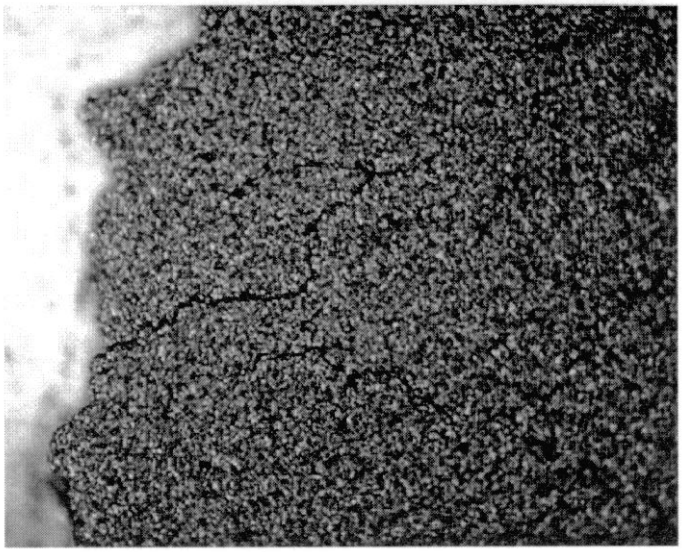

Figure 6 - Mechanical damage of sulfidic film by high velocity jet impingement.

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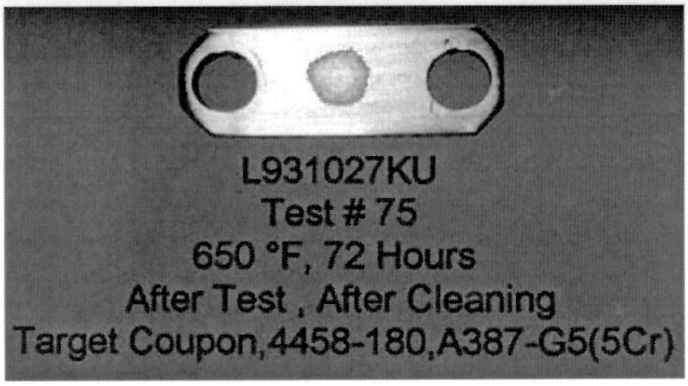

Figure 7a - Localized impingement attack produced by combination of mechanical and chemical attack of sulfide film: target coupon.

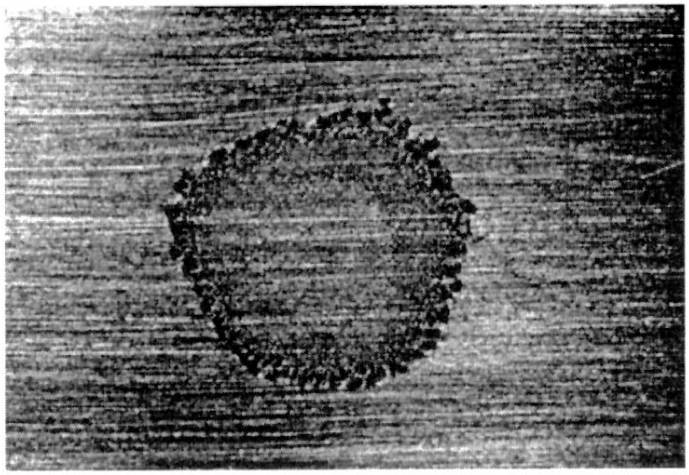

Figure 7b - Localized impingement attack produced by combination of mechanical and chemical attack of sulfide film: target coupon at higher magnification.

As discussed previously, the sulfide filming study revealed that naphthenic acids could chemically dissolve iron sulfide films on the surface of all steels ranging in chromium content from 0 to 18 percent. These losses were substantial and the percentage loss of scale weight increased with increasing chromium content of the material. The data in that study were generated in autoclave tests involving low velocity environments (<3 fps) where mechanical, flow-induced forces were minimal. Therefore, chemical dissolution of the iron sulfide films was the likely cause of this attack.

Visual examination of the target coupons from this portion of the program also showed evidence of chemical dissolution of the sulfide film. At high TAN and lower flow velocity, there was visual evidence of localized pitting and perforation of the sulfide film around the edges of the impingement attack. The local loss of this protective sulfide film resulted in regions of the substrate material being exposed to the naphthenic acid further resulting in initiation of impingement attack. By comparison, tests conducted at lower TAN and higher flow rates, showed visual evidence of mechanical fracture of the sulfide films on the surface of the material. The cracks produced in the sulfide film by the flowing media produced spalling of the sulfide film that resulted in areas of the substrate material being exposed to the corrosive media. These locations were where the impingement attack initiated.

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INFLUENCE OF H_2S AND SULFUR SPECIES ON NAPHTHENIC ACID CORROSION

The final experimental effort of the program involved an examination of the effect of H_2S and selected sulfur species on the corrosivity of hot oil under flowing conditions on 9Cr steel. A series of HOFL tests was chosen that investigated the following:

- One higher H_2S loading (from those used in Section 10.1) and its effect on impingement corrosion in 9Cr steel
- Two liquid sulfur species that were separately added to the Tufflo 1200 oil instead of H_2S on this material.

The results of these tests were compared with the results from those involving either no H_2S or a lower H_2S loading to better define the role of sulfur species on inhibition of naphthenic acid corrosion. These tests had the following boundary conditions:

- Base Oil – Tufflo 1200
- Naphthenic Acid – Kodak / Fluka
- TAN – 3.5
- Sulfur loadings – (See below)
- Temperature – 343 C (650 F)
- Velocity – 65 mps (200 fps)
- Target coupons - 9Cr steel

The test plan involved obtaining corrosion data on 9Cr steel target specimens at a condition that has been shown to provide substantial susceptibility to naphthenic acid impingement attack. The baseline test for this study were already run and reported in this section. They consisted of tests initially conducted at TAN 3.5 and 65 mps (200 fps) with no H_2S, then again at the same condition, but this time with 0.2 and 0.45 psia H_2S loaded to the reservoir of the HOFL. As described previously in this report, successful inhibition of naphthenic acid corrosion of 9Cr steel target coupons was obtained with both levels of H_2S loading.

The two sulfur species chosen for the study were selected on the basis of their boiling point that was used as a measure of their thermal stability and potential to form H_2S at the test temperature. Availability and cost were secondary issues that were also considered since we were approaching the end of the program. The details on the two sulfur compounds used in this study are described below:

- 1,9 – Nonanedithiol (NET) – 95%; $HS(CH_2)_9SH$; formula weight - 192.39; boiling point – 284 C (543 F). 200 ppm and 1000 ppm.
- Dibenzothiophene (DBT) – 99^+%; $C_{12}H_8S$; formula weight - 184.18; boiling point – 333 C (631 F). 20 ppm and 200 ppm.

At the test temperature of 343 C (650 F), it was expected that the compound with the lower boiling point (NET) would be likely to produce more H_2S than would the more thermally stable DBT. It was also suspected that, due to the high reactivity of H_2S, there might be a possible trend with H_2S in the off-gas that would dominate naphthenic corrosion and its inhibition in these environments. However, a different trend was also likely to be observed whereby the corrosivity and inhibition does not follow the H_2S level in the off-gas. In this event, a more complex situation could be present where direct reactions between the metal and sulfur species in the liquid phase enter significantly in the corrosion process.

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The data from the 9Cr target coupons in the tests involving various H_2S loadings are shown in Figure 2. They indicate that impingement attack was produced in the test where no H_2S was added, and significant reductions in the attack rate with additions of 0.2 and 0.45 psia H_2S to the test environment. After the conclusion of these tests, another test was conducted at a still higher H_2S loading in an attempt to determine the limit to the range of conditions where H_2S offers protection from naphthenic acid corrosion. With a still higher H_2S partial pressure addition (1.8 psia), the impingement attack rate on 9Cr steel increased dramatically to levels in excess of those that involved no H_2S loading..

Velocity Accelerated Attack. The impingement attack resulting from naphthenic acid corrosion was visually distinctive from that produced by sulfidic attack. The area of impingement produced by naphthenic acid attack was free of sulfide corrosion products. The area of velocity accelerated sulfidic corrosion contained a thin, dull gray surface film. Visual observations made in these tests indicated that the corrosion in the test with only naphthenic acid addition (without H_2S) involved both local dissolution and/or mechanical damage of the sulfide film in the area of impingement. This left the corroded area under the impingement nozzle essentially free of corrosion products. The two tests with intermediate levels of H_2S revealed dynamic film formation characterized by the presence of protective sulfide films. These films were characterized as consisting of local sheets of thin sulfide scale that appeared to interfere with the normal naphthenic acid corrosion process thereby producing an inhibitive effect on impingement (see Figures 8a and b). Finally, at the highest level of H_2S loading, the impingement attack reappeared, but it was differentiated from that in the test with no H_2S addition by having a thin gray film in the attack area. This latter type of corrosion appeared to be a formed by velocity accelerated sulfidic attack as described previously. It involved removal of the protective sulfide film on the coupon surface in the impingement zone and reaction of the bare material in this location with the environment containing a high H_2S concentration. This produced an impingement zone with dull gray coloration.

Figure 8a – Condition of 9Cr steel target specimen exposed to naphthenic corrosion conditions with intentional H_2S loading (before cleaning).

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Figure 8b – Same specimen shown in Figure 8a (after cleaning). No impingement attack – only slight staining at impingement site.

Effect of Sulfur Species. The combined results of the HOFL tests involving H_2S loadings and those from tests with liquid sulfur species (NET or DBT) showed consistent results. The tests where only a limited amount of H_2S was involved in the test (either from H_2S loading or from the liquid sulfur species added), impingement attack was observed. However, in the tests where intermediate levels of H_2S were involved, inhibition of impingement attack was observed. For the tests where a substantial amount of H_2S was involved, impingement attack reappeared. See Figure 9.

The data from both the initial tests with H_2S loading and those involving additions of DBT and NET are plotted versus the amount of H_2S in the off-gas at the end of the test. It can be seen that when all of the tests are taken into account, they show the inhibitive effect on naphthenic acid corrosion described previously for intermediate H_2S levels. It also shows the influence of very high levels of H_2S in the breakdown of this protection and the initiation of velocity accelerated sulfidic attack.

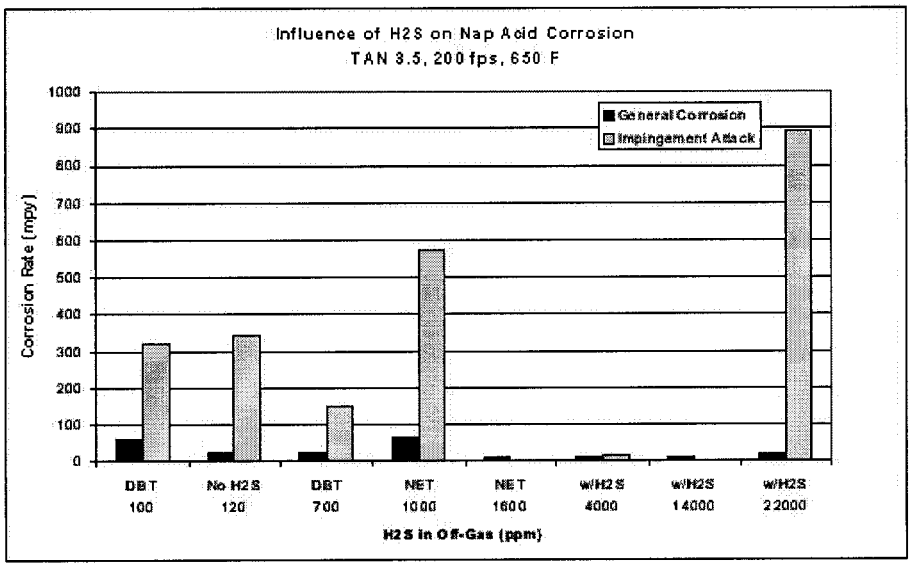

Figure 9 - General and impingement corrosion rates on 9Cr steel target specimens in tests with and without H_2S, DBT and NET. Note:100 fps = 30.5 mps

The influence of sulfur species on naphthenic acid corrosion appears related to their ability to decompose into H_2S at the exposure temperature. HOFL tests conducted with intermediate levels of H_2S from direct loading of H_2S gas resulted in inhibition of impingement attack in the HOFL tests. The range of H_2S off gas concentrations that produced this inhibition in these tests was 1,600 to 14,000 ppm (0.02 to 0.2 psia). The tests performed with additions of DBT did not

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produce high levels of H_2S in the off-gas [100 to 700 ppm (0.0015 to 0.01 psia)]. This was likely related to its relatively high boiling point relative to the test temperature. Consequently, high impingement attack rates (about 150 to 320 mpy) were observed in these tests. The tests conducted with addition of NET (with a lower boiling point than DBT) showed a transition from high attack rate at an H_2S level of 1,000 ppm (0.01 psia) in the off-gas to very low corrosion rate at an H_2S off-gas level of 1,600 ppm (0.02 psia).

These data suggest that sulfur species in the liquid phase that do not convert to reasonable levels of H_2S may not directly contribute to the inhibition of naphthenic acid corrosion. H_2S concentration in the off-gas are shown as a function of test duration for two tests involving addition of DBT and NET in Figure 9. In both tests, total sulfur levels were similar and nearly unchanged as a function of time. The major difference in the composition of the two test environments was in the concentration of H_2S in the off-gas. The concentration of off-gas H_2S decreased during the test with NET from about 6,000 to 1,000 ppm. By comparison, the test with DBT had a significantly lower H_2S off-gas concentration decreasing from about 1,000 to 100 ppm during the test duration. Hence, the availability of H_2S gas was noticeably lower in the test containing the DBT than with the lower boiling point and more unstable NET.

The data presented for 9Cr steel in the sulfur study combined with the tests with and without intentional H_2S loadings show three regimes of oil corrosivity:

1. Naphthenic acid corrosion where the availability to H_2S is limited.
2. Reduction (or inhibition) of naphthenic acid corrosion because of the presence of moderate levels of H_2S either evolved from the sulfur species in the oil upon heating or by direct loading of H_2S.
3. Acceleration of corrosion at high H_2S levels producing velocity accelerated sulfidic corrosion.

The data from this study also indicate that there is a continuum between naphthenic acid corrosion and sulfidic corrosion in high temperature flowing oil systems. The data from this program indicate that these two corrosion phenomena are linked by the ability to the material to form a protective sulfide film that can resist naphthenic acid attack. However, if the concentration of the reactive sulfur species is too high, then sulfidic corrosion can occur. These is also some suggestion that the susceptibility to velocity accelerated sulfidic corrosion may be enhanced by the presence of the naphthenic acid in the system. Whereas the data in this study are somewhat limited, they indicate definitive proof that there is a link between naphthenic acid and sulfidic corrosion. They also indicate that the resultant behavior at a particular temperature is produced by the availability and interplay of naphthenic acids and sulfur species combined with mechanical forces created by the flowing medium.

CONCLUSIONS

Based on the results described herein, the following conclusions were made:

1. Metallographic measurements of sulfide film thickness before and after exposure to a high TAN environment revealed that naphthenic acid has the ability to chemically dissolve sulfide films on the metal surface for all alloys examined thus leading to increasing corrosive attack.
2. The results of the HOFL tests conducted in the ultra-low sulfur base oil (Tufflo 1200) and reagent grade naphthenic acid (Fluke / Kodak) showed consistent data trends with well-defined thresholds (velocity vs. TAN) for the onset of impingement attack.

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3. The naphthenic acid corrosion behavior of the 5Cr steel and that of the 9Cr steel were similar in nature with respect to TAN and flow velocity limits. Both exhibited the onset of impingement attack at about a TAN value of 1.5 or higher, depending on the flow velocity in the HOFL apparatus. Results for 12Cr stainless steel indicated that this material was substantially more resistant to naphthenic acid impingement attack than either 5Cr or 9 Cr steels.
4. The lower limit for naphthenic acid corrosion of 5Cr and 9Cr steel in the HOFL tests was observed at about TAN 1.5, which was in close agreement with refinery experience for the onset of naphthenic acid corrosion of steels with intermediate alloy content.
5. Additions of H_2S to a test condition that produced severe naphthenic acid impingement attack (TAN 3.5 and 200 fps) significantly influenced the corrosion behavior of both 5Cr and 9Cr steels. Low levels of H_2S loading in the system were found to "inhibit" impingement attack for both materials. However, higher levels of H_2S loading provided inhibition of naphthenic acid corrosion for 9Cr steel but accelerated corrosion on 5Cr steel.
6. Visual examination of target specimens indicated that the mechanism of naphthenic acid corrosion was related to loss of the protective sulfide film on the metal surface. This loss of protection could arise from either (a) chemical dissolution by naphthenic acid or (b) mechanical action of the flowing fluid, or some combination of these phenomena.
7. The data from the tests with and without H_2S loading indicated that the corrosivity of the hot oil varied as a function of the H_2S off-gas in the HOFL. Local impingement attack rates were greatest under conditions without H_2S loading (i.e. naphthenic acid corrosion) and where the H_2S loading exceeded the resistance of the material for velocity accelerated sulfidic corrosion
8. The combined results of the HOFL tests involving H_2S loading and those from tests with liquid sulfur species (NET or DBT) showed consistent results. Impingement attack was observed in tests when little or no H_2S gas was evolved during the test. When intermediate levels of H_2S were evolved, inhibition of impingement attack was observed. For the tests where a substantial amount of H_2S was involved, impingement attack reappeared.
9. These results showed that the influence of sulfur species on naphthenic acid corrosion was related to their ability to decompose into H_2S at the exposure temperature combined with the resistance of the metal to sulfidic corrosion.

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