Crude Corrosivity: Parameters and Prediction – A Technical Recap

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***Key words**: crude corrosivity, sulfidation, naphthenic acid corrosion, distillation, corrosion model*

Introduction

High temperature sulfidation and naphthenic acid corrosion are considered as the main damage mechanisms in the hot systems (>204°C / 400°F) of crude distillation unit – for both atmospheric and vacuum sections. Total (active) sulfur concentration, total acid number (TAN), temperature and flow are key parameters affecting corrosivity in hot crude feed lines and side-cut lines. The general approach for assessment of crude/side-cut corrosivity is described in several normative documents like API RP 581[2] however it is lacking the accurate flow-corrosion representation. The flow plays an important role in crude corrosivity, particularly being responsible for removal of protective Fe_xS_y layer. It was documented in several papers that metal loss can be accelerated by increasing local turbulence. Therefore, a thorough assessment of the flow regime and key flow parameters - particularly wall shear stress - may help identify areas susceptible to corrosion. This paper briefly discusses crude corrosivity parameters and highlights the contribution of flow modeling to corrosion prediction through a selected modeling approach.

Key Process Parameters Influencing Crude Corrosivity

Temperature

It is widely accepted that crude corrosivity is most significant between approximately 230 °C and 400 °C. The lower temperature marks the onset of sulfidation, while the upper range corresponds to the decomposition of naphthenic acid and intensification of coke formation.

Within the above-mentioned temperature range the highest corrosivity is usually observed between 300-360°C (e.g. in VGO and HVGO side cuts), where naphthenic acid corrosion part typically reaches its peak. Presence of sulfidation and formation of FeS deposits changes the picture and final corrosion rate depends on balance between two damage mechanisms. There is a consensus that for low TAN (and low sulfur) the corrosion trends follow linear correlation, while for higher TAN (>1 mgKOH/g) and temperature >300°C / 572°F, corrosion rate seems to follow the side-cut TAN distribution profile. Increasing the sulfur content, and hence likelihood to formation of protective layer of sulfides, at TAN below c.a. 1mgKOH/g, slows down the corrosion rate which is known and confirmed phenomenon – see Figure 1.

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[2] *American Petroleum Institute Recommended Practice: Risk-Based Inspection Methodology, latest ed.*

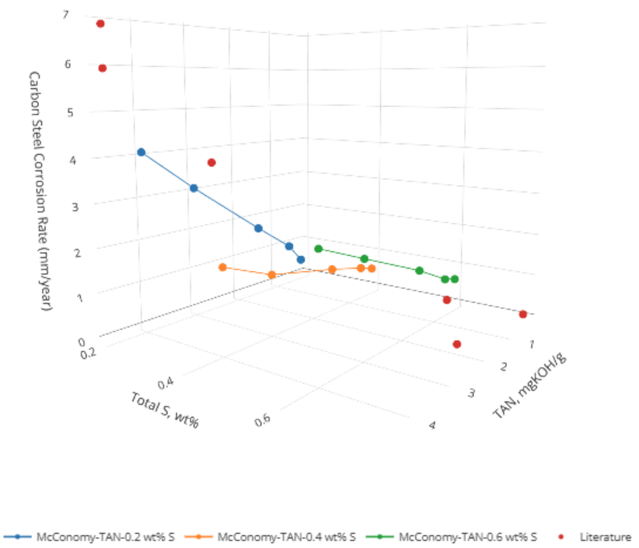


Figure 1 Comparison of modified McConomy (with nap acid impact) and literature results (carbon steel, T= 300-320 ℃, S = 0.2, 0.4 & 0.6 wt.%)

Most authors consider 400 °C (approximately 750 °F) as the upper limit for crude corrosivity. At this temperature, most naphthenic acids are expected to be fully decomposed, and the rate of sulfidation corrosion generally decreases. Sulfidic corrosion can still occur at higher temperatures (>500 °C), but such conditions are uncommon in typical refinery units, except in specialized processes such as coking).

For more details, please refer to the ***Knowledge Library*** - register now for free access.

Active Sulfur & Naphthenic acid structure

Over the last few decades, several studies have supported the concept of 'active sulfur' or 'active sulfur species' as primary drivers for sulfidic corrosion. Subsequently, researchers have delved into each group of active sulfur compounds to establish mathematical relations between their concentrations, operating parameters (predominantly temperature), and sulfidation rates.

The main groups of sulfur compounds identified in crude oil and its fractions include:

- Thiophenes
- Sulfides
- Thiols (mercaptans)
- Other (Sulfones/sulfoxides, Thiadiamandoids, $S1O_x$ type compounds etc.)

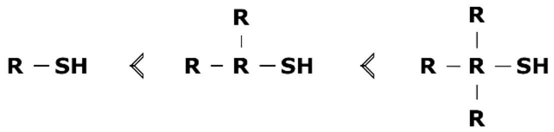
Each exhibits varying levels of 'reactivity' towards sulfidation, and within them, researchers have distinguished several sub-groups characterized by different functional groups and hydrocarbon chain structures, leading to different sulfidation activities.

Among these, Thiols (mercaptans) with the generic structure R-S-H are identified as the most reactive (active) sulfur compounds and are responsible for the major sulfidation impact in refinery processes. Numerous studies on mercaptans' reactivity and sulfidation rates have led to the following generic conclusions:

- The activity of primary mercaptans generally diminishes with increasing chain length (i.e., increasing molecular weight):

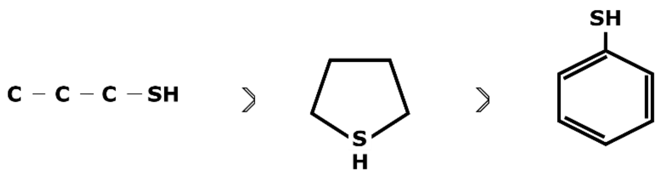
C – SH > C – C – SH > C – C – C – SH

- ❖ The branching of the hydrocarbon chain typically results in higher activity, and this is further influenced by the length of individual branches:



This phenomenon is explained by considering the stability of primary, secondary, and tertiary radicals, with the highest stability observed for tertiary radicals .

- ❖ Cyclic structures (such as cyclopentyl and cyclohexyl mercaptans) are less active than open-chain structures due to the stabilizing effect of the ring, which is further enhanced with unsaturation (e.g., phenyl mercaptan):



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The concentration and types of naphthenic acids is the second puzzle which impacts crude corrosivity. When considering the structure of naphthenic acid only and its impact on corrosion rate, we can assume the following:

- MW_{NAP} < c.a. 300au – expect higher corrosivity (sometimes referred as α-acids)
- MW_{NAP} > c.a. 300au – expect lower corrosivity (sometimes referred as β-acids)

This is, however, a generic statement and must be used with caution. The impact of the naphthenic acid structure is far more complex and in fact not yet fully understood. First, the naphthenic acid “soup” in the crude oil and side cuts, may comprise number of various structures while laboratory evaluations are performed mostly on individual acidic species. Second, the molecular weight itself hardly can be used as a factor that decisively impact on reaction paths or rates.

Hence, it is feasible to look for some other parameters (boiling point, structures etc.) that could better explain certain behavior of naphthenic acids in corrosion reactions. One of such parameters could be Molecular Complexity (MC) factor. The Molecular Complexity, however, not yet properly defined and empirically established (in terms of Complexify calculation) is used successfully in e.g., drugs synthesis. The MC approach has yet to be implemented at an industry level (currently in the experimental stage) due to the limited accessibility of data on individual naphthenic acid corrosion. However, it holds the potential to introduce new perspectives for studies on the correlation between naphthenic acid structure and corrosivity.

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Flow/wall shear stress

It was mentioned earlier that flow conditions (turbulence, single-multi phase etc.) may play an important role in determination of crude corrosivity. Fluid dynamics, typically expressed by flow velocity or by wall shear stress (WSS), influences primarily the sulfidation part of crude corrosivity. It is generally accepted that, in fully liquid-phase lines, fluid velocities below 6–7 m/s (approximately 20 ft/s) are unlikely to cause significant flow-accelerated sulfidic corrosion (removal of sulfide layer). This consensus, which is not limited to sulfidation, also recognizes that local turbulence at weld protrusions, elbows, tees, or other flow restrictors generally increases the propensity for corrosion by removing loose surface scale or deposits and enhancing erosion phenomena. Such local thinning is difficult to detect during routine inspections, and in its most hidden form - preferential weld attack - it poses a significant threat to the integrity of crude units.

Popular referencing document API RP 571[3] does not provide any guidance on velocity limits in crude corrosivity regime. Some feedback may be found in API RP 939C[4] referring to sulfidic corrosion component and presence/removal of protective sulfide film. It is mentioned that at flow velocity above c.a. 60 m/s, the sulfide layer will not be formed leading to intensification of sulfidic corrosion. This is somehow reflected in API RP 581[5], where the crude corrosivity calculation route includes correction factor "5" for velocities above 30 m/s (c.a. 100 fps). Note that the velocity limit specified in API RP 581 is 50% of one mentioned in API RP 939C.

Published laboratory tests, in general, under high flow velocities (>30m/s / 100ft/s) show very poor corrosion resistance of carbon steel to naphthenic acid and sulfidic corrosion. Alloyed steels like 5Cr and 9Cr, in general are more resistant than carbon steel, but may also exhibit kind of "swinging" resistance which basically depends on specific S/TAN configuration.

Austenitic stainless steels type 316 show good to very good resistance under high flow velocities (>30-40m/s) at TAN in range of about 1-2 mgKOH/g and total sulfur <2-3wt%. Type 317L with higher Mo and Cr content shows very good to excellent corrosion resistance to naphthenic acid attack and is typically a first-choice material for the equipment and pipelines working under most severe TAN/S-flow regimes (transfer lines, furnace tubes, bottom of the vacuum column etc.). It is therefore clear that corrosion risk assessment, a key element in developing Integrity Operating Windows, Corrosion Control Documents, and Inspection Strategies, must be supported by accurate and comprehensive flow characterization.

For more details and specific references, please see the ***Knowledge Library*** - register now for free access.

Our newly launched crude corrosivity prediction model, ***Crude-Corrology®***, is now integrated with advanced flow modeling tools. An example demonstrating how our latest ***Crude-Corrology®*** model compares against published corrosion–flow data is provided at the end of this paper.

Crude-Corrology®

The Crude-Corrology® model provides a structured framework in which flow modeling is integrated with key process parameters (T, S, TAN) to evaluate crude corrosivity. By integrating these parameters with flow characteristics, the model enables more accurate evaluation of areas susceptible to increased corrosion.

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[3] *American Petroleum Institute Recommended Practice: Damage Mechanisms Affecting Fixed Equipment in the Refining Industry, latest ed.*
[4] *American Petroleum Institute Recommended Practice: Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries, latest ed.*
[5] *American Petroleum Institute Recommended Practice: Risk-Based Inspection Methodology, latest ed.*

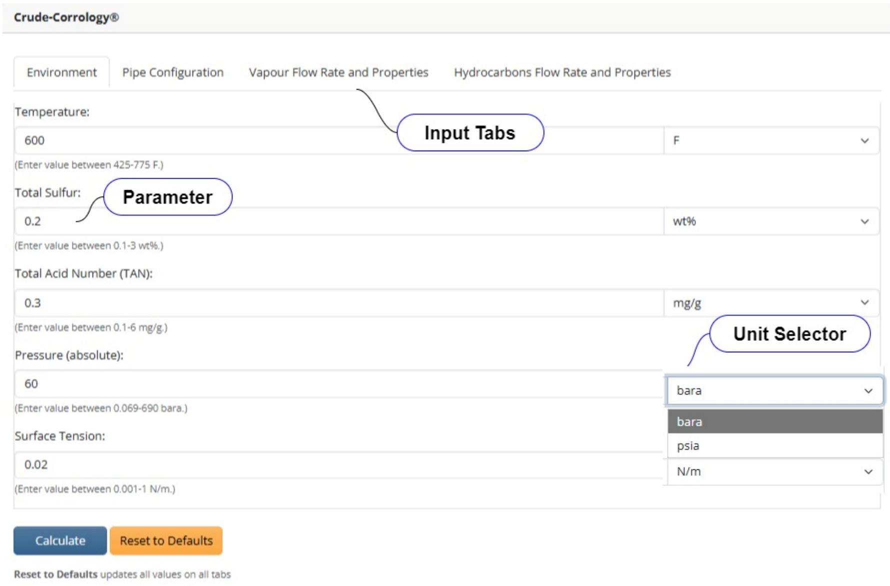
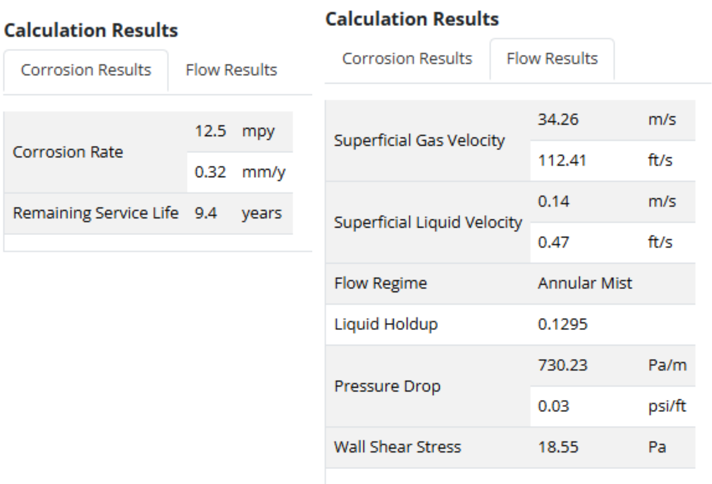


Figure 2 Example of Crude-Corrology® – Environment Configuration data input screen.

Figure 2 shows a screenshot of the input tab for Environment Configuration. By selecting the dedicated input tabs, the user can enter all relevant data for the operating environment as well as liquid and vapour properties. In the Unit Selector, the user can choose the appropriate engineering unit.

After completing all input fields across the tabs, clicking the **Calculate** button will display the Results screen, showing corrosion rate for selected material and flow parameters as illustrated in Figure 3.



Calculation Results

Corrosion Results | Flow Results

Corrosion Rate	12.5	mpy
	0.32	mm/y
Remaining Service Life	9.4	years

Calculation Results

Corrosion Results | Flow Results

Superficial Gas Velocity	34.26	m/s
	112.41	ft/s
Superficial Liquid Velocity	0.14	m/s
	0.47	ft/s
Flow Regime	Annular Mist	
Liquid Holdup	0.1295	
Pressure Drop	730.23	Pa/m
	0.03	psi/ft
Wall Shear Stress	18.55	Pa

Figure 3 Example of Corrosion and Flow results.

Table 1 presents a model verification, benchmarking predicted crude corrosivity against published corrosion data to evaluate accuracy under representative conditions.

Table 1 – Model verification: predicted corrosion rates benchmarked against published data.

Case	Material	T, C	TAN, mgKOH/g	S, wt%	Measured CR, mm/y	Predicted CR, mm/y
A	Carbon steel	340	0.2	1.55	1.13	1.01
B	Carbon steel	297	0.1	0.5	0.1-0.24	0.29
C	Carbon steel	340	2.7	0.4	1.12	1.3
D	5Cr	380	0.7	1.14	0.34	0.49
E	5Cr	330	0.1	0.3	0.1	0.14
F	5Cr	300	2.2	0.4	0.15	0.18
G	9Cr	204	0.4	2	<0.025	<0.025
H	316L	360	0.1	2.5	<0.025	<0.025