

Effect of sulphur and naphthenic acids on the corrosion of 9%Cr-1%Mo steels

Roberto Riva^{a*}, Giovanna Gabetta^a, Marino Tolomio^b

^a*Enitecnologie, via Maritano 26, 20097 San Donato Milanese, Italy*

^b*Venezia Tecnologie, via delle industrie 39, 30175 Porto Marghera, Italy*

**Corresponding author: e-mail rriva@enitecnologie.eni.it, fax +39 0252036347*

ABSTRACT

Refiners are interested in opportunity crude oils because they are cheap. They are cheap because they contain naphthenic acids and sulphur, which are potentially corrosive. Laboratory tests were carried out to investigate the interaction between sulphur and naphthenic acids, which gives rise to subtle changes in their corrosiveness depending on their relative concentrations. Corrosion tests of 9% Cr 1% Mo steel were carried out in a sealed autoclave. Two oils containing greatly different amounts of sulphur were used. The concentration of naphthenic acids, which is low in both oils, was increased by adding a mixture of synthetic acids. At a fixed concentration of naphthenic acids, there is a big difference in the appearance of the metal specimens after tests with the two oils. The high sulphur oil leads to the formation of thick black scales of sulphides, pointing to sulphidic corrosion, while the low sulphur oil leaves the surface of the metal smooth and free of damage, pointing to naphthenic acid corrosion. The difference in the weight of corrosion products that form on the metal surface and the sharp contrast in the behaviour of the corrosion rate versus concentration of the acids supports the above conclusions. The experimental results are therefore in agreement with the rough model that predicts the onset of sulphidic corrosion as the concentration of sulphur increases. On the other hand, the concentrations of naphthenic acids that were required to start naphthenic acid corrosion were far higher than those experienced in refinery plants. The experimental equipment used in these tests probably needs to be modified if the conditions set up in laboratory tests are to be made more similar to those of refinery plants.

Keywords : naphthenic acids, sulphur, interaction, laboratory tests.

INTRODUCTION

The distillation equipment of refineries can be severely affected by high-temperature crude oil corrosion. This tendency is compounded by the current spread of opportunity crude oils, which are cheap for the very reason that they are potentially corrosive. In general, the corrosiveness of a certain crude oil depends on its content of sulphur and naphthenic acids, both of which can be determined by chemical analysis. The corrosiveness of the oil is also affected by the type of sulphur containing compounds that are present. In fact, their tendency to decompose producing H₂S plays an important role in the corrosion process. For this reason H₂S evolution is often measured in addition to the total acid number (TAN) and the content of sulphur. Unfortunately, chemical analysis alone has so far proved insufficient to predict the corrosiveness of a certain crude oil. There is, in fact, a subtle interaction between sulphur and naphthenic acids, of which refiners have been aware for a long time and

which they have described in a simple model. This model can be summarized in a few statements. At a fixed concentration of naphthenic acids one expects naphthenic acid corrosion to take place, if the concentration of sulphur is low. At intermediate concentrations of sulphur naphthenic acid corrosion appears to be inhibited, while sulphidic corrosion sets in at higher sulphur concentrations. The understanding of this kind of interaction has led to the practice of blending high-TAN crude oils with lower-TAN oils, perhaps containing a fair concentration of sulphur in an attempt to inhibit naphthenic acid corrosion [1, 2]. The interaction of sulphur and naphthenic acids has also been investigated thoroughly in a series of experiments with a jet impingement flow loop [3].

However, the prediction of the corrosiveness of opportunity crude oils relies largely on past experience and a lot of effort is going into developing laboratory tests to assess their corrosiveness [4-6]. Flow conditions affect the corrosion process very strongly because erosion of the layer of corrosion products that builds up on the surface of the metal can favour further corrosion. The shear stress on metallic surfaces is the physical parameter that reflects the intensity of erosion-corrosion. It varies with fluid flow velocity and degree of vaporization. The various pieces of equipment in a refinery plant are consequently subject to different values of the shear stress and a different experimental setup is required to simulate the different shear stress conditions in the laboratory. Reportedly [4], the shear stress is expected to be highest in transfer lines and side cut piping, in which the fluid flow velocity is high and the degree of vaporization is low. Conversely, due to the high degree of vaporization, lower values of the shear stress occur in furnace tubes in spite of the high fluid velocity. The former conditions are best reproduced with a jet impingement flow loop, the latter with a rotating specimen in an autoclave. Finally, the condensation of naphthenic acids in distillation towers can be simulated by exposing metallic specimens to the vapour phase in an autoclave. Fluid velocity has virtually no effect on this last process.

This work focuses on the corrosion of furnace tubes and discusses the results of laboratory tests that were carried out on a rotating specimen in a sealed autoclave. The interaction between sulphur and naphthenic acids was investigated with a view to developing a laboratory test to assess the corrosiveness of crude oils and also to test the model sketched above.

EXPERIMENTAL

The specimens, made of 9%Cr-1%Mo steel, were abraded with 600 grit paper and rinsed thoroughly with deionized water and acetone before the tests.

Two different kinds of oil were used: Ural crude oil (sulphur 1.5 wt%; density 866.8 g/l; TAN 0.2 mg KOH/g oil) and DW05 lubricant base oil, which has a very low concentration of sulphur (sulphur 3.8 ppm in weight; density 845.9 g/l; TAN 0.16 mg KOH/g oil, distillation temperatures between 388 and 475°C). Values of TAN between 1 and 15 mg KOH/g oil were obtained by adding a mixture of synthetic naphthenic acids (Fluka 70340, mean molecular weight 230) to the oil. Tables 1 and 2 list the measured TAN of a few mixtures; the TAN corresponding to higher concentrations of naphthenic acids can be obtained with linear extrapolation. The velocity of the rotating specimen was about 3 m/sec relative to the walls of the autoclave. The autoclave was purged with nitrogen and sealed before heating. The temperature was raised to 340°C and the pressure rose to about 20 bar during the tests.

At the end of the tests the specimen was rinsed with toluene in an ultrasonic bath for 10 minutes, dried and weighed. The sum of the weights of the remaining metal and the corrosion products adhering firmly to the surface was obtained in this way. Then the specimen was cleaned with the following procedure: a 10 minute treatment in a cleaning solution (500 ml HCl sp gr 1.19, 3.5 g hexamethylene tetramine, reagent water to make 1000 ml) was followed by 10 minutes' ultrasonic cleaning in reagent water to remove loose products. The above procedure was repeated until the specimen had regained its original metallic colour, that is up to 4 times. It was weighed again and the cleaning procedure was carried out once more to check that its effect on the bare metal was negligible. The final weight was then measured. The rate of corrosion was calculated from the weight loss of the specimen with the ordinary formula [7].

The rate of corrosion of 9%Cr-1%Mo steel in the cleaning solution was also measured in a separate test. It is in the order of 2 mm/year and results therefore in a negligible weight loss during the cleaning procedure described above.

The composition of the corrosion products was investigated by means of energy dispersive x-ray fluorescence spectroscopy (EDXRF). The spectra were acquired with a portable spectrometer, EIS modello XRS P/N 0211. The specimen was in air during the measurement.

Table 1: total acid number (TAN) of mixtures of naphthenic acids (Fluka) and Ural crude oil

| Acids/Ural (g/l) | TAN (mg KOH/g oil) |
|---------------------|-----------------------|
| 3.85 | 1.19 |
| 18.75 | 5 |

Table 2: total acid number (TAN) of mixtures of naphthenic acids (Fluka) and DW05 lubricant base oil

| Acidi/DW05 (g/l) | TAN (mg KOH/g oil) |
|---------------------|-----------------------|
| 14.9 | 5.4 |
| 29.8 | 9.9 |

RESULTS

Irrespective of the concentration of naphthenic acids, there is a big difference in the appearance of the specimens after the tests in the Ural crude oil, having a high concentration of sulphur, or in the low-sulphur oil. After being exposed to the Ural oil the metal is covered by thick black scales that tend to flake off. The surface is badly damaged. In contrast, after the tests in the low-sulphur oil the surface is smooth and free of damage. It is only slightly brownish. This difference in appearance suggests that a different corrosion phenomenon must have occurred in the two different oils. A high concentration of sulphur is detected with x-ray fluorescence spectroscopy in the black scales that form in the Ural oil (figure 1). Sulphur is no longer present in the spectra after the specimen has been cleaned (figure 2). This leads to the conclusion that a black layer of iron sulphide builds up during the tests in the Ural oil and is removed by the cleaning procedure. Sulphidic corrosion appears therefore to take place in the Ural oil. In contrast, the smoothness of the surface after the tests in the low-sulphur oil points to naphthenic acid corrosion. In fact, iron naphthenate, which is the corresponding

corrosion product, is soluble in oil and leaves the surface free of corrosion products [1, 3, 8].

The weight of the corrosion products that stick firmly to the surface of the metal is very different after the tests in the high-sulphur or in the low-sulphur oil, table 3. On average, it is far higher for the high-sulphur than for the low-sulphur oil: 7.8 against 1.1 mg/cm². This is consistent with the difference in the appearance of the specimens, the black scales being much thicker than the smooth brownish film. The corrosion rate is plotted versus TAN in figure 3. The response of the rate of corrosion to changes in the total acid number (TAN) is very different in the two oils. The rates measured in the Ural oil are scattered and show no definite trend. In contrast, the corrosion rate increases with TAN in the low-sulphur oil. This behaviour confirms that naphthenic acid corrosion occurs in the low-sulphur oil but not in the Ural oil. It is also worth noticing that the corrosion rate depends on TAN at values higher than those observed in refineries, i.e. TAN below 6 [1,2]. The highest corrosion rate measured (about 1 mm/year at TAN=14.8) corresponds to a moderate attack in spite of the high TAN.

Only general corrosion was observed in all the tests.

Table 3: results of the corrosion tests.

| specimen | Oil | TAN (mg KOH/g oil) | Length of the test (days) | Corrosion rate (mm/year) | Weight of corrosion products (mg/cm ²) |
|----------|------|-----------------------|---------------------------------|--------------------------------|---|
| U1 bis | Ural | 1,2 | 9,5 | 0,19 | 9,2 |
| U2 | Ural | 1,2 | 3 | 0,62 | not measured |
| U3 | Ural | 4,9 | 3,5 | 0,75 | 5,3 |
| U5 | Ural | 4,9 | 4,5 | 0,93 | 12,2 |
| U8 | Ural | 4,9 | 4 | 0,55 | not measured |
| U9 | Ural | 4,9 | 4,5 | 0,50 | 4,9 |
| U1 pr.6 | Ural | 4,9 | 6 | 0,95 | 9,8 |
| U11 | Ural | 10 | 7,5 | 0,39 | 5,3 |
| U12 | Ural | 9,8 | 6,8 | 0,67 | 7,7 |
| U13 | DW05 | 5,4 | 4,5 | 0,10 | 1,2 |
| U13 bis | DW05 | 5,4 | 7 | 0,06 | 0,6 |
| U14 | DW05 | 9,9 | 7 | 0,33 | 1,3 |
| U15 | DW05 | 14,8 | 7 | 1,03 | 1,6 |
| U17 | DW05 | 14,8 | 7 | 0,90 | 0,8 |

Figure 1: x-ray fluorescence spectrum of a specimen tested in Ural oil and rinsed in toluene.

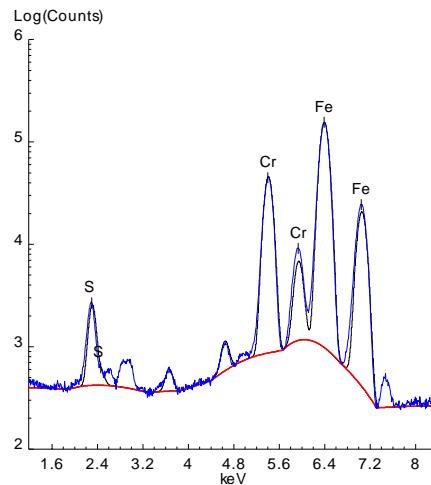


Figure 2: x-ray fluorescence spectrum of a specimen tested in Ural oil, rinsed in toluene and cleaned with the HCl solution.

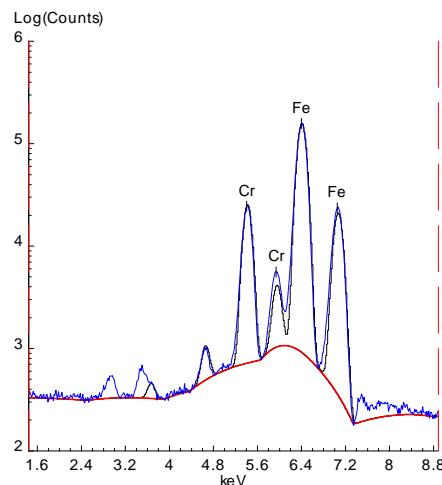
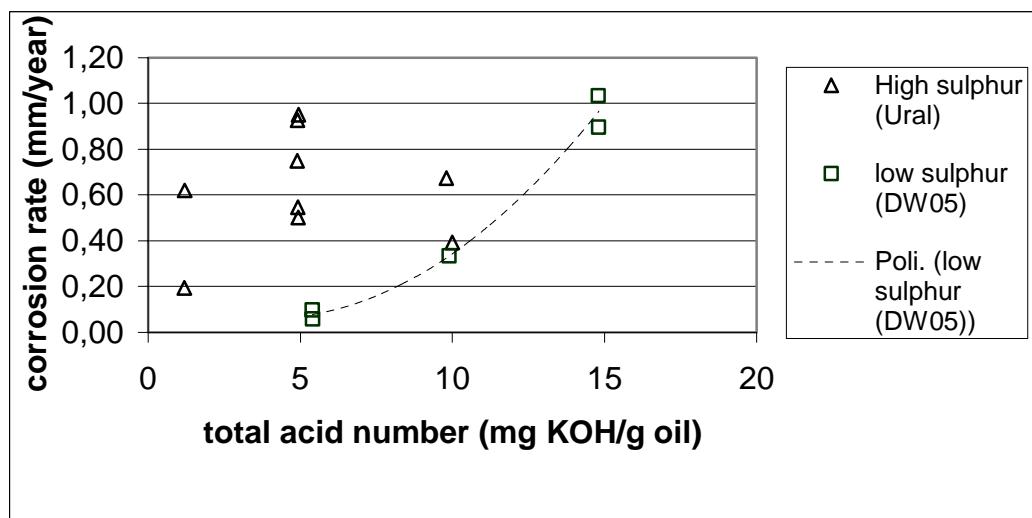


Figure 3: rate of corrosion versus total acid number (TAN).



DISCUSSION

The rate of corrosion and the weight of corrosion products can be put together to calculate the naphthenic acid corrosion index (NACI), proposed by Craig et al. a few years ago [8, 9]. The index is defined as:

$$\text{NACI} = [\text{rate of corrosion (mpy)}]/[\text{weight of corrosion products (mg/cm}^2\text{)}]$$

According to Craig, the NACI index allows naphthenic acid corrosion to be distinguished from sulphidic corrosion. The index takes on low values for sulphidic corrosion, since the denominator of the fraction is large. The weight of corrosion products that adhere firmly to the metal is, in fact, large for sulphidic corrosion. In contrast, high values of the index correspond to naphthenic acid corrosion because of its lack of surface corrosion products, which makes the denominator small. The type of corrosive attack can be distinguished according to the following criteria:

$\text{NACI} \leq 10$ sulfidation or, perhaps, oxidation

$10 < \text{NACI} \leq 100$ moderate naphthenic acid attack, perhaps inhibited by sulfidation

$\text{NACI} > 100$ severe naphthenic acid attack.

The NACI index was calculated for all the specimens except two (table 4). It is plotted versus total acid number (TAN) in figure 4. The tests in the Ural oil yield low values of the index, which correspond to sulphidic corrosion. In the low-sulphur oil the index increases with TAN and exceeds the threshold set by Craig for naphthenic acid corrosion. However, in agreement with the remarks that were made in the previous section, the highest values of the NACI index obtained in these tests correspond to a moderate attack only. The NACI index appears therefore to be a reliable tool to distinguish and evaluate the type of corrosive process that takes place in laboratory experiments.

A very low sulphur concentration (3.8 ppm in weight) and a very high concentration of naphthenic acids ($\text{TAN} \approx 15$) were needed for the onset of naphthenic acid corrosion. Sulphidic corrosion prevailed in the Ural oil (containing 1.5 wt% sulphur) even at TAN as high as 10. While this behaviour is roughly in agreement with the model that was sketched in the introduction, which depicts a competition between sulphur and naphthenic acids, the TAN values that were required for naphthenic acid corrosion to start are far higher than those experienced in refinery plants. Oils with TAN as low as 0.5 are in fact potentially corrosive. It is likely that this discrepancy can stem from the fact that the tests were carried out in a sealed autoclave. The compounds containing sulphur will in fact tend to decompose gradually during the test at 340°C , the H_2S partial pressure will rise as a result and favour sulphidic corrosion [4]. The conditions set up in laboratory tests could probably be made more similar to those of plants through two different approaches. Either a pressure relief valve can be fitted on the autoclave to prevent the pressure increasing excessively or the fluid can be continuously changed to prevent the H_2S partial pressure building up during the test [4-6].

The very high concentrations that were necessary to bring about naphthenic acid corrosion could partly be due to the tendency of naphthenic acids towards decomposition at high temperature [10]. The TAN of the liquid was therefore measured after a few of the tests. It was found that the liquid maintained a high acidity to the end of the tests (table 4) but a decrease in TAN not attributable to corrosion was indeed

observed. For example, the total acid number decreases from 4.9 to 1.96 during the test of specimen U3, even though corrosion (rate: 0.75 mm/year) was put down to sulphidic attack, which does not involve naphthenic acids and therefore should not affect the TAN. The concentration of naphthenic acids was lower than expected, although still fairly high, after the tests in the low-sulphur oil too, during which naphthenic acid corrosion took place. This conclusion can be drawn by examining the data of table 4. The value of TAN expected at the end of the tests is in fact equal to the difference between TAN and CAN (table 4). CAN stands for corrosive acid number and reflects the amount of naphthenic acids that would be consumed to bring about the measured weight loss of the specimen. This is then converted into the amount of KOH that would neutralize the corresponding solution [8,9]. Based on the weight loss, the values of TAN expected at the end of the test for specimens U13 and U17 are 5.2 (=5.4-0.2) and 11.6 (=14.8-3.2) respectively. They are far higher than the values measured at the end of the tests: 2 and 4.5 respectively. This suggests that decomposition of the naphthenic acids plays a part in the decrease of TAN during the tests in the low-sulphur oil too. Continuous change of the fluid in the autoclave could probably avoid this effect.

Figure 4: naphthenic acid corrosion index (NACI) versus total acid number (TAN).

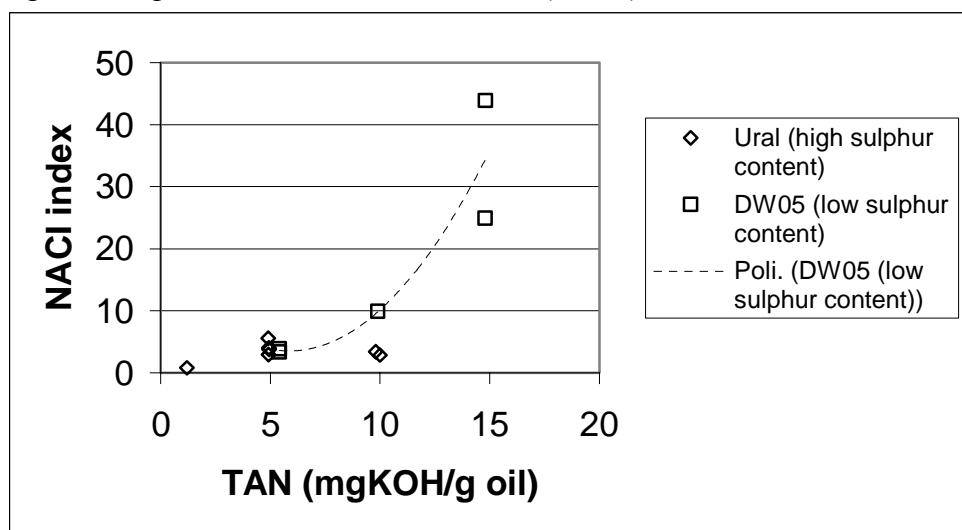


Table 4: naphthenic acid corrosion index (NACI), total acid number (TAN), corrosive acid number (CAN), after Craig et al. [8, 9].

| Specimen | Oil | NACI index | TAN | TAN |
|----------|------|------------|--|-------------------------|
| | | | At the start of the test (mg KOH/g oil) | CAN (mg KOH/g oilio) |
| U1 bis | Ural | 0,83 | 1,2 | 0,84 |
| U2 | Ural | Not det. | 1,2 | 0,83 |
| U3 | Ural | 5,58 | 4,9 | 1,34 |
| U5 | Ural | 3,00 | 4,9 | 2,13 |
| U8 | Ural | Not det. | 4,9 | 1,12 |
| U9 | Ural | 4,06 | 4,9 | 1,16 |
| U1 pr.6 | Ural | 3,81 | 4,9 | 2,92 |
| U11 | Ural | 2,88 | 10,0 | 1,53 |
| U12 | Ural | 3,43 | 9,8 | 2,34 |
| U13 | DW05 | 3,37 | 5,4 | 0,23 |
| U13 bis | DW05 | 3,92 | 5,4 | 0,21 |
| U14 | DW05 | 9,89 | 9,9 | 1,2 |
| U15 | DW05 | 24,93 | 14,8 | 3,7 |
| U17 | DW05 | 43,89 | 14,8 | 3,21 |
| | | | | 4,5 |

CONCLUSIONS

The experiments have confirmed the interaction between naphthenic acids and sulphur. Moderate naphthenic acid corrosion occurred in mixtures containing a very low sulphur concentration (3.8 ppm in weight) and a very high concentration of naphthenic acids (TAN≈15). Even such a low concentration of sulphur appears therefore to partially inhibit naphthenic acid corrosion in sealed autoclave tests. A far higher concentration of sulphur (1.5 wt%) favoured sulphidic corrosion, even in the presence of very high concentrations of naphthenic acids (up to TAN≈10). This behaviour is only roughly in agreement with the model sketched in the literature for this kind of interaction. In fact, the very high concentrations of naphthenic acids that were necessary for the onset of naphthenic acid corrosion, even at very low sulphur concentrations, contrast with refinery plant experience, which shows that crude oils with TAN values as low as 0.5 can be severely corrosive.

This discrepancy probably stems from the fact that a sealed autoclave was used, which gives rise to a build-up of the H₂S partial pressure during the tests as a consequence of the gradual decomposition of compounds containing sulphur. As a result, sulphidic corrosion is favoured over naphthenic acid corrosion. The experimental set-up needs to be modified, if plant conditions are to be reproduced more closely. The results of the tests are also affected to some degree by the tendency of naphthenic acids towards decomposition at the test temperature (340°C).

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