Corrosion and Materials Selection for Bitumen with Heavy Naphthenic Acid in Canadian Oil Sands

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Canada's oil sands contain one of the largest reserves of oil in the world. According to recent estimates, there are nearly 180 billion barrels of oil in the Canadian oil sands trapped in a complex mixture of sand, water and clay. More than 40 companies have been currently operating or developing oil sands facilities since the first production in 1967.

The process of oil sands upgrading is similar with down stream refinery, but the corrosion environment in upgrading refinery is often more severe than in the refinery because of high chlorides, mineral contents, carbonic acid, heavy viscosity and fouling, higher naphthenic acid [NA-R(CH$_2$)nCOOH], and greater sulfur contents.

Naphthenic acid corrosion (NAC) which is one of the most critical corrosion issues in up & downstream refinery plants was observed for the first time in 1920's in refinery distillation processes of Rumania, Azerbaizan (Baku), Venezuela, and California. As a first API report, the 11th annual meeting stated sources and mechanism of NAC in early 1930's. API has been developing the risk base standards, such as API RP580, 571, and Publication 581 which are based on the worst NAC damage in the world since 2000.

Nevertheless not only the NAC phenomena and control in Canadian sands oil process are not much widely known but also there are still no engineering guidances for the Canadian sands oil in API standards.

This paper will give NAC phenomina and materials selection guidance against NA environment in Canadian oil sands upgrading processes.

Keywords : *naphthenic acid (NA), NAC, materials selection, stainless steel, sulfur (S), molybdenum (Mo), oil sands, refining, erosion, AGO (atmospheric gas oil), LVGO/MVGO (light & medium vacuum gas oil), HVGO (heavy vacuum gas oil), SAGD (Steam Assisted Gravity Drainage), mpy (mils per year; 40 mpy=1 mm/y)*

1. Introduction

Although having been studied for approximately 80 years, NAC continuous to be a problem in the refinery industry; its mechanism and how different variables affect it are not completely understood. NAC and high temperature crude corrosivity in general is a reliability issue in refinery distillation units. The presence of NA and sulfur compounds considerably increases corrosion in the high temperature parts of the distillation units. The difference in process conditions, materials of construction and blend processed in each refinery and especially the frequent variation in crude diet increases the problem of correlating corrosion of a unit to a certain type of crude oil.

The influence of NAC at 221-399°C (430-750°F) in several fired heaters, piping systems and a vacuum tower have been assessed. Typically, the higher the acid content, the greater the sensitivity to erosion-corrosion in areas of high wall shear stress. The characteristic attack is frequently observed in locations of high shear stress (erosion-corrosion), such as elbows and thermowells, and generally is more severe where the physical state of the acids is changing (vaporization or condensation). The higher NA produces more severe corrosion.

There are several methods for the determination of organic acid concentrations. The typical evaluation is by a caustic titration technique (using potassium hydroxide, KOH) to produce Total Acid Number (TAN), also called Neutralization Number, which are expressed as milligrams of KOH required to neutralize the acidity in one gram of oil. There are two standard ASTM tests for TAN measurement, ASTM D974 (a colorimetric titration method) and ASTM D664 (potentiometric titration method).

Traditionally there are at least three corrosion environments in refinery plants where NAC has been a problem:
(i) furnace tubes and transfer lines (for atmospheric col-

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umn and vacuum column) where erosion-corrosion is dependent on velocity and vaporization and is accelerated by NA.

(ii) vacuum column where corrosion occurs at acid boiling temperatures, is independent of velocity and increases with NA concentration; mainly in light and heavy vacuum gas oil (LVGO & HVGO) and vacuum residue at higher than 200°C (392°F).

(iii) side cut piping where corrosion is dependent on NA content and is believed to be inhibited somewhat by sulfidic corrosion; mainly in light and heavy vacuum gas oil (LVGO & HVGO) and vacuum residue at higher than 200°C (392°F).

Several hot oil corrosion tests have been conducted by several companies since 1999 using various hydrocarbons to evaluate the resistance of different materials, primarily to NAC and high temperature sulfidation, at different conditions.

These tests were also run more recently, as part of this particular study, on 316 and 317 SS samples at 332°C (630°F) using hydrocarbon produced by a SAGD operation.
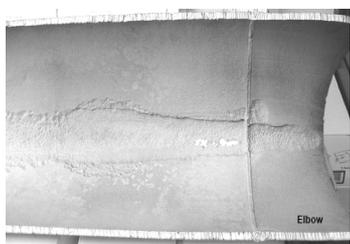
2. What is naphthenic acid (NA)?

2.1 General

The term "Naphthenic Acid", as commonly used in the petroleum industry, refers collectively to all of the organic acids present in crude oil. The name is derived from the early discovery of monobasic carboxylic acids, based on

(a) NAC "Pitting" & "Grooving"

(b) Absence of Scale and Grooving are Characteristic of NAC in Carbon Steel

Fig. 1. Appearance of NAC

Table 1. Types and Characteristics of Acids in Refinery Process[2),3),4)]

Designation	Structural Formula	Boiling Point, °C	Molar Mass	Carbon Number
Cylopentane Arboxylix Acid		216	114	6
Cyclohexane Carboxylic Acid		232	128	7
Cyclohexane Acetic Acid		242	142	8
Cyclohexane Propionic Acid		276	156	9
Cyclohexane Butyric Acid		-	170	10
Commercial Mixture of NA	General $R - (CH_2)_n - COOH$ 3 Rings 4 Rings 5 Rings	270 -324	180 -350 / 258 / 270 / 324	10 to 18

a saturated single-ring structure, in petroleum. Most crude oils can however contain a large variety of organic acids that includes low molecular weight fatty acids, as well as saturated and unsaturated acids based on single and multiple five and six-membered rings. The term "organic acid" therefore applies to a broad range of organic chain compounds which contain the organic acid radical .COOH. The hydrocarbon part of the compounds can be one of the following:[1)]

- Aliphatic (fatty) acids: R.COOH (where R is a straight or branched)

- Aromatic acids: Ar.COOH (where Ar is a benzene ring or substituted benzene rings)
- NAs: X.COOH (where X is a cycloparafinic ring)

Fig. 1 shows a typical appearance (pitting and grooving) of NAC.

Table 1 shows types and characteristics of acids in oil refinery process.

2.2 Properties of NA

- Formula of NA : $C_nH_{2n-1}COOH$
- Molecular Weight : 180-350
- Melting Point : 30°C (86°F)
- Specific Gravity : 0.95
- Solubility in Water : slightly soluble liquid at distilled grade/
  brown viscous liquid at semi-distilled grade- Vapor Density : 6.92
- Refractive Index : 1.47
- Flash Point : 140°C (284°F)
- Appearance : brown viscous liquid at crude grade/ clear to yellow
  viscous liquid at distilled grade/ brown viscous liquid at semi-distilled grade.

3. Mechanism of naphthenic acid corrosion (NAC)

The classical model characterizes the corrosion mechanism (Fig. 2) in the presence of H_2S as three competing reactions.[5]
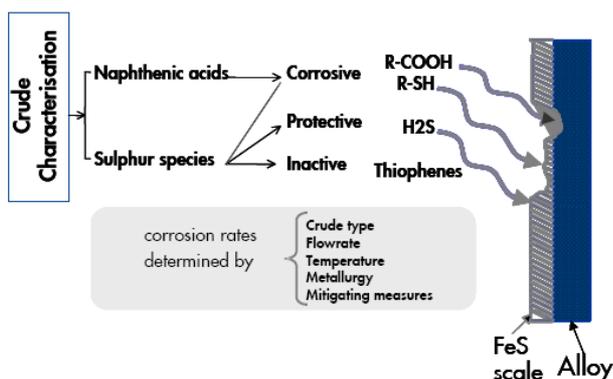
$$Fe + 2RCOOH \rightarrow Fe(RCOO)_2 + H_2 \qquad (1)$$

$$Fe + H_2S \rightarrow FeS + H_2 \qquad (2)$$

$$Fe(RCOO)_2 + H_2S \rightarrow FeS + 2RCOOH \qquad (3)$$

The iron naphthenates are soluble in oil and the surface is relatively film free. In the presence of H_2S a sulfide film is formed which can offer some protection depending on the acid concentration.

The net reaction processes described by the above equations could apply equally to chemical or electrochemical reactions. The distinction with respect to the latter is that there are separate anodic and cathodic reaction processes with movement of ions through the solution and electrons through the metal. To distinguish the relative contributions of electrochemical and chemical processes to the corrosion rate, the ideal approach would be to apply a sufficiently high anodic current to the specimen and compare the mass loss with that predicted from Faraday's law. Alternatively, apply a cathodic current to retard dissolution and compare with the mass loss rate. The use of the linear polarization method is thwarted somewhat by uncertainty in measurement of potential in these fluids at the operating temperatures.

NA is usually very soluble in the acids or oil media, leaving a corroded surface typically without any corrosion products or films.

The NAC process can be divided into four steps:[7]

1. Transportation of acid molecules toward the metal surface
2. Absorption of acid molecules at the active locations on the metal surface
3. Reaction with metal at those active locations, and
4. Dissolution of corrosion products

The researchers also found the corrosion rate of the carbon steel increased with increasing length of the $-(CH_2)n-$ group when the NA structure was described by $R-(CH_2)n-COOH$. The corrosivity appeared to peak at $n = 3$ and then began decreasing again. The research was able to establish a degree of correlation between molecular structure and corrosivity.[8]

Fig. 3 shows the most common areas exposed to NAC.
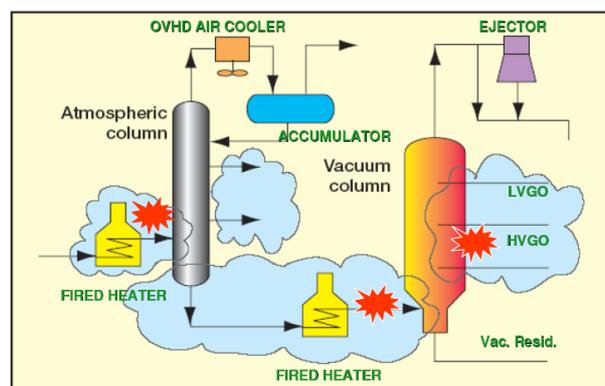

Fig. 2. Schematic Illustration of NAC[6]

Fig. 3. NAC Exposed Area in Refinery Plant

The effect of different variables involve in any of the steps for this damage mechanism process has been largely studied by different investigators[6),7),8),9)] for more than 50 years. This could be summarized as follows.

4. Variable factors of conventional nac

4.1 Corrosion rate equation

The overall corrosion rates are calculated as the addition of NA and sulfidic corrosion, mitigated by the formation of protective scales. Hence,

$$CR = (CRNAP + CRS + CRHSR) \times ff \times fsc \times fal$$

where CRNAP, CRS and CRHSR represent the corrosion per temperature induced by NAs, sulfur and mercaptans, respectively. ff is the flow enhancement factor, fsc is a scale factor that reflects the protectiveness of iron sulfide, and fal is the alloy factor, i.e., the ratio of the corrosion rate of an alloy to that of carbon steel.

These factors are not independent: for example, the effect of flow, scale protection and alloy composition depend on the relative importance of the NA and sulfidic components of the corrosion rates.

4.2 Temperature

In general, corrosion rate of different materials increases with increase in temperature. In the case of NAC, high temperatures promote primarily the transportation of acid molecules toward the metal surface and its reaction with active metal locations (endothermic reaction). At temperatures above 400°C (750°F), corrosion damage is usually not seen, most probably because of the decomposition of the acids or formation of a protective coke film at the
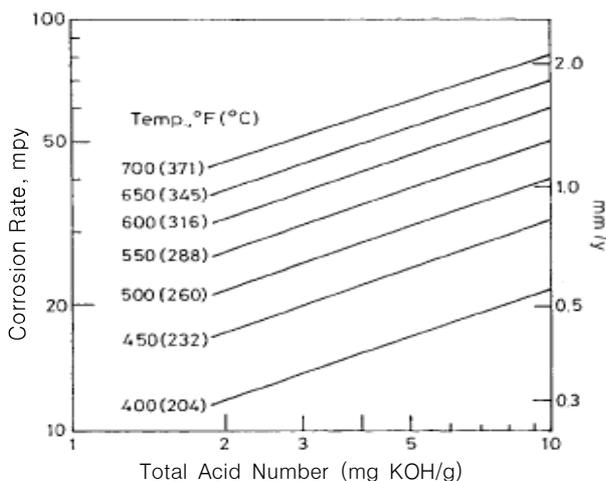
metal surface that protects it.[10)] Fig. 4 illustrates the effect of temperature in the corrosion rate of different materials.

4.3 Velocity

It has been recognized for many years that high velocities or turbulence, and more importantly wall shear stress, can accelerate NAC, particularly in two-phase flow conditions, by enhancing the transportation of molecules and promoting the dissolution/disruption of protective corrosion products. Wall shear stress tends to be more accurate to predict corrosion behavior since it takes into account the density and viscosity of the liquid and vapor, the degree of vaporization and geometry. So, in order to predict the corrosivity of a specific crude or blend, it is important to know or calculate the shear stress in both the units where this crude is being used and the unit where is planned to be used for comparison. In general, corrosion rates are directly proportional to shear stress and the sensitivity to velocity typically increases with the acid content.[1)] Wall

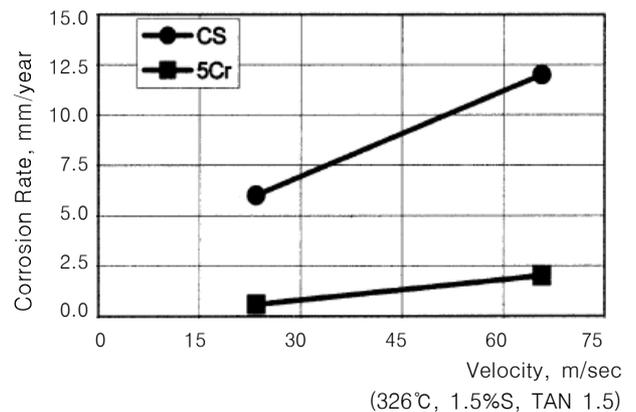**Fig. 5.** Effect of Velocity in Transfer Line[12)]

Fig. 4. Effect of temperature in the NAC of Carbon Steel[9)]
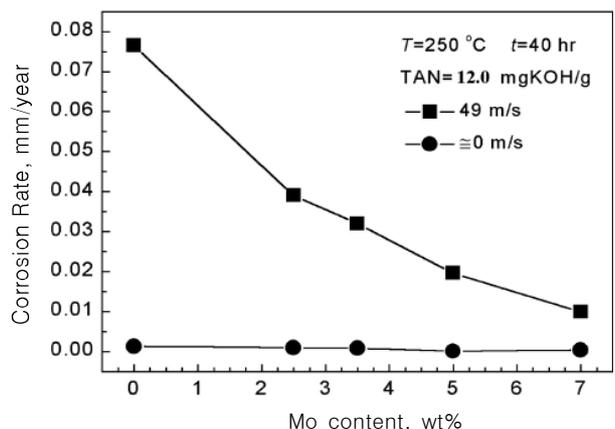

Fig. 6. Dependence of NAC rate on the Mo content in stainless steels (TAN = 12.0 mg KOH/g; testing time: 40 hours)[13)]

shear stress also takes also into account the physical properties of the flowing media, such as density and viscosity which could be affected by the degree of vaporization and temperature.[11]

Fig. 5 shows the velocity effect of CS and 5Cr steel on transfer line.[12] Fig. 6 indicates the velocity effect on several Mo containing steel.[13] It shows Mo can reduce the NAC at the high velocity zone.

4.4 Exposure time

Fig. 7 shows the dependence of NAC rate on the soaking during at 250°C (484°F) for the CS. The values shown were the mean of the corrosion rates measured on the three samples. It was found that the corrosion rate initially increased rapidly, remained comparatively constant from 30 to 100 hours, and after then, decreased slightly.[7]

4.5 Sulfur compounds

Sulfur is one of the most abundant elements in petroleum and may be present as a single element or forming compounds such as hydrogen sulfide, other sulfides, polysulfides, and mercaptans. At a level of 0.2 wt% and above is known to be corrosive to carbon and low alloy sulfidation. At high temperatures, both sulfidation and NAC compete with each other giving the following possibilities, depending on sulfur or acids concentrations, material being corroded, and other variables.[1,10,11]

- Only NAC where sulfur compounds have little or no effect, if they are present.
- High temperature sulfidation, accelerated by the presence of NAs through the following reaction:

$$Fe(RCOO)_2 + H_2S \rightarrow FeS + 2(RCOOH)$$
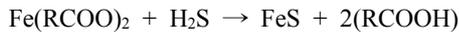
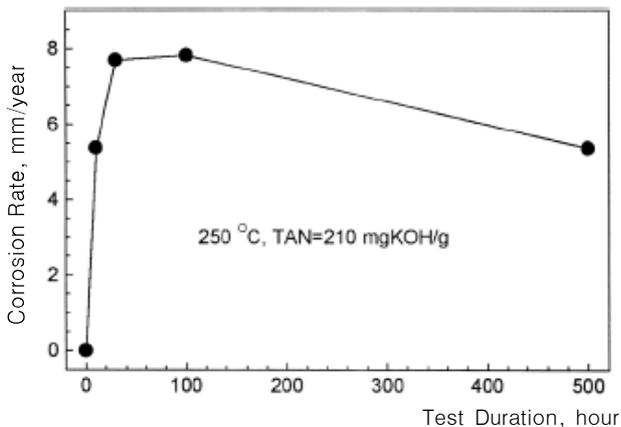In this case, soluble iron-naphthenate will react with hydrogen sulfide to form iron-sulfide and to regenerate NA.

The presence of the organic acids disrupts the sulfide film promoting corrosion due to sulfidation, even in alloys that are expected to be resistant to this damage mechanism (high chromium content alloys).

Only sulfidation in which NAC is suppressed by the formation of stable sulfide films that protect the metal as a barrier coating.

4.6 Cr effects in materials

Fig. 8 illustrates Cr effect. The curves for temperatures 277°C (530°F) and 338°C (640°F), taken from that report, represent data collected by means of steel coupons placed in furnaces in actual plants.

steels at temperatures from 230 to 455°C (450 to 850°F) by

The curve for 413°C (775°F) was drawn with data from the same report but originated from a different work.

Gutzeit[10] suggested that the curve would tend to move upward, as NAC became predominant (Fig. 8). The fact that moving from carbon steel (CS) through 5Cr-0.5Mo, 9Cr-1Mo and 12Cr does not help much in preventing NAC has been demonstrated with plant experience, where upgrading to 316 SS was required to solve the problem. However, from this upper limit where only 316 SS or even 317 SS are the alloys that work, to the situation of pure sulfidation, where 5Cr-0.5Mo or even CS gives an acceptable life, there are many intermediate cases.

Most opportunity crude oils can be placed in this intermediate space between these two extreme limits and the challenge is to find out, for distillation units designed to deal only with sulfidation or those not fully protected against NAC, which ones can be processed and which ones should not be processed at all, unless the unit is "fully
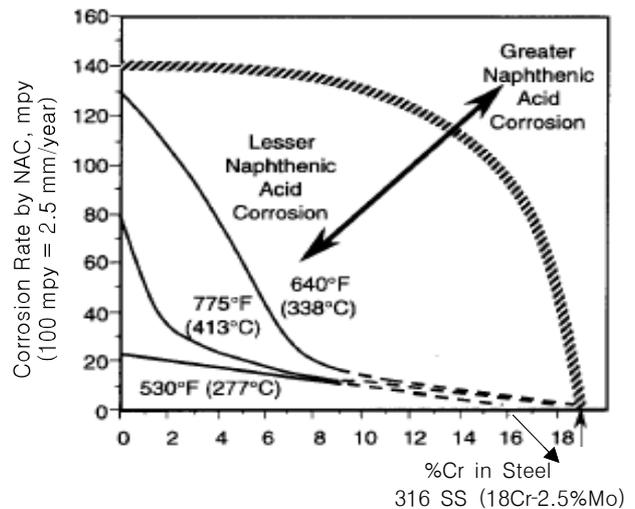

Fig. 7. Soaking time effect of NAC in CS.

Fig. 8. Effect of chromium on the relative corrosion rates of steels[2]

protected". It is important to emphasize that the final decision does not depend entirely on the type and acidity of the feedstock's but also on the actual process and plant conditions, in particular the flow velocity and turbulence for tubes and piping. The situation for vacuum tower internals is becoming different in the sense that some regions in the tower must be protected with 316 SS, irrespectively of the low acidity of the feedstocks, particularly with modern packed tower having high throughput and wash oil rates.[2]

4.7 Mo effects in materials

Considering that NAC has been characterized as a very localized corrosion damage in the form of pitting, flow induced grooving, striation or lake-type attack,[10,14] another important factor to be considered in the beneficial effect of Mo is related to stabilizing the protective passive film of stainless steels and nickel alloys. This will improve the resistance of these materials to pitting and crevice corrosion, particularly in some acids and chloride containing environments. There are different theories that have been developed trying to explain this effect. Some of them have been reviewed by X. Wu et al[7,15] in their work and are primarily associated with the formation of a protective passive film containing Mo oxides or other Mo compounds at anodic or active weak locations in the Cr rich passive film and the synergism between Mo and Cr compounds to produce a more stable protective film. Even though this is not completely understood, it has been widely recognized that Mo improves the pitting and crevice corrosion resistance of stainless steels and nickel alloys and has to be also beneficial to the NAC resistance of these materials.

Fig. 6 showed the Mo is very effective at the high velocity zone.

Finally, as it was explained by X. Wu et al,[7] another contribution of Mo to the NAC resistance of stainless steels could be the affinity of different metal atoms (M^+ ions) to react with the organic acid ($RCOO^-$ ions) to form M-naphthenates. They showed that Fe has higher affinity to form compounds with $RCOO^-$ ions compared with other metallic elements (Cr, Ni, Mn and Mo) in the steel. For instance, increasing the addition of any of these elements in the steel will reduce the amount of Fe to form Fe-naphthenate. This also greatly retards the bonding between the Fe^+ and $RCOO^-$ ions and the corrosion reaction, as indicated by the authors.

Material selection for high temperature applications in crude distillation units will depend primarily on the amount of organic acids present in the crude oil. For low levels of acids (<0.5 TAN), materials are chosen based on predictive corrosion rates using McConomy curves for

| HVGO Draw Tray | Packed Bed Vac. Tower | Atm. Heater Transfer Line | Vac. Heater Transfer Line |
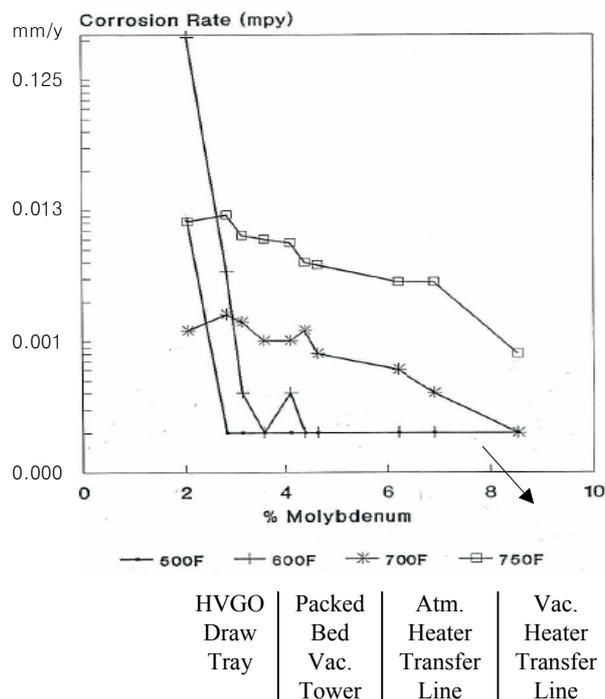
Fig. 9. Effects of Mo content on the corrosion rate of different materials from field tests using coupon racks exposed to various conditions.[4,9]

high temperature sulfidation. As indicated previously, higher alloys than the ones predictive by these curves, particularly those containing greater chromium and molybdenum, are used if organic acids are present. A rule of thumb for this particular service has been the use of austenitic stainless steels with at least 2.5 wt% Mo content (316 or 317 SS) based on what has been reported in the past by different investigators.[3,16]

The data presented by Craig related to laboratory and additional field tests show a gradual reduction of corrosion rate versus Mo content for different conditions. This is illustrated in the same Fig. 9 for the atmospheric and vacuum transfer line. The same behavior was presented more recently by X. Wu et al[7,15] with extensive laboratory test data for different alloys.

5. Review of api standards

API RP 571[14] paragraph 5.1.1.7 NAC has a good description of damage with critical factors that mention condensing vapors. Mo content is also mentioned. Unfortunately the Mo content mentioned, 2 wt% to 2.5 wt%, is not consistent with API Publication 581, which describes minimum 2.5 wt% Mo as having the best resistance. Another shortcoming is that most of the discussion concerns carbon and low-alloy steel but includes austenitic stainless steel

Table 2. Considerable Zone of Sulfur Dominated NAC (white) in CS & 5Cr, < 6 m/sec (20 fps) (Canadian Sands Oil)

Sulfur	TAN	Temperature (°F/°C)							
(wt.%)	(mg/g)	400-450 /204-232	451-500 /233-260	501-550 /261-288	551-600 /288-316	601-650 /316-343	651-700 /344-371	701-750 /372-399	> 750 / 399
< 0.2	< 0.7	1	1	1	2	3	4	5	6
	0.71-1.5	1	2	2	4	4	5	6	8
	1.6-2.1	2	4	5	8	10	15	15	20
	2.1-4.0	3	6	10	12	15	20	20	25
	> 4.0	5	8	12	15	20	25	30	30
0.21-0.6	< 0.7	1	1	2	3	4	6	7	8
	0.71-1.5	1	1	2	4	5	7	8	10
	1.6-2.1	2	2	3	5	8	8	10	10
	2.1-4.0	3	3	5	8	10	10	12	15
	> 4.0	4	5	8	10	10	12	15	15
0.61-1.0	< 0.7	1	1	2	3	5	8	9	10
	0.71-1.5	1	2	3	5	8	10	10	10
	1.6-2.1	2	3	5	8	10	10	10	15
	2.1-4.0	3	5	8	10	10	15	15	15
	> 4.0	5	8	10	10	15	15	20	20
1.1-2.0	< 0.7	1	1	2	4	6	10	10	15
	0.71-1.5	1	2	3	5	7	10	15	15
	1.6-2.1	2	4	4	6	8	12	15	20
	2.1-4.0	3	6	5	8	10	15	20	20
	> 4.0	5	8	10	12	15	20	20	25
2.1-3.0	< 0.7	1	1	3	5	7	10	15	15
	0.71-1.5	1	2	4	6	8	10	15	15
	1.6-2.1	2	4	5	8	10	15	15	20
	2.1-4.0	3	6	10	12	15	20	20	25
	> 4.0	5	8	12	15	20	25	30	30
> 3.0	< 0.7	1	1	2	5	8	10	15	15
	0.71-1.5	1	3	5	8	10	15	15	20
	1.6-2.1	3	5	10	12	15	20	20	25
	2.1-4.0	5	8	12	15	20	25	30	30
	> 4.0	7	9	15	20	25	30	35	40

without stating which factors apply to which material.

Discrepancies like this are common in the petroleum refining industry and can lead to confusion. The affect of NAC on the different alloy systems is a function of two completely different protective passive films, namely FeS and Cr_2O_3.

The API 581 G.7 High Temperature Sulfidic and NAC tables have been generated from industry data and include qualifiers that the corrosion rates (mpy = 1/000 inch per year) are an order of magnitude, only.[17] Table 2 shows the considerable zone of sulfur dominated NAC (white) in CS & 5Cr, < 6 m/sec. (20 fps).

6. Nac in canada athabasca oil sands

6.1 Experience (Materials of Construction by Field Data Survey)

As part of this material selection process, several locations in examples are:

These locations are summarized as follows:
- Pump suction and discharge piping in the HVGO pump-around circuit of a Vacuum Tower.
- Flow meter of this piping
- Diluent tower of a Vacuum Unit with 316 SS cladding and internals in the bottom section.

Metal loss areas in these locations were negligible, indicating that there is not currently a NAC or other corrosion mechanism problem in these locations.

In general, NAC has not been a problem in Canadian Oil Sands facilities since its start up in the mid 1960's,

even in the most aggressive process streams on different materials. Some particular examples are:

- 12Cr pump casings in the HVGO pump around circuit of a Vacuum Unit (288°C (550°F), TAN 4.5; 4wt%S).
- 12Cr pump casings and 5Cr-1/2Mo discharge piping in Coker Heater charge pumps (316°C (600°F); TAN 2.4; 3.5~4.0wt%S).
- 5Cr-1/2Mo and 9Cr-1Mo tubes and CS outlet piping in Diluent Recovery Unit Fired Heaters (316°C (600°F), TAN 2.4, 4.7wt%S).
- 9Cr-1Mo Vacuum furnace tubes (349°C (660°F), TAN 2.3, 4.8wt%S).

Similar situations have been reported in other North Alberta oil industries in the past.[18] B. Messer et al[8] attribute this fact to the particular characteristic of Canada Athabasca oil sands bitumen crudes.

They have proposed a new theory in which the corrosivity of NAs in these crudes is a function of its molecular weight, molecular structure, true boiling point, reactive sulfidic species, and local environment, rather than TAN. According to the authors, Athabasca crudes could be associated with two different types of NAs: low molecular weights or so called α type-NAs, characterized as corrosive, and high molecular weights or β type-NAs, considered to be non-corrosive and inhibitive.

The hot water washing process to extract the sand from the bitumen, particular for the Oil Sands Industry, appears to preferentially remove the higher water-soluble α fraction leaving the less corrosive, less water-soluble, β fraction. They have also proposed that acids surviving after thermal hydroprocessing tend to be of the inhibitive β type. Table 3 shows the comparison of NA between conventional and Canadian sands oil.

Even crudes that are considered very corrosive or are well known to contain high NAs, such as Venezuelan and Californian crudes, could behave differently depending on operating conditions rather than acid content. As reported by Hopkinson and Penuela,[19] materials different than Mo containing austenitic stainless steels, such as 304 SS or 410 SS, have been successfully used in petroleum refining distillation units processing these crudes, justifying the use of 316 SS only in non-vaporizing oil/acid systems where some impingement conditions could be present (transfer lines). For tower internals, where different acid concentrations could occur, higher alloys would be required.

6.2 Laboratory corrosion test 1 - Athabasca river crude in alberta, canada

Supplemental chemical analyses were performed on the hydrocarbon prior to and after testing. The analyses performed included the TAN (ASTM D664), Total Sulfur (ASTM D4294), Mercaptan Sulfur (UOP 163) and Dissolved H_2S (UOP 163). Additionally, the H_2S concentration in the off-gas was determined upon test start-up and after test completion. The pre-test hydrocarbon was also analyzed for sulfur compound determination and for NAs using FAB-MS (Fast Atom Bombardment-Mass Spectroscopy) techniques.

Fig. 10 shows Materials, conditions, crudes characteristics and corrosion rates of coupons from hot oil corrosion tests conducted using different hydrocarbons at different conditions in one plant of Canads Athabasca sands oil upgrading plant.

Results of Test 1

The following conclusions are derived from lab test and in-situ measuring data:

In general, corrosion rate increased with temperature in all materials, as it was expected. Additionally, the corrosion resistance of the materials increased with increasing the chromium content.

The dominant corrosion mechanism in the majority of the tests was sulfidation.

For all cases, corrosion rate in 316 SS and 317 SS was relatively low (below 0.14 mm/yr (5.5 mpy)). The highest corrosion test values (0.14 mm/yr (5.4 mpy)) were obtained in 316 SS on test conducted at 360°C (680°F) using oils with high sulfur content but relatively low TAN. For

Table 3. Comparison of Each Type of NAs

	α-NAs (Conventional)	β-NAs (Canadian Sands Oil)
molecular weight	low	high
solubility in water	moderate to high	moderate to low
solubility in oil	low	high
Carboxyl group in aqueous solutions	readily ionizes	poorly ionizes
Neutralizing	to form salts	difficult
Iron naphthenate	highly soluble in oil	difficult to form
True boiling point	up to 385ºC (725ºF)	357-816ºC (675-1500ºF) typically above average crude true boiling point
protective film formation	difficult	readily
# of HC chains	1 to 2	3 to 5
NAC Model	Classic (API standards)- by Sulfur and TAN combination	Unique (Only Canada Athabasca region) – Sulfur dominated
Corrosivity	Very High	Medium
Velocity Effect	High	High
Mo Effect	High	Medium
Cr Effect	High	Medium to High

Bitumen, 5.5%S, TAN 2.1 @ 550°F

API Publ.581 Table G-17 Estimated Corrosion Rates for CS (mpy)

Sulfur	TAN	Temperature (°F/°C)							
(wt.%)	(mg/g)	400-450 /204-232	451-500 /233-260	501-550 /261-288	551-600 /288-316	601-650 /316-343	651-700 /344-371	701-750 /372-399	>750 /399
>3.0	≤0.5	2	8	20	40	60	100	140	160
	0.51-1.0	8	15	25	45	65	120	150	170
	1.1-2.0	20	25	35	65	120	150	180	200
	2.1-4.0	30	60	60	120	150	160	240	240
	>4.0	40	80	100	160	180	200	280	300

(a) Bitumen, 5.5%S, TAN 2.1 @ 288°C (550°F) (40 mpy = 1 mm/yr)

Bitumen, 5.5%S, TAN 2.1 @ 680°F

API Publ.581 Table G-17 Estimated Corrosion Rates for CS (mpy)

Sulfur	TAN	Temperature (°F/°C)							
(wt.%)	(mg/g)	400-450 /204-232	451-500 /233-260	501-550 /261-288	551-600 /288-316	601-650 /316-343	651-700 /344-371	701-750 /372-399	>750 /399
>3.0	≤0.5	2	8	20	40	60	100	140	160
	0.51-1.0	8	15	25	45	65	120	150	170
	1.1-2.0	20	25	35	65	120	150	180	200
	2.1-4.0	30	60	60	120	150	160	240	240
	>4.0	40	80	100	160	180	200	280	300
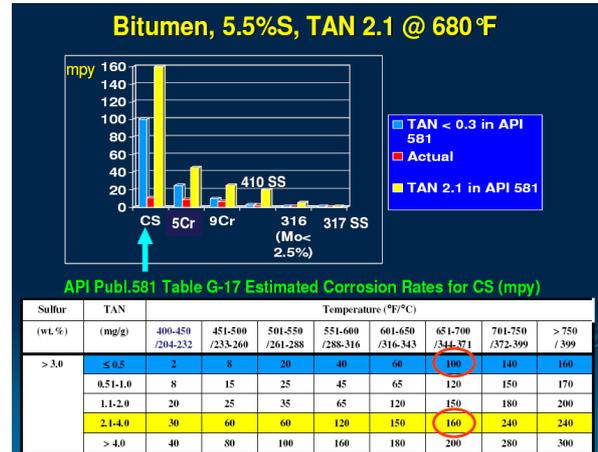
(b) Bitumen, 5.5%S, TAN 2.1 @ 360°C (680°F) (40 mpy = 1 mm/yr)

LVGO, 2.3%S, TAN 2.4 @ 550°F

API Publ.581 Table G-17 Estimated Corrosion Rates for CS (mpy)

Sulfur	TAN	Temperature (°F/°C)							
(wt.%)	(mg/g)	400-450 /204-232	451-500 /233-260	501-550 /261-288	551-600 /288-316	601-650 /316-343	651-700 /344-371	701-750 /372-399	>750 /399
2.1 - 3.0	≤0.5	2	7	20	35	55	95	130	150
	0.51-1.0	7	10	30	45	60	120	140	170
	1.1-2.0	15	20	40	60	75	140	170	200
	2.1-4.0	20	35	60	90	120			
	>4.0	35	50	80	120	150	200	260	280
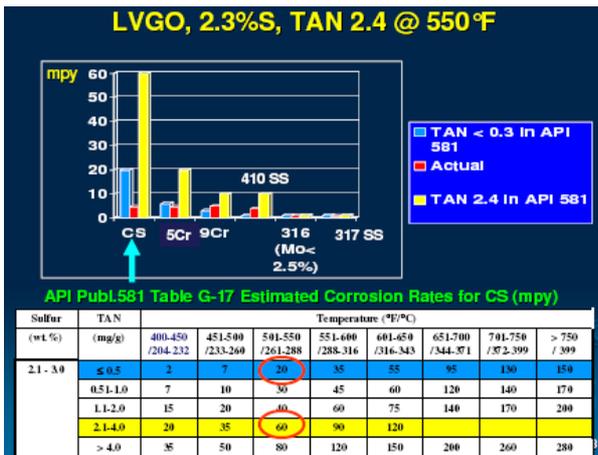
(c) LVGO, 2.3%S, TAN 2.4 @ 288°C (550°F) (40 mpy = 1 mm/yr)

LVGO, 2.3%S, TAN 2.4 @ 680°F

API Publ.581 Table G-17 Estimated Corrosion Rates for CS (mpy)

Sulfur	TAN	Temperature (°F/°C)							
(wt.%)	(mg/g)	400-450 /204-232	451-500 /233-260	501-550 /261-288	551-600 /288-316	601-650 /316-343	651-700 /344-371	701-750 /372-399	>750 /399
2.1 - 3.0	≤0.5	2	7	20	35	55	95	130	150
	0.51-1.0	7	10	30	45	60	120	140	170
	1.1-2.0	15	20	40	60	75	140	170	200
	2.1-4.0	20	35	60	90	120	200	260	280
	>4.0	35	50	80	120	150			

(d) LVGO, 2.3%S, TAN 2.4 @ 360°C (680°F) (40 mpy = 1 mm/yr)

HVGO, 4.4%S, TAN 4.7 @ 550°F

API Publ.581 Table G-17 Estimated Corrosion Rates for CS (mpy)

Sulfur	TAN	Temperature (°F/°C)							
(wt.%)	(mg/g)	400-450 /204-232	451-500 /233-260	501-550 /261-288	551-600 /288-316	601-650 /316-343	651-700 /344-371	701-750 /372-399	>750 /399
>3.0	≤0.5	2	8	20	40	60	100	140	160
	0.51-1.0	8	15	25	45	65	120	150	170
	1.1-2.0	20	25	35	65	120	150	180	200
	2.1-4.0	30	60	60	120	150	160	240	240
	>4.0	40	80	100	160	180	200	280	300

(e) HVGO, 4.4%S, TAN 4.7 @ 288°C (550°F) (40 mpy = 1 mm/yr)

HVGO, 4.4%S, TAN 4.7 @ 680°F

API Publ.581 Table G-17 Estimated Corrosion Rates for CS (mpy)

Sulfur	TAN	Temperature (°F/°C)							
(wt.%)	(mg/g)	400-450 /204-232	451-500 /233-260	501-550 /261-288	551-600 /288-316	601-650 /316-343	651-700 /344-371	701-750 /372-399	>750 /399
>3.0	≤0.5	2	8	20	40	60	100	140	160
	0.51-1.0	8	15	25	45	65	120	150	170
	1.1-2.0	20	25	35	65	120	150	180	200
	2.1-4.0	30	60	60	120	150	160	240	240
	>4.0	40	80	100	160	180	200	280	300

(f) HVGO, 4.4%S, TAN 4.7 @ 366°C (680°F) (40 mpy = 1 mm/yr)

(g) Vacuum Resid, 3.7%S, TAN 4.3 @288°C (550°F) (40 mpy = 1 mm/yr)

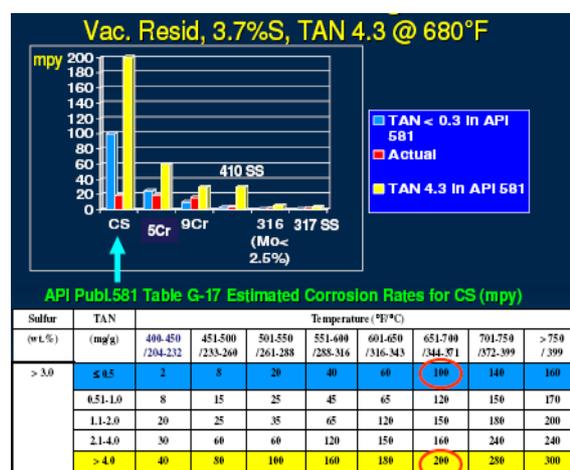(h) Vacuum Residue, 3.7%S, TAN 4.3 @ 360°C (680°F) (40 mpy = 1 mm/yr)

Fig. 10. Comparison Actual Corrosion Rate vs. API Guidelines

the case of the SAGD hydrocarbon test, both materials showed relatively low and very similar corrosion rates (0.06 mm/yr (2.4 mpy)). It is important to mention that, for the SAGD hydrocarbon test, Mo content in the materials tested was at the lower end of the corresponding allowable ranges ($\approx$ 2.0 wt% for 316 SS and $\approx$ 3.0 wt% for 317 SS).

6.3 Laboratory corrosion test 2 - Cold lake crude in alberta, canada

6.3.1 Legend;
API - RBI: Predicted API 581 corrosion rate for sulfur and TAN in fraction.
API - TL: Predicted API 581 corrosion rate using "Top Line" (<0.3 TAN) and actual sulfur in fraction.
IC - Ex: Lab test data for fractions derived from Cold Lake Crude.

Results of Test 2

The following conclusions are derived from lab test data:

The corrosion rates in Cold Lake area are very similar with those of Athabasca river sands oil. Both of them show the sulfur dominated corrosion mechanism that is the NAC is not much severe compared to conventional NAC.

Table 4 shows the cost comparison if candidate materials in NAC environment. It tells the higher Mo containing, the higher cost with better NAC resistance.

7. Results and discussion

1) In general, NAC has not been a problem in processing Canada Alberta oil sands bitumen. Materials different than

**Table 4. Cost of Candidate Materials in NAC Environment**

Material	%Cr	%Ni	%Mo	%Fe	Cost Ratio*
CS				99	1.0
5Cr	5		0.5	94	3
9Cr	9		1	89	4
410 SS	12			87	4-8
304/304L SS	19	10		70	4.5
316/316L SS	17	12	2	67	7
316L SS, Mo>2.5	17	12	2.5	67	8
317/317L SS	19	13	3	64	9
317LM	19	15	4	61	10
904L	21	25	4	45	13
6Mo	20	22	6	49	14-20

* The percents of element and cost ratio of material are based on average of seamless piping.

Mo-bearing stainless steels, such as 12 Cr, 5Cr-1/2Mo and 9Cr-1Mo, have been used in most areas where NAC might be expected without problems.

2) Even though most conventional articles require min. 2.5% Mo contained austenitic stainless steel in the severe NAC environment, as the results of laboratory test, the 316(L) SS equipment and piping with 2 to 2.5%Mo in Canada Athabasca River and Cold Lake area has been proving an excellent NAC resistance during the last several decades.
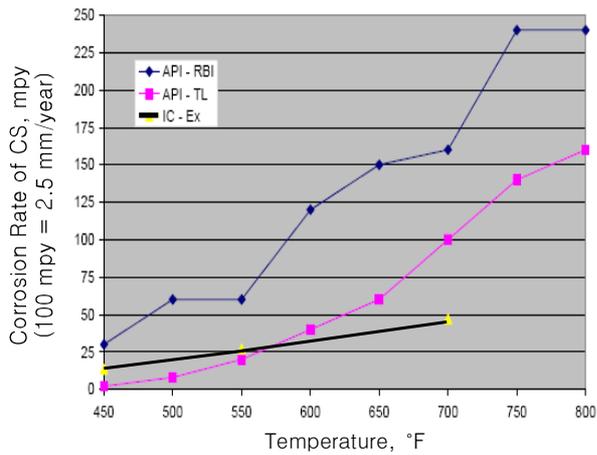
3) This study is not covered the quantitative corrosion mechanism per the several types of naphthenic acid even if the number of chain may be a critical factor in the se-
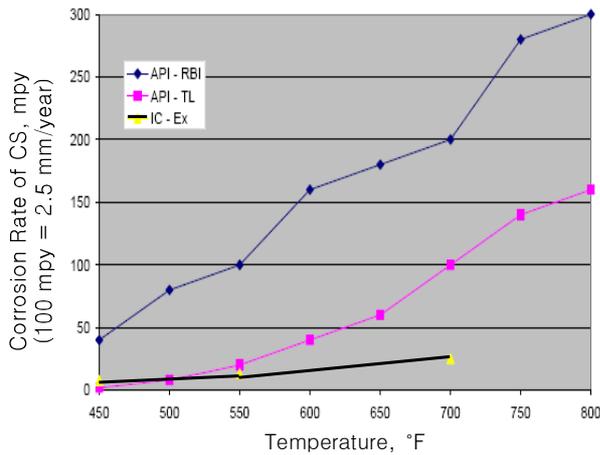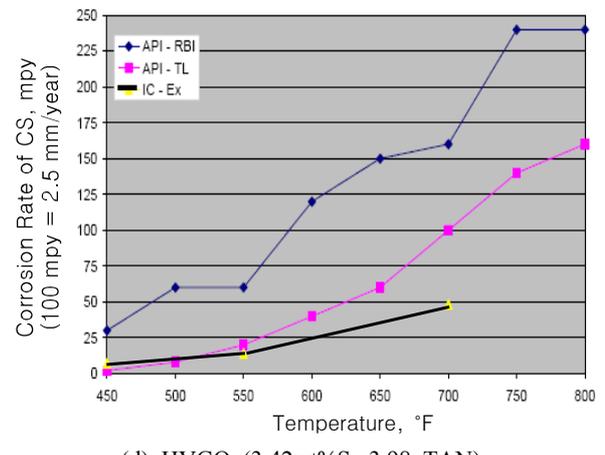
(a) Bitumen (5.54wt%S, 4.74 TAN)
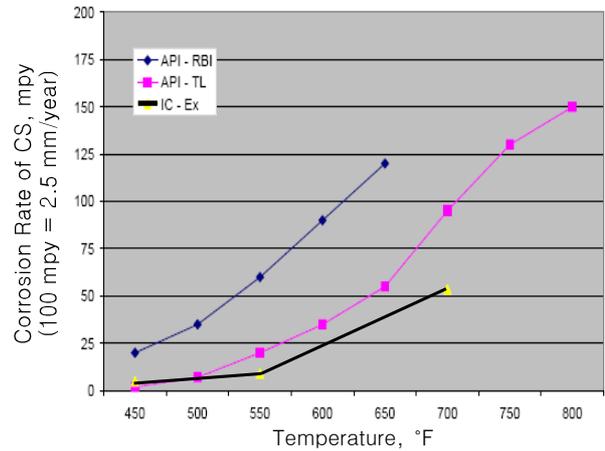
(b) LVGO (2.3wt%S, 2.39 TAN)

(c) Vacuum Residue (5.54wt%S, 2.09 TAN)

(d) HVGO (3.42wt%S, 3.98 TAN)

Fig. 11. Comparison Actual Corrosion Rate vs. API Guidelines

verity of NAC.

4) This study is evaluated in the low and medium velocity (< 15 m/sec) and liquid phase flow because there are no data in-situ (317 SS has been using for high velocity and multi-phase flow during the last several decades) as well as in laboratory tests (it is very difficult to set up the test equipment).

8. Conclusions

1) API Publication 581 may have to get some correction factors for Canadian Sands Oil because of the greatly sulfur-dominated condition.

2) Hot oil corrosion tests conducted in different hydrocarbons at different conditions have indicated that the dominant corrosion mechanism to be high temperature sulfidation with Mo-bearing stainless steels (316 SS and 317 SS) showing better corrosion resistance with little influence from the Mo content.

3) More recent studies in NAC have demonstrated that the beneficial effect of Mo in the resistance of stainless steels is primarily related to the increase in hardness and resistance of the material to erosive and impingement conditions as well as the contribution of Mo in stabilizing the protective passive film. Resistance of the material will depend on changes in operating conditions, particularly flow velocity and impingement conditions, temperature and/or concentration of acid, which could compromise the stability of the passive film.

4) After evaluating previous experiences in using 316 SS and lower alloyed materials in similar services as well as the results of different hot oil corrosion tests conducted, and having a better understanding about the beneficial contribution of Mo in the resistance of stainless steels to NAC,

it was concluded that 316 SS may be a recommendable substitute for 317 SS in specific areas of the upgrading process.

5) The effects of high velocity (> 15 m/sec) and two phase (liquid + vapor) flow should be continuously studied.

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