

**A Major**  
**Project Report On**  
**Studies of Naphthenic acid Corrosion**

A project report submitted in the partial fulfillment  
of the requirements for the award of the degree of

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**IN**  
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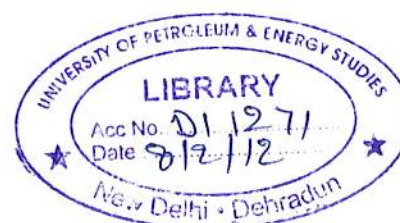
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## SUMMARY

Naphthenic acid corrosion (NAC) and high temperature crude corrosivity in general is a reliability issue in refinery distillation units. The presence of naphthenic acid increases corrosion in the high temperature parts of the distillation units and causes problems such as desalter upsets, preheat and reactor bed fouling, side-cut stability, increase downtime, lower production, creation of unexpected plant shutdown and unsafe working conditions, product loss etc. The corrosion has been undertaken with respect to the role of crude oil composition, temperature, fluid velocity, physical state (vapour or liquid), pressure, and materials of construction, difference in process conditions, materials of construction and blend processed in each refinery which is processing high acid crude oils.

The project includes the proper mitigation strategies, metallurgy and /or the application of naphthenic corrosion inhibitors, corrosion monitoring techniques, dilution methods etc to get benefit while processing high acid crudes which are generally known as "Opportunity crudes".

## CONTENTS

S.NO	TOPIC NAME	PAGE NUMBER
1	<b>INTRODUCTION</b> NAPHTHENIC ACID NAPHTHENIC ACID CORROSION AREAS SUSCEPTIBLE TO NAPHTHENIC ACID CORROSION ATTACK HOW NAPHTHENIC ACID IS FORMED? WHAT ARE HIGH ACID CRUDES? CRUDE ECONOMICS WHY WE SHOULD STUDY ABOUT NAPHTHENIC ACID CORROSION?	6
2	<b>ADVANCED TECHNOLOGIES - REVIEW PAGE</b>	21
	<b>2.1 NAPHTHENIC ACID CORROSION OF MILD STEEL IN THE PRESENCE OF SULFIDE SCALES FORMED IN CRUDE OIL FRACTIONS AT HIGH TEMPERATURE</b>	22
	<b>2.2 GE RCM ALLOWS REFINERY TO PRECISELY MEASURE PIPE CORROSION WHEN PROCESSING HIGH ACID OPPORTUNITY CRUDES</b>	37
	<b>2.3 BP-ADVANCED METHODS OF CONTINUOUS MONITORING AND INHIBITION OF NAPHTHENIC ACID CORROSION</b>	32
	<b>2.4 CORRELATION OF HYDROGEN FLUX AND CORROSION RATE MEASUREMENTS CARRIED OUT DURING A SEVERE EPISODE OF CORROSION-EROSION ATTRIBUTABLE TO NAPHTHENIC ACID.</b>	37
	<b>2.5 PROJECTS UNDER IMPLIMENTATION IN THE FIELD OF STUDY OF NAPHTHENIC ACID CORROSION</b> POWER, ENVIRONMENTAL & ENERGY RESEARCH CENTER, CALIFORNIA INSTITUTE OF TECHNOLOGY.(PEER-PROJECT). NAPHTENIC ACID CORROSION STUDIES AT ENI TECHNOLOGIE BY DR.ROBERTO RIVA (ET PROJECT)	42
3	<b>CASE STUDIES</b> A CASE STUDY ON THE GRANE HIGH ACID CRUDE OIL A CASE STUDY ON BAKER PETROLITE'S SMARTGUARD NAPHTHENIC ACID CRUDE PROCESSING PROGRAMME SITUATION	47
4	<b>CONCLUSION</b>	51
5	<b>BIBLIOGRAPHY</b>	52
6	<b>APPENDICES</b>	53

## INTRODUCTION

### ABOUT NAPHTHENIC ACIDS

**Definition:** Naphthenic acids is defined as a mixture of the aliphatic, condensed cycloaliphatic, and condensed aromatic carboxylic acids fraction of crude oil resins.

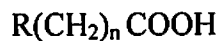
They have the general formula:  $C_nH_{2n+2}O_2$

where  $n$  = carbon number,

$z$  = hydrogen deficiency.

These are saturated or unsaturated five or six membered single or fused rings having a –COOH group attached through the alkyl chain.

Most of these acids have the chemical formula :



where R = cyclopentane ring

$n \geq 12$ .

Many different NSO-containing acids (i.e. alkyl phenols, alkyl benzene suffocates, etc...) are present in the naphthenic acid fraction.

The naphthenic acids possess mobility in both oil and aqueous phases due to the amphiphilic nature (fat-loving and water-loving). When naphthenic acids come in contact with neutral or basic water it gets dissociated into the aqueous phase. Naphthenic acids are soluble at neutral pH and ionize in basic solutions. 3% wt of crude oil is acids, of which naphthenic acids are most abundant. Oil and bitumen naphthenic acids are mixtures with diverse solubility and partitioning coefficients.

Naphthenic acid being non-volatile contributes to environmental degradation, increased organism exposure, bioaccumulation, and toxicity. Unsaturated and poly aromatic acids are more toxic than saturated acids.

Bio accumulated toxicants can persist in lean fish lipid tissue for more than 83 months, despite efforts of deparating water-soluble.

Toxic responses to neutral and acidic water-soluble range from decreased appetite to mutagenic effects and ultimately death.

Typical naphthenic acid (NA) bearing crude may have more than 1500 types of naphthenic acids.

The average molecular weight of naphthenic acids is 200-400.

Different grades of naphthenic acids are characterized by their TAN number, viz., 170, 230 etc.

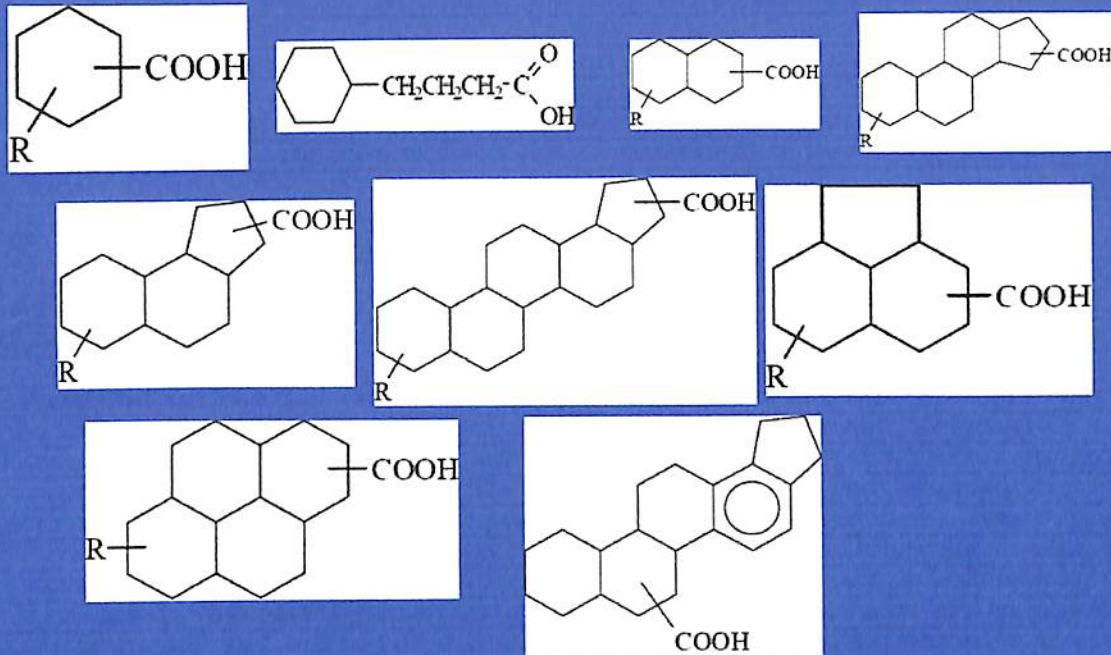
Higher grades, low mol wt naphthenic acids are found in kero & LGO boiling range and are highly corrosive than high mol wt naphthenic acids.

Typical approximate characteristics and properties and gasoline potential of various crudes.

CRUDE SOURCE	PARRAFINS (%VOL)	AROMATICS (%VOL)	NAPTHENES (%VOL)	SULFUR (%WT)	API GRAVITY (APPROX.)	NAPH. YIELD (% VOL)	OCTANE NUMBER (TYPICAL)
Nigerian (light)	37	9	54	0.2	36	28	60
Saudi (light)	63	19	18	2	34	22	40
Saudi (heavy)	60	15	25	2.1	28	23	35
Venezuela (heavy)	35	12	53	2.3	30	2	60
Venezuela (light)	52	14	34	1.5	24	18	50
USA Midcont. Sweet	-	-	-	0.4	40	-	-
USA (W. Texas Sour)	46	22	32	1.9	32	33	55
North Sea (Brent)	50	16	34	0.4	37	31	50

The following figure shows the examples of different naphthenic acid Structures.

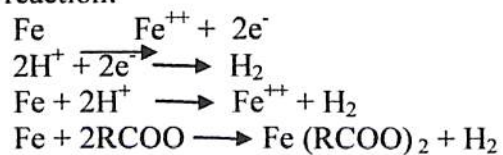
## Examples of Naphthenic Acid Structures



### ABOUT NAPHTHENIC ACID CORROSION

Corrosion is a chemical process of degradation and deterioration of essential properties in a material due to reactions with its environment. It is the loss of electrons of metals reacting with water or oxygen. Corrosion also includes the dissolution of ceramic materials and can refer to discoloration and weakening of polymers by the sun's ultraviolet light.

Corrosion is based on electrochemical reaction:



Crude oil corrosion is a critical issue in refining and economics. Refineries have to process economically high density crudes oils with high contents of sulfur, naphthenic acid, and numerous chemicals introduced during the production.

Acid content, sulfur content, velocity, temperature, and alloy (i.e. Cr and Mo) content of the material of construction are the main factors affecting the corrosion process.

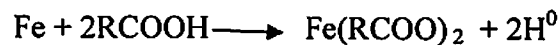
At lower temperatures, it appears that certain sulfur compounds may reduce the severity of naphthenic acid attack by forming a protective sulfide film, whereas at higher temperatures, naphthenic acids increase sulfide corrosion on alloys. Even at very low naphthenic acid content high velocities combined with high temperatures, dramatically increase the corrosive attack.

The naphthenic acids vaporize at widely varying temperatures which make prediction of crude corrosivity at varying operating conditions quite difficult. At elevated temperature sulphur compounds decompose to form hydrogen sulphide. Thus, sulfur content do not correlate to corrosion.

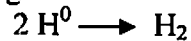
#### (1).NAPHTHENIC ACID CORROSION MECHANISM

Naphthenic acids cause corrosion between the temperature ranges of about 350°F (180°C) to 790°F (420°C). At higher temperatures naphthenic acids are in the vapor phase and the rate of de carboxylation increases..

Iron attacked by naphthenic acid forms iron naphthenate and atomic hydrogen



Atomic hydrogen diffuses through the metal and then recombines on the external surface to form molecular hydrogen.



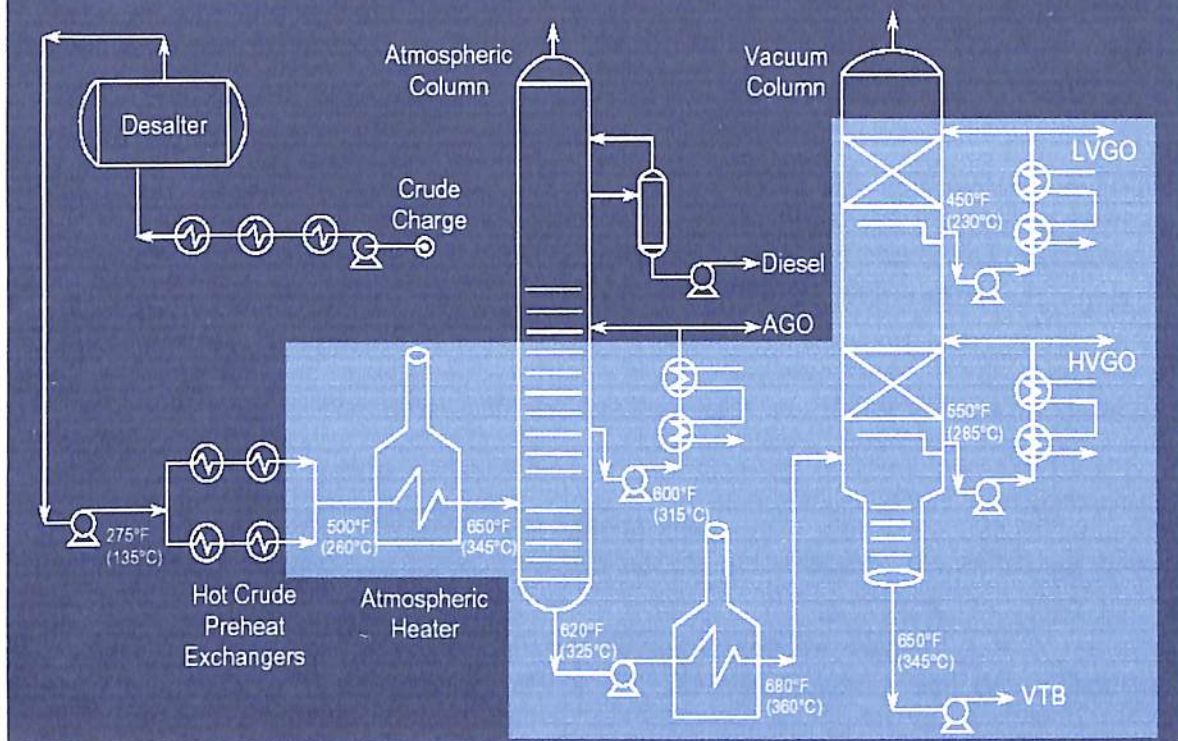
Structural alloys corrode from exposure to moisture in the air, but the process can be strongly affected by exposure to certain substances .Corrosion can be concentrated locally to form a pit or crack, or it can extend across a wide area to produce deterioration.

#### AREAS SUSCEPTIBLE TO NAPHTHENIC ACID CORROSION ATTACK

The following figure shows the typical areas of the crude unit susceptible to naphthenic acid corrosion which is represented by Sky blue color.



## Typical Areas of Crude Unit Susceptible to Nap Acid Corrosion



Source:www.nalco.com

### FURNACE TUBES AND TRANSFER LINES

Vaporization and fluid velocity are very high in furnace tubes and transfer lines. The high temperature conditions activates even small amounts of naphthenic acid in oil increasing corrosion significantly. Thus, at furnace tubes and transfer lines, the influence of temperature, velocity and degree of vaporization is quite large. Process conditions such as load and steam rate and especially turbulence greatly affect corrosion. The corrosion mechanism at the furnace tubes, transfer lines, areas of high turbulence such as thermo wells and pumps, is an accelerated corrosion due to the velocity and the two-phase flow. Simulation of these conditions in the laboratory requires conditions of high degree of vaporization and relatively low wall shear stress. A rotating electrode, with samples in the vapor phase simulates the high velocity conditions found in the field.

### VACUUM COLUMN

Preferential vaporization and condensation of naphthenic acids in the vacuum column, increase Total Acid Number of condensates. There is little effect of velocity. Corrosion



takes place in the liquid phase. It is condensate corrosion and is directly related to content, molecular weight and boiling point of the naphthenic acid. Corrosion is severe at the condensing point corresponding to high Total Acid Number and high temperature. Simulating vacuum tower corrosion requires the samples to be exposed in the condensing phase and not in the vapor or liquid phase. This requires apparatus common to corrosion studies in the chemical industry.

### **SIDE CUT PIPING**

Conditions of low vaporization and medium fluid velocity exist in side-cut piping. Some studies show a possible inhibition of NAC by sulfur compounds. An increase in velocity increases corrosion rates up to the point where impingement starts and corrosion is accelerated. The process of corrosion is dependent on flow, temperature, materials of construction and naphthenic acid and H<sub>2</sub>S content.

A stirred autoclave or flow loops with jet impingement are typically used to simulate these conditions.

### **NAPHTHENIC ACID CORROSION DURING DESALTING**

In general high acid crude oils are more difficult to desalt due to the following three reasons:

- (i) the surface activity of naphthenic acid salts or saponified organic acid,
- (ii) higher rates of addition of additives at the production site which can affect the surface activity of the crude oil,
- (iii) higher percentages of salt and water in the raw crude.

The above characteristics can be managed with the application of an appropriate demulsifier.

### **How actually Naphthenic Acid Crude is formed ?**

Naphthenic acids are carboxylic acids formed mainly by either aerobic or anaerobic biodegradation:-

#### **Aerobic biodegradation**

micro-organisms metabolize hydrocarbons (often as their sole source of energy) in the presence of oxygen:-

Areas of origin:

- Shallow reservoirs e.g. San Joaquin Valley, Duri, Alba over North Sea
- Reservoirs penetrated by meteoric waters (oxygen containing) e.g. Niger Delta, Gulf of Mexico, Venezuela

#### **Anaerobic biodegradation**

micro-organisms metabolize hydrocarbons without the presence of oxygen:-

Areas of origin:

- Deep water reservoirs where no meteoric waters are present e.g. some Gulf of Mexico, Angola.
- Light Paraffin's first then intermediate hydrocarbons are biodegraded leading to heavy oils.

### What Are High Acid Crudes?

The **Total Acid Number** is the amount of potassium hydroxide in milligrams that is required to neutralize the acids present in one gram of oil. It is an important quality measurement of crude oil. This value indicates to the crude oil refinery the potential of corrosion problems. High Acid crudes are defined as those crudes with a TAN of 1.0 or higher. It is a number derived from a standard test indicating the acid or base composition of lubricating oils also known as corrosion number. Acid number (or "neutralization number" or "acid value" or "acidity") is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of chemical substance. The acid number is a measure of the amount of carboxylic acid groups in a chemical compound such as a fatty acid. In a typical procedure, a known amount of sample dissolved in organic solvent is titrated with a solution of potassium hydroxide with known concentration and with phenolphthalein as a color indicator. The acid number is used to quantify the amount of acid present, for example in a sample of crude oil. It is the quantity of base, expressed in milligrams of potassium hydroxide that is required to neutralize the acidic constituents in 1g of sample.

$$\text{Acid Number} = (A_{eq} - C_{eq}) M 56.1/W$$

Where  $A_{eq}$  = the amount of titrant (ml) consumed by the crude oil sample and 1ml spiking solution at the equivalent point,

$C_{eq}$  = the amount of titrant (ml) consumed by 1 ml spiking solution at the equivalent point, and 56.1 is the molecular weight of KOH

$M$  = Molarity of titrant.

$M = 1000 W_{KHP} / (204.23 A_{eq})$

$W_{KHP}$  = Weight of Potassium hydrogen phthalate

$W$  = Weight of oil in grams.

204.23 is the molecular weight of Potassium hydrogen phthalate.

### **CRUDE ECONOMICS**

One particular study focused on operating costs at a single small refinery (53,000 barrels/day), concentrating on the costs related to environmental protection. This project quantified air emissions, water discharges, and other wastes generated at the facility. Moreover, it identified a range of options to reduce or prevent those releases, some of which appeared more cost-effective than those required by existing rules. At most refineries, operating costs are dominated by crude oil. Even small fluctuations in the price of crude oil can overshadow other operating costs of the refinery. As a result, it is customary at the refinery level to track "non-crude operating costs," excluding the cost of feedstock. The non-crude operating costs of this refinery are shown in table

<b>ENVIRONMENTAL COST CATEGORY</b>	<b>PERCENTAGE OF 1992 NON-CRUDE OPERATING COSTS</b>
Waste Treatment	4.9
Maintenance	3.3
Product Requirements	2.7
Depreciation	2.5
Administration, Compliance	2.4
Sulphur Recovery	1.1
Waste Disposal	0.7
Non-Recurring Costs	4.0
<b>TOTAL</b>	<b>21.6%</b>

The analysis estimates that total environmentally related costs are 21.6 percent of total non-crude operating costs. This total focuses primarily on capital, operating, and maintenance costs, and excludes contingent liability costs. If these costs were added, the total could be higher. Remediation expenses are recorded as "non-recurring costs."

Maintenance costs (40 percent of which can be attributed to corrosion control) were estimated in the study to be 3.3 percent (rounded to 3 percent) of the non-crude operating costs (table 4). When scaling up to all processes, this figure becomes:  
0.03 fraction maintenance costs / 0.216 fraction environmental operating costs = 13.9% of the total operating costs due to maintenance

$\$5.51/\text{bbl operating costs} \times 13.9\% = \$0.76/\text{bbl maintenance costs}$

$\$0.76/\text{bbl maintenance costs} \times 40\% \text{ due to corrosion control} = \$0.31/\text{bbl operating costs for corrosion control}$

When multiplied by the annual refinery output in the United States (5.7 billion barrels in 1997), the total cost of corrosion is ( $\$0.31 \times 5.7 \text{ billion} =$ ) \$1.767 billion per year.

Vessel turnarounds, during which a processing vessel is emptied, inspected, repaired (if necessary), and put back into service, are mandatory in most cases due to U.S. Department of Transportation (DOT) regulations, primarily due to suspected corrosion damage inside the vessels. The costs for these operations are capitalized rather than included in the maintenance budget.

One refiner estimated the total cost of the turnarounds at one of their refineries (a 260,000-bbl per day plant).

For the 3,000 processing vessels in this refinery, the total cost of turnarounds (5-year intervals for each individual vessel) was \$118 million. Therefore, turnaround costs per barrel are:

$(\$118,000,000/\text{yr} \times 1 \text{ turnaround}/5 \text{ years}) / (260,000 \text{ bbl}/\text{day} \times 365 \text{ days}/\text{yr}) = \$0.25/\text{bbl}$   
 $\$0.25/\text{bbl} \times 5.7 \text{ billion bbl}/\text{yr} = \$1.425 \text{ billion}/\text{yr} \text{ for turnaround costs}$

It should be noted that the trend in this activity is to move toward risk-based inspections and longer intervals (10 to 20 years) between turnarounds, which would significantly reduce the cost of corrosion maintenance, but increase the risk factor dramatically.

### **What is the global production, demand and supply position of high acid crudes ?**

#### **Global High Acid Crude (HAC) production and Supply/Demand Balance:**

- HAC are plentiful in most global regions and are increasing their% of total crude supply.
- Crude oils from California, Venezuela, North Sea, Western Africa, India, China, and Russia have typically a high naphthenic acid content.
- In India Reliance petroleum company processing high acid crudes.
- The Mediterranean currently imports only approx. 180 mbd of HAC.
- With increasing West African and America's production, the Mediterranean refiners are likely to take more HAC.
- South America is a net exporter of approx. 2.5 MMbd of crude. A large percentage of this is High Acid crude blends. Approx.500 mbd is refined in South America, mostly local production.
- North West Europe which has traditionally been a net exporter of HAC's is now balanced (increased refinery HAC runs) :-
  1. HAC's from NWE are exported to the USEC, USGC, Mediterranean and even the Far East.
  2. HAC's are imported from West Africa & South America.
- The Far East has moved from being a net importer of 25-40 mbd for the refining market to being long due to increased production from Bohai Bay and Penglai.

Note approx. 250 mbd of Far East HAC production goes into the burning market. There are now some exports to the USWC. Far East refiners are beginning to process HAC.

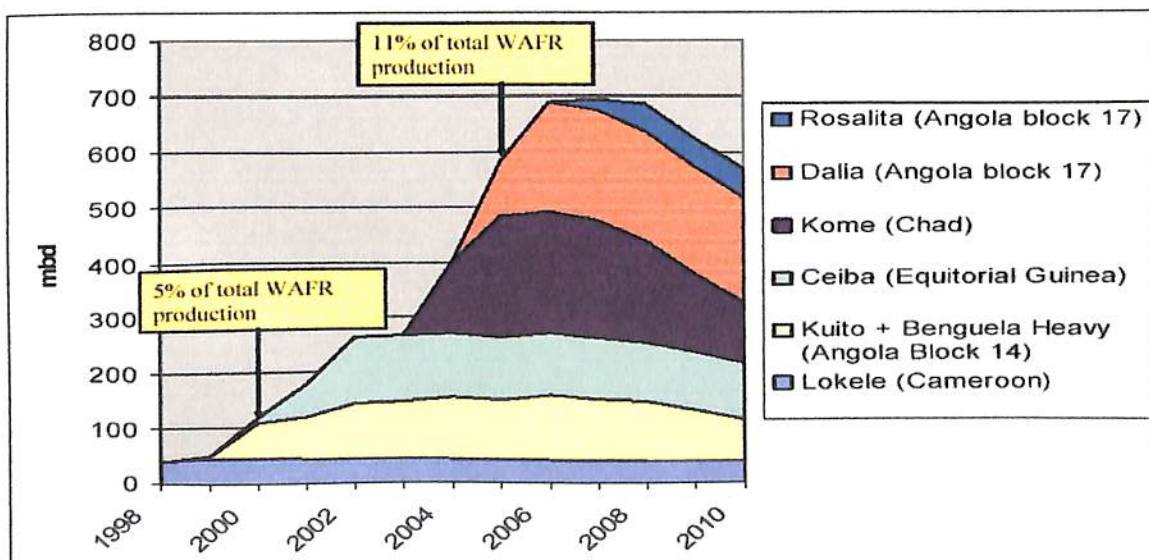
- There is no known HAC production in the Middle East (except 1 field offshore Saudi), Mediterranean or the FSU. Fujairah is the only Middle East refinery processing HAC's.

**High Acid crude supply:** There is a sizeable and increasing global supply of HAC's  
 6.3 million Bbls per day -2002  
 8.1 million Bbls per day -2005  
 9.2 million Bbls per day -2010 (expected).

**Economics of running High Acid Crudes:**

- Since these are available at cheap the investment cost of crude oil will be increasing.
- . Sizeable and increasing supply of HAC
- . Limited ability or willingness to run HAC
- Solutions are available to the HAC problem – Metallurgy - Corrosion inhibition etc.

**High Acid crude oil production and supply in various places in different years**

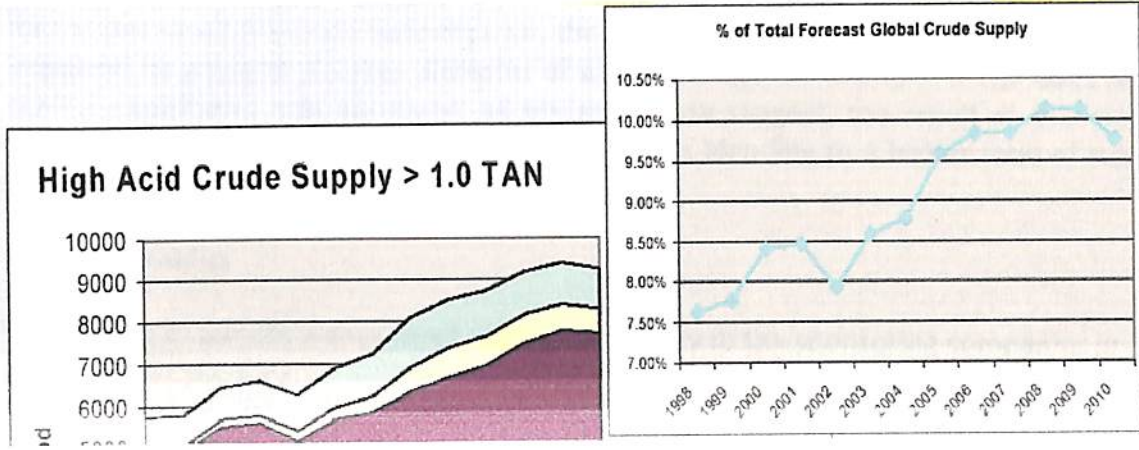


Source: www.petroindustry.com



## West Africa (WAFR) HAC (>1.0 TAN) Production

Source: [www.chevron.com](http://www.chevron.com)



A second area of benefit is the improvements in the operational limits of the existing refinery. The results will provide data upon which decisions about increased through put can be made more predicatively. For example, the data may show that through put can be increased to a desired amount if the alloy of critical components is increased to allow for the increased flow rate (velocity). Or, the data may show that a transfer line can be improved by going to a larger diameter of a lower alloy, for example. If H<sub>2</sub>S does help control naphthenic acid corrosion, as literature data suggest, the result of this study may show the economic value to a given refinery in blending to a higher ratio of sulfur crudes to naphthenic acid crudes.

### 3. Fringe Benefits

A third area of benefit is that which will come directly to the sponsoring companies in terms of the following:

1. Knowledge of the interaction between naphthenic acids and various crude oil feed stocks as a basis for engineering decisions as well as future in-house investigations.
2. Availability of highly characterized and reproducible naphthenic acids on a commercial basis for their in-house research efforts and testing programs

### The factors or parameters affecting Naphthenic Acid Corrosion

The chemistry, content, boiling point distribution, and decomposition temperature of naphthenic acid and sulfur compounds have a direct effect on the high temperature corrosion of the distillation unit. Process conditions such as velocity, degree of vaporization and temperature, and alloy composition are also important factors affecting the corrosion process.

#### (1).Naphthenic Acid Chemistry

Naphthenic acid is a generic name used for all the organic acids present in crude oils. Most of these acids are believed to have the chemical formula  $R(CH_2)_nCOOH$  where R is a cyclopentane ring and n is typically greater than 12. However, a multitude of other acidic organic compounds are also present and not all of them have been analyzed to date. Because of this chemical nature of naphthenic acid they lead to corrosion. So, it is better to determine the naphthenic acid content through laboratory tests.

There are several methods for the determination of naphthenic acid content. Unfortunately, these methods lead to different results.

1. The ASTM procedures for Total Acid Number (TAN) also called Neut number were not developed for crude oils. They were used for determining the oxidation of petroleum products and lubricants. ASTM D974 is a colorimetric

titration method and has a reproducibility of 15%. ASTM D664 is a potentiometric titration method with reproducibility of 20 to 44% depending on the end point (buffer or inflection), type of oil (used or fresh), and titration mode (automatic or manual). Inorganic acids, esters, phenolic compounds, sulfur compounds, lactones, resins, salts, and additives such as inhibitors and detergents interfere with both methods. In addition, these ASTM methods do not differentiate between naphthenic acids, phenols, carbon dioxide, hydrogen sulfide, mercaptans, and other acidic compounds present in the oil.

2. In the UOP procedures, sulfur compounds are removed before analysis of acid number. UOP 565 is a by potentiometric method and UOP 587 is a colorimetric method.
3. In the chromatographic method or Mobil method naphthenic acid are expressed by weight percent. The acids are extracted by liquid chromatography and then analyzed by IR spectroscopy. Unfortunately, the instrument is calibrated with standard naphthenic acid, which might not have the same composition and molecular weight as the sample. Thus, the weight percent can be used for comparison purpose only.
4. Another variation of the chromatographic method is the Naphthenic Acid Number (NAN) or Naphthenic Acid Titration (NAT) whereby the sample is extracted by chromatography and then titrated per ASTM D664.

The Fast Atom Bombardment Mass Spectroscopy (FAB-MS) analysis determines the molecular weight distribution of the naphthenic acid extracted from the oil. This method is mainly used to fingerprint crude oils from around the world. Research is still underway to apply this technique to corrosivity prediction.

The naphthenic acids are most active at their boiling point and the most severe corrosion generally occurs on condensation. Crude oils with a TAN higher than 0.5 and cuts with a TAN higher than 1.5 are considered to be potentially corrosive between the temperature of 450 to 750F. However, there are many cases including high velocity, high TAN and others where these rules of thumb break down and correlating the TAN of specific cut to their corrosivity is still far from being reached.

## **(2).Sulfur Compounds**

Other than carbon and hydrogen, sulfur is the most abundant element in petroleum. It may be present as elemental sulfur, hydrogen sulfide, mercaptans, sulfides, and polysulfides. The total sulfur content is generally analyzed with ASTM D4294 method using X-ray fluorescence. Halides and heavy metals interfere with this method.

Sulfur at a level of 0.2% and above is known to be corrosive to carbon and low alloy steels at temperatures from 230 ° C (450 ° F) to 455 ° C (850 ° F). When sulfur is the only

contaminant, McConomy curves, with the help of correction factors, are used to predict the relative corrosivity of crude oils and their various fractions as well as the effect of operational changes on corrosion rates already experienced in the field. Sulfur content of the cuts and more advanced analysis of specific sulfur compounds such as H<sub>2</sub>S, mercaptans, sulfides, polysulfides when correlated to field data appear to help predict crude corrosivity much better. Hydrogen sulfide evolution tests were also used to predict crude corrosivity. As early as 1953, it was found that the H<sub>2</sub>S evolved at 850F correlated very well with experienced corrosion of 21 out of 22 oils tested. Piehl's work also showed that there was a good correlation of corrosion with H<sub>2</sub>S evolution. A standard procedure for the hydrogen sulfide evolution with temperature is not currently available.

At high temperature, especially in furnaces and transfer lines, the presence of naphthenic acids may increase the severity of sulfidic corrosion. The presence of these organic acids may disrupt the sulfide film thereby promoting sulfidic corrosion on alloys that would normally be expected to resist this form of attack (i.e., 12 Cr and higher alloys). In some cases, such as in side cut piping, the sulfide film produced by H<sub>2</sub>S is believed to offer some degree of protection from naphthenic acid corrosion.

### (3).Temperature

In general, corrosion rate of all alloys in the distillation units increases with increase in temperature. Naphthenic acid corrosion occurs primarily in high velocity areas of crude distillation units in the 220 to 400 ° C (430 to 750 ° F) temperature range. No corrosion damage is usually found at temperatures above 400 ° C (750 ° F), most probably because of the decomposition of naphthenic acids or protection from the coke formed at the metal surface.

### (4).Velocity

Velocity and more importantly wall shear stress is a main parameter affecting NAC. Fluid flow velocity lacks predictive capabilities. Data related to fluid flow parameters such as wall shear stress and Reynolds's Number is more accurate because the density and viscosity of liquid and vapor in the pipe, the degree of vaporization in the pipe and the pipe diameter are also taken into account.

To estimate wall shear stress, it is necessary to know the density and viscosity of the liquid and the vapor, the degree of vaporization and the pipe diameter. The chart of Diameters versus Roughness and chart of Friction Factors (Moody Diagram) are also needed. First, the Reynolds's Number for field flow conditions in a pipe is calculated by the following equation:

$$R_e = D \rho V / \mu \quad \text{where } R_e = \text{Reynolds's Number}$$

$\rho = \text{density of fluid (Kg/m}^3\text{)}$

$D = \text{diameter of pipe (m)}$

$V = \text{velocity of fluid (m/s)}$        $\mu = \text{dynamic viscosity (Kg/m.s, 1 Poise = 0.1 Kg/m.s)}$

With the Reynolds number known, the Relative roughness ( $e/D$ ) is obtained from the chart of Diameters versus Relative Roughness and the Friction factor ( $f$ ) is then obtained from the Moody Diagram. Finally, the Shear Stress ( $t$ ) is calculated by the following equation:

$$T = f L V^2 / 2$$

To use plant corrosion data of a specific crude or blend as a way to predict its corrosivity for another plant: (1) Calculate shear stress for plant with known corrosion data, (2) calculate shear stress for plant which is planning to run the specific crude or blend and (3) compare both shear stress. Corrosion rates are directly proportional to shear stress. Typically, the higher the acid content, the greater the sensitivity to velocity. When combined with high temperature and high velocity, even very low levels of naphthenic acid may result in very high corrosion rates.

#### **(5). Materials of Construction**

Above 288 ° C (550 ° F), and very low naphthenic acid content, 5 Cr or 12 Cr cladding is recommended for crudes over 1% sulfur when no operating experience is available. When hydrogen sulfide is evolved, an alloy containing a minimum of 9% chromium is preferred. In contrast to high-temperature sulfidic corrosion, low-alloy steels containing up to 12% Cr do not seem to provide benefits over carbon steel in naphthenic acid service. 316 SS (with 2.5% Mo minimum) or better 317 SS with a higher Mo content (3.5% minimum) cladding of vacuum column is recommended when TAN is above 0.5 mg KOH/g and in atmospheric column when the TAN is above 2.0 mg KOH/g.

## **Review Page**

High temperature crude corrosivity of distillation units is a major concern to the refining industry. The presence of naphthenic acid and sulfur compounds considerably increases corrosion in the high temperature parts of the distillation units and equipment failures have become a critical safety and reliability issue. The difference in process conditions, materials of construction and blend processed in each refinery and especially the frequent variation in crude diet increases the problem of correlating corrosion of a unit to a certain type of crude oil.

With proper mitigation strategies, metallurgy and / or the application of naphthenic corrosion inhibitors, opportunity crudes can now be safely processed. The high acids crude oils which are usually known as "Opportunity Crudes" ..



On the basis of literature survey and some laboratory tests the following mitigation methods were adopted to successfully processing the high acid crude oils.

**Upgrading unit metallurgy-** more resistant alloys can effectively reduce NAC rates.

**Chemical inhibition** is often the most economical choice for mitigation of NAC.

**Crude oil blending** – addition of low acid crudes to high acid content crudes also reduces this problem by diluting crude oil.

Besides all these mitigation techniques corrosion monitoring is also most important to take relevant prevention techniques. The advanced techniques in the field of studies of reduction of naphthenic acid corrosion are as described in the coming headings.

## **2. NAPHTHENIC ACID CORROSION OF MILD STEEL IN THE PRESENCE OF SULFIDE SCALES FORMED IN CRUDE OIL FRACTIONS AT HIGH TEMPERATURE**

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### **Introduction**

Increasing demand on the oil market has raised interest in oils with high naphthenic acid (NAP) concentration. These oils were previously considered of lower quality due to their corrosive character. Processing such oils at elevated temperatures encountered in refineries (300-350°C) may cause aggressive corrosive attack on the inside walls of equipment such as pipes and distillation towers.

Naphthenic acid corrosion attack is a non aqueous corrosion process and can be retarded by sulfur containing compounds inherently present in crude oil fractions in the form of soluble sulfides. Although these sulfides can be corrosive as well, they can also form iron sulfide scale on the metal surfaces potentially offering a degree of protection against naphthenic acid attack.

However the iron sulfide scales can be removed from metal surfaces under the combined effects of high velocity flow and NAP attack. This study has focused on the role of iron sulfide scales formed in different crude oil fractions on samples made from mild as well as chromium containing steels. They were exposed to naphthenic acid attack under high flow rates at high temperature.

### **About the study**

This study starts from the hypothesis that sulfur containing compounds mitigate corrosion by forming iron sulfide scale on the metal surface. However this effect diminishes under combined effect of strong acidic attack and high velocity when the scale loses its protectiveness.

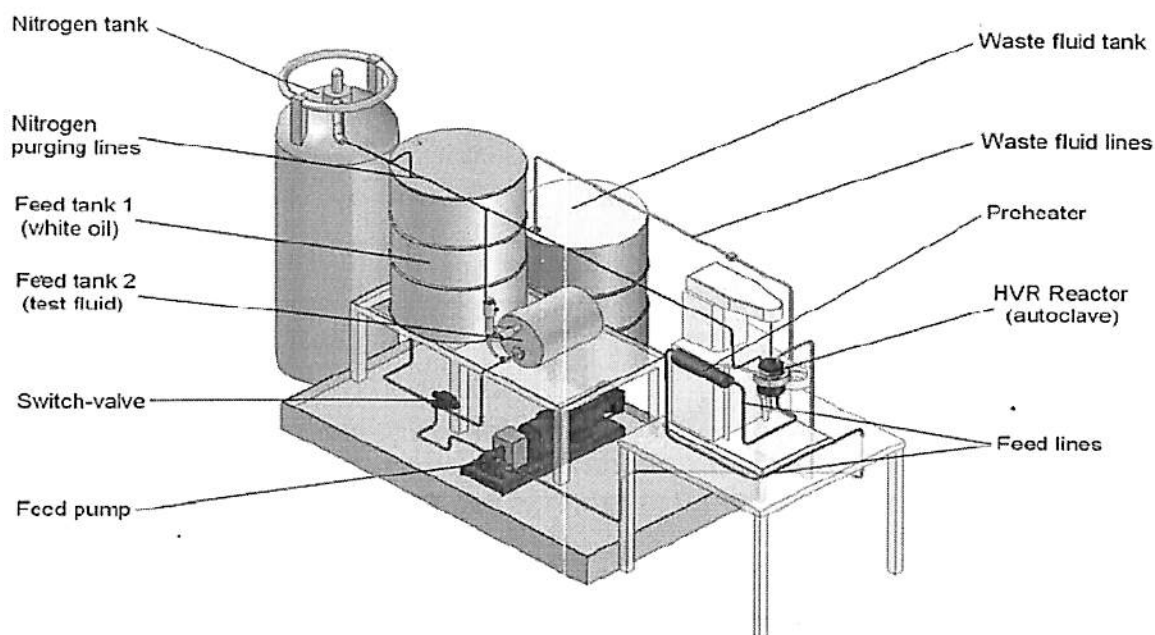
In order to verify this hypothesis it was decided to form iron sulfide scales and attack ("challenge") them with crude oil fractions containing naphthenic acids under experimental conditions close to those found in distillation towers.

In the experiments described below the iron sulfide scale was performed on steel samples by using real crude oil fractions containing significant amounts of sulfur compounds and little naphthenic acid. These were then "challenged" by model oils containing no sulfur but with higher naphthenic acid content.

The following sections will describe the experimental setup and procedures in detail followed by a discussion of the results for both model oil and real fraction tests.

### **Experimental Setting and Procedure**

Experimental apparatus used for naphthenic acid corrosion tests called the High Velocity Rig (HVR) is schematically presented in FIGURE 1.



**FIGURE 1. High Velocity Rig used for naphthenic acid corrosion tests under high velocity and temperature conditions. The HVR autoclave was used for challenging with naphthenic acids preformed iron sulfide scales on CS and 5Cr samples.**

### **The Principle**

The HVR is designed to reproduce the flow, pressure, temperature and shear stresses conditions usually encountered in liquid side streams of atmospheric and vacuum distillation units.

The main part of the HVR loop is an autoclave where ring samples made from steel are mounted on a rotating cylinder and flushed with testing fluids at high temperature. Operating pressure of the autoclave is from 0 to 500 psig and temperature up to 370°C (700°F). The fluid flow rate provided by the HVR pump is controllable over the range of 5 to 20 cm<sup>3</sup>/min. Ring samples are rotated in the autoclave at 2000 rpm during the experiments. The entire experimental rig and the fluids used are purged with an inert gas before the tests.

The test protocol calls for pre-treating (pre-sulfidation) the steel ring sample *ex-situ* in sulfur containing fluids which form iron sulfide scale on the steel surface. Ex-situ pre-sulfidation of the steel rings is done in separate autoclaves at the same high temperature 370°C (700°F) as used in the subsequent challenge phase. The HVR is used for challenging the pre-sulfided steel rings in a sulfur-free environment. All the tested crude oil fractions and their total corrosive sulfur and acidic contents are listed in TABLE 1.

**TABLE 1**

### **MODEL OILS AND REAL CRUDE OIL FRACTIONS USED IN SULFIDATION-CHALLENGE TESTS**

Tested Fluid	Total Acid Number (mg KOH/gr oil)	Corrosive Sulfur (%wt)
1. White Oil (Model oil)	0	0
2. Yellow Oil (Model oil)	0	0.25
3 Naphthenic acids	~230	0
4. Fraction A	1.75	0.18
5. Fraction B	<0.1	0.6
6. Fraction C	1	1.51
7. Fraction D	0.2	0.7
8. Fraction E	0.2	0.92

Note: Fluids 1 and 2 have no appreciable naphthenic acid or metals. For the results in Figures 2-5, the TAN level in fluid 2 was increased to 0.1 using commercial naphthenic acid.

Ring samples are fabricated from carbon steel (CS) and 5Cr steel (5Cr, 0.5 Mo) and with the outer diameter OD = 81.75 mm. Six ring samples were used in every test (3 of each steel type). Before every test, samples were polished using 400 and 600-grit silicon carbide (SiC) paper under isopropanol flushing, then dried with nitrogen, and finally weighed before being inserted into the autoclave. Corrosion rates were evaluated by sample weight loss measured as the difference between sample weight before and after the tests. Samples final weight was evaluated at the end of every test by removing iron sulfide scale completely from the steel surfaces using mechanical and chemical means. The very loose scale was mechanically removed from sample surfaces by rinsing them with organic solvents (toluene and acetone) and then brushing with a stiff plastic brush. At the end of mechanical cleaning samples were weighed again. Strongly adherent scale that survived the mechanical cleaning was chemically removed later using Clarke solution<sup>(2)</sup> (ASTM G 1-90) when the final weighing was done. Two samples (one of each steel type) were saved at the end of every test and prepared for further analysis that included scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX).

### Experimental Data Calculations

Corrosion rates of the samples were evaluated by weight loss, calculating the difference of samples weight before and after the test, according to Equation (1), with the final result being expressed in *mm/y*:

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

where

CR - the corrosion rate [mm/y],

IW - initial weight [kg],

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

$\rho_{Fe}$  - iron density [kg/m<sup>3</sup>],

$A_c$  - sample area exposed to acidic oil during challenge (outer ring area) [m<sup>2</sup>],

$t$  - time of the experiment [hr].

Because the experiments consist of two separate phases *i.e.* sulfidation followed by challenge, final corrosion rates have to express exclusively the effect of NAP acid corrosion. Therefore in Equation (1) initial weight  $IW$  used for calculations represents the difference between initial weight of samples before any experimental phase and the weight loss corresponding to separately run sulfidation phase. Thus the weight loss of interest *i.e.* caused by naphthenic acids attack excludes the weight losses of presulfidation. From weight loss measurements, a hypothetical scale thickness was calculated for both "total" and "adherent" scale by assuming that the iron sulfide scale was perfectly compact and dense. It is referred to below as the "calculated scale thickness". Total scale includes both the loose scale that could be removed by simple mechanical means (rubbing, brushing) and the strongly adherent scale which could be removed only chemically (Clarke solution). The total scale was calculated with Equation (2) using weight difference between weight after solvent rinsing and final weight of the sample.

$$\delta_T = \frac{(W_{Rinse} - FW) \times 10^6}{\rho_{FeS} \times A_T}$$

where

$\delta_T$  - thickness of total scale [ $\mu\text{m}$ ],

$W_{Rinse}$  - rinse weight, weight after solvent rinse, rubbing, brushing [kg],

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

$\rho_{FeS}$  - iron sulfide density [ $\text{kg}/\text{m}^3$ ],

$A_T$  - total area of the sample (total ring area) [ $\text{m}^2$ ].

Finally, the adherent scale was evaluated using the weight difference between sample weight after rubbing (mechanical removal) and sample final weight after last cleaning with Clarke solution ("clarking") - Equation (3).

$$\delta_A = \frac{(W_{Rub} - FW) \times 10^6}{\rho_{FeS} \times A_T}$$

where

$\delta_A$  - thickness of adherent scale [ $\mu\text{m}$ ],

$W_{Rub}$  - rinse weight [kg],

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

$\rho_{FeS}$  - iron sulfide density [ $\text{kg}/\text{m}^3$ ],

## Conclusion

The final corrosion rates for all the tested crude fractions and model oil are summarized in Figure 5 for carbon steel and Figure 6 for 5Cr steel. Both figures include also the "pure TAN" corrosion rate that was generated under pure naphthenic acids attack in the



absence of sulfur, representing the maximum expected corrosion rate under the given set of conditions.

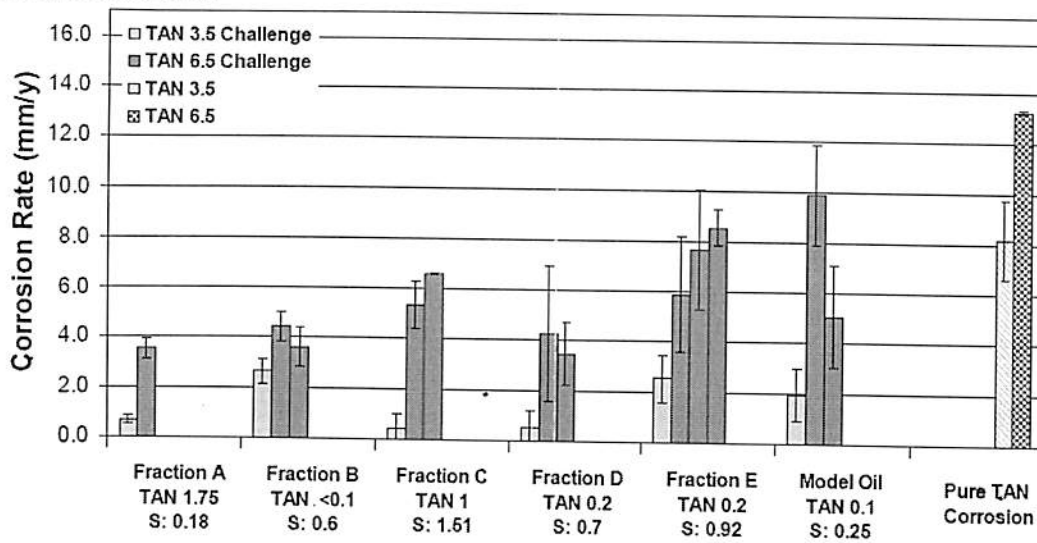


FIGURE 5. Corrosion rates for CS samples that were pre-sulfidized in autoclave with crude oil fractions and then challenged at high velocity with naphthenic acids at TAN 3.5 and TAN 6.5. Plot includes also corrosion rates generated with pure naphthenic acids dissolved in white oil (sulfur free environment) at identical temperature and velocity conditions to all other tests.

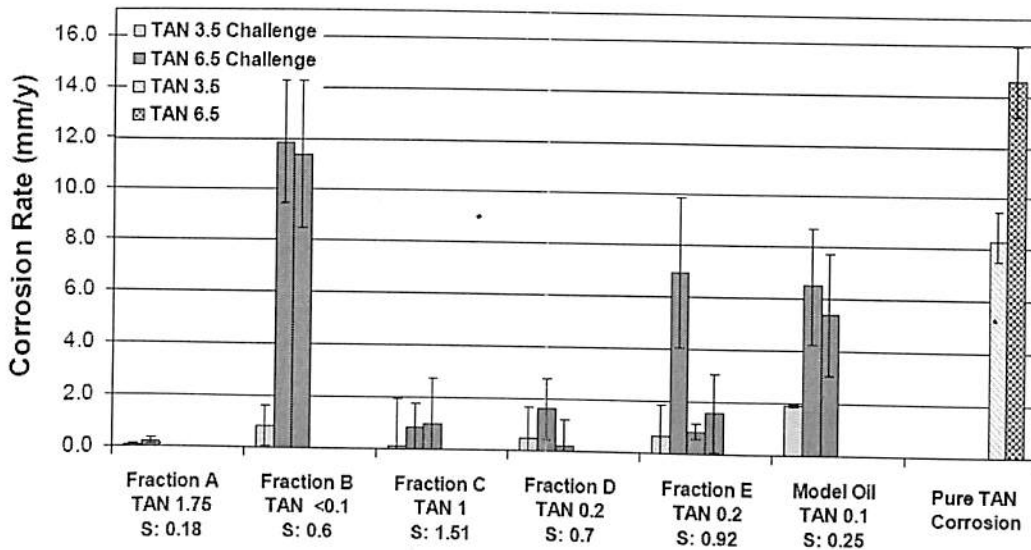


FIGURE 6. Corrosion rates for 5Cr samples that were pre-sulfidized in autoclave with crude oil fractions and then challenged at high velocity with naphthenic acids at TAN 3.5 and TAN 6.5. Plot includes also corrosion rates generated with pure naphthenic acids dissolved in white oil (sulfur free environment) at identical temperature and velocity conditions to all other tests.

Some general conclusions can be drawn:

- For all crude oil fractions tested as well as the model oil, the pre-sulfidation resulted in sulfide scale which was somewhat protective resulting in a lower corrosion rate compared to that seen on a bare metal.

- Corrosion rates seen after pre-sulfidation with crude oil fractions were different and varied unpredictably when compared to those obtained in a model oil.

The following observations can be made upon reviewing of FIGURE 5 for carbon steel:

- The TAN 6.5 challenge always resulted in a higher corrosion rate than the TAN 3.5 challenge.
- None of the crude oil fractions have formed a sulfide scale that could withstand the TAN 6.5 challenge.
- When considering the TAN 3.5 challenge, pre-sulfidation with crude oil fractions A, C, D did provide considerable protection. Scale formed in crude fractions B, and E provided similar but reduced level corrosion protection. Thus TAN 3.5 challenge differentiates the protectiveness of iron sulfide scales formed on carbon steel.

From FIGURE 6 for the 5Cr steel it can be seen that:

- The TAN 6.5 challenge results in a higher corrosion rate than the TAN 3.5 challenge for crude oil fraction B. For the other crude oil fractions, results for the different TAN values are close within experimental variability.
- Crude oil fractions A, C, D formed protective scales which were very protective and withstood the challenge by TAN 6.5.
- When considering the TAN 3.5 challenge, pre-sulfidation with crude oil fractions A, C, and D resulted in very good protection and very low corrosion rate while pre-sulfidation with crude oil fractions B and E did significantly reduced the corrosion rate but not as much as with the other crude oil fractions.
- Comparing the two challenges data it is obvious that in case of 5Cr steel it was TAN 6.5 challenge that differentiate the protectiveness of iron sulfide scales formed on steel surface.

Test results demonstrated that it is difficult to predict protectiveness of iron sulfide scale based only on sulfur content of crude oil fractions generating the scales. As a general conclusion, it can be said that in the case of all crude oil fractions tested, the iron sulfide scales could protect the steel against TAN 3.5 challenge to a similar degree. The TAN 6.5 challenge clearly differentiated between more and less protective scales.

## **2.2 GE RCM Allows Refinery to Precisely Measure Pipe Corrosion When Processing High Acid Opportunity Crudes**

**The principle:**

The operation of this system is based on the measurement of changes to electrical potential drop caused by the removal of material due to corrosion. The system developed has been shown to be capable of acquiring accurate corrosion data during plant operations. Measurement process data acquired from plant operation and laboratory experiments are as discussed below.

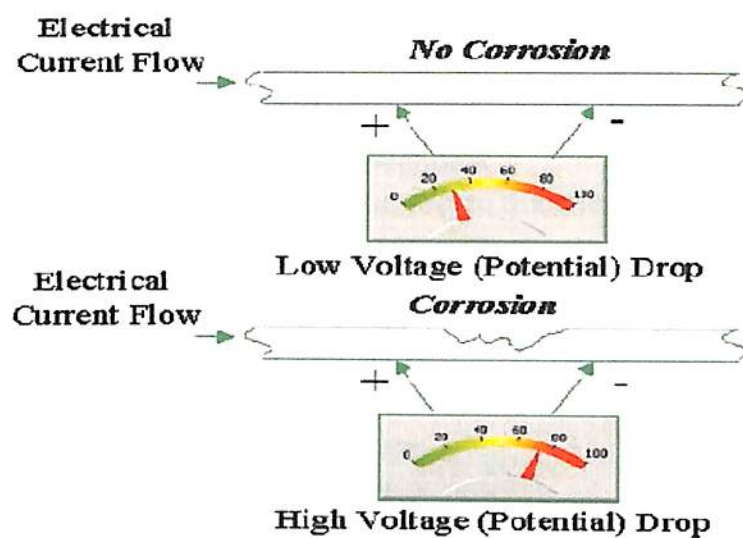
**Back ground of invention:**

In piping systems, this naphthenic acid corrosion can lead to leakage of the vaporized crude oil, an extremely dangerous event. Many companies, such as GE Water and process Technologies, have developed corrosion mitigating chemicals that are injected into the flow of the vaporized oil providing protection to naphthenic acid corrosion. Occasionally, regions of the crude unit are not suitably protected from these chemicals and it becomes necessary to be able to detect this type of corrosion so that refineries can process the high acid crude oil safely. Typically, the remaining wall material is measured occasionally using ultrasonic thickness inspection. These measurements can be made during plant outages. Thickness measurements taken using ultrasonic methods during plant operations require a great deal of planning in order to insure the safety of the inspector. For high temperature applications, it would be preferred to make use of an online inspection system. Online measurements allow the facility operators to understand the condition of the assets in the refinery and make decisions about how best to safely operate the facility. The temperatures of the components in the crude unit do not allow the use of traditional online inspection probes such as ultrasonic probes. This type of online measurement requires a probe to remain viable at temperatures reaching 900 degrees F and provide reliable measurements for a period of up to 20 years.

To accomplish this measurement, a resistance corrosion monitoring (RCM) system was developed by GE. This system makes use of the component, itself, as the probe. In the case of piping, the wall of the pipe is the probe and the system measures the electrical resistance within the wall of the pipe. As the wall thickness changes due to corrosion, the electrical resistance changes. This system uses high temperature wiring and attachments to connect the data acquisition system to the pipe. Electrical current, generated by a low voltage high amp hour rated battery, provides the means to determine the electrical resistance of the pipe or vessel wall of a specified region where electrical attachments provide for the measure of electrical potential. A plurality of electrical attachments, in the region of interest on the vessel or pipe, provides the signal path to the data acquisition system. The data acquisition system developed for this measurement provides for online monitoring of the measurements and can provide data to the facility operator indicating severe corrosion issues. The remainder of the

publication will be devoted to data collected from a prototype system and the means to evaluate the data to provide a reliable measure of the remaining wall thickness in the component displaying naphthenic acid corrosion.

**Results:** Use of the electrical resistance of the material has been used as a means to evaluate the condition of material [as shown in figure]. This method of material evaluation makes use of current flowing through the material to be evaluated. Along the axis between the point of current supply and ground, a series of pairs of electrodes are used to measure the voltage or potential drop between the pair of electrodes. The following figure shows a schematic example of the potential drop measurement.



Schematic demonstration of the resistance corrosion measurement

The voltage measured in using this technique is typically in the microvolt range, depending on the current injected and the geometry of the component. Commercially available systems have been shown to be subject to measurement noise caused by a variety of sources. Noise sources can include thermocouple voltage, current fluctuations as well as electromagnetically induced noise from plant operation. These noise sources can produce voltages equal to and sometimes greater than the voltage indicating changes to the material thickness. With these noise sources in mind, the GE acquisition system was designed to acquire the data from the component with the sensitivity to the microvolt signal level while reducing the sensitivity to noise sources. The system can be configured to provide up to 1 square meter of material inspection coverage. Typically, two or more of the system channels available are used as reference channels. The reference data acquisition channels are connected to the reference sample that is attached to the component and is made from the same material as the component. The reference sample is at the same temperature as the component but is suspended to allow reference measurements prior to allowing the current to enter the test component.



The acquisition system contains a microprocessor to control the acquisition, the high current switching, analog to digital conversion and data storage. The data is collected on a conventional USB memory stick for transport to an analysis computer. All system channels are sampled simultaneously rather than multiplexed. Although this makes for a larger system platform, it allows for all channels to detect signal from the component without concern for fluctuations in current flow in the component. It is well known that when batteries are used for high current applications, the voltage produced by the battery will “sag” or diminish in value. In multiplexed systems, it is typical that the battery is required to supply high current for the period of time required to switch through all channels completing the data acquisition cycle. By simultaneously acquiring all channels of data, the battery is required to produce high current for short period of time. The method of acquisition avoids battery voltage sag as well as preserves the battery charge for subsequent acquisition periods.

The steps involved in this method are

- (1). Calculate the potential drop from the component.
- (2). Normalization of component data with respect to the reference sample
- (3). Determination of material removed by corrosion

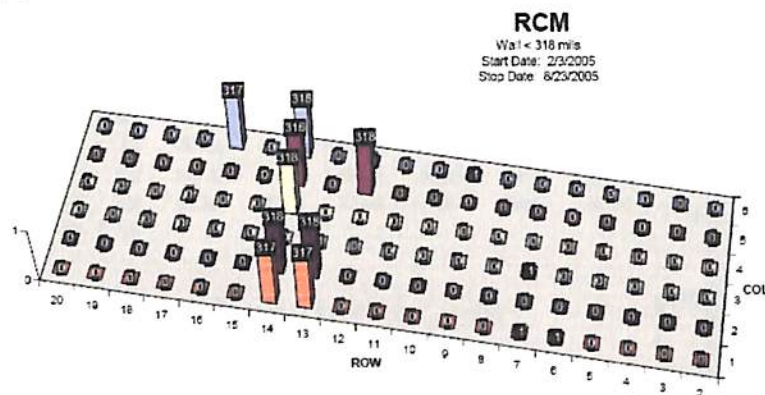


Figure 1: RCM Results Wall Thickness

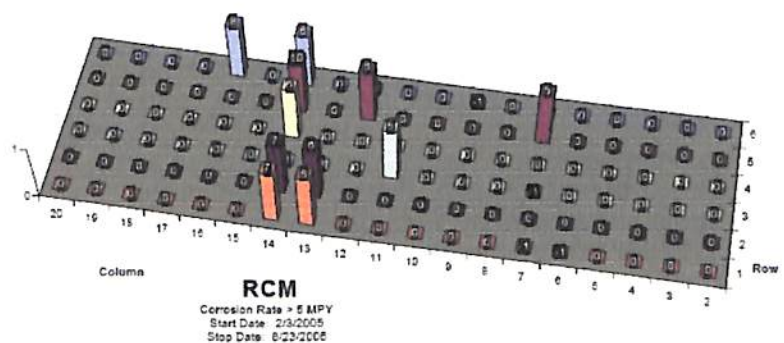


Figure 2: RCM Corrosion Rates

**Benefit of this method:** The resistance corrosion monitoring system developed at GE has been proven to be an effective tool for the determination of remaining wall thickness of components subject to corrosive attack. This system has been shown to be sensitive to the changes in material thickness while insensitive to plant and facility



noise. The design of the system allows for online measurement of material thickness at temperatures reaching as high as 900 degrees F and can be programmed to provide the data necessary for assisting the safe refining of high acid crude oil.

### Process Capability Analysis for ER Probe Cor

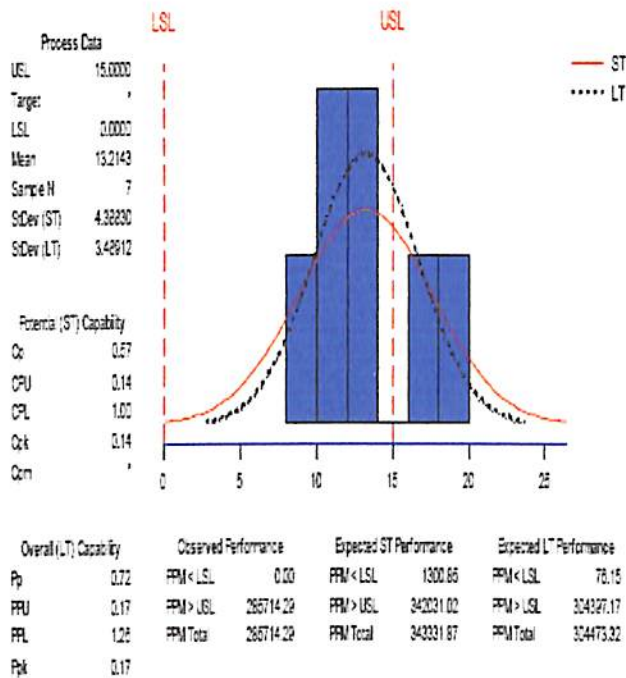


Figure 3: Process Capability Analysis for ER Probe Corrosion

### RCM % Change

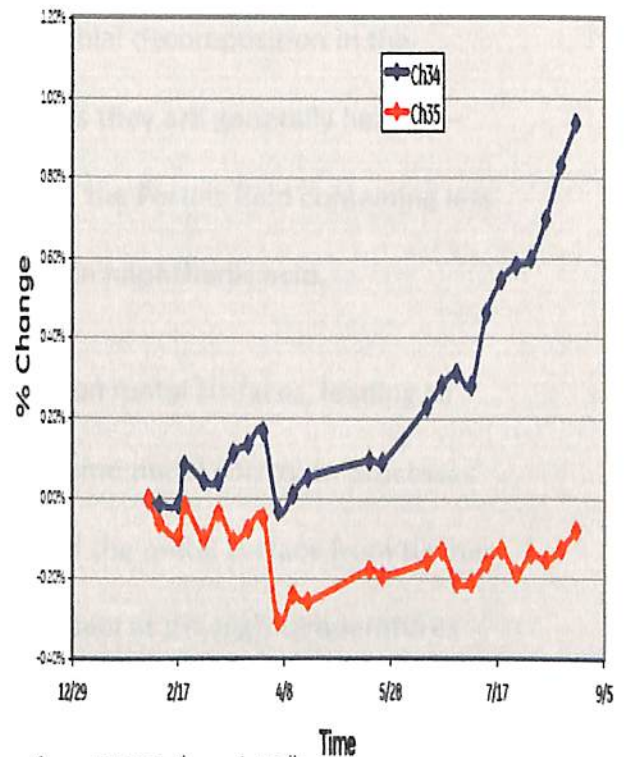


Figure 4: RCM % Change in Wall Loss

## 2.3 BP-Advanced methods of Continuous monitoring and inhibition of Naphthenic acid corrosion

**Introduction:**

Oil refineries are designed to run on a range of blends of crude oil.

Feedstock by buying in a variety of different crude, refinery operations can be optimized, giving the flexibility to keep processing units full to meet changing market requirements.

Not surprisingly, oil companies are constantly looking for technical innovations that will give their purchasing and refining strategies an economic edge.

One such project, successfully undertaken by BP and which promises to benefit refineries around the world, has been to investigate ways of safely including more 'acid crudes' in the blends being processed. Acid crude oils are found in many parts of the world in shallow oil fields that have experienced microbial decomposition in the reservoir. The resulting crude oils are cheaper to buy as they are generally heavier – more viscous – than standard blends such as that from the Forties field containing less desirable hydrocarbons, and, more significantly, contain **naphthenic acid**.

This aggressive compound engages in chemical attack on metal surfaces, leading to corrosion of refinery pipe work and vessels. Unlike some metal corrosion processes which tend to produce a semi protective scale to shield the metal surface from further corrosion, naphthenic acid reacts with iron in carbon steel at the high temperatures found in refining operations to form iron naphthenate, a compound soluble in oil. The metal surfaces are therefore continually exposed to more of the acid, leading to abnormally high corrosion rates. In areas where there are high fluid velocities and a vapour-liquid hydrocarbon mix, pitting soon develops as high speed droplets of

hydrocarbons containing the acids rain on the metal surface. Some stainless steels can withstand the attack but in most cases, upgrading the metallurgy to cope with naphthenic acid would be too expensive to justify the refining of cheaper acid crudes. As a result the proportion of acid crudes blended into feeds is usually kept below a certain limit defined by the total acid number or TAN (the number of milligrams of Potassium hydroxide required to neutralize a certain quantity of the acidic material). The refining industry commonly applies crude oil TAN limits of 0.3 to 0.5. BP, however, was keen to see if the TAN limits could be raised without increasing the risk of disruption due to corrosion of equipment.

To Monitoring the corrosion BJ identified a device which had been successfully used to monitor online sub sea pipelines and other generally inaccessible offshore systems for corrosion. This device was originally designed for upstream applications below 502C, there followed 18 months' further development work with the manufacturer to give us the reliability we needed at refinery conditions and temperature, around 350'C.

The system, known as the Field Signature Method (FSM) was developed by Norwegian corrosion specialist company, Corr Ocean of BJ. Ten of the newly developed high temperature FSM-IT units are located at strategic locations around the Grange mouth Testing Refinery of BJ..

### **Description of the method:**

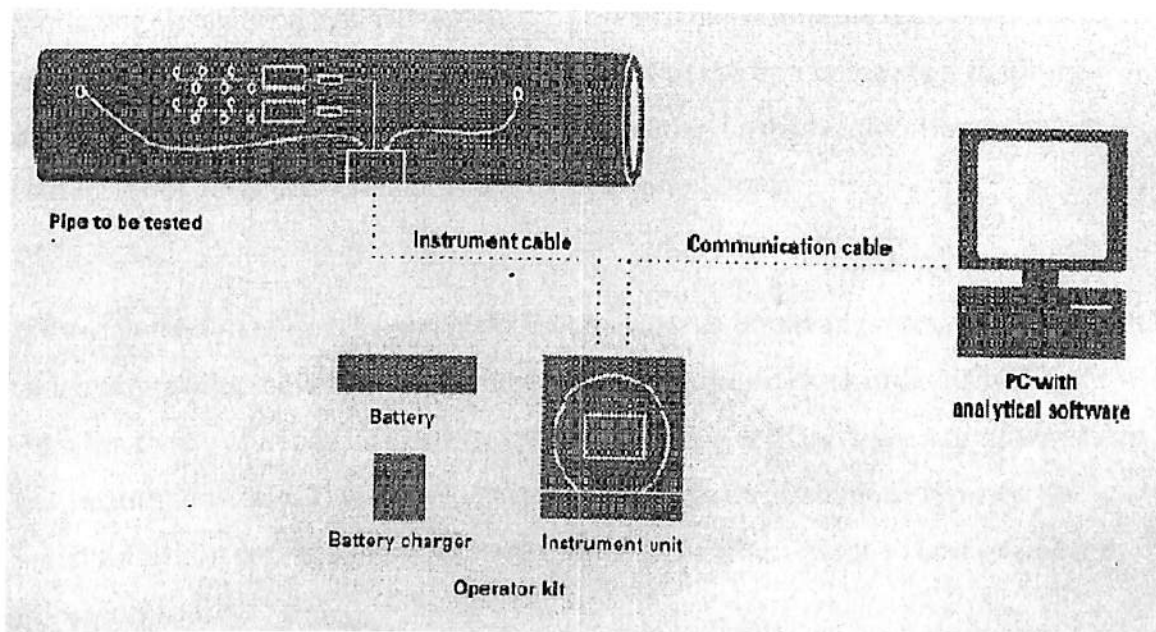
FSM (Field Signature Method) is a non-intrusive method for monitoring corrosion, erosion or localized attacks/cracks inside pipelines, process piping or vessels.

The Field Signature Method has been in industrial use since 1991, and used subsea since 1994. The field signature method is based on feeding a current through a selected section of the structure to be monitored and sensing the electric field pattern by measuring small potential differences set up on the surface of the monitored object<sup>1</sup>. The first measurement in time (signature) is unique to the geometry of the object, and later measurements are compared to this first reading. When general or local corrosion takes place, the pattern of electric field will change and can be compared to the

signature. By proper interpretation of the changes in the potential differences, conclusions can be drawn, e.g. regarding general wall thickness reduction or localized corrosion.

Each FSM sensor consists of a matrix of up to 50 metallic pins which are welded to the outer wall of the pipe, hedgehog-fashion in a rectangular pattern. A small current is passed from one side of the matrix to the other and the voltage developed across each pin and its neighbor is monitored. This gives a unique electric-field signature which depends on the geometry and thickness of the pipe and the electrical conductivity of the metal.

Any changes in the field - or signature - resulting from internal corrosion or erosion are revealed as a drop in voltage across the sensor pins. To provide reference measurements and additional assurance on pipe integrity, conventional electrical resistance probes of measuring corrosion were also inserted into the pipelines.



Schematic of the Field Signature Method(FSM) equipment used to monitor NA corrosion

The FSM data, compensated for temperature changes, are processed by proprietary software to give a three-dimensional map of the metal thickness. In addition to giving early warning of the effects of process changes on corrosion conditions; the

## FSM

devices offer a number of practical advantages. The non-intrusive devices are located outside the harsh environment of the process fluids and are easily fitted to any part of a piping system vessel wall, covering a relatively large area to provide greater accuracy of measurement. CorrOcean claims the system is sensitive enough to detect pitting in metal surfaces measuring less than one five-thousandth of the wall thickness. For instance, as little as 0.0125 millimeters of metal loss can be detected in a pipewall 12.5 millimeters thick.

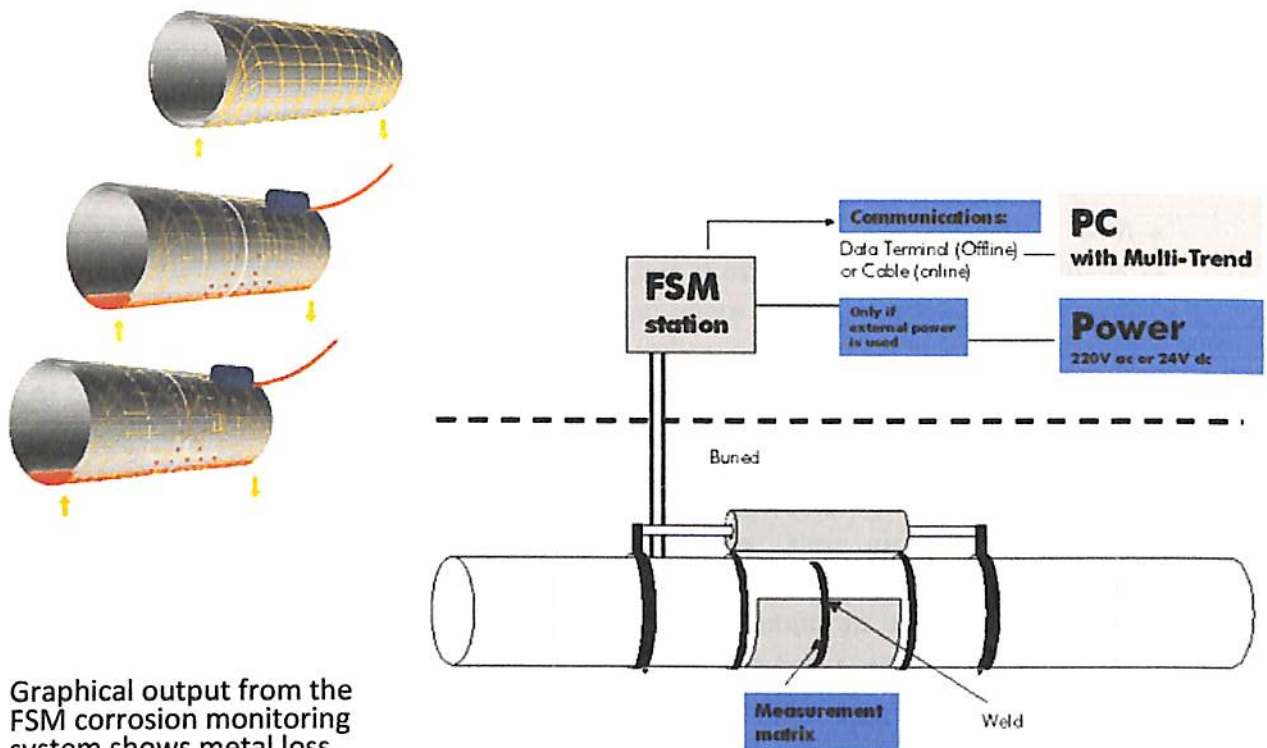
## Passive resistance

Along with the corrosion monitoring programmed, the other key activity within the project was to evaluate the effect of injecting novel 'passivating' chemicals into the process stream that would inhibit the naphthenic acid corrosion reaction. One way of protecting steel piping against naphthenic acid is to blend into the feed other crudes with a high sulphur content. The sulphur reacts with the iron in the steel to form a protective layer of insoluble iron sulphide, preventing further attack. However, this coating is not particularly robust and is easily washed away.

Chemicals manufacturers have developed phosphorus-based additives - or passivators - which can reduce the effects of naphthenic acid corrosion. Passivator chemicals are from the family of phosphate esters which decompose with increasing temperature to form phosphoric acid. This in turn reacts with the weak iron sulphide layer on the metal surface to create a more resilient passive layer which is not so easily removed from the surface.

BP is working with US chemicals supplier Betz Dearborn, employing its passivator chemicals in Grange mouth to establish the most effective ways of using the additives. A foundation dose of the chemicals is applied to the process system before acid crude is introduced, after which a low level maintenance dose is injected via 'quills' projecting into pipe work at strategic locations.

Using additives adds a further cost element. 'Regular use in a refinery would cost hundreds of thousands of dollars per year, so the plan is to inject it only when necessary. Our approach is to monitor the corrosion rate with the corrosion sensors and, if this rises above acceptable levels, apply passivation chemicals to control corrosion and maintain safe operating tolerances.'



Graphical output from the FSM corrosion monitoring system shows metal loss around

the pipe. The plot shows the 20 location of the pin pairs on the matrix, identified by pair row and clock position. The metal loss from the pipe wall is compared with a reference metal, and is identified on the vertical axis identified by parts per thousand metal loss. Benefits of this method is that because it can directly displayed the output data in the form of user understanding the technical people can take the correct action at right time like inhibition of chemical etc and one more benefit is that it can continuously monitoring the naphthenic acid corrosion under high temperature conditions of crude oil processing.



## **2.4 CORRELATION OF HYDROGEN FLUX AND CORROSION RATE MEASUREMENTS CARRIED OUT DURING A SEVERE EPISODE OF CORROSION-EROSION ATTRIBUTABLE TO NAPHTHENIC ACID.**

### **Introduction:**

Over a six month period, UT measurements at a matrix of measurement sites on a Fractionation column indicated that it was suffering from severe internal corrosion. It was decided to monitor hydrogen flux at all measurement points on a frequent basis. The resulting flux profiles broadly co-trended. Time averaged flux and longer term corrosion rates correlated well. In a more sophisticated treatment, flux data was converted into hydrogen activity at the corroding face, to compensate for hydrogen permeation through the steel, thus normalising any variations in steel temperature and thickness.

Again the correlation of activity and shorter term corrosion rate was good, with a correlation factor that was closely comparable to that obtained from laboratory data. In short, the data illustrates that, at temperatures where naphthenic acid corrosion can take place, hydrogen flux may provide a keen indication of the corrosion rate in near real time, with the diffusive delay in flux stabilization upon a corrosive change typically being one hour.

In this study, we focus upon a case of naphthenic acid corrosion (NAC) in an oil refinery visbreaker fractionator, which was monitored over time using hydrogen flux measurements<sup>2</sup>. In this study, we will concentrate on correlation of the corrosion with the flux. Specifically, we will consider the errors and assumptions associated with every step in the sequence from the generation of naphthenic acid corrosion through to the recording of a measurement of a high temperature hydrogen flux. By this means, we will know how confident we can be in assessing NAC from flux measurements and how the correlation between the two should be qualified.

The sequence of chemical reactions and movements of the hydrogen atom leading to flux measurement of NAC is depicted in Figure 1. These can be summarized as follows:

1. Corrosive formation of hydrogen on a corroding steel surface
2. Hydrogen entry into the steel wall
3. Hydrogen permeating the steel wall
4. Hydrogen exit onto an external steel surface
5. Hydrogen association and desorption on the external surface
6. Hydrogen flux measurement.

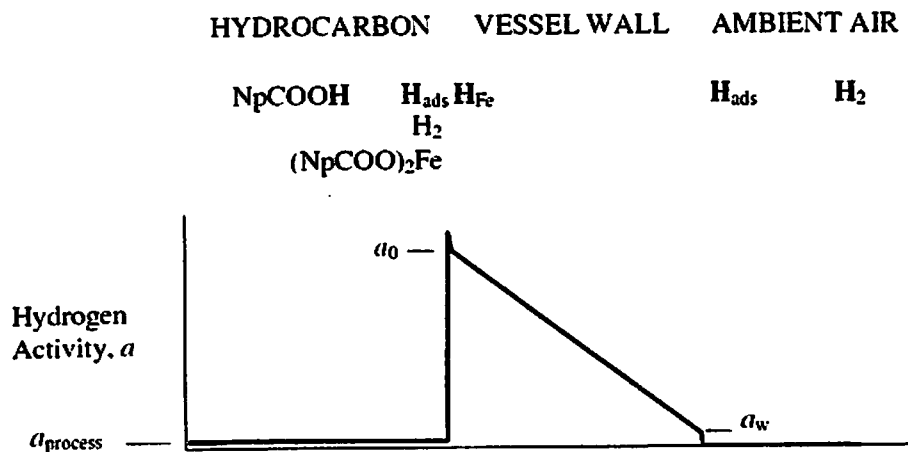
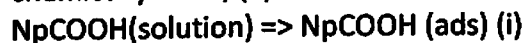


FIGURE 1. Schematic illustration of high temperature corrosion (NAC) induced hydrogen permeation, as discussed in the text.

#### FORMATION OF ATOMIC HYDROGEN IN STEEL

During NAC, naphthenic acid, represented as  $\text{NpCOOH}$ , is considered to physically adsorb on steel (i), then chemically react, (ii):



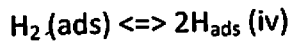
The subscript 'ads' is used to depict chemical adsorption.

It has been suggested that corrosion reaction (ii) could proceed electrochemically. However, given the very low conductivity of production fluids subject to NAC, any anodic and cathodic reactions would have to take place over very small distances, and therefore it is almost certain that, during NAC, hydrogen only forms on steel according to (i), (ii), and not through any semiconducting product layer. We will further assume that hydrogen atoms are formed on the surface of the steel in stoichiometric proportion to the oxidation of the steel, *ie* two  $\text{H}_{\text{ads}}$  per Fe atom. This is a crucial assumption affecting directly the correlation of flux with corrosion. Are there any ways in which iron could be oxidized or removed, or hydrogen formed, other than by equation (ii)? NAC is specific to locations where the shear velocity of the process stream is sufficient to erode away corrosion product to reveal more steel by which corrosion can progress. Thus for example, corrosion in the visbreaker fractionator was most severe at the splash zones. Erosive iron loss has not been reported in situations where NAC has been eliminated with a suitable corrosion resistant alloy.

Other acid corrodants such as  $\text{H}_2\text{S}$  and mercaptans will produce hydrogen and consume iron in the same proportion as in (ii). However, a process stream containing hydrogen could deliver hydrogen flux without iron loss:





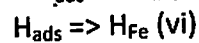
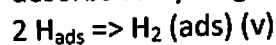


In the visbreaker fractionator, as in other NAC locations, the only source of hydrogen in the process stream was likely to be from cracking of hydrocarbons. In the case of the visbreaker, we estimated a maximum partial pressure of 0.1 mbar hydrogen, in view of the extremely short residence times of fluids expected within the fractionator.

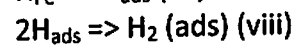
The maximum hydrogen activity in steel,  $a_{\text{process}}$ , caused by equilibration of this process hydrogen through equilibration of reactions (iii), (iv) and (vi) (see below), was then 0.01  $\text{bar}^{1/2}$ , delivering a flux of a few  $\text{pL}/\text{cm}^2/\text{s}$  at  $200^\circ\text{C}$  through steels of typical thickness. The effect was therefore discounted.

#### HYDROGEN PERMEATING STEEL

Adsorbed hydrogen,  $\text{H}_{\text{ads}}$ , either associates to form molecular hydrogen (v), which desorbs as hydrogen gas, or enters steel  $\text{H}_{\text{Fe}}$  in (vi):



Hydrogen entering the steel by (vi) diffuses through the wall, emerging at the external surface of the steel and exiting into air:



To obtain a correlation between flux and corrosion rate, one must reconcile the relative rates of hydrogen entry and dissociation from (v) vs (vi). At low temperatures, it has been established that at steel thicknesses greater than a few millimeters, steady state flux  $J_{\text{ss}}$  ( $\text{pL}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ ) varies in inverse proportion with steel thickness  $w$  (cm).

This is because the flux of hydrogen entering steel at the corroding surface (vi) and exiting at the external surface in (vii) is sufficiently low for it not to effect the concentration of  $\text{H}_{\text{ads}}$  at the corroding surface. Under these conditions, the hydrogen flux is determined by the permeability  $P$  ( $\text{pL}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}\cdot\text{cm}\cdot\text{bar}^{-1/2}$ ) of hydrogen through the steel:

$$J_{\text{ss}} = P \cdot (a_0 - a_w) / w \text{ (ix)}$$

where  $a_0$  and  $a_w$  ( $\text{bar}^{1/2}$ ) are the activities of hydrogen just under the corroding face and external face respectively.

With the assumption that  $a_w$  is zero, this simplifies to

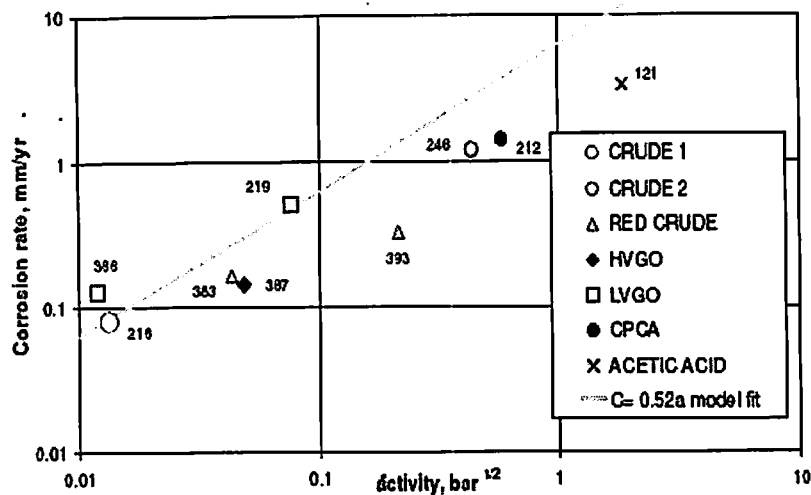
$$J_{\text{ss}} = P \cdot a_0 / w \text{ (x)}$$

The permeability of steels was investigated by Grabke and Riecke. We adopt their value for mild steel from which the fractionator walls were fabricated,

$$P = 1.76 \times 10^6 \exp(-4125/T) \text{ pL}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}\cdot\text{bar}^{-1/2} \text{ (xi)}$$

$T$  is the steel temperature (K). Riecke and Grabke's data suggests that variance in mild steels should not cause permeability to vary more than  $\pm 10\%$ . Adjusted values of the pre-exponential in (xi) are required for chrome alloy steels typically used in high temperature service, for 10% Cr being about half that of mild steel. Activity  $a_0$  is 'normalized' for the effect of steel thickness and temperature and can be derived from field measured and experimentally determined parameters in (x) and (xi).

### Experimental Data:



**FIGURE 2.** Correlation of corrosion rate and  $a_0$  deduced from laboratory experiments with various corrosive liqueurs under reflux as detailed elsewhere<sup>7</sup>. Numbers refer to maximum temperature. Mild steel of  $w = 0.2$  cm was tested. The correlation used in this work is shown by the line.

Data is presented in Figure 2.

A fairly linear relationship is established between activity and corrosion rate, which was particularly satisfactory given the range of test temperatures.

The correlation  $C = 5.2 a_0$  (xii)

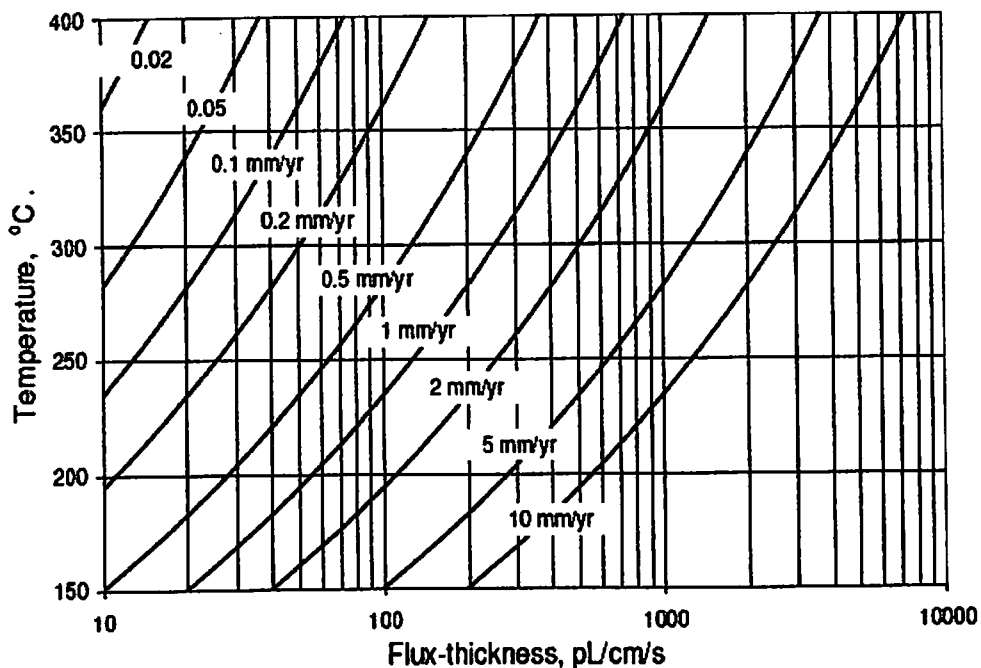
is shown by a solid line, and was adopted in this study. Equation (xii) overestimates the corrosion rate as obtained from the laboratory data, but was considered applicable to field measurements.

## FLUX-CORROSION RATE CORRELATION

Combining (ix) with (xi) and (xii) we obtain,

$$C = 2.96 \cdot 10^6 J_{SS} \cdot w \cdot \exp(4125/T) \text{ pL} \cdot \text{cm}^{-1} \cdot \text{s}^{-1} \cdot \text{bar}^{-1/2}$$

A graph enabling prediction of corrosion rate from flux x thickness using above equations is shown in Figure 3.



**FIGURE 3.** Chart for estimating corrosion rates from flux-thickness between 150 and 400 °C. for mild steel<sup>(3)</sup>. For example, a flux of 500 pL/cm<sup>2</sup>/s through 1 cm steel at 300 °C is indicative of a corrosion rate of 2 mm/yr. The correlation should be used with cautiously until further field data is obtained.

The above narrative indicates that the predicted corrosion rate using the roaming field probe was probably correct to within a factor of two. A much improved correlation would be obtained with a larger fixed probe, under insulation, as skin temperature effects and 'wind stripping', and positional variability would then be eliminated.

## **2.5 PROJECTS UNDER IMPLIMENTATION IN THE FIELD OF STUDY OF NAPHTHENIC ACID CORROSION**

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(8)

**(1). Power, Environmental & Energy Research Center, California Institute of Technology (PEER-Project).**

**Project Topic:      NAPHTHENIC ACID REMOVAL FROM CRUDE OIL**

### **Background:**

It has been known that carboxylic acids are present in crude oil and contribute to the acidity of oil products. The existence of these compounds e.g. naphthenic acids in oil has been recognized as one of the major sources of corrosion that occurs in transportation pipelines and distillation units in refineries. Consequently, the oil products with high concentrations of naphthenic acid are labeled as poor oil quality and have a lower price in the market. The conventional method to remove naphthenic acid is based on a caustic wash. However, this treatment results in the formation of emulsion. Once it is formed, this emulsion is very difficult to be broken.

### **Goal of the project:**

The aims of the current project are to develop cost-effective methods to remove naphthenic acids from rude oil.

Two objectives are targeted:

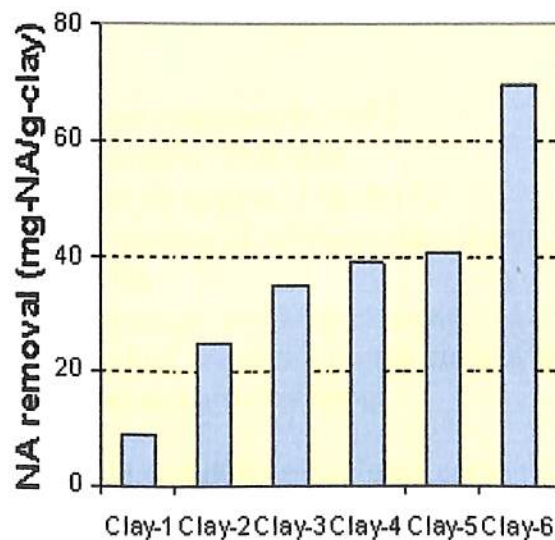
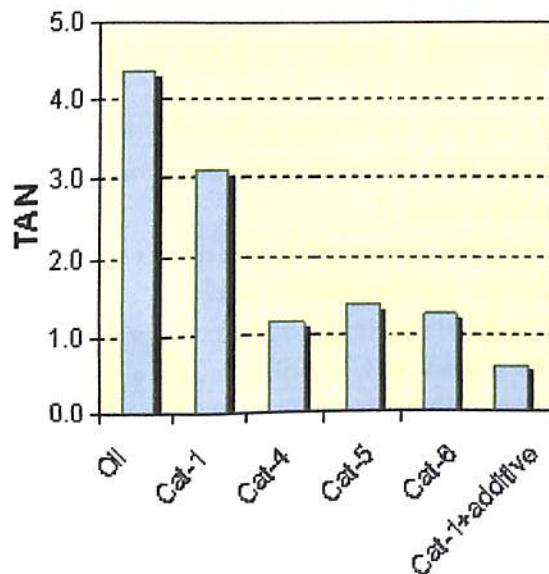
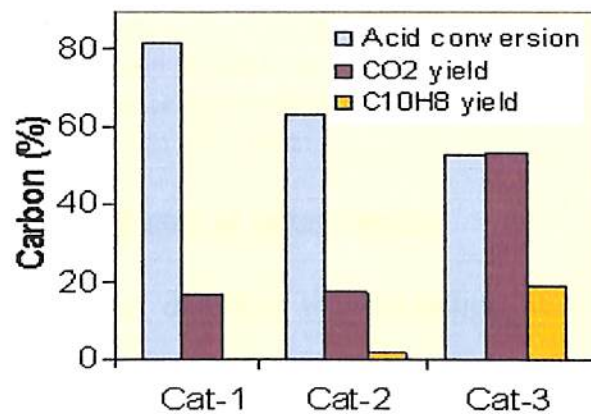
- 1) To develop a novel decarboxylation process through a catalytic reaction to convert these acids to non-corrosive components.
- (2) To remove naphthenic acids via a chemical adsorption process by using solid absorbent

### **Approaches:**

Catalytic decarboxylation use commercial available chemicals or self-prepared materials as catalysts to test their effectiveness with model compound first and then approach to the real oil. NA solid absorption Target naturally abundant, low cost materials such as clays to explore their probability for the selective adsorption of naphthenic acid from

crude oil. Theoretical modeling use sophisticated computational tools to investigate the possible reaction pathways and to obtain the fundamental understanding of the interaction among the reaction species

**Promising results :** With the model acid reaction, e. g.  $C_{10}H_7COOH \rightarrow C_{10}H_8 + CO_2$ . Several metal oxide catalysts have been found to be very effective to the catalytic decarboxylation, which were verified by the formation of  $CO_2$ . A newly developed catalyst with an additive was able to reduce the total acid number (TAN) of a heavy crude oil from 4.38 to 0.60 at  $300^\circ C$  for 4 hours. Flow reaction test shows that one of the catalysts they developed can maintain its effectiveness for 12 hours at  $250^\circ C$ . Several natural occurring clays showed promise as adsorption agents to the selective removal of acids. The adsorption capacity of one of the clays was as high as about 70 mg-NA/g-clay.



Some of the results during this PEER project are as shown in the figures above.

## **(2). Naphtenic acid corrosion Studies at Eni Technologie by Dr.Roberto Riva (ET project)**

**Project Topic: Naphthenic acid corrosion of 9%Cr 1%Mo steel and interaction of naphthenic acids and sulfur compounds.**

### **Background:**

Opportunity crude oils are cheap, but potentially corrosive because they may contain naphthenic acids and a high concentration of sulphur. Chemical analysis alone cannot predict their corrosivity; still, the total acid number (TAN) and the content of sulphur are key parameters. There is a subtle interaction between naphthenic acids and sulphur, which can be described by a simple model. At a fixed concentration of naphthenic acids the model predicts

- 1) Naphthenic acid corrosion at low S content
- 2) Inhibition of naphthenic acid corrosion at intermediate S content
- 3) Sulphidic corrosion at high S content

### **Aims of the experimental work of Enitecnologie:**

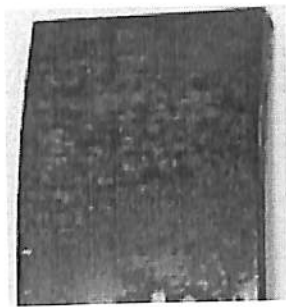
Testing the model that describes the interaction between naphthenic acids and sulphur.

Developing a laboratory test capable of predicting the corrosivity of opportunity crudes, which could become a planning tool for refineries. We focus on furnace tubes.

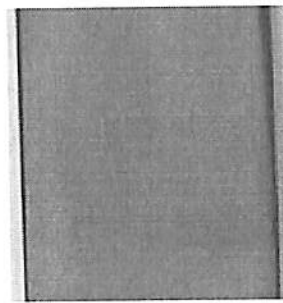
### **Experimental procedure – Requirements:**

- Rotating specimen (9% Cr, 1% Mo) in a sealed autoclave at 340°C.
- Two kinds of oil: 1) Ural crude oil (1.5% wt sulphur, TAN=0.2)  
2) Lubricant base oil (3.8ppm wt sulphur, TAN=0.16).
- Acidity is increased through addition of a mixture of synthetic naphthenic acids (Fluka 70340, average molecular weight 230).
- Evaluation of the rate of corrosion through weight loss after cleaning.
- Evaluation of the weight of corrosion product deposited on the surface of the metal: difference between weight after test and after cleaning.

**Equal concentration of naphthenic acids (TAN=4.9), but different sulphur content**



High content of sulphur



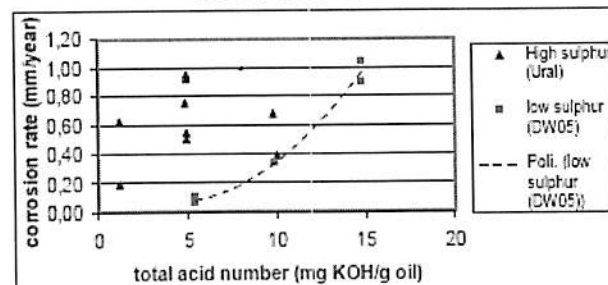
Low content of sulphur

### Weight of corrosion products

High sulphur content  
Average weight of corrosion products (9 tests with various TAN values)  
**7.8 mg/cm<sup>2</sup>**

Low sulphur content  
Average weight of corrosion products (5 tests with various TAN values)  
**1.1 mg/cm<sup>2</sup>**

### Corrosion rate

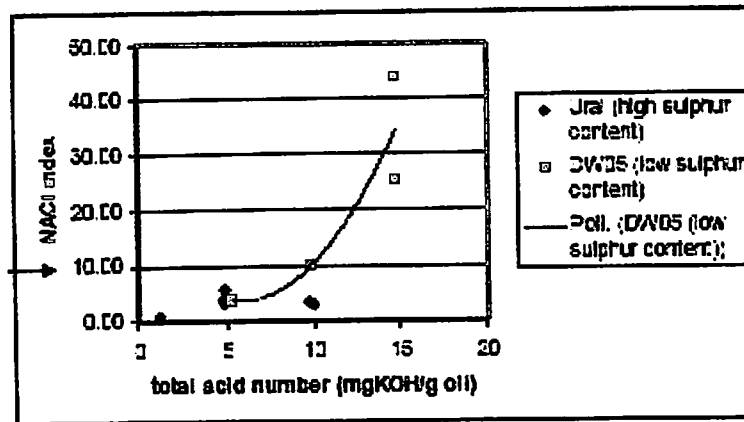


Through their experiments they had given a concept of Naphthenic Acid Corrosion Index (NACI) to decide the type of the corrosion.

NACI experimental formula and division of NACI values to decide the type of the corrosion is as follows.

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

NACI	TYPE OF CORROSION
< 10	sulphidation or, perhaps, oxidation
10 to 100	moderate naphthenic attack, perhaps inhibited by sulphidation
> 100	severe naphthenic attack



**NACI Vs TAN**

Theshold naphthenic acid corrosion

### Discussion of the experimental results:

The experimental results are roughly in agreement with the model given in the literature for the interaction between sulphur and naphthenic acids. For example:

- High sulphur content and TAN=10 lead to sulphidic corrosion
- Low sulphur content and TAN=10 lead to naphthenic acid corrosion.

. In contrast, far lower concentrations can give rise to naphthenic acid corrosion in refinery plants.

- The experiments have confirmed the interaction between sulphur and naphthenic acids. The results are roughly in agreement with the model given in the literature.
- Very high concentrations of naphthenic acids (TAN10) were required for the onset naphthenic acid corrosion. Such behavior is surprising even for 9% Cr-1% Mo steel, which is quite resistant to naphthenic acids. Far lower concentrations (TAN0.5) are potentially corrosive in refinery plants. The experimental set-up probably needs modifying, if plant conditions are to be reproduced.

At last they finalize that sulphidic corrosion leads to the formation of sulphidic corrosion scales and no surface corrosion products after naphthenic acid corrosion.



## CASE STUDIES

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### **(1). A case study on the Grane High acid crude oil**

#### **The Grane Crude Oil Characteristics:**

Grane is a heavy, naphthenic, low sulphur North Sea crude oil with a total acid number of 2.2 mg KOH/g, similar to e.g. Alba and Captain. The naphthenic character, the yield structure and the acidity assume blending with other, ideally parafinic crude oils. Norsk Hydro internal and external investigations and analyses by among others UOP Limited and Ondeo Nalco Energy Services have shown that Grane could account for about 10% of most refiner's crude slate, even in light of the most stringent European product specifications, provided an adequate corrosion control programmed is in place. In refineries with high conversion, hydro treatment capabilities and/or markets with less stringent specifications, higher percentages might be run.

Grane has low naphtha but high middle distillate and vacuum gas oil yield. The vacuum residue yield is high. The middle distillates have excellent cold properties but limited burning characteristics. The VGO is expected to be well suited for HC- and FCC-processing. There are strong indications that Grane to a certain but limited extent has the potential to produce naphthenic base oils and, if blended with a light sweet crude oil, anode grade coke.

**They are also focused on naphthenic acid corrosion in desalting unit.** In general high acid crude oils are more difficult to desalt due to:

- 1 The surface activity of naphthenic acid salts (saponified organic acid - soaps).
- 2 Higher additive additions at the production site which can affect the surface activity of the crude oil.
- 3 Higher levels of salt and water in the raw crude.

The above characteristics can be managed with the application of an appropriate demulsifier. The results of water separation tests of a typical Grane crude slate (30% Grane, 70%Ekofiskblend) against a Forties standard demonstrate that similar performance with respect to water separation can be obtained

## **(2). A case study on Baker Petrolite's SMARTGUARD Naphthenic Acid Crude processing programme situation**

### **Introduction:**

Refiners processing naphthenic "opportunity" crudes using the SCORPION® II program without having upgraded the metallurgy of the transfer lines, furnace tubes or tower internals of the crude and vacuum units. The metallurgy of these areas is generally either carbon steel or 5% Chrome which does not protect against naphthenic acid attack.

### **Programme:**

SCORPION® II program risk assessments were performed on the refineries by Ondeo Nalco Energy Services Ltd. personnel to identify potential areas of high temperature corrosion. The assessments also located suitable points for injection of the SCORPION® II corrosion inhibitor, sampling points and corrosion monitoring

### **Objective of the programme:**

Baker Petrolite's SMARTGUARD Naphthenic Acid Corrosion Control Program is designed to allow you to take full advantage of discounted opportunity crudes and reduce the risks associated with processing a higher percentage of naphthenic acid crudes oils in your feedstock blend.

### **Corrosion Impact Assessments:**

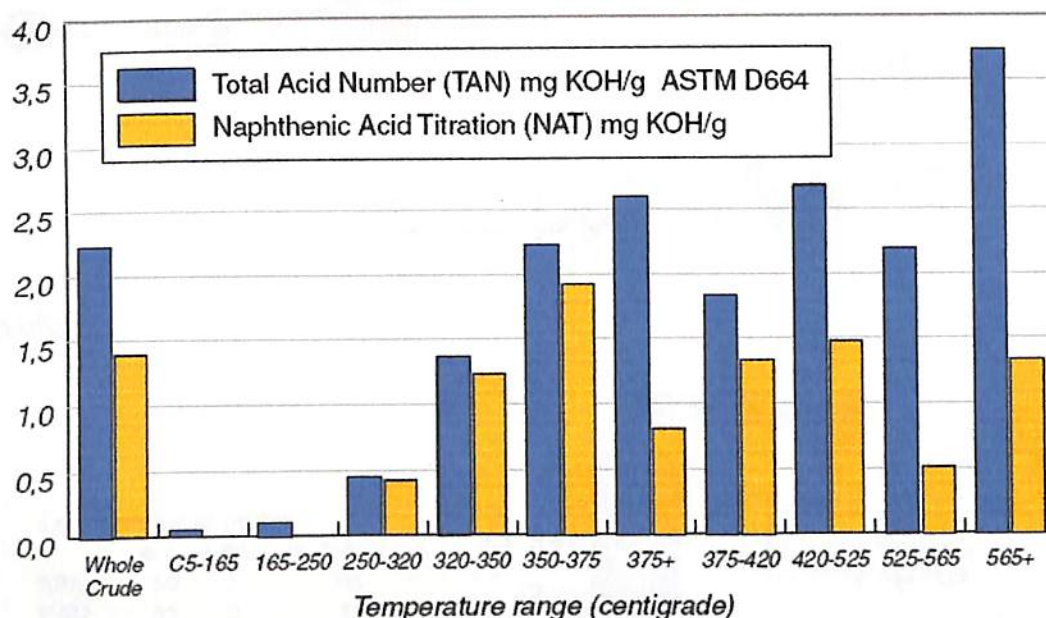
Baker Petrolite uses a systematic engineering approach to assess the impact of processing High acid crude oils. The assessment is used to establish processing limits and to focus corrosion mitigation and monitoring efforts. The corrosion impact assessment begins with a thorough data collection campaign. They review unit P&IDs, metallurgical records and inspection reports, corrosion rate data, plus operational data such as flow rates and temperatures. We measure and document stream metals content, sulfur and total acid number (TAN) data and also conduct interviews with operating and technical personnel. Baker Petrolite has developed a proprietary **specific carboxylic acid number (SCAN)** test method which directly measures the acid contribution from the naphthenic acids in a hydrocarbon stream, and is a more accurate predictor of potential NAC than the standard TAN method.

### **Applications:**

The injection points, utilizing a propriety injection quill system for high temperature corrosion applications, were selected depending on temperature, stream flow velocity and such that all areas susceptible to naphthenic acid attack were protected. Similarly ONES, using various methods, one of which is proprietary, monitored all areas

## Refining Grane Acid Crude Oils

Grane has a total acid number of 2.2 mg KOH/g. The content of the naphthenic acids based on Ondeo Nalco's NAT method is 1.4 mg KOH/g.



Source: [www.ones.com](http://www.ones.com)

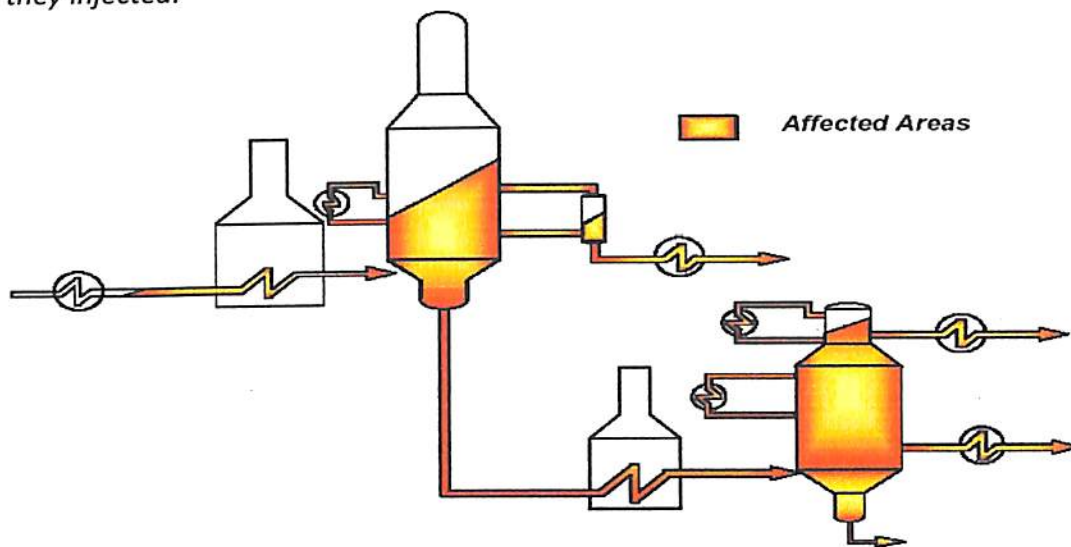
### Corrosion Testing

Through Ondeo Nalco Energy Services laboratory corrosion testing using high pressure, high temperature rotating cylinder autoclave equipment has been performed on the atmospheric residue fraction of the Grane crude oil (350°C +). In comparison to the corrosion rates of uninhibited samples the corrosion rates of carbon steel and 5% Chrome in the presence of a commercial inhibitor were reduced by 88% and 74% respectively.

### Ondeo Nalco Energy Services Case Study Success.

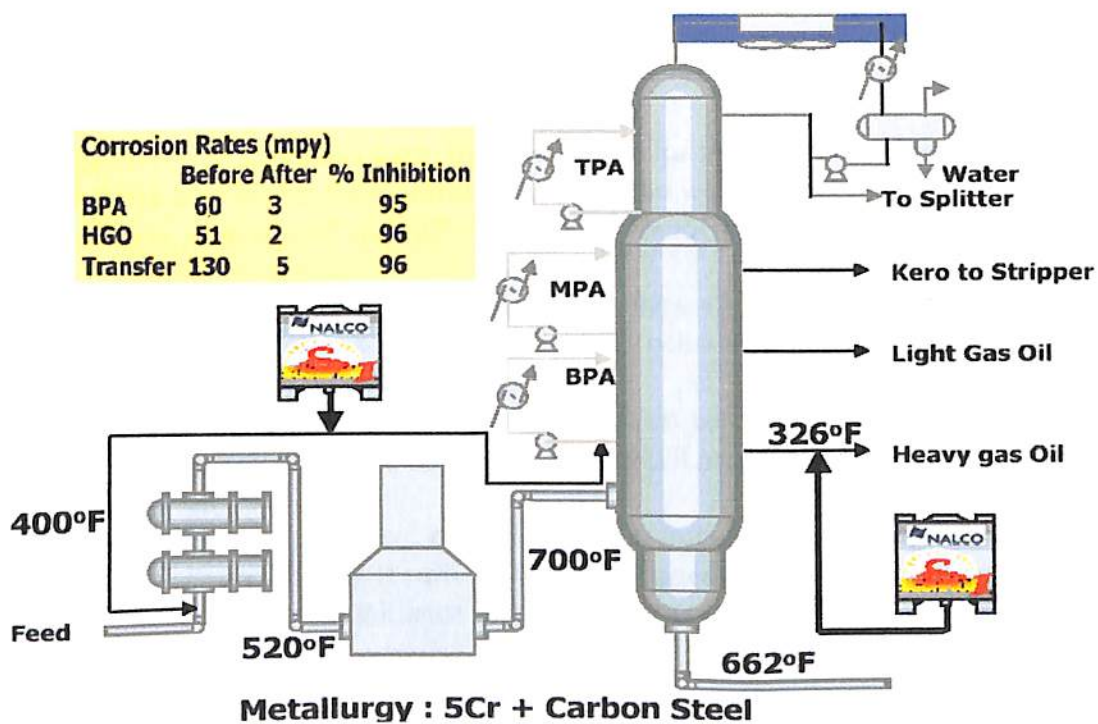
The impact of using a high acid crude can be successfully managed with a good corrosion monitoring programme and the use of one or a combination of the above methods. This is demonstrated by a generic case study as shown above.

susceptible to naphthenic acid attack for corrosion. *The following figure shows where they injected.*



**Results:**

Corrosion Rates (mpy)			
	Before	After	% Inhibition
BPA	60	3	95
HGO	51	2	96
Transfer	130	5	96



The refineries have successfully processed naphthenic crudes at 100% of the crude slate and shutdown inspectors have verified the success of the SCORPION® II corrosion management programme in place at the refineries. And this is found to be very effective inhibitor to naphthenic acid corrosion.

## CONCLUSION

- (1). High temperature naphthenic acid corrosion is a complex problem. There are at least three corrosion mechanisms corresponding to: (i) furnace tubes and transfer lines where corrosion is dependent on velocity and vaporization and is accelerated by naphthenic acid, (ii) vacuum column where corrosion occurs at condensing temperature, is independent of velocity and increases with naphthenic acid concentration, and (iii) side cut piping where corrosion is dependent on naphthenic acid content and is inhibited somewhat by sulfur compounds.
- (2).The industry still relies heavily on previous experience and readily available data on TAN and sulfur of cuts when processing opportunity crudes.
- (3).The uniqueness in process conditions, materials of construction and blend processed in each refinery and especially the frequent variation in crude or blend processed does still not allow an accurate correlation of plant experience to chemical analysis and laboratory corrosion tests.
- (4).In addition to corrosion data, there is a need for better monitoring and recording of the process conditions (temperature, velocity, and vaporization) and the analytical data (TAN of cuts, type of acid and sulfur compounds present).
- (5).Some advanced monitoring methods like BP's should be applied for continuous monitoring of naphthenic acid corrosion while processing the high acid crudes.
- (6).There is necessary to develop methods which can remove naphthenic acids from high acid crude before sent for processing, like PEER project etc.
- (7).Because of the presence of this harmful impurities "Opportunity crudes" are available at cheap cost .So, if sufficient are developed then the economy of the refinery will be increase. In India Reliance petroleum company processing high acid crudes by using SCOR



*Studies on Naphthenic acid corrosion in a petroleum refinery*



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## **Appendices:**

### **Glossary of some important words**

<b>ASTM</b>	<b>American Society for Testing and Materials</b>
<b>DR</b>	<b>Digital Radiography</b>
<b>FAB-MS</b>	<b>Fast Atom Bombardment Mass Spectroscopy</b>
<b>FSM</b>	<b>Field Signature Method</b>
<b>HAC</b>	<b>High Acid Crude</b>
<b>HPLC</b>	<b>High Performance Liquid Chromatography</b>
<b>MPY</b>	<b>Mils Per Year</b>
<b>NA</b>	<b>Naphthenic Acid</b>
<b>NAC</b>	<b>Naphthenic acid corrosion</b>
<b>NACI</b>	<b>Naphthenic Acid Corrosion Index</b>
<b>NAN</b>	<b>Naphthenic Acid Number</b>
<b>NAT</b>	<b>Naphthenic Acid Titration</b>
<b>RCM</b>	<b>Resistance Corrosion Monitoring</b>
<b>SCAN</b>	<b>Specific Carboxylic Acid Number</b>
<b>TAN</b>	<b>Total Acid Number</b>
<b>UOP</b>	<b>Universal Petroleum Products</b>