Measuring naphthenic acid corrosion potential with the Fe powder test

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Abstract   Results are presented of experiments performed using a new method to measure the naphthenic acid corrosion potential. The method consists of adding pure iron powder into a small autoclave containing the crude or oil sample. The test is then performed at a given temperature for one hour, after which the oil sample is filtered and the remaining liquid is sent for iron content determination (ppm). The tests are run at 7 different temperature levels, 3 more are run as repeated tests. A best-fitted curve is drawn through these 10 experimental points and the maximum point is thus determined. This becomes the main outcome of the test and it is used to give a measure of the naphthenic acid corrosion potential. The same general trends as observed in the past using the neutralization number or TAN (Total Acid Number) is obtained. However, this new test seems capable of detecting anomalous cases where oil samples having larger values of TAN exhibit less corrosivity than others having much lower values of TAN or where they show completely different corrosivity despite having similar or the same TAN.

Keywords   Naphthenic acid corrosion. Total Acid Number (TAN). The Fe powder test.

Medición del potencial de corrosión por ácidos nafténicos mediante el ensayo del polvo de hierro

Resumen   Se presentan los resultados de experimentos realizados con un nuevo método para medir el potencial de corrosión por ácidos nafténicos. El método consiste en añadir hierro puro en polvo a una muestra de crudo o aceite, en un autoclave pequeño. El ensayo se realiza a una temperatura dada durante una hora; luego se filtra la muestra de aceite y el líquido filtrado se envía para medir la concentración de hierro disuelto (ppm). El ensayo se reitera para siete temperaturas diferentes y se repiten tres más para determinar su reproducibilidad. Con estos 10 puntos experimentales se dibuja la mejor curva de ajuste y se determina un máximo de hierro disuelto. Este máximo se convierte en el resultado principal del ensayo y se usa para dar una medida del potencial de corrosión por ácidos nafténicos. Se obtienen las mismas tendencias generales observadas en el pasado al utilizar el número de neutralización o NAT (Número de Acidez Total). Sin embargo, este nuevo ensayo parece ser capaz de detectar casos anómalos, donde la muestra de aceite, que contiene altos valores de TAN, exhibe menos corrosividad que otras que contienen valores mucho más bajos de TAN; o donde ellas muestran un corrosividad completamente distinta a pesar de tener un TAN similar o igual.

Palabras clave   Corrosión por ácidos nafténicos. Número de Acidez Total (TAN). Ensayo del polvo de hierro.

1. INTRODUCTION

In 1956, Derungs[1] stated that naphthenic acid corrosion was first observed in the 1920's. If so, corrosion engineers in the petroleum refining industry have been dealing with this phenomenon for 80 years or more. The naphthenic acid content is commonly determined by titration with potassium hydroxide (KOH), as described in ASTM D 974 (color-indicator titration) and D 664 (potentiometric titration). The value obtained is referred to as neutralization number or more commonly as the Total Acid Number (TAN), which is expressed in milligrams of KOH required to neutralize the acid constituents present in one gram of sample. During this very long time span,

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many technical papers have been written on the subject suggesting that naphthenic acid corrosion is predictable from TAN[2 and 3].

A rule of thumb using TAN is commonly used, which consider crudes with TAN higher than 0.5 as potentially corrosive to distillation equipment made of carbon steel or alloyed to deal only with sulfidation attack. Based on actual field experience, however, others have adopted the criterion that crude slates with TAN less than 0.3 can be processed in distillation units made primarily of carbon steel. Continuous processing of feed with TAN in the range of 0.3-0.5 is said to require the use of alloy and even austenitic stainless steels in some critical areas of the distillation units. For feed with TAN higher than 0.5 it is said that it can be processed only in fully protected units. By full protection it is meant to have austenitic stainless steel type AISI 316 (17Cr-12Ni-2.5Mo) or even 317 (19Cr-13Ni-3.5Mo) for all parts or equipment in the unit operating in the temperature range of 230-400 °C. This is a rather expensive approach.

Since some crude with low TAN can be more corrosive than others with higher TAN, the use of TAN to predict corrosivity has been questioned. When the TAN is adjusted by adding commercially available low-sulfur naphthenic acids in sulfur-free white oil or mineral oil, the correlation between TAN and corrosivity seems to be evident. The higher the TAN the greater the corrosivity. However, with actual crude oil samples, it does not always produce the same trends and sometimes even produces quite unexpected results. Alternative methods have been proposed based on autoclave test and weight lost measurement. Lee Craig[4] proposed the use of a corrosive acid number (CAN), determined by calculating the equivalent weight of iron lost by corrosion, and of a naphthenic acid corrosion index (NACI). This is a ratio of the corrosion rate to the weight of corrosion product. The principle is that there are two competing corrosion mechanisms acting together, sulfidation and naphthenic acid corrosion. While sulfidation produces an insoluble corrosion product naphthenic acid corrosion is said to produce an oil-soluble corrosion product. Thus, a value of NACI between 10 to 100 is said to correspond to moderate naphthenic acid corrosion while those higher than 100 correspond to severe naphthenic acid corrosion. Low values of NACI, less than 10; mean that sulfidation is the predominant corrosion mechanism.

The use of autoclave tests and of a closed loop circuit for hot oil to provide dynamic testing conditions have been proposed as a mean to assess crude corrosivity. This has been the main tool used in a multi-client sponsored research effort[5] on crude corrosivity prediction initiated in 1993. Althought the final report with the complete results of this research program has not yet been made public, as a sponsor it is known that it has produced clear laboratory evidence showing a very complex interaction and inhibiting effect of sulfidation on the naphthenic acid corrosion phenomenon. When the interacting effect of sulfur is present, the use of TAN to indicate corrosivity may be misleading.

Notice that measuring corrosion rate by weight lost does not make the necessary discrimination between sulfidation and naphthenic acid corrosion. This is important because using Cr-Mo steels or stainless steel type 410 or 12 Cr usually solves high corrosivity problems due to sulfidation. In contrast, use of austenitic stainless steel type 316 or even 317 must be made to solve high corrosivity problems due to naphthenic acid corrosion.

The task group T-8-22 formed during the 1996 Fall Committee Week, NACE International T-8 Refining Industry Corrosion Group, recently published its results[6] on the literature review on naphthenic acid corrosion. They concluded that the concerns associated with naphthenic acid corrosion continue to exist today, that there are still difficulties on predicting this type of corrosion, and that a more accurate prediction tool or method will have to be developed. Some approaches have been different to traditional ones. For instance, a recent paper[7] was published of a methodology of better crude oil corrosivity predictions based on origin, evolution, and maturity (crude history). The iron powder test is another different approach to this very old problem. This paper describes the principles and the potential use of the method to predict corrosivity. It also updates the information regarding the latest stages that have been completed in the development process of this new method.

2. THE Fe POWDER TEST

The original idea behind the Fe powder test (patent pending) was to expose a much large surface area than available in any steel corrosion coupon used when applying the weight lost

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method. This was followed by another idea of using a fundamental approach of chemical kinetics to study the rate of the chemical reactions of the naphthenic acids with iron in the corrosion process[8]. In the iron powder test, all compounds that can react with iron at the testing temperature should do so during the test. However, only those producing oil soluble corrosion products contribute to the measured result, which is the amount in ppm (part per million, weight) of dissolved iron. If any other chemical reactions or corrosion processes occur and produce solid products, like sulfidation that produces FeS, it should be ignored because only the dissolved iron will be measured. Since the naphthenic acids react with iron to produce oil-soluble iron naphthenates, it is believed that the method is capable of giving an indication of the naphthenic acid corrosion potential. As mentioned earlier, the weight lost methods give a total corrosivity indication. Based on this perception, an effort was made to try to use the iron powder test to assess corrosivity[9]. Most recently, it was used for classifying crude oils[10] according to their corrosivity potential, as measured by the iron powder test method.

3. EXPERIMENTAL PROCEDURE

The tests are currently performed with 25 g of oil sample and 2.5 g of iron powder placed in 50 ml autoclaves with an axial flow impeller rotating at 100 rpm to induce fluid motion and bring about uniformity. The iron powder is added in excess so that the naphthenic acids are the limiting reactant. To eliminate oxygen entrapment in the reactor, N_2 is bubbled during 5 minutes. Then, the valves are closed and the temperature is increased. When reaching 90 % of the set temperature, the recording of the reaction time is started. At the end of the reaction time, the reactor is cooled. After opening the autoclave, the mixture is filtered to separate the remaining iron powder. If the oil sample is too heavy, Xylene is used to dilute it before filtering. The Fe concentration in the filtered liquid is determined by inductive coupled plasma (ICP) emission spectroscopy (ASTM D-5708-95) and the result is expressed as a function of the oil sample weight as ppm.

The testing procedure consists of conducting the several tests, as just described, at a constant time of one hour and at different temperatures. A curve of the amount of dissolved Fe against temperature is then plotted. The final response of the test is the point of maximum amount of dissolved Fe for one-hour test at the corresponding testing temperature. The testing temperature is selected in steps of 40 °C from 140 to 380 °C, given a total of 7 tests. At least 3 tests are replicated for accuracy. An initial point is added corresponding to 30 °C and the initial amount of Fe contained in the virgin oil sample. Since the type, size and particular shape of the iron particles in the powder influence the result, all tests need to be performed with the same iron powder brand and type.

Even though it is possible to convert the result into a corrosion rate expressed as thickness lost per year, this might be misleading and it is therefore not recommended in the procedure. Steels used in the oil refining industry have alloying elements that may change the material performance as compared with pure iron. Also, actual field conditions involve velocity/turbulence effect in piping and acid condensation in vacuum tower. These two factors plus the condition implying a continuous fresh hydrocarbon stream contacting the metal are rather difficult to simulate in the laboratory. This test is performed in autoclave using a very limited amount of oil sample continuously in contact with the same iron powder for as long as the test lasts at the testing temperature.

4. RESULTS

The results summarized in figure 1 were produced by performing the Fe powder test with low-sulfur paraffinic white oil (less than 10 ppm sulfur and with a TAN less than 0.05) with addition of low-sulfur commercially available naphthenic acid. This acid has a TAN of 230 mg KOH/g. The samples were produced by adding weighed amount of this commercially available naphthenic acid to make up 250 ml of paraffinic oil. An equivalent TAN was calculated, as a reference. The maximum amount of iron dissolved found after the test is shown in the vertical axis in a logarithmic scale in figure 1a and in a linear scale in figure 1b.

Notice that the addition of 0.2 % naphthenic acid resulted in a maximum amount of iron dissolved of 8 ppm. Doubling the addition of naphthenic acid to 0.4 %, resulted in a maximum amount of iron dissolved of 20 ppm. Increasing the addition of naphthenic acid to 1.0 % resulted in a maximum amount of iron dissolved of 85 ppm. These amounts of naphthenic acid added correspond

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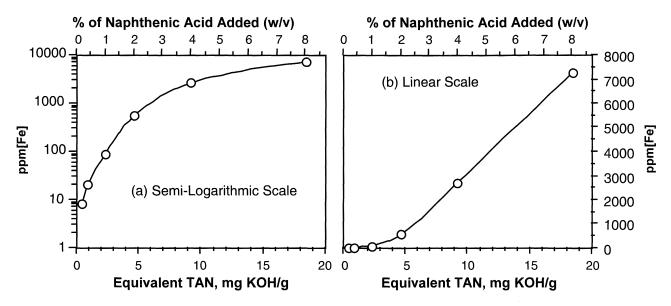*Rev. Metal. Madrid Vol. Extr. (2003) 116-123*

Figure 1. Maximum amount of iron dissolved as a function of the naphthenic acid added into white oil, after performing the Fe powder test. (a) Semi-Logarithmic scale and (b) Linear scale.

Figura 1. Cantidad máxima de hierro disuelto en función de la cantidad de ácido nafténico añadido en el aceite parafínico, después de realizar el ensayo del polvo de Fe. (a) escala semilogarítmica y (b) escala lineal.

to values of TAN of about 0.5, 0.9 and 2.3 mg KOH/g, respectively. Up to here, the relationship between dissolved iron and TAN fits a second order polynomial.

The addition of 2, 4 and 8 % naphthenic acid corresponds to values of TAN of 4.6, 9.2 and 18.4 mg KOH/g. The temperature at which the maximum iron dissolution occurred varied. It was 180, 200, 220, 250, 260 and 270 °C for the oil samples with naphthenic acid additions of 0.2, 0.4, 1.0, 2.0, 4.0 and 8.0 %. The maximum amount of iron dissolved was 8, 20, 85, 620, 2700 and 7300 ppm, respectively.

The point at which the addition was 2 % naphthenic acid (TAN = 4.6) represents a transition above which the relationship between the maximum amount of dissolved iron and TAN fits a straight line. Most common crude oils have TAN below 5.0 but heavy vacuum gas oil (HVGO) and the first liquid collected in the bottom bed of a vacuum distillation tower may have values of TAN up to 8.0 when processing long residues derived from these crude oils. So the experiments in figure 1 do represent conditions similar to those actually found in oil refineries, when processing naphthenic acid containing crude oils, at least in regard to naphthenic acid content and TAN.

Table I shows real crude oil samples tested with this method. All except three are Venezuelan crude oils from heavy such as Boscan and Tía Juana
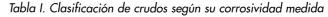
Pesado to lighter ones such as Mesa and Lagomar. All the oil samples shown in table 1 have total sulfur content exceeding 1.0 %. The TAN varies from the lowest measured of 0.13 for Mesa to the highest measured of 4.6 for Tía Juana Pesado.

Assuming that the amount of dissolved iron gives an indication of the naphthenic acid corrosion potential, a comparison between the results in figure 1 and table I shows that having the same TAN does not necessarily correspond to the same corrosivity level. For instance, BCF 17 (Bolivar Coastal Field 17) has a TAN of about 2.1 and dissolved 42 ppm of iron. Notice that the addition of 1.0 % naphthenic acid was equivalent to a TAN of 2.3, which dissolved 85 ppm of iron. That is, although they have similar TAN values, the latter dissolved twice the amount of iron. The case of TJP is even more revealing. Both TJP and the oil sample produced by adding 2 % naphthenic acid have a TAN of 4.6 and yet, this sample dissolved 620 ppm, as compared with TJP that dissolved 217 ppm of iron. Some scatter was obtained in the test with TJP, giving an error of about ±64 ppm. The synthetic oil sample produced by adding 2 % naphthenic acid dissolved more than twice as much iron than TJP in spite of the fact that they both have the same TAN.

Figure 2 shows the comparison of the results obtained by testing real crude oil samples and the synthetic mixture of paraffinic oil with addition of

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Table I. Classification of crude oils according to their measured corrosivity

Tabla I. Clasificación de crudos según su corrosividad medida

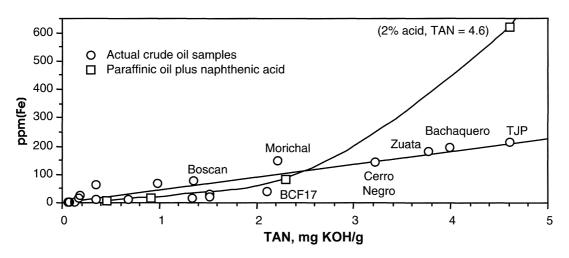|	Crude Oil Name	Sulfur %	API Gravity	TAN [mg KOH/g]	ppm [Fe]	°C
1	Mesa	1.06	28.5	0.13	< 5	–
2	LagoTreco	1.97	23.9	0.67	12	380
3	Foreign Crude 1	2.27	24.0	0.34	16	280
4	Lagomar	1.37	30.8	0.17	18	260
5	Menemota	2.54	20.4	1.33	19	312
6	BCF22 (Bolivar Coastal Field 22)	2.19	21.8	1.51	25	320
7	Foreign Crude 2	4.10	22.8	0.18	30	285
8	Merey	2.56	16.1	1.51	33	300
9	BCF17 (Bolivar Coastal Field 17)	2.22	17.9	2.10	42	320
10	Foreign Crude 3	3.75	17.5	0.34	68	310
11	Boscan	5.70	10.0	1.35	82	350
12	Tia Juana Pesado (TJP)	2.66	10.9	4.60	217	300

Figure 2. Comparison between the results obtained with the Fe powder test for real crude oil samples and for the mixture of paraffinic with addition of commercially available low-sulfur naphthenic acid.

Figura 2. Comparación entre los resultados obtenidos con el ensayo del polvo de Fe, para muestras de crudos reales y para la mezcla de aceite parafínico con ácido nafténico comercial con bajo azufre.

commercially available low-sulfur naphthenic acid. A regression line was fitted for the points produced by real crude oil sample testing. The experimental points corresponding to synthetic mixture were joined by a hand-fitted curve. There are differences when comparing the straight line with this curve below about a TAN of 2.6. For instance, with a value of TAN equal to 2.1, the regression line predicts 97 ppm; the hand-fitted curve predicts 70 ppm, as compared with the actual one obtained for BCF17 of 42 ppm. Despite these differences, in the graph in figure 2 they appear closer because of the large scale used in the ordinate, 0-650 ppm.

Above a TAN of 2.6, the results from the synthetic mixture depart farther away from the real crude oil sample ones. None of the heavy crude oils Cerro Negro, Zuata, Bachaquero, and TJP exhibit the same corrosion potential than the values predicted by the hand-fitted curve for the synthetic mixture. With 2 % naphthenic acid the equivalent TAN is 4.6 as compared with values of TAN of 3.21, 3.77, 3.99, and 4.60, for Cerro Negro, Zuata, Bachaquero, and TJP, respectively.

Figure 3 shows again the straight line correlation found between values of TAN and the maximum amount of iron dissolved in the Fe powder test applied to real crude oil samples. However, this time a logarithmic scale was used for the ordinate to better reveal the differences.

Notice that the general trend suggests what is already known that the higher the TAN the
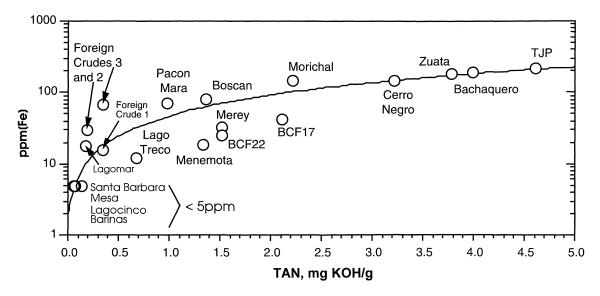
Figure 3. Correlation between the maximum amount of iron dissolved, as determined in the Fe powder test, and the TAN for real crude oil samples.

Figura 3. Correlación entre la cantidad máxima de hierro disuelto, determinada según el ensayo del polvo de Fe, y el TAN para muestras de crudos reales.

greater the corrosivity. However, some points do not follow the correlation very well, particularly below a TAN of 2.6. Thus, crude oils such as the foreign crude 3, Pacon Mara, and Boscan, that have similar or even much lower values of TAN, appear more corrosive than Merey, BCF22, and BCF17. This matches field experience. Merey, BCF22, and BCF17 are found in actual field experience that they are not as corrosive as the foreign crude 3 and Boscan. Foreign crude 2 (30 ppm [Fe]) appears with similar corrosivity than Merey (33 ppm [Fe]) despite the fact that the former has a TAN of only 0.18 as compared with 1.51 of Merey. Crude oils such as Lago Treco (12 ppm [Fe]) and Menemota (19 ppm [Fe]) are known not to be very corrosive and this is also reflected in the results shown in figure 3.

Figure 4a shows the correlation between the maximum amount of iron dissolved, as determined in the Fe powder test, and the API gravity of real crude oil samples. Figure 4b shows the correlation between the TAN and the API gravity for the same crude oil samples. There are several points that do not fit the regression curve. However, although the correlation is far from perfect, the general trend is evident. The heavier the crude oils the higher the TAN and the higher the corrosivity, which is also known from experience.

Although the test is being developed since early 1998 and has already gone through several stages, it still needs further development. The effort

to produce a simple standard procedure continues in order to reduce data scattering, which sometimes has been a problem. Also, the main challenge is to find how to translate these results into actual field applications. The questions to be answered are several. There is one related to the level of ppm [Fe] below which carbon steel is acceptable or above which the need arises to upgrade to higher alloy steels. There is another one related to the level of ppm [Fe] above which stainless steel type 316 becomes necessary or above which even this steel does not provide the necessary protection.

The translation from the Fe powder test results into reality needs to be done as to know which piping, vessel, heat exchanger shell and tube bundle, and distillation tower wall and internals require upgrading to higher alloy steels. This would imply testing not only the raw crude but also the long residue and all the distillates to determine the levels of ppm [Fe] below which 5 Cr-0.5 Mo or 9 Cr-1 Mo steels suffice or above which upgrading to stainless steel type 316 becomes necessary. So there is still a long way to go but the work is in progress.

The propensity has been to use it in comparison with the known corrosivity of what has been processed for many years. That is, say that a new crude slate is tested and dissolved twice or three times more than the current crude slate. If the latter is producing so many mils per year (mpy) of corrosion rate in a particular area of the distillation

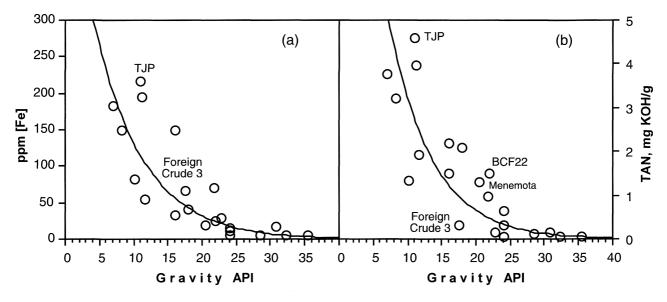*Rev. Metal. Madrid Vol. Extr. (2003) 116-123*

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Figure 4. Correlation between the maximum amount of iron dissolved, as determined in the Fe powder test, TAN, and the API gravity of real crude oil samples.

Figura 4. Correlación entre la cantidad máxima de hierro disuelto, determinada según el ensayo del polvo de Fe, y el TAN y la gravedad API de muestras de crudos reales.

unit, it is predicted that the new crude slate will produce twice or three times higher corrosion rate. Although the prediction could sometimes be successful, the approach has not yet been proved and it is not recommended.

5. CONCLUSIONS

This new method of measuring the naphthenic acid corrosion potential produces results that agree with existing knowledge about this phenomenon. That the higher the acid content corresponds to greater corrosivity has been observed in the field and in laboratory test results. However, by the same nature of the test procedure, the Fe powder test reveals results that have caused much confusion in traditional laboratory test results and in failure analysis interpretation. This refers to cases where oil samples that have the same or similar values of TAN do not show the same corrosivity. It also refers to cases where oil samples having larger values of TAN exhibit less corrosivity than others having much lower values of TAN.

The Fe powder test seems capable of detecting the above mentioned cases. This is because unlike KOH, which does not only react with naphthenic acids but also with other compounds such as hydrolyzable salts, iron naphthenates, inhibitors and detergents, the iron powder is likely to react more with all those species also capable of producing

corrosion on actual steels. If the naphthenic acids present are stronger it is expected to produce a larger amount of dissolve iron than in another oil sample having weaker organic acids. In this way, it is somewhat capable of distinguishing between different acids.

Unlike conventional corrosivity tests based on weight lost and steel coupons, if some corrosion reactions occur that produce insoluble corrosion products (like sulfidation does), the Fe powder test should not record this contribution. In this way, it should give a much better indication of the naphthenic acid corrosion potential than conventional corrosivity tests, since these produce a total corrosion rate that have both the contribution of sulfidation and naphthenic acid corrosion.

Whether the effect is due to an inhibiting effect of sulfur species or not, it is outside the scope of this work. The fact is that sulfur-free paraffinic oil having values of TAN higher than 2.6 appears much more corrosive than real crude oil samples that have a total sulfur content greater than 1.0 % and similar or even higher values of TAN.

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also wish to express recognition to R. Callarotti, R. Lorenzo, and M. I. Specht for previous contribution to the development of this new test method and to M. Ledezma who has administered the project under which this method has been developed.

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