NAPHTHENIC ACID CORROSION IN REFINERIES

A PROJECT REPORT

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May, 2007

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CERTIFICATE

This is to certify that the project work entitled **"NAPHTHENIC ACID CORROSION IN REFINERIES"** submitted by Mr. Rohit Joshi is partial fulfillment of the requirements for the degree of Master of Technology (Refining & Petrochemical Engineering), college of Engineering, University of Petroleum & Energy Studies, is a record of the work carried by him at UPES under the guidance of **"Dr. R.P. Badoni, Distinguished Prof. COE, UPES".**

To the best of my knowledge, the content of this project work did not form as basis of the award of my pervious degree by any one else.

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Rohit Joshi

ROHIT JOSHI

PREFACE

This report is focused towards developing a perspective to the crude oil industry which is facing a numerous amounts of challenge viz-engineering, costing, and availability of crudes etc. My emphasis is towards the engineering challenges focused by the crude oil refinery industry, specially speaking about the high temperature "***Naphthenic Acid Corrosion***". This is one of the major challenges faced by the refineries due to availability of economic but high acid crude. Which are comparatively cheap but an emerging technological hurdle in terms of corrosion, equipment failure, high maintenance cost etc.

The report is been described in forms of eight chapters wherein:

- First Chapter Provides Information About Naphthenic Acid Chemistry.
- Second Chapter Concentrates on Naphthenic Acid Corrosion & Area Affected by NAC.
- Third Chapter Deals With Parameters Affecting Naphthenic Acid Corrosion and Methods for Determination of NAs Content in Crude Oil.
- Fourth Chapter Focuses on NAC Mechanism.
- Fifth Chapter Provides Information About Mitigation Techniques for NAC.
- Sixth Chapter Gives an Idea About Improved Processes to Recover Naphthenic Acids From Middle Distillates and Industrial Application of Naphthenic Acids.
- Seventh Chapter Deals With Monitoring and Inspection for NAC Control

Along with these informative chapters, the report is accompanied by number of graphs, charts, tables and for the ease of reader; the data have been supported by relevant information in appendices and annexure. There by developing a set of constrictive recommendation beneficial to the refining sector and emphasis towards dealing with naphthenic acid not just a problem but a challenge for future to generates value to the industry.

ABSTRACT

Modern Refineries are currently investigating the possibility of processing "Opportunity Crudes" and one of such refineries is Reliance Industries Limited, Jamnagar, India which has started processing such crudes to increase GRM and hence increase profitability. One of the problems, which may result from the processing of these crudes, is naphthenic acid corrosion. Crude from Venezuela, California, Russia, Canada, and the Gulf Coast have been identified as naphthenic acid-bearing crudes. New crudes from the Far East and Africa are also indicating high total acid number (TAN) in crude assays. Naphthenic acid corrosion occurs in the higher temperature processing areas (>250^{0}C). The severity of the corrosion is influenced by alloy type, velocity, turbulence, and increasing temperature.

To mitigate acid corrosion one has to resort to either metallurgical modifications and / or use corrosion inhibitors. There is no established and field tested laboratory method for screening or short listing of best corrosion inhibitor from amongst a variety being offered by chemical suppliers; as a result the refiners has to rely on vendors claims and time consuming trial and error methods. Therefore need of the hour is to develop a quick and a reliable method for screening and recommending cost effective best corrosion inhibitor.

Another value addition option is to recover naphthenic acids from crude oil. It will not only assist refiners in avoiding corrosion of processing units but also add value to its profit margins. Some of the international companies like Merichem, USA use dilute caustic solution to recover valuable naphthenic acids from middle distillate as sodium naphthenate and recover by acidifying with H_2SO_4 or HCl and subsequently purifying for a variety of end use applications such as oil field corrosion inhibitors, metal soaps of naphthenic acids as emulsifiers in cutting oil, lubricity additives in fuels, driers in paints and inks etc.

CONTENTS

ABBREVIATIONS

NAC: Naphthenic Acid Corrosion
HAC: High Acid Crude
TAN: Total Acid Number
NAN: Naphthenic Acid Number
NAT: Naphthenic Acid Titration
GRM: Gross Refinery Margin
NA: Naphthenic Acid
SC: Sulphidic Corrosion
CS: Carbon Steel
SS: Stainless Steel
MO: Metal Oxide

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CHAPTER 1. NAPHTHENIC ACID CHEMISTRY

1.1 Introduction

The name naphthenic acid (NA) derives from the first observation of the acidity in naphthenic-based crude from the Baku Region, of Russia in 1920's.

Although the term "naphthenic" traditionally was used to classify only acids with cycloaliphatic derivatives, in the petroleum industry it refers normally to all the organic acids (aromatic, olefinic, hydroxy and dibasic acids are present as minor components of naphthenic acids) present in crude oil [38].

Naphthenic acids are mixtures of alkyl-substituted acyclic and cyclic structures with the general chemical formula $C_nH_{2n+z}O_2$, where n indicates the carbon number and Z is zero, in the case of fatty acids, or negative, depending on the number of condensed and/or aromatic rings. Figure1 displays some examples of possible monoprotic naphthenic acid structures for different Z values [38].

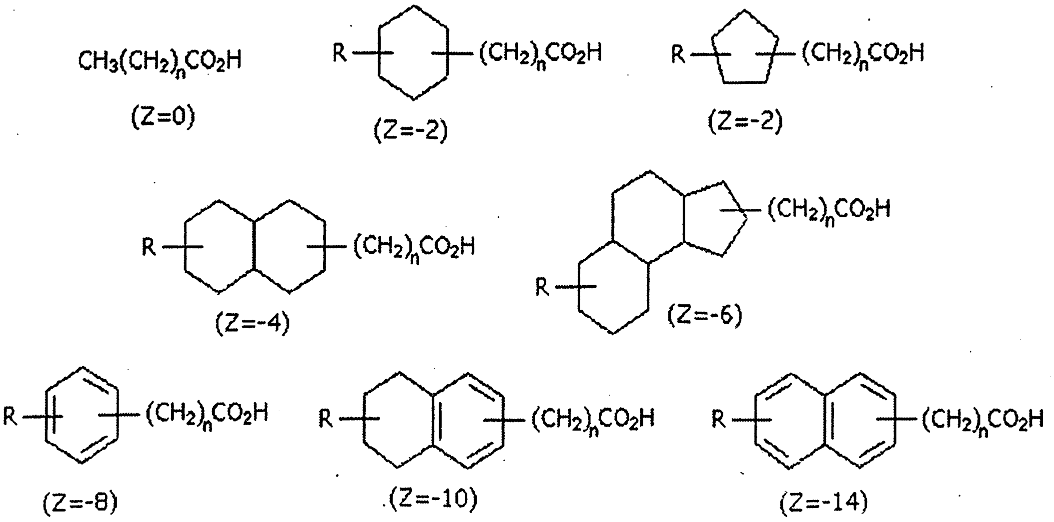


Figure 1: Naphthenic acid structures where Z describes the hydrogen deficiency, R is an alkyl chain, and n the number of CH_2 units.

1.2 Generation of Naphthenic Acids in Crude Oils

Naphthenic acids are normal constituents in nearly all crude oils, typically ranging from 0-4 %wt. The acids are predominantly found in immature heavy crudes, whereas paraffinic crudes normally have low acid contents. The naphthenic acids are assumed to generate from in-reservoir biodegradation of petroleum hydrocarbons. This suggestion has been supported by discovery of naphthenic acids in deposits in naturally biodegraded crude oils and in crude oils that have been biodegraded under laboratory conditions.

1.3 Reason for Corrosive & Toxic Nature of NAs

The amphiphilic hydrocarbon backbone and oxygen-containing polar head-group functionalities promote naphthenic acid mobility in oil and aqueous phases.

For example, when in contact with neutral or basic water, naphthenic acids can dissociate and partition into the aqueous phase. Conversely, naphthenic acids molecularly solvate asphaltenes in the oil phase. Naphthenic acids achieve this through interaction between their acid groups with basic groups of asphaltenes. The asphaltene solvation and dispersion properties directly relate to the composition of the acid functionality for the naphthenic species.

The amphiphilic properties of naphthenic acids result in a variety of negative industrial and environmental consequences such as metal surface corrosion and toxicity [38].

1.4 Challenges Associated with High Acid Crude Processing

An opportunity crude oil is a crude that is priced below market value because such crude contains undesirable high content of naphthenic acid. There are many disadvantages of processing opportunity crudes (high acid crudes) in refinery. Refiners have discovered that processing these high content naphthenic acid crudes impacts both operational reliability and equipment integrity. Some operational impacts experienced are given below:

- Reduced desalter efficiency.
- Equipment fouling (exchanger fouling)
- Catalyst poisoning (auto-oxidation of the catalyst)
- Poor wastewater quality (low molecular weight compounds present in the waste water have shown to be toxic to a variety of aquatic organisms)
- Off specification finished product quality (Diesel fuel have low cetane index and smoke point)

Some principle equipment impacts have been given below:

- High temperature corrosion
- Piping failure
- Loss of product containment

The most significant of these risks being high temperature naphthenic acid corrosion (NAC), as naphthenic acids are highly corrosive to the process equipment. Left unchecked, high-acid corrosion can damage equipment, lower production and, in the extreme, create unexpected plant shutdowns and unsafe working conditions.

CHAPTER 2. NAPHTHENIC ACID CORROSION (NAC)

2.1 Introduction

Many opportunity crudes are known to contain naphthenic acids. 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 250^0C to 450^0C, which can cause corrosion in high temperature regions within the refinery normally around the crude and vacuum towers. Because of this corrosion, and the absence of a method to predict corrosion, crudes high in TAN (Total Acid Number) are discounted. Some refineries are taking advantage of the economically attractive nature of these crude oils by processing them at high levels while working towards maintaining unit reliability.

Naphthenic acid corrosion is a localized corrosion. The nature of corrosion due to naphthenic acids is in the form of sharp-edged holes and streamlined grooves [1, 10, 17-18]. Long grooving corrosion, sometimes described as "comet tails" starts out in these pits. Initially, the corrosion starts out as a pit. Sometimes, these pits are associated with surface discontinuities in the equipment.

In 1956, Derungs [31] assembled a summary of the technology dealing with naphthenic acid corrosion up to that time. He described the appearance of the naphthenic acid corrosion as "...highly characteristic, varying with increase in stream velocity from sharp-edged, crater-like holes to sharp-edged streamlined grooves."

2.2 Some Examples of NAC in Refineries

Initial observation of naphthenic acid corrosion dates back to the 1920's. Its occurrence in these early years was confined primarily to processing crudes from California, Venezuela, Russia and Romania. In recent years, however, that list has been expanded to include crudes from the North Sea, West Africa, China, and India.

- The Sun Marcas Refinery which runs sweet crude and expecting no corrosion due to naphthenic acids. But in December turn-around during 1990, when vacuum tower was opened, it was found corroded due to naphthenic acid [4].
- From a report in 1983 it was seen that the Amuay refinery in California was running naphthenic acid crude since last 30 years and detected a lot of corrosion in different parts of the process equipments [9].
- To overcome naphthenic acid corrosion California refinery used metallurgical solutions by cladding vacuum column in 317SS.
- U.S. Southern Gulf Coast refinery processes a blend of Venezuelan crude oils, and was experiencing naphthenic acid corrosion in the vacuum heater transfer lines, the heavy vacuum gas oil section of the vacuum tower, and in the pumparound piping as well [35].

2.3 System Assessment

System assessment is also known as "risk assessment". To safely run high acid crude oils in the refinery it is important to first assess the susceptibility of system and equipment to undergo naphthenic acid corrosion. Typically, data is reviewed to establish potential corrosion rates which could be used to estimate the remaining life on the refinery process, pressure pipelines, pumps and vessels [31].

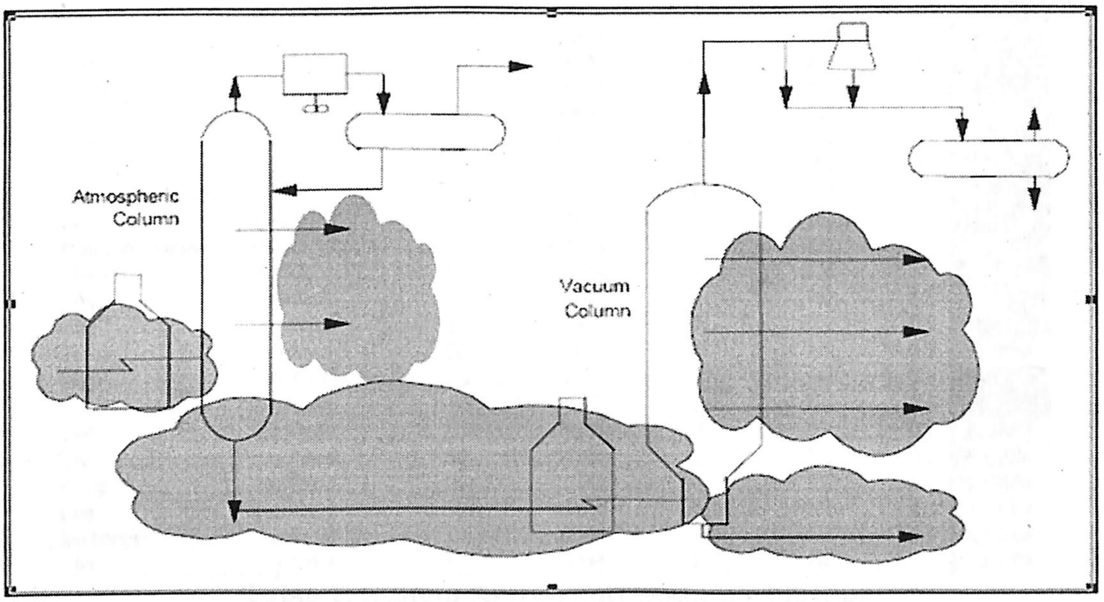


Figure 2: Highlighted Areas Affected by NAC

Unfortunately, experience has shown that it is difficult to correlate corrosion rates for particular crudes from refinery to refinery. This is due to the differences in equipment design, operating temperatures, flow velocities and other crudes present, which may provide a natural passivating effect to the system.

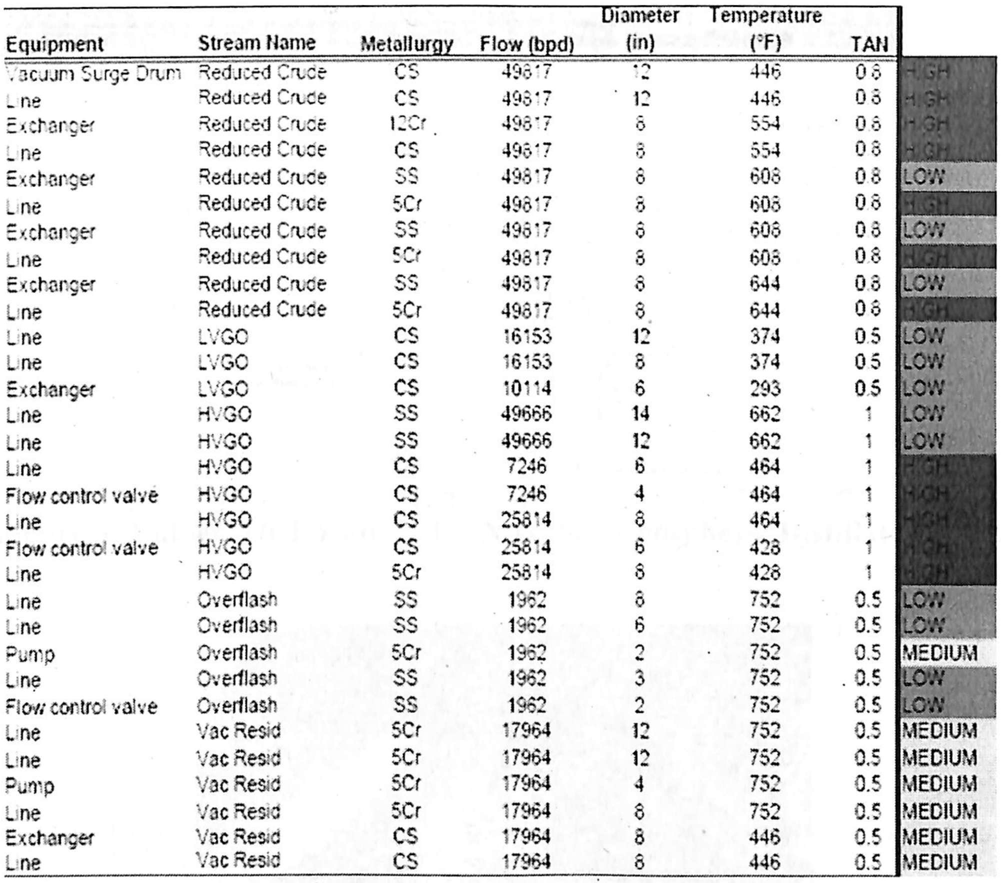
There are several important variables to consider while performing a risk assessment on a Unit: stream analysis, temperature, velocity, metallurgy, flow regimes, etc. Each and every variable must be analyzed before the best mitigation strategies can be developed.

System Assessment discrete Analysis conducted on circuit –by- circuit basis. First discrete "break points" (Temperature, metallurgy, pipe size etc) are identified. The circuit details are captured in assessment spreadsheet and calculations are performed to determine the severity of the risk. Each circuit is assigned a risk potential

- Low (Green)
- Medium (Yellow)
- High (Red)

From the given Table1 it is evident that concern levels are inter-dependent. For example

- High sulfur offsets high TAN.
- High Velocity can offset moderate TAN.



Equipment	Stream Name	Metallurgy	Flow (bpd)	Diameter (in)	Temperature (°F)	TAN	
Vacuum Surge Drum	Reduced Crude	CS	49817	12	446	0.8	HIGH
Line	Reduced Crude	CS	49817	12	446	0.8	HIGH
Exchanger	Reduced Crude	12Cr	49817	8	554	0.8	HIGH
Line	Reduced Crude	CS	49817	8	554	0.8	HIGH
Exchanger	Reduced Crude	SS	49817	8	608	0.8	LOW
Line	Reduced Crude	5Cr	49817	8	608	0.8	HIGH
Exchanger	Reduced Crude	SS	49817	8	608	0.8	LOW
Line	Reduced Crude	5Cr	49817	8	608	0.8	HIGH
Exchanger	Reduced Crude	SS	49817	8	644	0.8	LOW
Line	Reduced Crude	5Cr	49817	8	644	0.8	HIGH
Line	LVGO	CS	16153	12	374	0.5	LOW
Line	LVGO	CS	16153	8	374	0.5	LOW
Exchanger	LVGO	CS	10114	6	293	0.5	LOW
Line	HVGO	SS	49666	14	662	1	LOW
Line	HVGO	SS	49666	12	662	1	LOW
Line	HVGO	CS	7246	6	464	1	HIGH
Flow control valve	HVGO	CS	7246	4	464	1	HIGH
Line	HVGO	CS	25814	8	464	1	HIGH
Flow control valve	HVGO	CS	25814	6	428	1	HIGH
Line	HVGO	5Cr	25814	8	428	1	HIGH
Line	Overflash	SS	1962	8	752	0.5	LOW
Line	Overflash	SS	1962	6	752	0.5	LOW
Pump	Overflash	5Cr	1962	2	752	0.5	MEDIUM
Line	Overflash	SS	1962	3	752	0.5	LOW
Flow control valve	Overflash	SS	1962	2	752	0.5	LOW
Line	Vac Resid	5Cr	17964	12	752	0.5	MEDIUM
Line	Vac Resid	5Cr	17964	12	752	0.5	MEDIUM
Pump	Vac Resid	5Cr	17964	4	752	0.5	MEDIUM
Line	Vac Resid	5Cr	17964	8	752	0.5	MEDIUM
Exchanger	Vac Resid	CS	17964	8	446	0.5	MEDIUM
Line	Vac Resid	CS	17964	8	446	0.5	MEDIUM

Table 1: System Assessment – Sample Output

2.4 Areas Affected by Naphthenic Acid Corrosion

Literature reviewed and experience indicates that pipelines and equipment containing crude, light diesel, heavy diesel, atmospheric residue, light and heavy vacuum gas oil and vacuum residue operating at temperatures higher than 200°C were possible areas for naphthenic acid attack [31].

Enrichment of the acids into the gas oils makes these cuts particularly corrosive. The characteristic localized attack is frequently observed in locations of high shear stress, such as elbows and downstream of thermowells In general, the corrosion problem is more severe where the physical state of the acids is changing e.g. vaporizing, as in a transfer line, or condensing, as in a vacuum tower. Brief discussion on common areas affected by NAC in crude unit is given below.

- **Atmospheric Distillation Unit:** In atmospheric distillation unit preheat furnace, exchanger channels and bottom of the atmospheric distillation column are the potential attack location for NAC. Naphthenic acid crude also reduce the desalter efficiency.

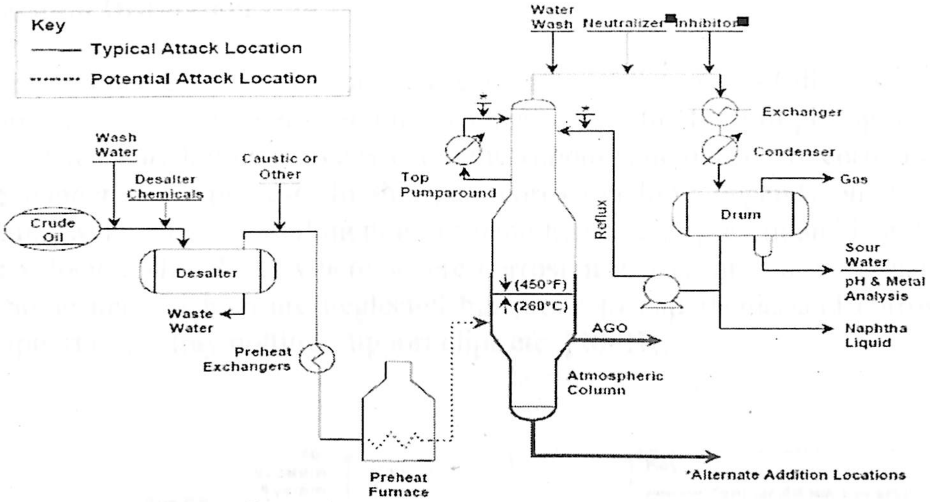


Figure 3: Vulnerable Locations for NAC in Atmospheric Distillation Unit [42]

Figure 4: Chevron Refinery CDU. Severe Corrosion of Exchanger Channel (5 Cr- ½ Mo) Side Cut @ 650^{0}F (343^{0}C) [42]

❖ Desalter Efficiency

When acidic crude is processed and NaOH is used for desalter pH control, it is important to not let the pH get above 9. Above 9 pH, sodium naphthenate can plate out on the electric insulators in the desalter vessels. These salts are conductive and can cause a short circuit of the electrical system.

Crude oils contain various amounts of naphthenic acids, which have a high molecular weight. The lighter acids tend to be water soluble. When the light acid content is proportionately higher, the acids affect the pH on the desalting system. The pH may go as low as 3.0 to 5.0, which may create emulsion problems. As the pH of the water inside the desalter increases, the sodium naphthenate can form very stable emulsions which are difficult to break. Thus naphthenic acid crude processing reduced the desalter efficiency. To get rid of this problem choice of right demulsifier is important.

➢ Vacuum Distillation Unit

Severe naphthenic acid corrosion was seen in vacuum towers of distillation column at temperature 290°C to 350°C and the damage was in the form of pitting. It was seen that these acids are highly active when in the vapour state but severe corrosion is seen in the condensation process. In this part corrosion limit depends on the content, molecular weight and the boiling point of naphthenic acids present and is independent of the velocity. The places where severe corrosion is seen are the condensing point [19]. Some items, which are neglected but prone to naphthenic acid corrosion, are tray support rings, tray bolting, support clips etc. [20-21].

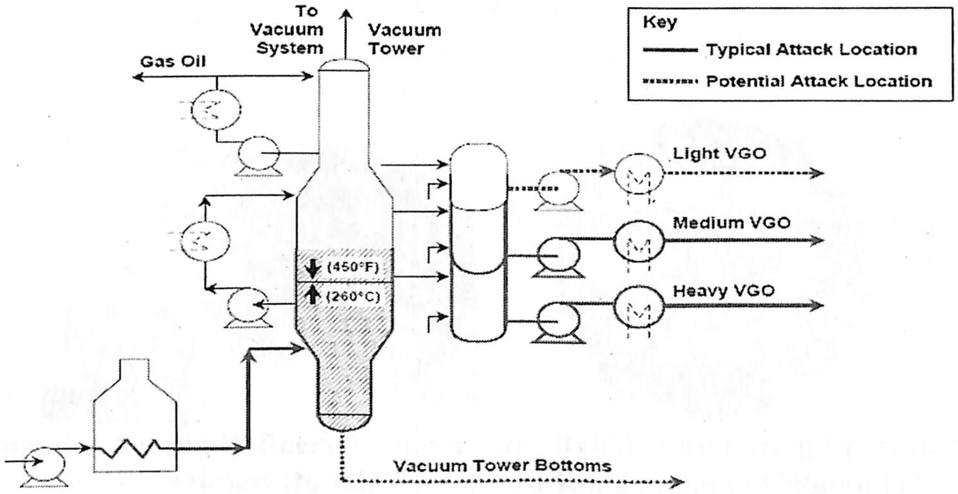


Figure 5: Vulnerable Locations for NAC in Vacuum Distillation Column [42]

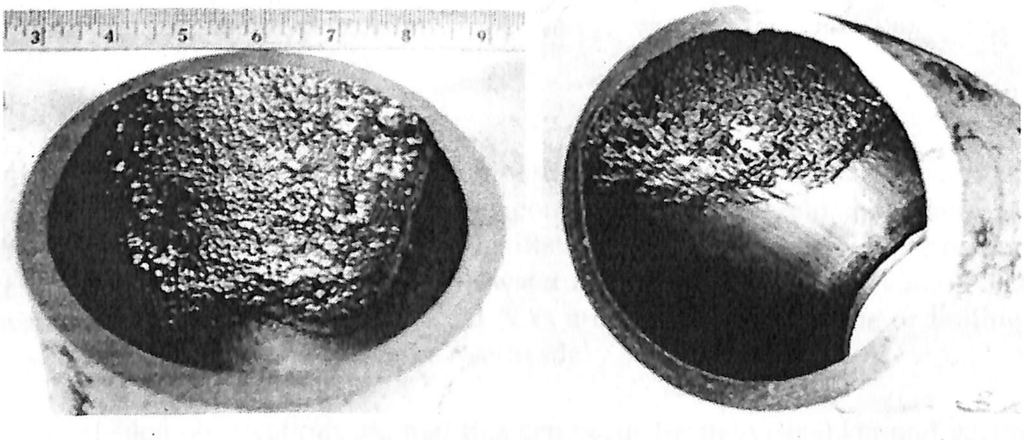


Figure 6: Chevron Refinery Vacuum Unit: Severe Corrosion of 5 Cr-1/2Mo on an Outer Bend of an Elbow (Just Upstream of the Collection Header) [42]

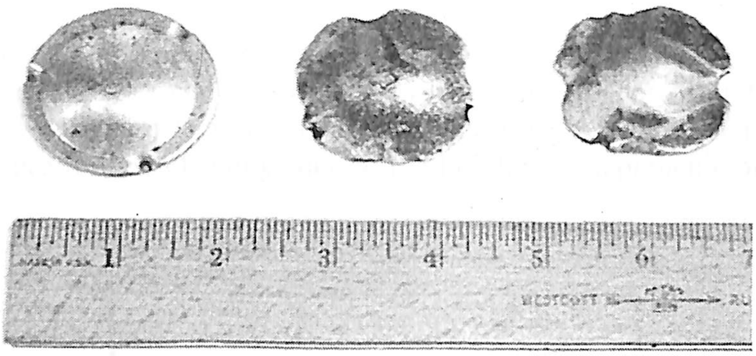


Figure 7: Cage Tray Caps after Six Month in Prefractionator Column Processing NAs Crude [42]

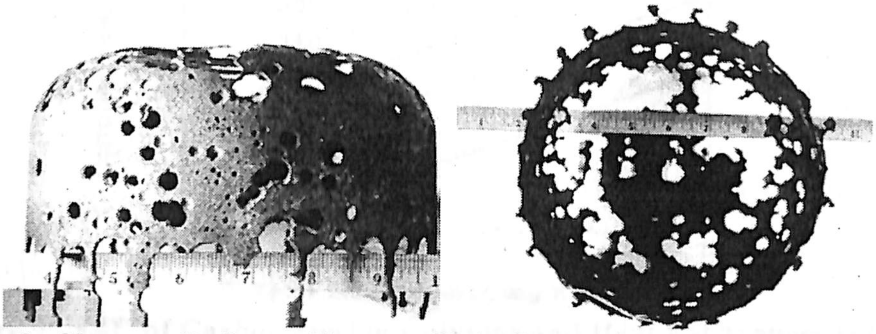


Figure 8: Chevron Refinery Vacuum Unit: Bubble Cap pitting Corrosion of Type 410 Stainless Bubble Cap from a Resid Stripper Column [42]

- **Bubble Caps:** Attacks on bubble caps are due to impinging droplets of condensing naphthenic acids.

- **Pumps:** In pumps the affected points are galling between mating wear rings, suction line and discharge line.

- **Overhead Corrosion**

Above 420°C naphthenic acids decompose at an increasing rate but concern has been expressed that the light organic acid compounds (acetic acid, propanoic acid and butanoic acid) generated end up in distillation fractions and they could be corrosive. These acids are all readily soluble in water and will partition readily into condensing water while higher molecular weight NAs are hydrocarbon soluble or boiling points are such that they do not reach the overheads.

Ondeo Nalco observations are that this can occur for the visbreaker and vacuum unit fractionator's overheads. This may require a change in approach to the traditional techniques of corrosion control applied in these areas.

❖ Fouling

In addition to the fouling potential due to asphaltenes in the crude, fouling can also occur in downstream units due to corrosion by-products. The corrosion by-product of naphthenic acid corrosion is iron naphthenate. Corrosion mitigation is required to prevent premature fouling/cleanings due to the buildup of naphthenic acid corrosion by-products.

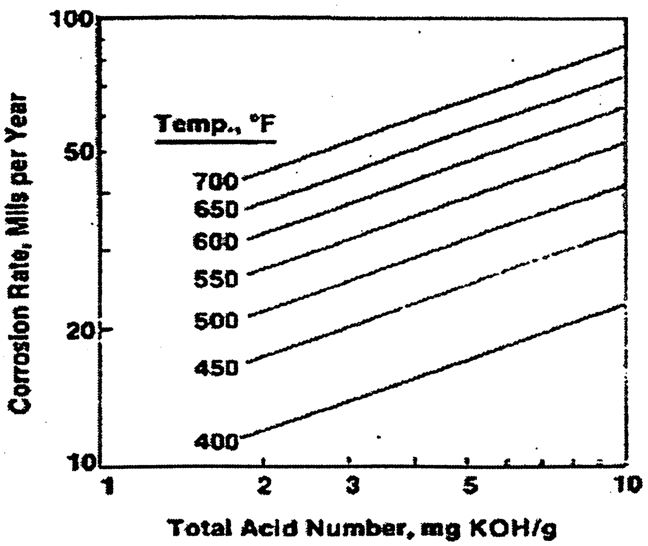


Figure 9: NAC of Carbon Steel in Columns and Heat Exchangers [42]

➢ Exchangers

Heat exchangers are the other most affected area by NAC where corrosion rate increases with increase in temperature as well as TAN (figure 9). The affected points of exchangers by NAC are shelve, tubes, baffles and tie road [20].

➢ Side Cut Piping

Here if the velocity increases, corrosion also increases and it was seen that the presence of sulphur reduces the corrosion. 317L SS up-gradation reduces the corrosion. Also the orifices, valves, thermo-wells and other instruments are affected and need to be up-graded [19-20].

➢ Furnace Tubes of Transfer Lines

The intensity of corrosion depends on the temperature of the system, velocity and the degree of vaporization. Also parameters like load & steam rate and turbulence do affect the corrosion rate. The mechanism is an accelerated corrosion mechanism. To avoid this carbon steel piping clad with 317SLSS is used. The most affected areas are the thermo-wells in the furnace outlets and the transfer lines [19-20].

➢ Side-cut Stability

Polymerization, auto-oxidation, corrosion, and thermal decomposition are some adverse effect of NAs present in crude that affects the end product quality (like cetane index, colour, odour etc).

❖ Oxidation of VGO

If high level of naphthenic acid crude processed, potential exist for destabilization of VGO. In some circumstances processing high levels of naphthenic acid crudes has led to oxidation of the VGO causing it to turn black within hours. The increased acid number was essentially resulting in oxidation of VGO.

Solution: Ondeo Nalco has treated this condition successfully with a chemical stabilizer (200 ppm of EC5300) to the problem stream.

❖ Low Cetane Index and Smoke Point in Distillates

Another common side-cut stability problem is low cetane index and smoke point for most of the high TAN crude available in market [42]. Consequently, crude oils with high naphthenic acid concentrations are considered to be of poor quality and marketed at a lower price.

To meet diesel (gas oil) specifications allowance has to be made either for the use of a cetane improver or an amount of higher cetane gas oil available in the refinery pool for blending.

Crude Source	Merey	Alba	Kuito	Gryphon	Heidrun
Cetane	41	42	40	39	40
TAN	1.05	2.6	2.1	4.4	2.7
Sulphur %	1.5	0.6	0.4	0.3	0.4

Table 2: Cetane Index for Various HAC [42]

From the table 2, it is significant that high acid crude, like gryphon, has lowest cetane number. As the TAN increases the cetane number is decreases.

Solution: Now a day, naphthenic acid recovery from distillates is also a very convenient approach to get rid of this problem. In addition to reducing corrosion in the refinery, naphthenic acid recovery from the petroleum distillates, primarily kerosene and diesel fractions is necessary to improve the burning qualities, storage stability, and odor of the finished kerosene and diesel fuels.

CHAPTER 3. PARAMETERS AFFECTING NAPHTHENIC ACID CORROSION

The main factors which govern the onset and severity of the corrosion are: naphthenic acid, acid number, temperature, velocity, metallurgy, sulfur content and physical state of NAs.

3.1 Naphthenic Acids [The 'villain of the piece']

Naphthenic acids are normal constituents in nearly all heavy crude oils, typically ranging from 0-4 %wt. The naphthenic acids are complex mixtures, showing variations in structure and molecular weight (Figure 10 & table 3).

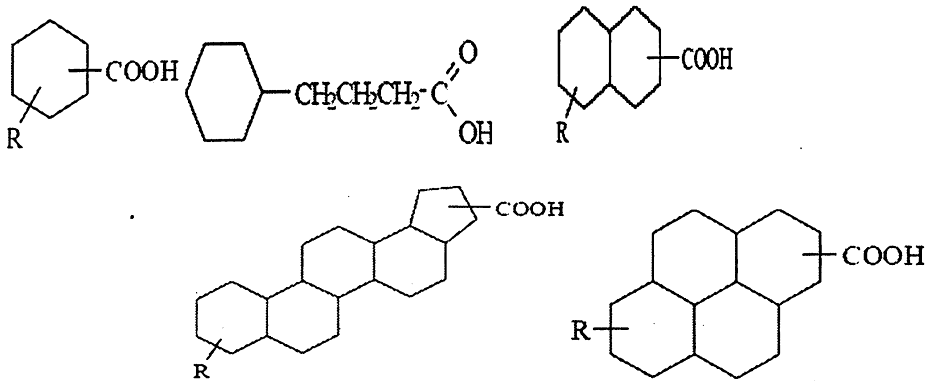


Figure 10: Some Naphthenic Acid Present in High Acid Crude

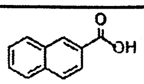
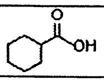
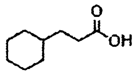
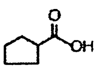
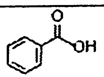
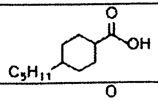
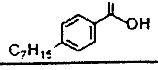
Carboxylic Acids	Structures	Molecular Weight	MP(°C)	BP(°C)
2-Naphthoic acid		172 18	185.5	>300
Cyclohexane carboxylic acid		128 17	31.5	232.5
Cyclohexanepropionic acid		156 22	16.0	276.5
Cyclopentane carboxylic acid		114 14	4.0	216.0
Benzoic acid		122.12	122.4	249.2
Trans-Pentylcyclohexanecarboxylic acid		198 31	51-53	110 0
4-Heptyl benzoic acid		220 31		

Table 3: Structures and properties for several NAs

On an average, a typical NA bearing crude may have more than 1500 types of naphthenic acids. Some are very corrosive others are relatively inert. Low molecular weight NAs are highly corrosive than high molecular weight. Average molecular weight of naphthenic acids typically ranging from 200-400.

❖ Boiling Point Distribution of NAs

Different NA species distil at different temperatures and can concentrate in specific areas in the refinery. The naphthenic acids are most active at their boiling point and the most severe corrosion generally occurs on condensation.

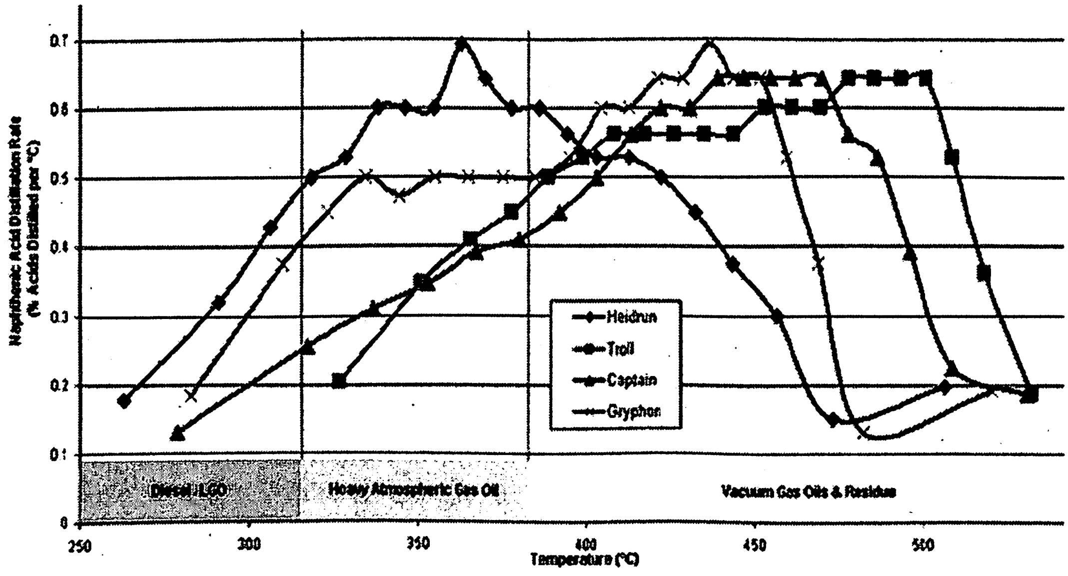


Figure 11: NA Distribution Profile for Various North Sea Crude Oils [65]

Boiling point distribution of NAs varies from crude to crude. Distribution mainly depends on the type of NAs (high/ low molecular weight). For Heridrun crude, NA distillation rate is maximum at 360^{0}C while 440^{0}C for Gryphon crude (figure 11).

➢ Acid Number/ Neutralization Number (TAN)

The most common method of indexing crudes according to acid content is a titration method to determine total acid number **(TAN)** which is a measure of the number of mg KOH required neutralizing one gram of oil. The exact amount of acid needed to cause a problem is still in question. Nevertheless, some useful guidelines have been reported (Table 4).

Craig has reported data shelving that calculated by converting the equivalent weight of iron lost in the corrosion process to an equivalent number of milligrams of KOH per gram of oil [48, 62].typically only about 5% of the naphthenic acids present in crude are corrosive. He defines a corrosion acid number (CAN) which is He defines a **corrosion acid number (CAN)** which is calculated by converting the equivalent weight of iron lost in the corrosion process to an equivalent number of milligrams of KOH per gram of oil.

Lit. Reference	**Crude Type**	**Threshold Value (TAN)**
Heller, Material Performance, 2(9),1963	Not given	0.5
Derungs, NACE 1956	Not given	0.5
IIP/ IFP Paper 1986	General and Nigerian	0.5-0.8 and 0.3
Gutzeit, Corrosion 1976,1981	Not given	0.5
PL Piehi, NACE 1988	US West Gulf Coast and California	1.5-1.8

Table 4: Crude Type and Threshold Value

These threshold values are helpful, but should not be taken as absolutes.

❖ Correlation of Corrosivity and TAN

Since the naphthenic acids are a mixture in any particular crude and vary considerably from crude to crude, two different crudes with the same TAN will not necessarily have the same corrosivity [39]. From figure 15(a), it is clear that there is no direct correlation between TAN and corrosivity (represented by color and shape) with the overall percent relative abundance of the carboxylic acids.

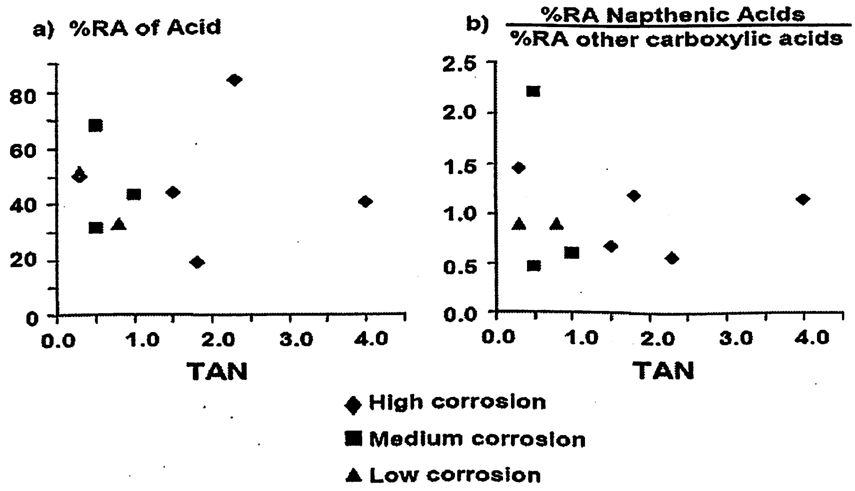


Figure 12: Plot of percent relative abundance of COOH group containing species vs. TAN (a) and the ratio of percent relative abundance of naphthenic acids to percent relative abundance of other carboxylic acids vs. TAN (b)

Next, the abundance of the naphthenic acids was examined by plotting the ratio of naphthenic acid percent relative abundance to the percent relative abundance of all other carboxylic acids vs. TAN {figure15 (b)}.

- **Naphthenic Acid Number vs. Total Acid Number**

TAN titrations measures many other species along with naphthenic acid or it gives the total acid content a crude oil. So TAN titrations give no perfect information on the volatility of the naphthenic acid. For these reasons, crude assay TAN can serve as a "red flag," but it is not predictive of when or where corrosion will occur.

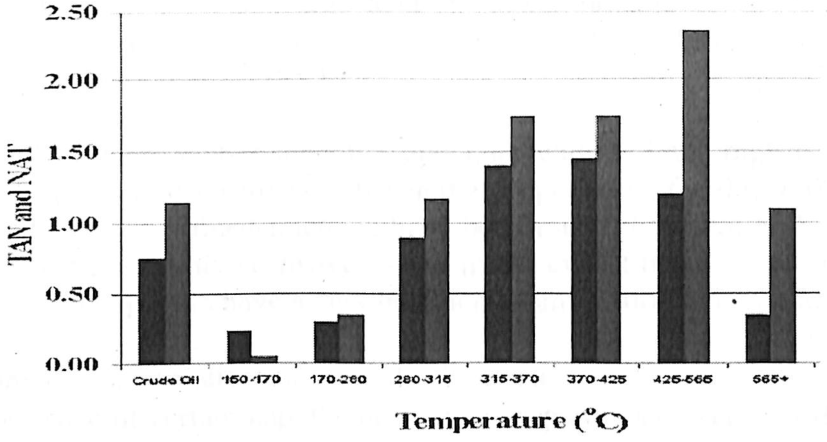
To overcome this problem of TAN titration, naphthenic acid titration (NAT) comes into the picture. NAT is also known as NAN (naphthenic acid number). The TAN and naphthenic acid content (from the Naphthenic Acid Titration, or NAT) for most crude oils varies with the temperature of distillation fraction. NAT represents only the naphthenic acids within the TAN.

Boiling Range	Total Acid Number (TAN) mg KOH/g	Naphthenic Acid Titration (NAT) mg KOH/g
Whole Captain Crude	2.5	2.2
IBP - 260 deg C	0.25	0.3
260 - 302 deg C	0.9	0.85
302 - 343 deg C	2.1	2.0
343 - 390 deg C	2.8	2.5
390 - 482 deg C	3.8	2.6
482 - 565 deg C	3.8	2.0
565 - deg C +	2.5	0.6

Table 5: TAN vs. NAT Captain Crude oil and Fractions

There are many different naphthenic acid species, and some are more corrosive than others. Testing the whole crude and the side cuts shows where the different naphthenic acids will concentrate. Table 4 shows the TAN vs. NAT for Captain Crude oil as whole crude and typical fractions. Figure 13 shows the same TAN vs. NAT profile, this time for a crude blend consisting of 37% Heidrun crude. Notice that for the whole crude, NAT represents only 60% of the TAN, while at the vacuum gas-oil temperatures the NAT numbers are concentrated and much closer to 90% of the TAN at those temperatures. The distribution of naphthenic acids is provided in Figure 14. Note the NAT numbers in the 329-350 and 350-375 °C cuts represent almost all the TAN, whereas the hotter cuts show the NAT becoming a smaller percent of the TAN. Similar trend is also observed for Venezuelan crude (Figure 15).

Figure 13: TAN and NAT profiles for crude slate containing 37% Heidrun



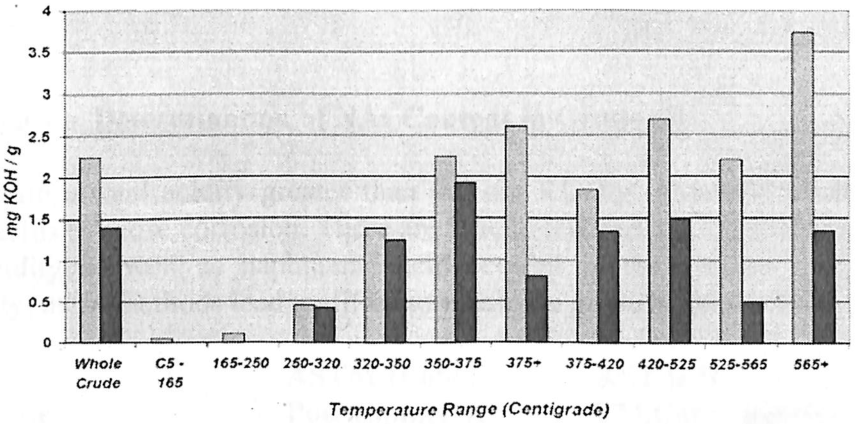


Figure 14: TAN/NAT Profile for Typical High Acid Crude (Grane Crude)

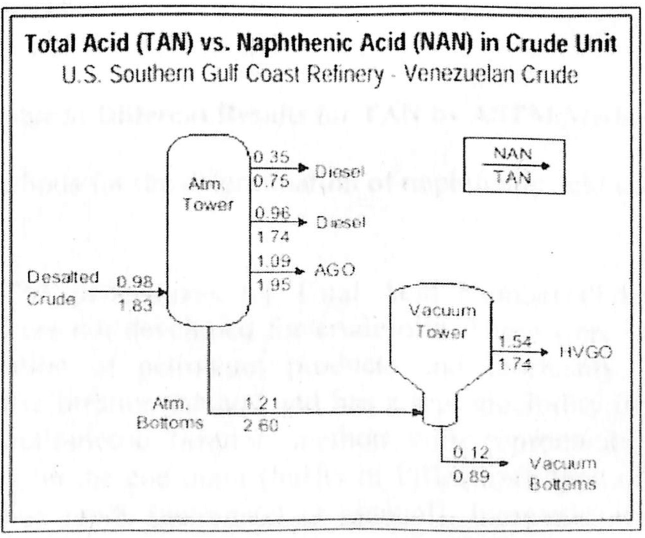


Figure 15: TAN and NAN in Crude Unit of US Southern Gulf Coast Refinery

As temperature increases the corrosion rates may increase until the temperatures are hot enough to break down the naphthenic acids to lower organic acids. The differential between TAN and NAT then begins to widen with the NAT decreasing. This usually starts to happen at above 420°C (788^{0}F).

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 750^{0}F. But some sources of crude oil and refined fractions have been found that have high TAN values, but appear not to be as highly corrosive as one might expect based solely on their TAN value. These crudes appear to have a very beneficial combination of conditions:

- The presence of sufficient sulfur in the fractions.
- The presence of certain naphthenic acids with particular structures those are less corrosive.

3.2.1 Methods for Determination of NAs Content in Crude oil

Crude oils with a total acidity greater than 0.5 mg KOH/g, generally contains enough naphthenic acids to cause corrosion. There are special test methods available to determine the total acidity as well as naphthenic acid content in the process stream [11-14]. Unfortunately, these methods lead to different results as given below in Table 6.

Crude	**ASTM D-664, Potentiometric**	**ASTM D-974,Colorimetric**
South Beiridge	9	6.4
Cyrmic Heavy	8.2	6.5
Cyrmic Light Heavy	8	6.4
Midway Special	8.4	6.4

Table 6: Different Results for TAN by ASTM Method

There are several methods for the determination of naphthenic acid content.

1. **The ASTM procedures** for Total Acid Number (TAN) also called neut number were not developed for crude oils. There 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, mercaptan, 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.

3.2.2 Improved Methods for Measuring Crude Oil Corrosivity

- **The Fast Atom Bombardment Mass Spectroscopy (FAB-MS) of NAs.**

This method is also known as Shell method FAB-MS (details being furnished by SGS, USA). Shell method considers isolation of nap acids and measurement is done based on mol wt distribution through mass spectra of the naphthenic acid extracted from the oil. This method is mainly used to fingerprint crude oils from around the world [37].

- **Nalco NAT (Nap acid titration) Method.**

On a query to Nalco, it was stated that their method would be shared only to clients using their inhibitor program to combat HAC corrosion. Some results of Nalco NAT methods is given above under the heading of NAN vs. TAN [32].

- **Radioactive tracer technology (RATT)**

RATT is used to measure crude oil corrosivity with much greater accuracy than conventional methods. With RATT, test coupons are irradiated to develop suitable tracers for detection using on-line gamma ray spectroscopy. Corrosion is measured by monitoring the buildup of radioactivity in a closed-loop system as a function of test time [42].

Advantages of RATT:

- Detection and measurement of corrosion in real time.
- Shorter test times (typically 4 hours vs. 24–48 hours with conventional testing).
- No degradation of crude properties during testing.
- Allows for safer and more reliable use of opportunity crudes.

Research is still underway to determine which type of naphthenic acid is potentially corrosive and to predict the cuts where these naphthenic acids will concentrate during distillation of the crude oil. During distillation and chemical analysis, sampling, H_2S evolution with temperature and the naphthenic acid and sulfur compounds decomposition with temperature depend also on the heating steps and temperature holding time which is arbitrarily chosen since the process conditions are different in each refinery.

➢ Sulfur Compounds

Other than carbon and hydrogen, sulfur is the most abundant element in petroleum. Sulfidic corrosion by various sulfur compounds at temperatures between 260 and 540°C is another type of high temperature corrosion in many petroleum-refining processes and occasionally in petrochemical processes. Sulfidic corrosion (SC) is in the form of uniform thinning, localized attack, or erosion corrosion.

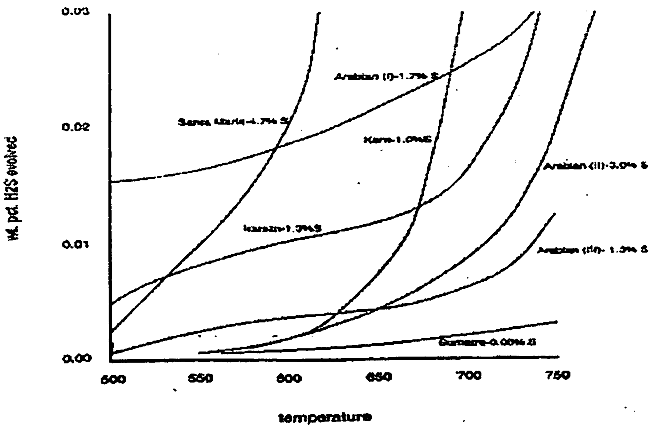
Sulfidic corrosion temperature range overlaps naphthenic acid corrosion, starting at about 500^0F (260^0C) and increasing from there. Since virtually all crudes have some sulfur, the effects of sulfidic and naphthenic acid corrosion can be confounded. Several people have observed that higher sulfur content will mitigate naphthenic acid corrosion, presumably because of stabilization of iron sulfide scale which the naphthenic acids tend to dissolve.

❖ H_2S Evolution

Hydrogen sulfide evolution test results could be correlated with crude corrosivity if enough refinery experience evolution versus corrosivity of typical crudes is available. However, crude corrosivity is function of the hydrogen sulfide dissolved in oil rather than in the vapor phase. If a linear relationship between the content of H_2S in oil and in the vapor (at equilibrium) is assumed, then H_2S evolution can be used as a predictive tool. Otherwise, analysis of H_2S dissolved in each cut, in addition to TAN, might be more useful for assessing crude corrosivity [37].

As early as 1953, it was found that the H_2S evolved at 850^0F 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_2S evolution**. A standard procedure for the hydrogen sulfide evolution with temperature is not currently available.

Figure 16: H_2S Evolution Data of Different Crude Oils



The presence of sulfur-containing compounds in hydrocarbon fractions can inhibit naphthenic acid corrosion. The most important factor in this effect appears to be sulfur speciation and the ability of the sulfur species present to provide reactive sulfur (H_2S) to inhibit the naphthenic acid corrosion under the process conditions (Figure 17). For example, in side cut piping, the sulfide film produced by H_2S is believed to offer some degree of protection from naphthenic acid corrosion.

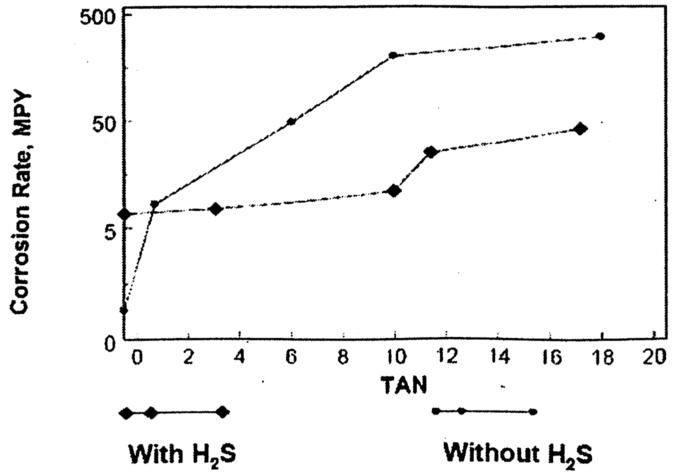


Figure 17: Effect of H_2S on NAC [42]

Naphthenic acid corrosion is either reduced or augmented depending on [37]:

- Acid species like H_2S, CO_2, acid salts, etc do not contribute to naphthenic acid attack. Further, on a query, it was stated that no correlation had yet been established to say organic chlorides when present in crudes had any influence on nap acids attack.
- Wt. % sulfur present in crude oil.
- Amount of "reactive" (lighter) sulfur species present along with naphthenic acid.

Higher sulphur level is generally considered to be beneficial for the inhibition of naphthenic acid attack. However, increased concentrations of reactive sulphur may trigger high temperature sulphidic corrosion.

➢ Velocity

Velocity and wall shear stress is a main parameter affecting NAC. Both sulfidic and naphthenic acid corrosion can be accelerated by velocity of the flowing process environment or by local turbulence. The wall shear stress produced by the flowing media contributes an added mechanical means to remove the normally protective sulfide films.

Fluid flow velocity lacks predictive capabilities. Data related to fluid flow parameters such as wall shear stress and Reynold'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 Reynold's Number for field flow conditions in a pipe is calculated by the following equation:

$$\mathbf{R_e = D\ r\ V / m}$$

where R_e = Reynold's Number
D = diameter of pipe (m)
r = density of fluid (Kg/m^3)
V = velocity of fluid (m/s)
m = 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:

$$\mathbf{t = f\ r\ V^2 / 2}$$

To use plant corrosion data of specific crude or blend as a way to predict its corrosivity for another plant:

- Calculate shear stress for plant with known corrosion data,
- Calculate shear stress for plant which is planning to run the specific crude or blend
- Compare both shear stresses.

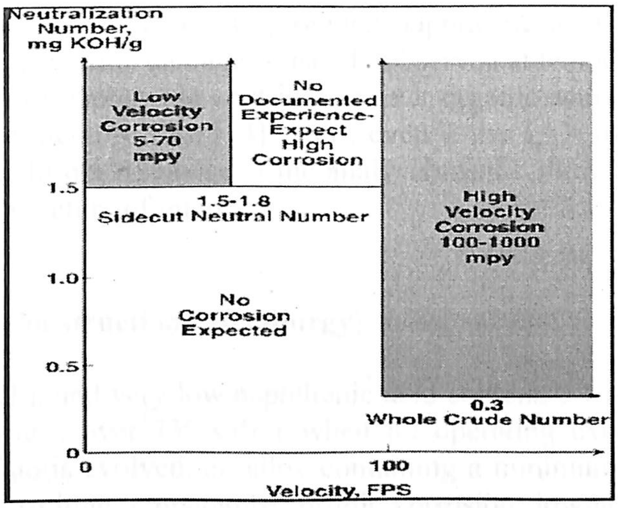


Figure 18: Velocity Effect on Naphthenic Acid Crude [42]

Corrosion rates are directly proportional to shear stress. Typically, the higher the acid content, the greater the sensitivity to velocity (Figure 18). When combined with high temperature and high velocity, even very low levels of naphthenic acid may result in very high corrosion rates [24].

- **Physical State**

Gutzeit in his paper indicated that liquid phase corrosion decreases slightly with increase in velocity due to loss of naphthenic acid as vapors whereas vapour phase corrosion increased drastically with increase in velocity because of more vapors are formed due to agitation and thereby caused more of condensation. But increasing velocity above 4m/s-vapour phase corrosion rate decreased as formation of naphthenic acid rich condense film is prevented due to centrifugal force[22, 24].

- **Temperature**

Naphthenic acid decomposition with temperature is an additional test that may predict the severity of naphthenic acid corrosion as a function of temperature. The relationship between temperature and corrosion rate at a constant TAN is fairly linear - to a point (figure 14). Naphthenic acid corrosion is normally not a concern much below 200°C (392^{0}F). Naphthenic acid corrosion is found to occur in the temperature range from 230-420°C in high velocity areas. In the Q&A session of NPRA congress in 1990, it was reported that several refineries experienced naphthenic acid corrosion at temperatures as low as 177°C [10].

In general, corrosion rate of all alloys in the distillation units increases with increase in temperature.Gutzeit has tentatively concluded that naphthenic acid corrosion continues to increase with temperature up to 385°C provided naphthenic acid are not lost through vaporization [22]. No corrosion damage is usually observed at temperatures above 400°C, due to decomposition of naphthenic acid into smaller organic acids or protection due to coke formation on the metal surface [24]. Thus, even if the TAN of a cut is expected to be high, corrosion might not be severe if the analysis results show that the acids readily decompose at the temperature of interest.

➢ Materials of Construction (Metallurgy)

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.

❖ Rules of Thumb

A crude oil 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 450-750 ^{0}F. Some rules for materials recommendations are:

- Above 450^{0}F: Use 3 16SS (2.5 Mo minimum) clad in vacuum column if TAN is above 0.5 and also in atmospheric column if TAN is above 2.0.
- Above 550^{0}F: Use 5Cr or 12CR clad for crude over 1% sulfur content.
- Above 650^{0}F: Use 5Cr or 12Cr clad for 0.1 to 1% sulfur content.

However, there are many cases including high velocity, high TAN and others where these rules of thumb break down.

CHAPTER 4. NAC MECHANISM

Naphthenic acid corrosion (NAC) and high temperature crude corrosivity in general is a reliability issue in refinery distillation units. The presence of naphthenic acid and sulfur compounds considerably increases corrosion in the high temperature parts of the distillation units. The corrosion mechanism is, generally condensate corrosion and is directly related to content, molecular weight and boiling point of naphthenic acids present in crude oil.

The NAC reaction process is generally described by:

$$\mathbf{Fe + 2RCOOH \longrightarrow Fe(RCOO)_2 + H_2}$$

The corrosion product is an oil-soluble iron naphthenate.

Since it could apply equally to chemical or electrochemical mechanism, the understanding of the NAC mechanism is still obscure. Turnbull attempted to distinguish the relative contributions of electrochemical and chemical process based on the conductivity and current density measurement. It is concluded that NAC is more likely to be a chemical mechanism. However, Wu et al. suggested that the naphthenic acids could dissociate into $RCOO^-$ and H^+ even in oil media at high temperature, which indicated that electrochemical mechanism is also possible.

4.1 Electrochemical Mechanism:

At low temperature, NAC should be mainly a chemical reaction since little naphthenic acid is dissociated and the conductivity is low. At high temperature, more naphthenic acid is dissociated into $RCOO^-$ and H^+ and the conductivity increased significantly with temperature as noticed by Turnbull. Electrochemical NAC thus became possible [33]. The anodic reaction should be

$$\mathbf{Fe + 2RCOOH \quad = \quad Fe(RCOO)_2 + 2e^-}$$

The cathodic reaction should be

$$\mathbf{2H^+ + 2e^- \quad = \quad H_2}$$

4.2 Chemical Mechanism (Combined Effect of SC and NAC)

Pure naphthenic acid cannot be responsible for the high corrosion rates encountered in practice. The high corrosion rates experienced in refinery equipment are more likely the result of a combined action of sulphur (H_2S) and naphthenic acids. The role of these acids is assumed to be in converting the normally protective and stable oil-insoluble iron sulphide scale into an oil-soluble iron-naphthenate [33].The NAC mechanism can be explained as:

- Sulphur bearing stocks at low levels, provide a protective sulphide layer on metal surface.
- Naphthenic acids break down these layers, exposing fresh metal to further corrosion
- Naphthenic acid corrosion manifests as grooving or localized corrosion

These lines can be represented by the following reactions:

$Fe + 2RCOOH \longrightarrow Fe(RCOO)_2 + H_2$	NA attack
$Fe + H_2S \longrightarrow FeS$	Sulphidation
$FeS + 2RCOOH \longrightarrow Fe(RCOO)_2 + H_2S$	NA-S corrosion

This synergism between the organic (naphthenic) acid corrosion and sulphidation makes the reaction so severe.

4.3 Mechanism Based on Location Affected by NAC

There are at least three mechanisms of naphthenic acid corrosion. Each one is predominant in specific areas of the distillation unit.

Furnace Tubes and Transfer Lines

In furnace tubes and transfer lines, the influence of temperature, velocity and degree of vaporization is very large. Process conditions such as load and steam rate and especially turbulence affect corrosivity. The presence of any naphthenic acid most likely increases sulfidic corrosion. The corrosion mechanism at the furnace tubes, transfer lines, areas of high turbulence such as thermowells and pumps, is most likely an accelerated corrosion due to the velocity and the two-phase flow.

Vacuum Column

In the vacuum column, preferential vaporization and condensation of naphthenic acids increase TAN of condensates. The corrosion is similar to corrosion in very high TAN cuts and velocity has virtually no effect on the process. The naphthenic acids are most active at their boiling point but the most severe corrosion generally occurs on condensation. The corrosion mechanism is mainly condensate corrosion and is directly related to content, molecular weight and boiling point of the naphthenic acid. Corrosion is typically severe at the condensing point corresponding to high TAN and temperature.

Side Cut Piping

In side-cut piping, conditions of low vaporization and medium fluid velocity exist. In these conditions, an increase in velocity increases corrosion rates up to the point where impingement starts and corrosion is accelerated dramatically. Sulfur has been shown to inhibit somehow the corrosion.

4.4 The role of pseudo-passive film in combating the synthetic effect of SC and NAC

Corrosion film, or ''pseudo-passive film'' as it called, plays an important role in understanding the corrosion behavior in refining environments. Film composition varies with the crude. As discovered by Smart, no film was formed in pure oil containing naphthenic acid, but in crude oils the metal was able to react with oxygen and sulphur to form a mixed oxide–sulphide film. It was generally accepted that the forming of metal sulphides film could partly protect the metal from further attack such as NAC, erosion–corrosion, etc.

6.4.1. Naphthenic Acid Corrosion Index (NACI)

In order to study the effect of SC on NAC, ''naphthenic acid corrosion index'', a simple ratio of the corrosion rate to the weight of corrosion product film, was suggested to assess the severity of NAC [32, 69].

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

Based on this theory, three types of corrosion were found:

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

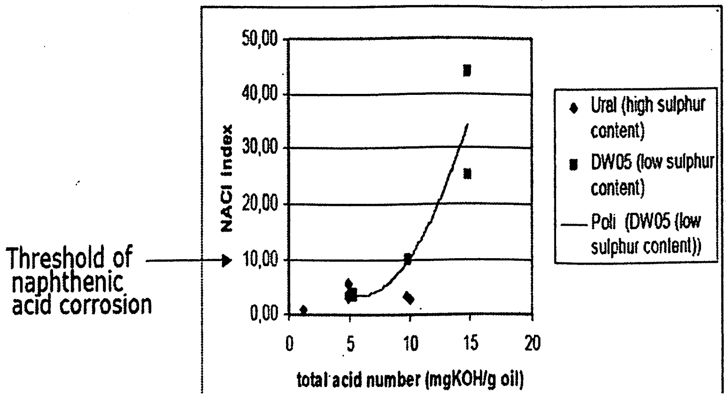


Figure 19: NACI index [63]

The experimental results are roughly in agreement with the model given in the literature for the interaction between sulphur and naphthenic acids [63]. For example:

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

But a very high concentration of naphthenic acids (TAN=10) is necessary for the naphthenic acid corrosion to start. In contrast, far lower concentrations can give rise to naphthenic acid corrosion in refinery plants.

CHAPTER 5. MITIGATION TECHNIQUES FOR NAC

In general, there are five control methods for NAC includes blending, neutralization inhibition, and process control and materials upgrading. Brief discussion on these mitigation techniques are given below.

5.1 Blending

Blending is nothing but a dilution of NA concentration in HAC. Blending is performed in a way that the crude, which enters the distillation column, should not have a neutralization number more than 0.5 to 1.0 or it may be used to reduce the naphthenic acid content of the feed by diluting high TAN crude with a low TAN one, thus reducing corrosion to an acceptable level.

But blending is not useful for vacuum tower internals operating in temperature range of 290-350°C. The sulphur content can also be increased using blending which reduces the naphthenic acid corrosion. Blending also changes shear stress parameters and reduces corrosion [1, 9].

This method involves blending the acidic crudes with low acid crude in order to get the TAN below the critical threshold value. The method is not always practicable because of limited availability of crudes for blending. Also, the concept of a safe, critical lower threshold might not be valid.

5.2 Partial Neutralization with Caustic

In neutralization caustic injection is given before desalter and at distillation furnace outlet. This method involves conversion of the acids to naphthenate by the addition of caustic. The disadvantage of this method is that the naphthenate can form very stable emulsion. Also, an excess of caustic can cause deposition, fouling, and caustic embrittlement [9]. Sodium contamination of resid is also a problem in desalters.

5.3 Materials in Refinery Construction

For long-term reliability, upgrading the construction materials is the best solution. The selection of materials for refinery construction depends on the type of refinery, the type of crude oil handled, and the expected service life for each vessel. As with all materials selection, the life-cycle cost must be considered in addition to purchase price. Table 6 lists some common alloys and their material costs.

Carbon steel (CS) is the most susceptible metal for refinery construction but CS can not give adequate protection against high temperature NAC. On the other hand, the most effective metallurgical remedy for surest protection against NAC is 317SS. This material is very similar to 316SS, but has molybdenum (Mo) content of 3-4%, compared to 2-3% for 316SS.

Based on field experience and laboratory experiments, molybdenum content of an alloy plays an important role in naphthenic acid corrosion mitigation. **Piehl** cites a critical Mo threshold of 2.5% for adequate protection from naphthenic acid attack.

According to a survey by **Cathleen Shargay** et al. (USA), at least 317 SS should be used in high velocity areas like furnaces and transfer lines. He also indicated that some places like side stream piping may require up-gradation to 317 SS or 316L SS with 2.5% Mo [9, 20]. Aluminum has also been useful, both as an alloying element and in aluminized coatings. Its use has been limited by its mechanical properties.

ALLOY CLASS	EXAMPLE	CONSTITUENTS										COST RATIO(9)
		Ni	Cr	Mo	Fe	Co	Ti	Cu	Cb	Al	V	
Carbon Steel	C10				>94							0.2
Low-Alloy Steel	1-1/4Cr 1/2Mo		1.25	0.5	balance							0.25
Fe-Ni-Cr + Mo	Type 316L	13.0	17.0	2.3	balance							1.0
	Alloy 800H	32.5	21.0		4.6							-
	20Cb-3	35.0	20.0	2.5	balance			3.5				3.8
Ni-Cr-Mo	Alloy C2	54.0	15.5	16.0								6.0
	Alloy C276	57.0	16.0	16.0	5.5							
	Alloy C4	54.0	16.0	15.5	3.0							
	Alloy 625	60.0	21.5	9.0					3.7			6.3
Ni-Cr-Fe	Alloy G	45.0	22.2	6.5	19.5			2.0				6.4
	Alloy 600	76.0	15.0		8.0							-
Ni-Mo	Alloy B2	balance	1.0	28.0	2.0	1.0						11.6
Ni-Cu	Alloy 400	65.1						32.0				-
Nickel	Alloy 200	99.9										-
Co-Base	ULTIMET (R)	9.0	26.0	5.0	3.0	54.0						27.2
Ti-Base	Ti-6Al-4V						90			6.0	4.0	-

Table 7: Common Alloys and Their Material Costs

- **Some Examples of Metallurgical up gradation in Refineries:**

1. To overcome naphthenic acid corrosion California refinery used metallurgical solutions by cladding vacuum column in 317SS.

2. In **Cross Oil & Refining Company**, the refinery metallurgy is mostly carbon steel with the exception of the following components, which were upgraded to 317 Stainless Steel [34]:

- Atmospheric Heater transfer line to atmospheric column replaced in 1999
- Atmospheric column Flash Zone clad in 1999
- Piping from Atmospheric column to Vacuum Heater replaced in 2001
- Vacuum Heater transfer line to vacuum column replaced in 2001
- Vacuum column flash zone to 9 stream draw tray clad in 2001

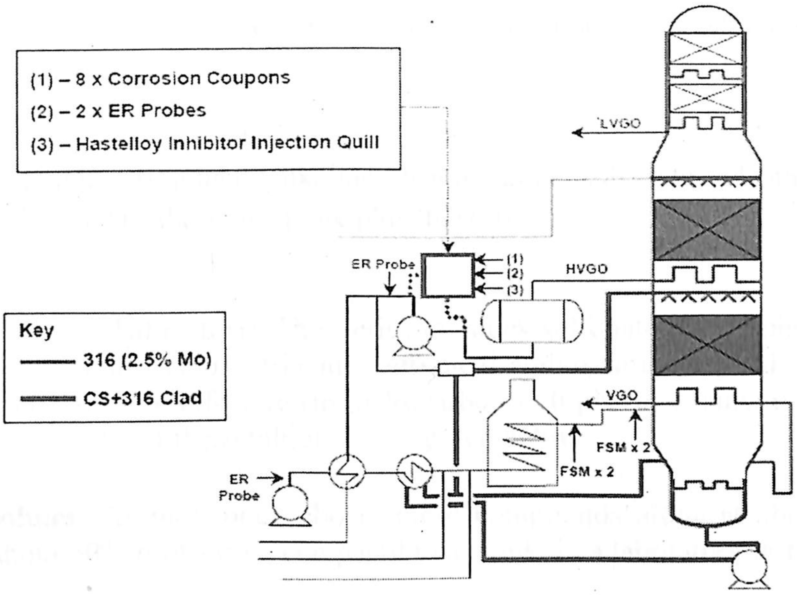


Figure 20: Western Europe VDU (Chevron Texaco) - Limited Metallurgical Upgrades

Since most of the systems are carbon steel, the challenge of corrosion control of high acid crudes is more difficult and challenging. It is very difficult for existing refineries to go for metallurgical up gradation since most of the systems are carbon steel (figure 23).

❖ **Alloy**

Nickel alloys containing high amount of Ni like Inconel 600 and Incoloy 800 are resistant against naphthenic acids but these have limited operational conditions [9]. In the Q&A session of NPRA (1990) representatives of different refineries mentioned their precautionary measures taken in respective refinery and was seen that some used up-gradation of equipment and some used blending, topping crude and neutralization methods to overcome the problem [18].

5.4 CHEMICAL INHIBITION

➢ **Classification**

Corrosion inhibitors are frequently used to control NAC in refineries. Literature survey indicated some organic corrosion inhibitors that are effective even at temperatures above 200°C whence the naphthenic acid corrosion problems become significant. These comprise of two categories:

1. **P Based Inhibitors:** The phosphorus-based inhibitors which have been reported in the corrosion literature and/or disclosed as patents use phosphate esters, phosphite esters, or phosphonate- phenate sulfides as the phosphorus source.

These formulations may also have other components. Some of phosphorus based inhibitors are given below:

- Phosphate ester plus amines
- Trialkylphosphate / alkaline earth metal phosphonate - phenate sulfide
- Di- or Tri-alkyl phosphite plus thiazolines

2. **Non-P Based Inhibitors:** This series includes sulfonated alkyl phenols, organic polysulfide, thio-hydroxy triazine, fatty acid amino amide etc, all of which have been claimed to be effective (in hydrocarbon rich phase) against naphthenic acid corrosion. Some of these inhibitors are given below.

- **Thiazolines.** As mentioned above, these compounds alone at about 1300 ppm gave about 50% protection, compared to a blank, in a laboratory test.
- **Organic polysulfides.** The preferred molecular weight is in the 300-600 range.
- **Sulfonated alkyl phenols.** The patent discloses use of alkyl phenol sulfonic acids as inhibitors in crude oils and gas oil with a TAN of 3.5 to 5.5.

One other application of chemical to alleviate naphthenic acid corrosion is the use of amines to make amides. Since this process involves a stoichiometric reaction between the carboxylic acid group and the amine functionality, it is not strictly speaking inhibition, but rather more like neutralization.

➢ Mechanism of Corrosion Inhibitors

As regards the phosphorus compounds, scanning electron microscope, studies revealed the presence of phosphorus on metal surface. Interaction of phosphate esters with metal (iron) surface has been postulated in the following manner:

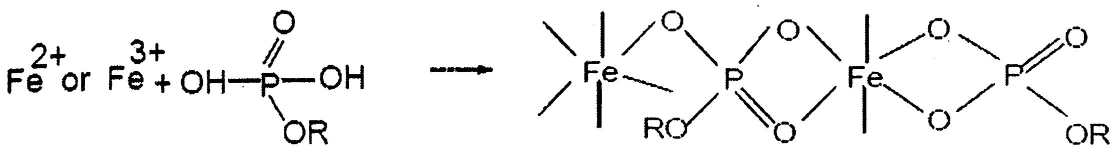


Figure 21: Mechanism of Corrosion Inhibitors

The above mechanism interferes with the reaction of iron with naphthenic acids. Instead of forming a hydrocarbon soluble iron naphthenate, insoluble iron phosphate is produced. Such complexes are very stable because of the strength of the Fe-P bond. This interaction eventually results in the formation of a tenacious film on the metal surface, which prevents naphthenic acid attack [4, 26-27].

➢ Benefits of the Sulphur-Based (Non-Phosphorus) Corrosion Inhibitor [34]

- Based on equipment inspections, UT probe analysis, ER probes, chemical and metallurgical analyses the sulphur-based corrosion inhibitor has provided corrosion protection similar to that of traditional state of the art phosphate ester inhibitors.
- The sulphur-based corrosion inhibitor has eliminated fouling that was experienced with previous inhibitors (P base inhibitors).
- The sulphur-based corrosion inhibitor has eliminated the source of catalyst deactivation.
- Controlling the fouling and corrosion have significantly reduced the refinery maintenance budget.
- Controlling fouling and corrosion have significantly enhanced the reliability of operations and worker safety.

➢ Use of Inhibitors

In the refining and petrochemical industry, SCORPION of Ondeo Nalco and SMARTGUARD of Baker Hughes are widely used for NAC control. It is stated that Nalco is the leader with 96% market share with 39 refiners using and "zero" failures in last 6yrs. despite TAN being as high as 6.5. Question arises when we should go for chemical inhibitors. In two situations refiner should go for chemical inhibition for NAC. When refiner is using

1. **HAC as a continuous feed stock**
    - Generally used until alloy upgrade can be made.
    - Used if NAs attack is limited and can be monitored.
    - Used when blend is moderately corrosive.

2. **Intermittent use of HAC**
    - Used when corrosion rates are excessive based on monitoring.

3. By using inhibitors refiner can protect their equipment from NAC and save money. (Cost is directly related to amount of equipment protected).

❖ Dosage of inhibitor [65]:

- Depends on severity of corrosion conditions.
- Typically 5 – 25 ppm.
- Pre-passivation is required.

❖ Application points for corrosion inhibitors

Corrosion inhibitors are applied to furnace, transfer lines, pump arounds and product side drawn [65]. In general corrosion inhibitors are applied

- Via suitable chemical injection quills with reflux.
- Upstream of anticipated area of risk

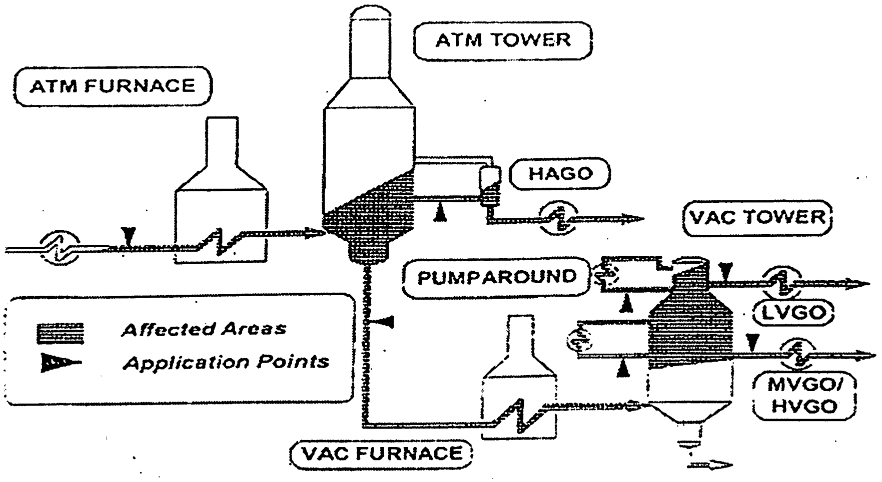


Figure 22: Typical Inhibitor Injection Points [28]

❖ Limitations of Corrosion Inhibitors

Shell observes the following limitations with inhibitor programme based on their studies till date.

- Inhibitor injection point could vary with type and distribution of nap acids in crude. In other words, multiple injection point will be essential.
- In some cases, pre treatment (with higher dosage of inhibitors) will be essential.
- Little or no vapour phase protection.
- There is a likely deactivation in HDS units. On a query with Nalco, it was stated that they did not have any problem at all in any HDS units including cat feed HDS
- Unproven effectiveness at high velocity / turbulent zones.
- Operating expenses.

➢ Process control changes

Ernesto and Brian have concluded that when a refinery is in processing naphthenic crude oils, operational changes can affect corrosivity, much more than with non naphthenic crude oils. Any proposed operational changes should be reviewed with material specialists to evaluate their impact [9].

CHAPTER 6. IMPROVED PROCESSES TO RECOVER NAS FROM MIDDLE DISTILLATES

6.1 Introduction

High Acid crude are much cheaper than sweet and non acidic crude and therefore can improve refinery margins significantly if acid corrosion is properly addressed and / or naphthenic acids, instead are recovered from the crude oil value added product. Recovery of NAs will not only assist refiners in avoiding corrosion of processing units but also add value to its profit margins.

Crude oil with high naphthenic acid content is a problem in terms of low cetane index and smoke point in petroleum distillates, primarily kerosene and diesel fractions. Consequently, crude oils with high naphthenic acid concentrations are considered to be of poor quality and marketed at a lower price.

Recovery of NAs compounds from crude oils is regarded as one of the most important processes in heavy oil upgrading. In addition to reducing corrosion in the refinery, recovery of NAs from the distillates is necessary to improve the burning qualities, storage stability, colour and odor of the finished kerosene and diesel fuels.

Naphthenic acids are obtained by caustic extraction of petroleum distillates, primarily kerosene and diesel fractions. In addition to reducing corrosion in the refinery, the caustic wash of the distillates is necessary to improve the burning qualities, storage stability, colour and odor of the finished kerosene and diesel fuels.

After removing NAs from diesel and kerosene stream, refiner can get more profit by selling this valuable product (NAs) in market (Detail in Section 8.9).

6.2 Conventional Methods of NAs Recovery and Their Disadvantages [39]

1. Current industrial practices either depend on dilution or caustic washing methods to reduce the TAN number of heavy crude oils. For instance, blending a high TAN crude oil with a low TAN one may reduce the naphthenic acid content to an acceptable level, but the acidic compounds remain and the value of the low TAN oil is diminished.
2. The conventional method of contacting two immiscible liquids- such as hydrocarbons and caustic- is to disperse one liquid thoroughly in the other as small droplets. The surface of the droplets lets contaminants pass between phases. As the droplets become smaller and more numerous, surface area increase and mass transfer from one phase to the other improves.

   Even when this dispersion- based system provides adequate treatment, separating the two phases is usually extremely inefficient. The mixture must remain in the phase separator until the caustic droplets settle out by gravity, a process that may take hours. As the treating requirement becomes more difficult, a higher pressure drop must be maintained, dispersion of the caustic phase must be more through, and the separation time becomes more longer.

Stable emulsions may even form in the separator vessel, resulting in the massive carryover. When carryover is excessive, expensive equipment must be installed downstream to remove caustic from the product, and treatment is often interrupted until the problem can be corrected. Process shutdowns, contaminated product, expensive coalescers- all are conventional problem that are normal with dispersive treatment methods.

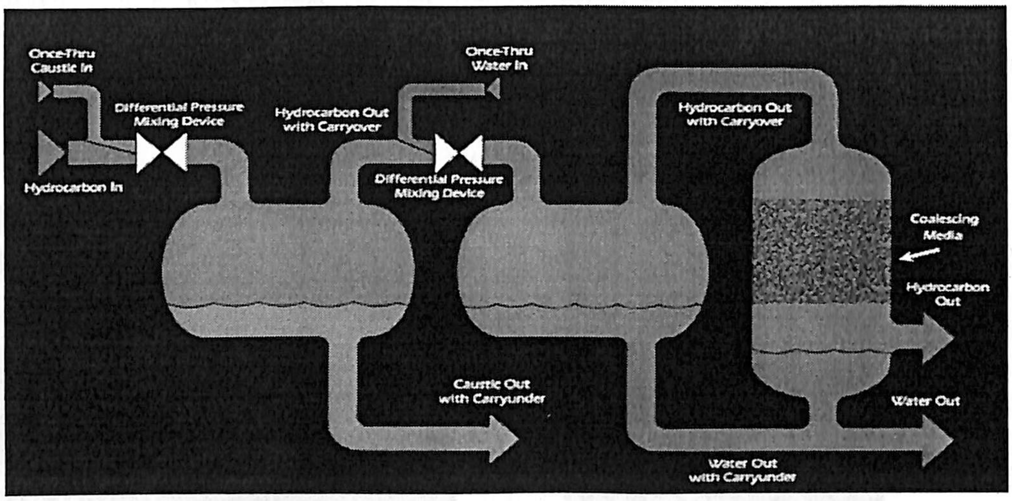


Figure 23: Conventional dispersive treatment process

Now a day, to overcome these problems a low-temperature and cost effective methods, including catalytic and adsorptive approaches, are developed to remove naphthenic acids from crude oil. In detail, objectives of these two processes are given below:

1) Caustic treatment of kerosene/ jet fuels streams using **Merichem FIBER-FILM™ Contactors** has proven to be practical and reliable, compared with conventional caustic washing systems. This prevents emulsion formation and results in minimum caustic carryover and high utilization of the caustic solution.
2) To develop a novel decarboxylation process to convert naphthenic acid compounds into non-corrosive components.
3) To remove naphthenic acid via a chemical adsorptive process by using solid adsorbents.

The naphthenic acid, existing in complex mixture of organic compounds, can be selectively extracted and condensed through solid adsorbents. If the two processes (2 & 3) can reach a complementary for each other, it would be an ideal concept for the process design [30].

6.3 Merichem's FIBER-FILM™ Contactors

The Fiber-Film process is a non-dispersive method of contacting two immiscible liquids without forming emulsions, which are the source of most difficulties inherent in dispersive treating. This unique technology solves a wide range of refinery and petrochemical treating problems:

- It improves mass transfer efficiency yet virtually eliminates aqueous phase carryover.
- With shorter settling times and less generation of dilute aqueous waste, it requires much smaller processing vessels, thus saving valuable plant space and reducing capital expenditures.
- Whether applied to caustic acid or water treating needs, this technology results in a high efficient, more profitable processing operation.

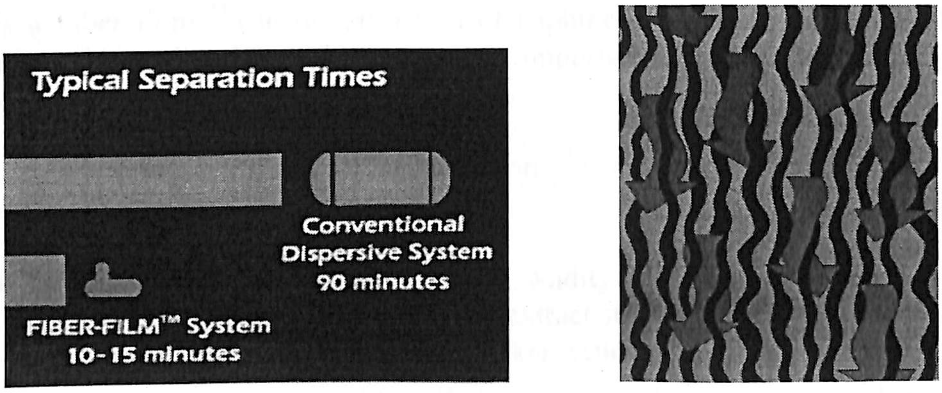


Figure 24: (a) Typical Separation Time of Fiber Film Contactor, (b) Heart of Merichem FIBER-FILM™ Contactors

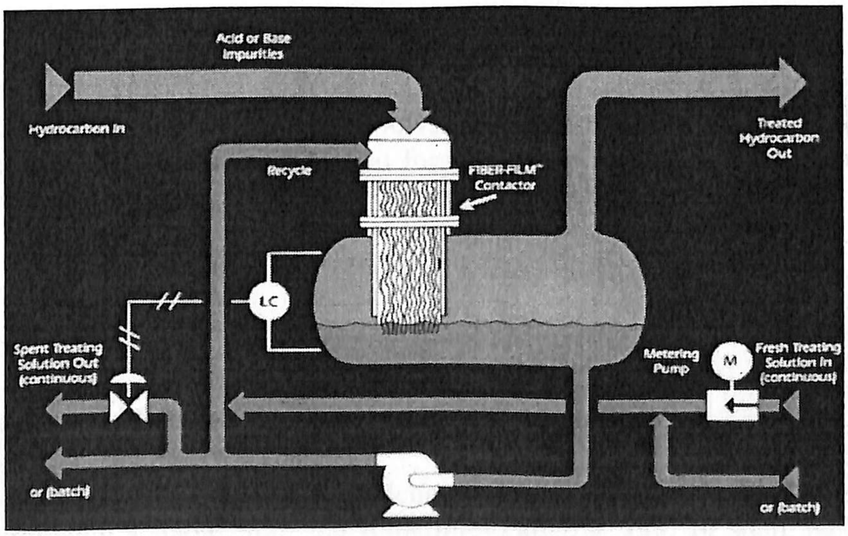


Figure 25: One Stage Merichem FIBER-FILM™ Extraction System.

Figure 24 (b) is known as the heart of Merichem FIBER-FILM™ Contactors is a column tightly packed with fine proprietary metal fibers. The constrained caustic phase (blue) wets the fibers while the free owing hydrocarbon phase (red) is purified as it passes through the array of wetted fibers.

Caustic treatment of middle distillate streams using FIBER-FILM™ Contactors has **proven to be practical and reliable, compared with conventional systems.** It a new and more efficient method of creating interfacial surface area that would avoid dispersion while at the same time allowing equilibrium constants and concentration driving force to be increased.

6.3.1 NAPFINING^{SM} Technology

It is a Fiber Film^{TM} caustic extraction of naphthenic acid from jet fuels, kerosene and virgin middle distillate. There are two important steps in wet treating of middle distillates:

- Total acidity reduction
- Mercaptan oxidation.

The processing step required when total acidity must be reduced is a weak caustic prewash which is designed specifically to extract strongly acidic compounds such as H_2S but in particular naphthenic acids from the kerosene/jet fuel.

❖ Objective of Merichem's NAPFINING Technology

By reducing the total acidity of the kerosene/jet fuel, the NAPFINING^{SM} pre-wash also provides a more easily sweetened feedstock for the mercaptan oxidation process that follows. The FIBER-FILM™ Contactor allows the caustic and naphthenic acids to react without dispersion of phases. This reaction forms sodium naphthenate, the chemistry of which is shown below:

$$RCOOH + NaOH \rightarrow RCOONa + H_2O$$

❖ Advantage of Merichem's NAPFINING Technology

- Sodium naphthenate has a great tendency to emulsify with the diesel and kerosene fuel producing a stable emulsion sometimes called a "rag" or soap, which is very difficult to break. if these soaps get into downstream mercaptan sweeteners, they can adversely affect their performance. These soaps also will cause the diesel, kerosene and jet fuel to fail other specifications such as water separation index if allowed to remain in the finished kerosene/jet fuel product. By using NAPFINING, refiner can overcome these problems.

- NAPFINING can be operated in the batch or continuous mode of fresh 5-10% caustic addition, but the most common mode is continuous addition by metering pump and continuous withdrawal of spent caustic on level control [39].

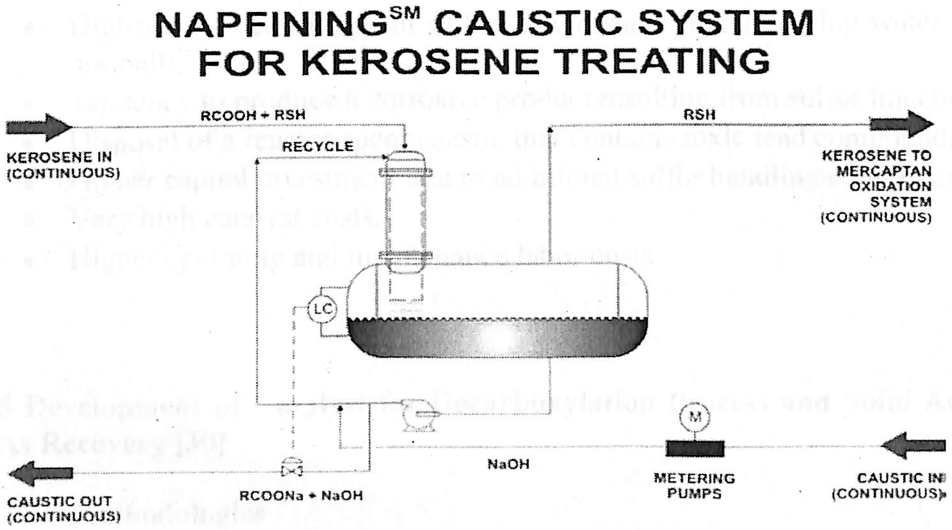


Figure 26: NAPFINING^{SM} Technology for Kerosene Treating

6.4 Disadvantages of Alternative Diesel and Kerosene Fuel Treating Processes

- **Hydrotreating:** Hydrotreating involves a much greater capital investment (10 to 20 times) and requires much higher operating costs (20 to 50 times) than "wet treating" which is the phrase often used to denote caustic treating with the attendant cleanup processes. For these reasons, refineries avoid hydrotreating whenever possible. The table below provides a cost comparison between caustic treating and Hydrotreating [39].

	U.S.D. Operating Costs/ 1,000 Metric Tons Processed	**U.S.D. Capital Costs/ 1,000 Metric Tons Capacity**
Chemical Treating	80 - 400	400,000 – 1,200,000
Hydrotreating	4,000 – 8,000	8,000,000 – 12,000,000

Table 8: Cost Estimation of Chemical Treating and Hydrotreating

Bender Treating: Although the bender process has been effective in producing kerosene/jet fuels in many refineries there are some disadvantages when compared to the NAPFINING^{SM}[39]:

- The electrostatic mixer settler approach used in the pre-wash step often results in shutdowns due to electrical short circuits caused by emulsions. As the feed neutralization number increases, so does the tendency for this to occur.
- Incomplete removal of naphthenic acids results in soaping of the bender reactor and downtime of washing.
- Under utilization of the caustic in the pre-wash due to ineffective contact of the phases.
- Higher water consumption of the electrostatic mixer settling water wash system normally used.
- Tendency to produce a corrosive product resulting from sulfur injection.
- Disposal of a reactor spent caustic that contains toxic lead compounds.
- Higher capital investment due to additional sulfur handling equipment.
- Very high catalyst costs.
- Higher operating and maintenance labor costs.

6.5 Development of Catalyst for Decarboxylation Process and Solid Adsorbent for NAs Recovery [30]

➢ Methodologies

❖ Model carboxylic acids and mixed acid solution

A set of carboxylic acids, including 2-naphthoic acid ($C_{10}H_7COOH$), cyclohexane carboxylic acid ($C_6H_{11}COOH$) and cyclohexane propionic acid ($C_6H_{11}C_2H_5COOH$) are selected as the model compounds to represent aromatic and saturated NAs. Naphthoic acid is used in most catalytic tests due to its proper physical property and similarity to the acidic compounds most often encountered in crude oils.

Table 9: Composition of the Mixed Acid Solution

Carboxylic acids	Concentrations in dodecane (wt%)
Cyclopentane carboxylic acid (CPCA)	2.471
Cyclohexane carboxylic acid (CHCA)	1.927
Benzoic acid (BA)	0.871
Pentyl-cyclopentane carboxylic acid (C_5H_{11}-CHCA)	1.099
Heptyl-benzoic acid (C_7H_{15}-BA)	1.107

A mixed hydrocarbon-acid solution is also prepared by dissolving five organic acids in dodecane to more closely model actual NA compositions in oils.

❖ Catalyst materials and catalyst preparation

1. Alkaline earth metal oxides
2. Oxidative metal oxides
3. Supported precious metal (Pt/SiO_2. Ni/Al_2O_3 and Cu/SiO_2)
4. Zeolite

Commercially available compounds such as MgO, CaO, Ag_2O, Cu_2O, and MnO_2 are used in this study. For MgO, it is calcined at 800°C for 10hrs prior to use for activation.

A strong acidic zeolite, ZSM-5 type zeolites are used as shown in Table 10. The high SiO_2/Al_2O_2 ratios indicate their strong acidities. Before the running, all of the three zeolites are activated at 450°C overnight. With this treatment, the ammonium type zeolites (CBV 3024E and CBV 8014E) could be converted to their hydrogen type.

Table 10: Data of ZSM-5 type zeolites

Catalyst	SiO_2/Al_2O_3 Mole ratio	Nominal cation form	Na_2O Weight %	Surface Area (m^2/g)
CBV 3020E	30	Hydrogen	0.10	400
CBV 3024E	30	Ammonium	0.05	400
CBV 8014E	80	Ammonium	0.05	425

Powder catalysts are mainly used in batch reactions, while granular ones with an average particle size of 28-65 mesh are loaded into a tubular flow reactor in order to reduce the resistance to flow during oil addition.

❖ Autoclave Reactor

For crude oil test experiments, as more sample amounts are needed for the TAN measurement, a different experimental procedure is established. An autoclave reactor with the volume of ca 40 ml is used to perform the reaction.

❖ GC Analysis

The reaction gas is collected and quantified in a vacuum line via a standard gas transfer method. The gas is then analyzed with a GC, which is connected with the vacuum line. CO_2 as well as other gaseous products could be quantified herein, from which, the yields of CO_2 and other gaseous products could be calculated. For the reaction residue, using dichloromethane to recover the un-reacted acids and then subject to another GC analysis, from which acid conversion could be calculated.

❖ Viscosity measurement

Brookfield DV-I viscometer is used for the oil viscosity measurement.

- **Fixed-bed flow through reaction**

Flow tests for crude oil and mixed-acid solution are conducted in a reaction line.

- **Crude oil sample**

All the crude oil tests are performed with a crude oil sample that is provided by ChevronTexaco.

- **TAN Measurement**

Determination of the Total Acid Number by ASTM standard method D664 is a key technology.

6.5.1 Adsorbent and adsorption measurement

- **Adsorptive application of clay minerals**

Clay minerals are aluminosilicates that predominate in the clay fractions of soils at the intermediate to advanced stages of weathering. Their major components are silica, alumina, and water, frequently with appreciable quantities of iron, alkali, and alkaline earth cations. Natural clays usually have high cation-exchange capacity (CEC) and surface areas. In addition, they are inexpensive and environmentally friendly.

Clay minerals may interact with many organic compounds to form complexes of varying stabilities and properties. The chemical affinity between the acid compound and the solid surface depends on structure (molecular weight, chain length, etc) of the acid molecule, functional groups present in the acid molecule such as hydrophobic groups (-C-C-C-C-), electronegative groups (-C=O, -C-O-C-, -OH), π bonds (-C=C-, aromatic rings), and configuration of the acid molecule.

Surface functional groups in clay minerals play a significant role in adsorption processes. Surface functional groups can be organic (e.g. carboxyl, carbonyl, phenolic) or inorganic molecular units.

Table 9 summarizes the results of NAs adsorbed onto the selected clay absorbents. The order of the affinity of various clays as adsorbents to NAs is: SepSp-1>SWy-2>SAz-1≥PF1-1> SCa-3 ≥SHCa-1 >SAz-2>IMt-1>IScz-1>KGa-2>ISMt-2.

In addition, in each test no significant adsorption is observed for tetradecane. This result shows that these clay adsorbents are highly selective toward NAs but not hydrocarbon.

The results show that Sepiolite (SepSp-1) and Na-montmorillonite (SWy-2) are potential efficient adsorbent for removing NAs from oil. On the contrary, illite-smectite mixed layer (ISMt-2) is found to be inactive towards the acid adsorption.

Table 11: Efficiency of acid removal from the selected clay absorbents

Adsorbent	NAs Adsorbed Percentage (%) NA1	NA2	NA3	NA4	Amount of NAs Adsorbed (mg/g)
KGa-2	5.5	6.6	11.1	1.9	9.7
IMt-1	15.7	24.5	19.1	8.1	25.7
ISCz-1	1.6	25.7	3.1	3.6	12.2
ISMt-2	0.0	0.0	0.0	0.0	0.0
PF1-1	20.1	34.3	20.2	26.9	38.9
SAz-1	21.2	46.7	23.7	13.5	40.0
SAz-2	15.4	30.8	22.3	8.5	29.3
SCa-3	16.1	30.6	19.4	8.7	34.1
SepSp-1	37.9	60.0	39.2	40.9	68.0
SHCa-1	17.4	40.4	19.4	11.8	33.9
SWy-2	17.7	47.0	23.3	49.8	53.0

NA1=Cyclohexanepropionic acid, FW = 156.23
NA2=Benzoic acid, FW = 122.1
NA3=Cyclohexanepentanoic acid, FW = 184.28
NA4=4-Heptylbenzoic acid, FW = 220.31

6.4.2.2. Adsorption of naphthenic acids from dodecane on metal oxides

Several metal oxides (MOs) are investigated as adsorbents/catalysts for the removal of naphthenic acids (NAs) in the oil. The adsorption of NAs onto metal oxide surfaces generally occurs through coordination via the carboxyl group, which acts as a ligand for vacant coordination sits of surface metal cations. **The coordination of a carboxylic acid usually occurs as the deprotonated carboxylate.** In general, the more metallic character an element has the more basic its oxide will be. Likewise, the more non-metallic character an element has, the more acidic its oxide will be. The metallic character of an element can be determined by its position on the periodic table as shown in Figure 27.

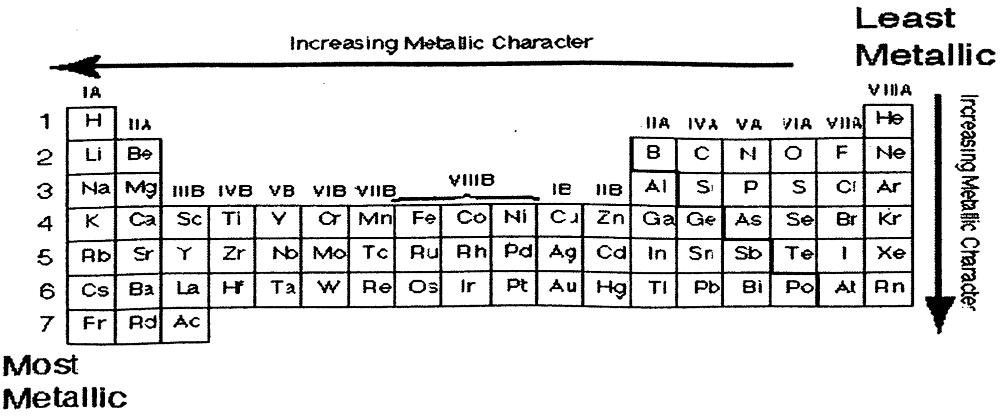


Figure 27: The Metallic Character of Elements

Several metal oxides are selected as adsorbents for the removal of naphthenic acids. These results are shown in Table 10. Metal oxides of Group 1A and 2A elements, such as Na_2O, MgO, and CaO are alkaline and can be shown to neutralize NAs. These alkali and alkali earth metal oxides perform as strong base which adsorb substantially all of the NAs onto surfaces based on the stoichiometric ratio.

Metal Oxide	N-compound	S-compound	NA1	NA2	NA3	NA4	Adsorbed (mg/g)
Al2O3	5.3	0.7	69.4	91.0	69.2	76.7	116.5
SiO2	98.2	3.5	75.3	86.6	74.5	69.4	116.5
PbO	0.0	0.0	0.0	4.2	0.3	2.3	2.4
SeO2	96.0	0.0	5.5	1.0	0.0	2.7	1.1
CuO	0.0	0.0	0.9	6.7	0.0	3.9	4.3
Cu2O	14.7	0.1	3.0	39.0	0.0	23.5	24.2
AgO	33.5	0.0	97.0	99.0	97.5	100.0	153.1
Ag2O	33.6	0.0	100.0	100.0	100.0	100.0	154.4
ZnO	10.6	0.0	62.9	79.7	72.7	97.2	120.4
Y2O3	13.4	1.9	92.0	97.3	91.4	95.9	145.8
La2O3	0.0	0.0	0.0	0.0	0.0	0.0	0
ZrO2	2.9	0.0	0.0	9.1	7.7	6.4	8.3
MnO2	2.3	1.2	0.0	5.6	2.1	1.7	3.3
Fe2O3	7.9	8.8	16.1	16.6	24.4	21.4	30.1
CeO2	0.0	0.0	7.8	4.8	0.0	5.6	5.8

Nitrogen compound=Quinoline, FW = 129.16

Sulfur compound=2-phenylthiophene, FW = 160.24

NA1=Cyclohexanepropionic acid, FW = 156.23;

NA2=Benzoic acid, FW = 122.1;

NA3=Cyclohexanepentanoic acid, FW = 184.28;

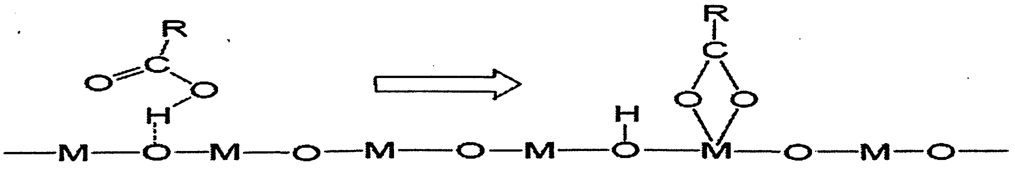
NA4=4-heptylbenzoic acid, FW = 220.31

Table 12: Efficiency of NAs removal from the selected metal oxides

For example 2RCOOH + MgO = $(RCOO)_2Mg + H_2O$, i.e. One mole of MgO can adsorb two mole of NA. Therefore, the removal efficiency is 100% for these metal oxides.

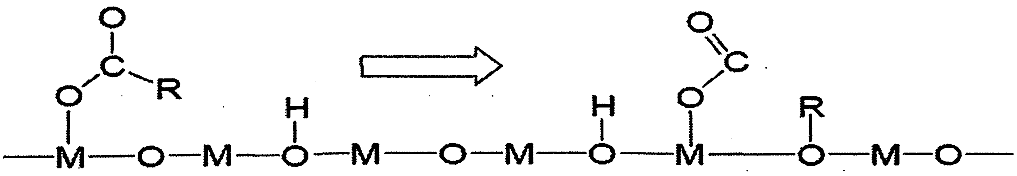
It is found that AgO and Ag_2O are very reactive with NAs. They showed great effect on the adsorption of NAs and minor effect on N-containing molecule, but no effect on S-containing molecule, such as 2-phenylthiophene. The adsorption of 2- phenylthiophene is very difficult on the metal oxide surfaces. The rest of MOs have little effect on the adsorption of NAs.

- **Theoretical studies of chemical processes on the oxide surfaces**
  1. Adsorption of acids on the oxide surface.
  2. Deprotonation of acids on the oxide surfaces.
  3. Decarboxylation of acids on the oxide surface.



M = Mg, Ca

Figure 28: Deprotonation process of an adsorbed acid on the oxide surface.



M = Mg, Ca

Figure 29: Decarboxylation of acids on the oxide surfaces

Figure 30 highlights the overall calculated energy profile of the benzoic acid (BA) and Cyclohexane Carboxylic Acid (CHCA) interact with the MgO and CaO surfaces.

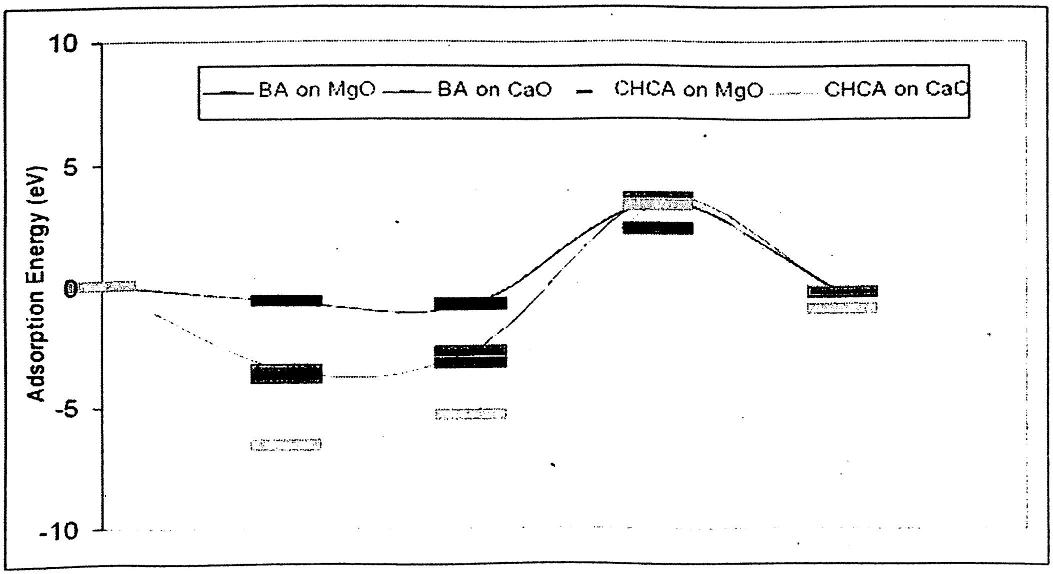


Figure 30: Summary of the calculated energy profile of carboxylic acids on the oxide surfaces.

From the theoretical studies following results are obtained.

- Adsorption of a carboxylic acid on CaO is much stronger than on MgO, indicating that CaO is a good solid adsorbent for the naphthenic acid.
- Decarboxylation is the most energetically demanded process, so it will be the rate-determining step in the overall reaction path.
- MgO could have a dual function characterization for both adsorption and decarboxylation for naphthenic acids.
- Adsorption of saturate on the oxide surface is in general stronger than aromatics.

6.5.2 Development of effective decarboxylation catalysts

❖ Alkaline earth metal oxides

Four alkaline earth metal oxides, CaO, MgO, SrO and BaO are tested with a model carboxylic acid, naphthoic acid ($C_{10}H_7COOH$). The catalytic activities of these compounds are determined by the extent of acid conversion and CO_2 yield. Here CO_2 yield is defined as the amount of organic carbon mole converted to CO_2 and it is an indication of the degree of the catalytic decarboxylation.

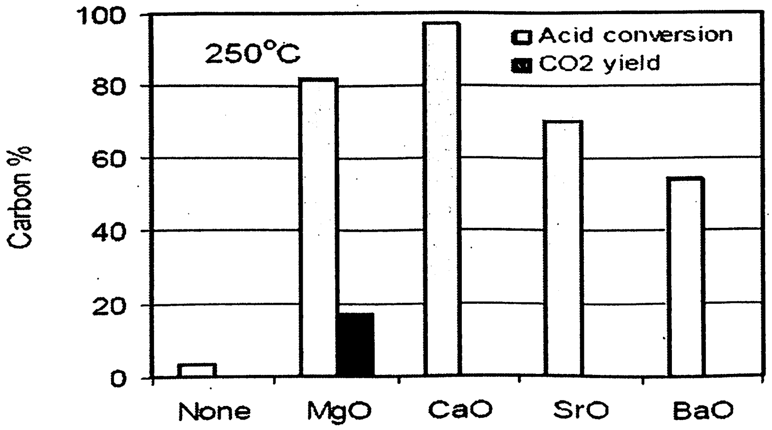


Figure 31: Reaction of naphthoic acid in the presence of alkaline earth metal oxides at 250°C.

Even with the MgO catalyst, the CO_2 yield is much lower than the converted acid amount. Regarding this phenomenon, two factors are considered to be responsible, 1) the strong combination ability of this series of metal oxides with CO_2, (i.e., as CO_2 is formed it tends to be combined with the metal oxides to form stable carbonate minerals (Equ-1)) and, 2) the reaction pathway might be multiple (e.g., in addition to the decarboxylation, other reactions such as neutralization and cracking may occur simultaneously). The high acid conversion obtained from CaO, SrO and BaO would mainly result from neutralization (Equ-2).

$$RCOOH \longrightarrow RH + CO_2 \xrightarrow{+MeO} MeCO_3 \qquad (1)$$

$$2RCOOH + MeO \longrightarrow (RCOO)_2Me - H_2O \qquad (2)$$

Figure 31 shows that compared with no catalyst addition, all four alkaline earth metal oxides result in high acid removal rates while CO_2 formation is only detected with MgO.

❖ Oxidative metal oxides (Ag_2O, Cu_2O and others)

Several metal oxides with multiple oxidative states are investigated in the catalytic decarboxylation of model compounds, naphthoic acid and cyclohexane pentanoic acid, the latter is considered to be more representative as the component of naphthenic acid in crude oil. The tested metal oxides include Ag_2O, AgO, MnO_2, Mn_2O_3, PbO_2, CuO, Cu_2O, Fe_2O_3 and Co_2O_3 (Table 14). Note that all of these metal oxides have variable oxidative states.

Acid (mg)		Catalyst (mg)		Temp (°C)	RT (hr)	Acid conv (%)	CO_2 yield (%)	$C_{10}H_8$ Yield (%)	$C_{20}H_{14}$
NA	60.0	Ag_2O	9.8	230	4	26.0	3.6		
NA	49.7	MnO_2	10.0	230	4	34.2	3.3		
NA	50.2	PbO_2	11.8	230	4	24.9	4.5		
NA	49.9	CuO	10.2	230	4	53.9	3.5		
NA	53.0			250	4	3.6	0.1		
NA	49.9	Ag_2O	10.4	250	4	53.1	53.7	19.4	
NA	54.3	MnO_2	10.9	250	4	51.9	14.6		
NA	56.6	Mn_2O_3	10.2	250	4	20.2	2.8		
NA	57.6	Cu_2O	10.7	250	4	59.2	6.7		
NA	49.8	CuO	10.5	250	4	63.3	17.2	1.6	
NA	49.5	Fe_2O_3	9.7	250	4	40.2	0.0		
NA	55.2	Co_2O_3	10.7	250	4	16.0	6.0		
NA	57.4			300	4	5.9	0.4		
NA	54.0	Ag_2O	10.8	300	4	93.9	96.9	66.2	detected
NA	48.3	AgO	10.2	300	4	16.1	15.4	2.2	
NA	49.7	MnO_2	11.5	300	4	74.3	17.1	0.5	detected
NA	52.6	Mn_2O_3	10.7	300	4	61.8	5.2		
NA	49.9	PbO_2	10.6	300	4	36.4	5.2		
NA	52.2	CuO	11.5	300	4	56.5	20.9	4.4	
NA	50.2	Cu_2O	10.1	300	4	63.6	22.9	13.7	
NA	50.3	Ag (Powder)	7.2	275	4	16.9	0.5		
NA	50.4	Ag+Air	10.0	275	4	16.7	7.7	0.3	
CHPA	64.0	Ag_2O	9.4	250	4	10.6	2.8		
CHPA	65.6	MnO_2	10.3	250	4	36.2	5.5		
CHPA	72.2	PbO_2	13.9	250	4	24.4	5.3		

NA, $C_{10}H_7COOH$, 2-naphthoic acid   CHPA, $C_6H_{11}C_4H_8COOH$, Cyclohexane pentanoic acid

Table 13: Catalytic decarboxylation of model carboxylic acid in the presence of oxidative metal oxides

❖ Zeolite based catalyst

As C-C cleavage is involved in decarboxylation reaction (R-COOH = RH+CO_2), acidic catalyst becomes one choice for scientists. On the other hand, the application of acidic zeolites in oil refinery has well been established, typically being represented by the famous FCC process.

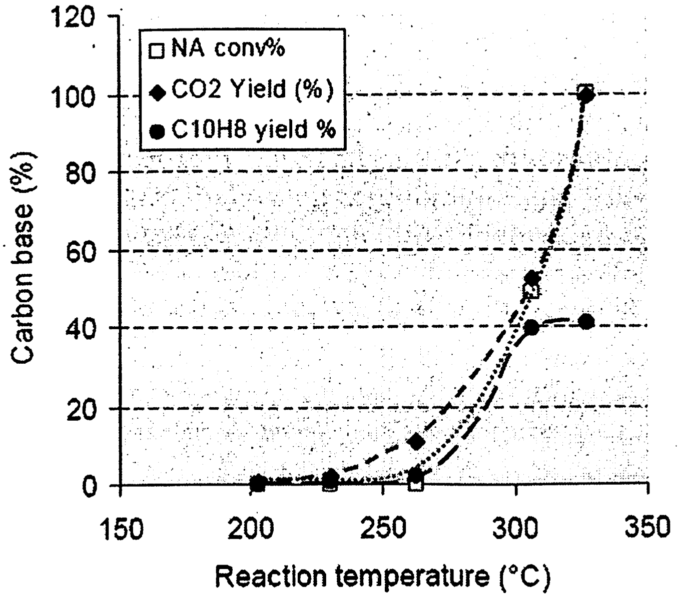


Figure 32: Effects of reaction temperature on acid conversion and product formation in the reaction of naphthoic acid over HZSM-5 catalyst

Acid (mg)	Catalyst		Temperature (°C)	Reaction time (hr)	Acid conversion (%)	CO_2 yield (%)	$C_{10}H_8$ yield (%)
57.4			300	4	5.9	0.4	0
51.5	CBV 3020E	10.3	300	4	65.4	71.4	41.5
55.3	CBV 3024E	10.0	300	4	49.5	46.1	29.9
67.1	CBV 8014E	11.0	300	4	38.7	34.8	25.6

Table 14: Catalytic decarboxylation of model carboxylic acid in the presence of the ZSM-5 type zeolite catalysts

Using the three zeolites, the decarboxylation experiments are conducted with naphthoic acid at 300°C for 4hrs. As shown in all of the three ZSM-5 catalysts are effective to the catalytic decarboxylation of naphthoic acid. The acid conversions reached from 65.4 to 38.7% for the three zeolites, while the blank run gave only 5.9% conversion CO_2 yields varied in the range of 34.8% to 71.4% and these values are well consistent with the acid conversions.

Naphthalene is also significantly formed as another decarboxylation product. The ratios of naphthalene yields to acid conversions fall in around 60%.

- **Supported precious metal catalysts**

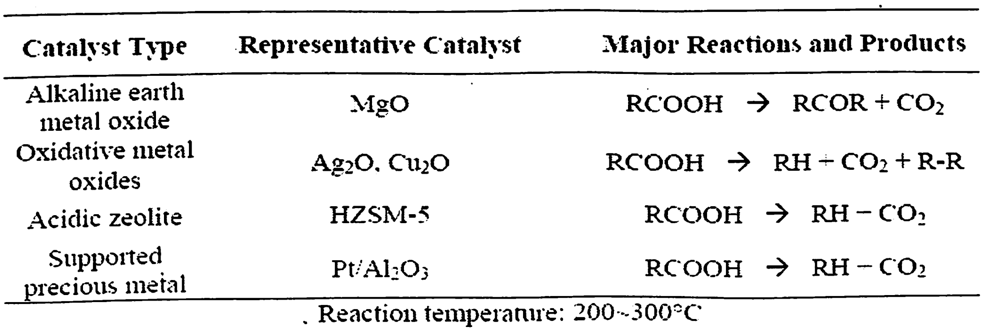
It is known that Pt has wide application and irreplaceable role in oil and environmental industries due to its excellence catalytic performance for the processes of hydrogenation, dehydrogenation, isomerization etc and therefore, it.

H_2 $PtCl_6$ is used as the precursor and Pt-loading is controlled at 0.5wt%. The experiment is carried out with naphthoic acid at 275°C for 4hrs. To determine the effect of Pt, the same experiment is run with the support Al_2O_3 alone. Table 15 listed the experimental condition and results. Compared to the result of blank experiment, CO_2 is clearly formed from Pt/Al_2O_3, and naphthalene is also slightly detected. This result strongly suggests that Pt is effective to catalytic decarboxylation. The data in Table 16 also shows that the acid conversions are almost as high as 100% on both of the catalysts. This might be due to the strong adsorption capacity of Al_3O_3.

Table 15: Catalytic decarboxylation of model acid in the presence of supported precious metal catalysts

Catalyst	Catalyst weight (mg)	Acid	Acid weight (mg)	Reaction Temp (°C)	Reaction time (hr)	CO_2 yield (%)	Acid conversion (%)	Naphthalene yield (%)
Pt/Al_2O_3	58.2	NA	50.5	300	4	9.0	100	1.2
Al_2O_3	58.6	NA	50.7	300	4	0.2	100	0.0

Pt/Al_2O_3: 0.5wt%



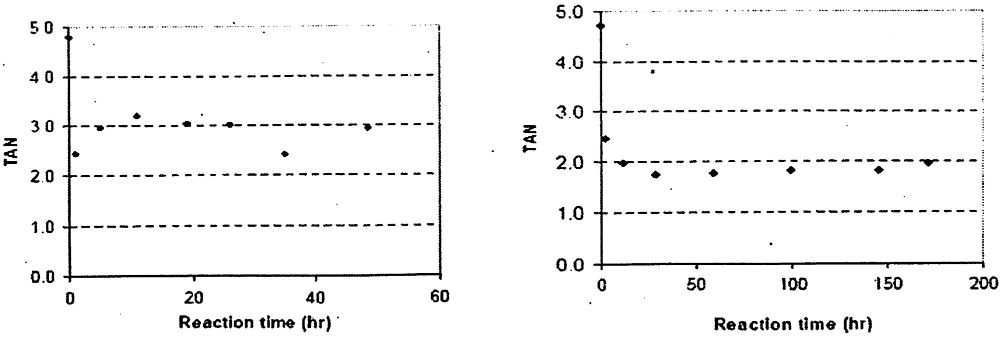
Catalyst Type	Representative Catalyst	Major Reactions and Products
Alkaline earth metal oxide	MgO	RCOOH → $RCOR + CO_2$
Oxidative metal oxides	Ag_2O, Cu_2O	RCOOH → $RH + CO_2 + R\text{-}R$
Acidic zeolite	HZSM-5	RCOOH → $RH - CO_2$
Supported precious metal	Pt/Al_2O_3	RCOOH → $RH - CO_2$

Reaction temperature: 200~300°C

Table 16: Four types effective decarboxylation catalysts

6.5.3 Naphthenic Acid removal from crude oil with MgO catalyst

With 1g MgO catalyst, whose particle sizes fell in a range of 20-60 meshes, the test is continuously run at 300°C for 54 hr and the flow rate of oil changed from 15.35 to 1.76ml/hr, mostly in the range of 2-5 ml/hr. The contact time of oil feed with the catalyst is calculated roughly to be 200-500 seconds. The total oil collected during the reaction is 206.23g. The TAN changes at different reaction stages are plotted as the Figure 33 (a).



(a)

(b)

Figure 33: (a) Reaction of crude oil over MgO catalysts at 300°C. (b) Flow reaction of crude oil over MgO catalysts at 350°C

To improve the catalytic behavior of MgO catalyst, the experimental condition is further modified. To accumulate longer retention time of the oil in catalyst bed, 2.0g catalyst is loaded into the reactor, and the flow rate is set slower at about 50µ/min. The contact time is calculated to be 33min. As shown in Figure 33 (b),

The experiment is continuously run at 350°C for 171.58 hr and the amount of the oil being collected reached 202.74g. For the treated oil, the TAN decreased from 4.74 to 1. 74 ~1.98, corresponding to about 63%~58% reduction rates. On the other hand, the viscosity measurement shows that the viscosity is also significantly decreased from 6300 cP for raw oil to 420~830 cP at 40°C. This greatly contributes to the improvement of the mobility of oil.

6.5.4 Results

- There are four types effective low temperature decacboxylation catalysts include MgO, Ag_2O/Cu_2O, HZSM-5 zeolite and Pt/Al_2O_3. All of these catalysts show excellent catalytic decarboxylation activities at relative low temperature ca. 200-300°C.

- MgO catalyze decarboxylation reaction through a ketonization mechanism with two moles of carboxylic acid, which give rise to the formation of one mole of CO_2. Ag_2O and Cu_2O are, most possibly, involved in decarboxylation process via a free radical mechanism.

- On the other hand, the high activities of zeolite towards decarboxylation would be caused by C-C cracking catalyzed by the strong acidic sites on zeolite. Due to the complexity of the oil composition and poison issues, not all of these catalysts can be directly applied in crude oil.

- MgO catalyst is identified to be effective to catalytic decarboxylation, naphthenic acid adsorption, flow reaction tests with a fixed bed tubular reactor are performed and the results revealed the effectiveness of MgO to naphthenic acid removal. At

300°C, with contact time in the range of 200-500 seconds, the TAN reduction rates could reach about 30~50% while the catalyst could keep its activity for more than 50hrs. Furthermore at 350°C with longer contact time ~ 33min, the TAN reduction rate reached as high as 70%

- **Clay minerals**, such as sepiolite and montmorillonite, have the potential to be used as adsorbents for the removal of naphthenic acids. In order to enhance the efficiency of adsorption of NAs by mineral clays, various species, such as metal-oxide pillars and organic or organometallic complexes should be incorporated into the structure of clay minerals to improve the adsorptive and/or catalytic properties of the products.

In summary, combining the catalytic and adsorptive approaches developed in this work; the NA in crude oil can be effectively removed and the quality of the oil can be upgraded.

6.6 Industrial Applications of Naphthenic Acids

NAs are frequently used as oil-soluble metal soaps for driers and other catalysts, wood preservatives, tire cord adhesion promoters, and in amine derivatives for corrosion inhibitors. Now these days, the petroleum industry uses naphthenic acid amine derivatives as surfactants for enhanced oil recovery and as corrosion inhibitors for refineries, pipelines, and downhole use.

MERICHEM: World's Largest Supplier of Naphthenic Acid [40]

MERICHEM headquarter is in Houston, Texas, USA. They are producing different kinds of NAs with some additional qualities as given below:

Types of Naphthenic Acid

- Crude Naphthenic Acid
- Semi-Refined Naphthenic Acid
- Refined Naphthenic Acid
- Custom blends

Properties of Naphthenic Acids

- Improved solubility and hydrolytic/oxidative stability
- Improved surface or pigment wetting
- Lower pour point
- More complete reaction

Advantages

Naphthenic acids can replace natural fatty acids, tall oil acids and synthetic acids in numerous performance-oriented applications requiring these advantages:

- Excellent oxidative stability and compatibility
- High solubility in hydrocarbons and oils
- Low solubility in water
- Low viscosity and surface active properties

Evaluation of Naphthenic Acids: When determining the type of naphthenic acid to evaluate for application, consider three key factors: acid number, color and unsaponifiables as given below.

PRODUCT GRADE	TYPICAL USES	ACID NUMBER (mg KOH/g)	COLOR	UNSAPONIFIABLES (% by Wt)
Crude	Corrosion inhibitors Wood preservatives	160–220	Dark—no color specification	7–30
Semi-refined	Lubricant additives Wood preservatives	180–260	Dark—no color specification	5–10
Refined	Driers for paints & inks Lubricant additives Fuel additives Heat/UV stabilizers Cutting oils	200–260	3 minimum	4–8
High Purity Refined	Tire cord adhesive promoter Driers for paints & inks Esters	220–310	3 minimum	3 maximum
Specialty Blends (naphthenic acids/non-naphthenics)	Driers for paints & inks	240–310	3 minimum	3–5

CHAPTER 7. MONITORING AND INSPECTION FOR NAC CONTROL

Monitoring and Inspection Program is composed of three technology platforms that allow for: **predicting** the impact a crude has on the refinery, **protecting** the refinery from those impacts and **monitoring** the results of the protection programs [36]. By using combination of these three technologies, the refiner can develop comprehensive strategies to safely and profitably process the opportunity crude to overcome risk and to take full advantage of the available profit potential.

7.1 Objectives of Monitoring and Inspection Program [64]

- Evaluate the effectiveness of corrosion control program.
- Establish operational constraints/ limits.
- Serve as an early warning of changes in system corrosion

7.2 Features of Corrosion Monitoring Program

Refining acid crudes requires good corrosion monitoring regardless of the methods for mitigating the acid. Fortunately, a good monitoring program is neither complicated nor expensive. A good corrosion monitoring program consists of the following:

- Information on the Acid Number in the crude and the various cuts.
- Information on the crude slate to the refinery including blends for acid numbers of no more than 0.5 mg KOH/g in the side cuts in the >400 F range.
- Corrosion monitoring probes or coupons at sensitive points where the distillate cut temperature is 400- 800 F and where high velocity exists. These most susceptible areas are sometimes difficult to identify (like turbulent areas in piping) and monitor (like furnace outlet headers).
- Plans to establish baseline corrosion rates and then gradually introduce the new crude while monitoring.
- Monitoring probes should be maintained in good working order and coupons checked periodically based on the baseline and probe data.

7.3 Monitoring Techniques

Several of monitoring techniques are used in refineries but no single monitoring technique will suffice [65]. Some of widely used monitoring techniques used in refineries are given below.

- Retractable coupons
- Electric resistance probes
- Flush ERP
- Field Signature Method (FSM) Technology

- Corrosion monitoring loop
- On Stream High Temperature UT/Radiography
- Metals Analysis
- Corrosion Monitoring Loops

7.4 Monitoring of NAC [64]: NAC monitoring is done by following way

Compositional measurement

- TAN, NAN and sulfur
- Phosphorous residual
- Metal level/ ratio

Metal Loss/ Corrosion Activity

- ER probes or weight loss coupon
- Ultrasonic thickness measurement
- Digital radiography
- Field signature method (FSM)
- Hydrogen permeation measurement

7.5 Disadvantages of Monitoring Techniques

Current Non Destructive Testing (NDT) inspection and monitoring technologies such as coupons, ultra-sound (UT), film radiography and electrical resistance (ER) probes are all limited in some form. For instance, UT measurements are extremely localized, allowing for typical measurements of only minute piping area, usually less than 0.05-0.1% of the total piping. Film radiography is used as a scanning technology to identify issues, but it lacks a quantitative measurement capability. Coupons provide little information on localized corrosion issues, and ER probes are limited in the coverage extent and may not be measuring conditions representative of the entire system [35]..

7.6 Latest Monitoring Techniques

Some technologies like FSM and Hydrogen permeation, RCM and digital radiography technologies are widely used in refineries. Brief descriptions of these two technologies are given below.

❖ Field Signature Method (FSM) Technology

- FSM is a non-intrusive corrosion monitoring method that has some particular advantages for Naphthenic Acid monitoring.
- Corrosion measurements are made on the actual process component, as opposed to using a probe that measures the corrosivity of the process.

In Chevron Texaco (Western Europe), FSM is installed at following locations:

- Crude heater transfer line to distillation column.
- Atmospheric resid piping ex distillation column bottom.
- VDU heater outlet elbows.
- VDU transfer line elbows- heater to tower.

Chevron Texaco (Western Europe) has experienced reliability problems with the temperature compensation modules. This is being dealt with by upgrading cables. Installations on other units have shown good correlation between known corrosion rates and FSM recorded value.

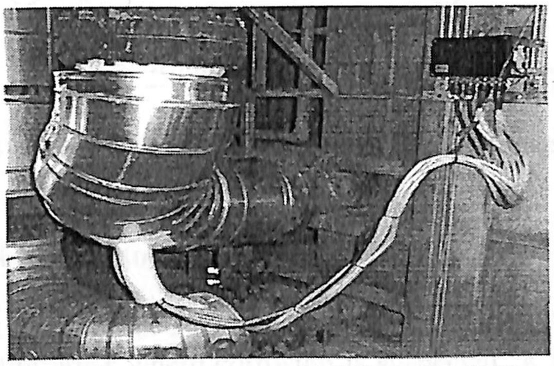


Figure 34: Chevron Texaco (Western Europe) FSM- VDU Heater Outlet Bend

❖ Hydrogen Permeation Measurement [64]

- It measures rates of hydrogen release at external wall of pipe and vessel.
- Rate of external hydrogen release is related to the corrosion activity occuring on the internal surface.

Hydrogen permeation is a function of:

- Temperature
- Metal thickness
- Metallurgy
- Corrosion mechanism

Baker Petrolite has developed a "corrosion index" which allows for comparison across the entire unit.

Advantages of Hydrogen Permeation Measurement

- Mobile and portable instrument.
- Temperature up to 1100°F (600°C)
- Non intrusive- measurement in minutes.
- Measurement reflects real- time corrosion activity
- Fixed collectors available used under insulation.
- Intrinsically safe for refinery operation.

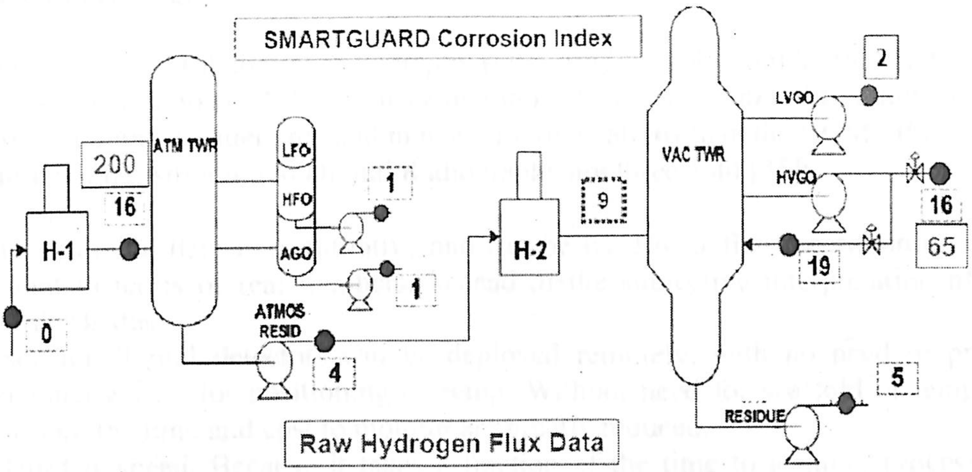


Figure 35: Hydrogen Permeation Measurements Monitoring Servey Results [64]

❖ Resistance Corrosion Monitoring (RCM)

The RCM is a proven front line tool for 24/7 continuous monitoring of pipe wall thickness in high temperature areas where corrosion is suspected. A picture of an RCM installed on a spool piece is shown in Figure 1. It is a stationary array covering approximately 1 m^2 of pipe area that can be located on a straight section of pipe, an elbow, across a T, etc. and in high temperature regions or other areas where naphthenic acid corrosion is predicted. It uses electric potentials to measure thickness changes to a 6-sigma measurement accuracy of 2% of the wall thickness. These changes in wall thickness can then be used to calculate a corrosion rate over time, and they provide a very direct and accurate assessment of time-to-failure of the pipe [35].

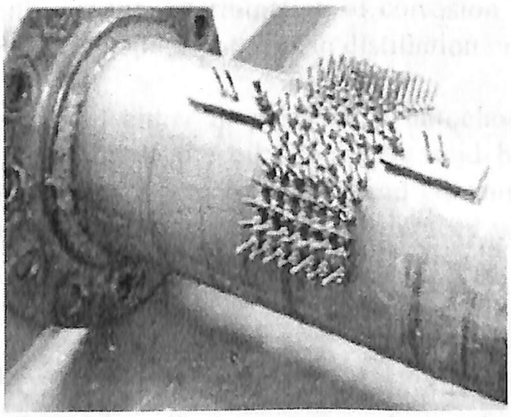


Figure 36: An RCM installation on a spool piece is shown above.

- **Digital radiography (DR)**

Augmenting the RCM is digital radiography (DR). Radiography, unlike the RCM, is not meant to be a continuous 24/7 stationary monitor. However, its mobility allows it to be deployed over a much wider area and in many more locations than the RCM [35].
The benefits of transitioning to Digital Radiography are three-fold [35]:

- First, digital data is quantitative and can be used to define the condition of the plant in terms of real numbers, instead of the subjective interpretation of gray scale shades.
- Second, digital detectors can be deployed remotely, with no need to provide manual access for positioning or setup. Without need for scaffold or temporary access, the time and cost to monitor are greatly reduced.
- Third is speed. Because it takes a fraction of the time to acquire, process, and display a digital radiograph, it can be done in near real time. With such increased efficiency, a much more comprehensive and complete monitoring can be undertaken in areas that were previously believed inaccessible.

7.7 Monitoring of NAC (Laboratory Corrosion Simulation Tests)

As per Gutzeit [22], the laboratory evaluation of naphthenic acid corrosion is carried out using various methods like:

- Continuous flow unit
- Rocking autoclave
- Distillation equipment

This type of tests for evaluating naphthenic acid corrosion suffers from following drawbacks:

a. These tests are used only for the determination of corrosion at different velocities in either a liquid environment or in vapour phase as in distillation unit.

b. These test methods are used either in pressurized autoclave or in distillation unit working at atmospheric pressure. White oil naphthenic acid blends are used in these studies. Under these conditions, the actual refinery feed containing naphthenic acid can not be used because of the likely-hood of cracking of the feed which in turn changes the composition of the feed.

7.7.1 Process Simulation

Several parameters need to be defined in planning a laboratory crude corrosion tests: (1) oil fraction, (2) temperature, (3) wall shear stress (velocity), (4) alloy composition, (5) exposure time and (6) testing procedure. Laboratory corrosion tests still need to be correlated to refinery experience [43].

There are at least three types of high temperature crude corrosion processes. They are simulated differently in laboratory tests.

Furnace Tubes and Outlets Headers

In furnaces tubes, the metal is between 100 to 300^0F higher than the bulk temperature of the crude. The degree of vaporization is very high and so is the fluid velocity. In addition to the crude composition, the corrosion process is dependent mainly on the temperature of the metal and its composition. Simulation of these conditions in laboratory corrosion tests requires the specimens, instead of the oil, to be heated and the test temperature to be controlled by the oil temperature to account for the heat capacity of the oil. At these conditions of high degree of vaporization wall shear stress is not expected to be severe even if the velocity is very high. Since the wall shear stress is dependent on the tube size, velocity, density and viscosity of the fluid, a rotation of the specimens of 15 ft/s to 20 ft/s easily simulate the 200 to 300 ft/s conditions found in the field.

Distillation Towers

Condensation of vaporized naphthenic acids occurs on the walls and trays of towers. The corrosion process is similar to corrosion in concentrated organic acids and velocity has virtually no effect on the process. Simulating distillation towers requires the specimens to be exposed in the vapor phase of an autoclave (see Figure 3) which is half filled with the oil tested. The vaporized naphthenic acid in the autoclave will condense on the specimens.

Transfer Lines and Side Cuts Piping

Under these conditions, flows start playing an important role. Conditions of high flow and medium degree of vaporization exits in the transfer lines while conditions of low flow and low degree of vaporization exit in the side cuts piping. The corrosion process is dependent on flow, temperature, materials of construction and naphthenic acid and H_2S content.

Laboratory Device for controlled velocity test in a vacuum distillation unit developed at IIP, Dehradun (Figure 37)

Jayaraman and coworkers have developed a device useful for conducting controlled velocity corrosion test in a vacuum distillation unit [23]. This ensures no change in the composition of petroleum feed during the distillation, such as the decomposition of naphthenic acid of the feed at higher temperatures. It is reported in literature that thermal decomposition of naphthenic acid can occur which may lead to corrosive low carbon number organic acids.

Advantages

- Stable composition of feed during Distillation
- Varying velocity of test metal in the form of disc
- Application in liquid and vapour pressure.

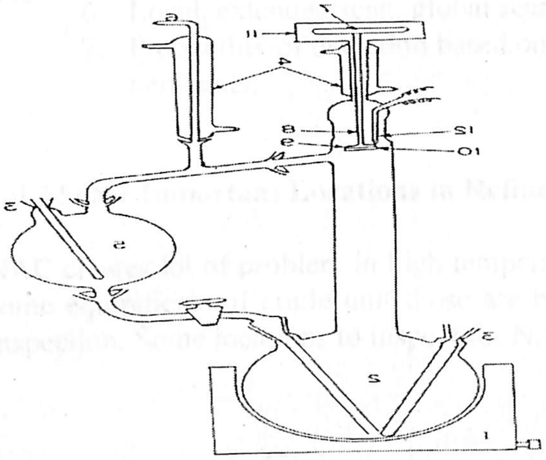
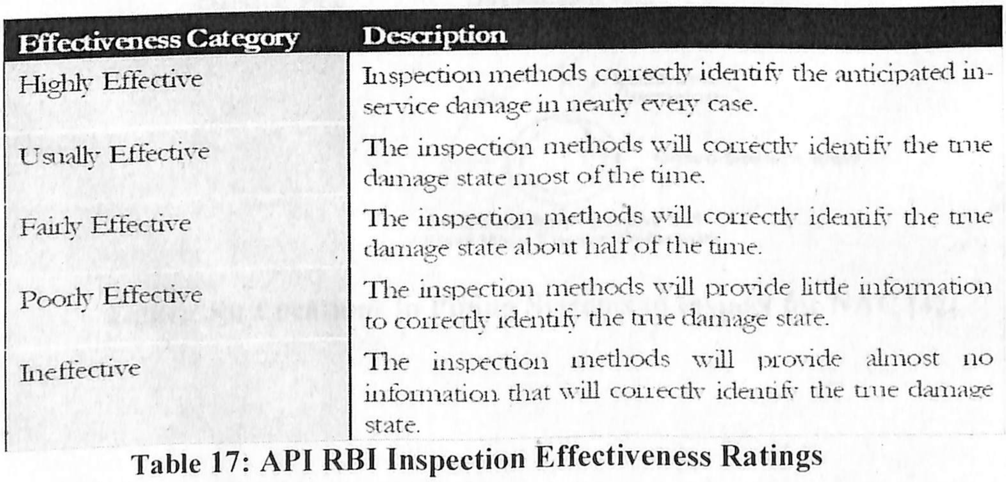


Figure 37: Laboratory Device for controlled velocity test
[Reference: A Jayraman and R C Saxena, Indian Pat. No. 1470/DEL/93]

7.9 Inspection

Inspection is a major challenge due to less than predictable combination of temperature, sulfidic components, material, velocities and flow regime. While these variables can lead to localized corrosion in the plant, often the corrosion morphology is general thinning that might lead to dangerous "blow-out" type failures rather than small leaks.



Effectiveness Category	Description
Highly Effective	Inspection methods correctly identify the anticipated in-service damage in nearly every case.
Usually Effective	The inspection methods will correctly identify the true damage state most of the time.
Fairly Effective	The inspection methods will correctly identify the true damage state about half of the time.
Poorly Effective	The inspection methods will provide little information to correctly identify the true damage state.
Ineffective	The inspection methods will provide almost no information that will correctly identify the true damage state.

Table 17: API RBI Inspection Effectiveness Ratings

7.9.1 Inspection Effectiveness: Inspection effectiveness is a combination of:

1. Predictability of damage locations for the mechanisms involved.
2. Inspection history of damage location.
3. Confidence in the inspection methods to be used.
4. Limitations (insulation, temperature, access).
5. Scanning Coverage.
6. Local, extended scan, global search.
7. Probability of detection based on NDT methods, procedure, equipment, personnel..

7.9.2 Some Important Locations in Refinery to Inspect for NAC

NAC creates lot of problem in high temperature as well as high velocity areas. There are some equipments of crude unit those are badly affected by NAC. So they need regular inspection. Some locations to inspect for NAC are given in below figures.

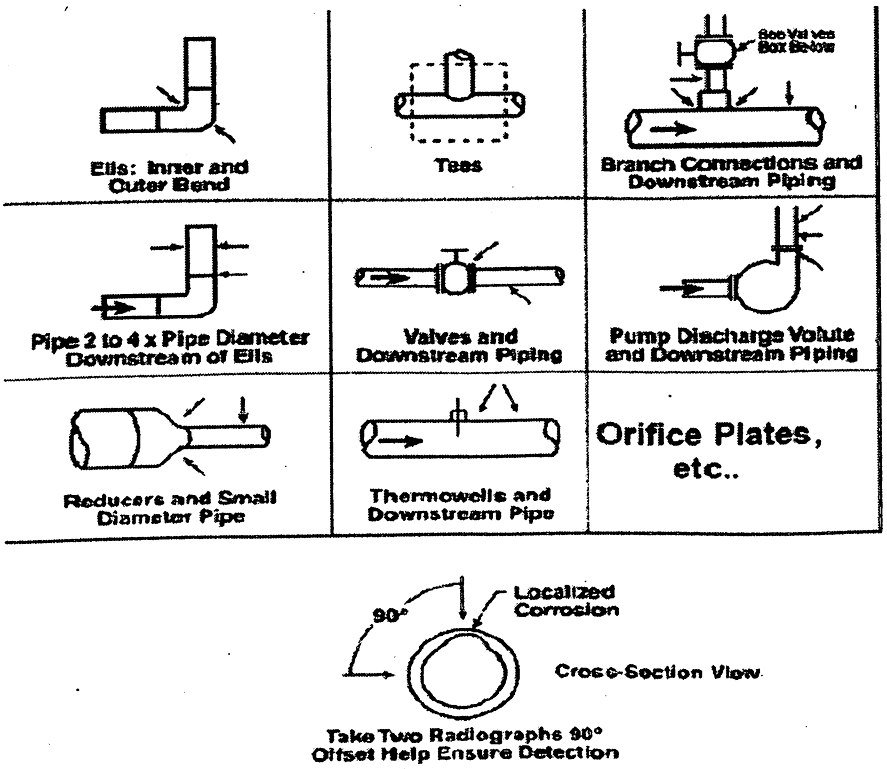


Figure 38: Locations in Piping Systems to Inspect for NAC [42]

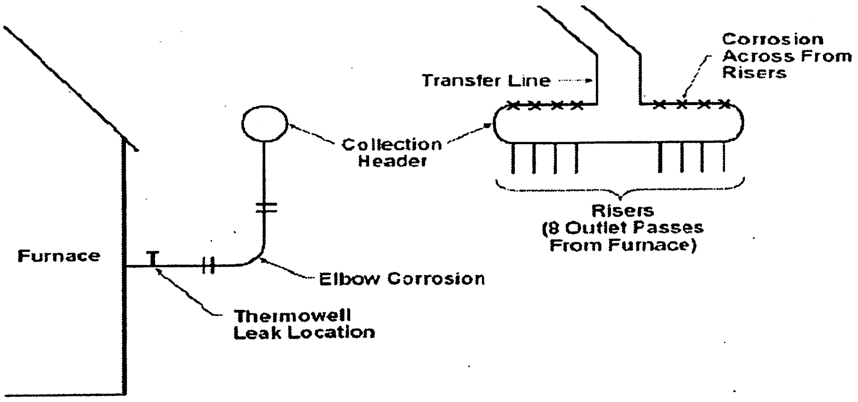


Figure 39: Establish Inspection Locations e.g. Vacuum Furnace Transfer Lines [42]

➢ NAC in Indian Context

Due to escalating crude prices and increasing energy demand, India as an energy deficit country can not perpetually afford its dependence on crude oil import. India needs to develop its own oil fields expeditiously. Indian refineries can process 0.5 mg KOH/g acid crude with the present metallurgy. North Gujarat crude has high naphthenic acid content (more than 0.5 TAN) and is diluted with non acidic crude before processing at Gujarat refinery. Reliance Industries Limited, Jamnagar, India has started processing such crudes to increase GRM and hence increase profitability. Reliance is also blending high TAN crude with low TAN crude to mitigate the NAC in crude unit.

In India, third party feasibility studies are needed for processing high TAN crudes because in India high acid crude processing is not in routine. Feasibility studies include identification of vulnerable areas, metallurgy requirement, inhibitor programme, injection points with corrosion monitoring locations and methods.

RECOMMENDATIONS

- The industry still relies heavily on previous experience and readily available data on TAN and sulfur of cuts when processing opportunity crudes. Despite their shortcoming, rules of thumb are still used mainly because of lack of resources and time of the plant corrosion engineer. So it is also necessary to rationalize the method for determination of true naphthenic acid content in crude oil as different methods used give different values.
- For long term reliability, use 316 and 317SS, higher chrome and/or molybdenum alloy, as upgrading the construction materials in refineries.
- Use of Sulfur based (non phosphorus) corrosion inhibitors to
    - ➢ Eliminate fouling that was experienced with previous inhibitors (P base inhibitors).
    - ➢ Eliminate the source of catalyst deactivation.
    - ➢ Control the fouling and corrosion that will significantly enhanced the reliability of operations.
- Refiner should have correct injection facilities available in case required.
- There is no established and field tested laboratory method for screening or short listing of best corrosion inhibitor from amongst a variety being offered by chemical suppliers; as a result the refiners has to rely on vendors claims and time consuming trial and error methods. Therefore need of the hour is to develop a quick and a reliable method for screening and recommending cost effective best corrosion inhibitor.
- Recovery of NAs compounds from crude oils is regarded as one of the most important processes in heavy oil upgrading. Recovery of NAs will not only assist refiners in avoiding corrosion of processing units but also add value to its profit margins.
- For NAs recovery there are four types effective low temperature decacboxylation catalysts include MgO, Ag_2O/Cu_2O, HZSM-5 zeolite and Pt/Al_2O_3. All of these catalysts show excellent catalytic decarboxylation activities at relative low temperature ca. 200-300°C.
- MgO catalyst is identified to be effective to catalytic decarboxylation, naphthenic acid adsorption, flow reaction tests with a fixed bed tubular reactor are performed and the results revealed the effectiveness of MgO to naphthenic acid removal.
- Clay minerals, such as sepiolite and montmorillonite, have the potential to be used as adsorbents for the removal of naphthenic acids.
- Caustic treatment of kerosene/ jet fuels streams using **Merichem FIBER-FILM™ Contactors** has proven to be practical and reliable, compared with conventional caustic washing systems.
- Full servey of the system and implementation of full monitoring program is required.
- In case of refinery design modifications, avoid bends and use length expanders to reduce fluid velocities.
- Further study is required on NAC for establishing synergistic and antagonistic effect of sulfur, nitrogen and other organometallic impurities present in crude oil.

CONCLUSIONS

- The amphiphilic properties of naphthenic acids result in a variety of negative industrial and environmental consequences such as metal surface corrosion and toxicity.
- Though present in small amounts, naphthenic acid causes significant amount of corrosion in process equipments in a temperature range of 230-400^{0}C.
- The naphthenic acids are most active at their boiling point and the most severe corrosion generally occurs on condensation.
- No corrosion damage is usually observed at temperatures above 400°C, due to decomposition of naphthenic acid into smaller organic acids or protection due to coke formation on the metal surface.
- Literature indicates that in vapour phase naphthenic acids cause more severe corrosion than in liquid phase.
- Velocity has an effect on corrosion rate through wall shear stress and corrosion also depends on the physical state of the acids present in the operating system.
- Two different crudes with the same TAN will not necessarily have the same corrosivity and there is no direct correlation between TAN and corrosivity
- Naphthenic acid crude processing reduced the desalter efficiency. To get rid of this problem choice of right demulsifier is important.
- Chemical inhibition can offer valuable, alternative protection in certain areas.
- Suitable corrosion monitoring is invariably required to check the effectiveness of any control measure.
- To mitigate acid corrosion one has to resort to either metallurgical modifications and / or use corrosion inhibitors.
- Combination of the catalytic and adsorptive approaches can be effectively removed NAs and the quality of the middle distillates can be upgraded.
- 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)

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