

An Enhanced Prediction Model for Simultaneous Naphthenic Acid and Sulfidic Corrosion Quantification

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ABSTRACT

Refinery operators face increasingly complex challenges in managing integrity of process units and assets – driven by the goal to achieve operational excellence and maximize asset performance while minimizing costs and maintaining the highest safety standards. Naphthenic acids (NAP) and organic sulfur compounds (OSC) present in crude oils pose serious hot oil corrosion problems in oil refineries, especially with the increase in processing of lower-quality, opportunity crudes. In oil at 400-750F (204-400C), simultaneous naphthenic acid plus sulfidation reactions (SNAPS) remove iron (Fe) from steel surfaces. In Corrosion/2021, the authors introduced a molecular mechanistic model that quantifies and predicts SNAPS corrosion rates. The current paper describes the molecular basis of the model's reactions, kinetics, and mass transport to vessel walls. Unlike empirical industry correlation models, the new model takes a radically different, molecular view of hot oil corrosion. The model captures concurrent reaction rates among carbon steel, NAP, OSC, and corrosion products. Competitive adsorption between NAP and OSC and the role of a nano-particulate barrier layer result in para-linear algorithms. Factors are applied to compensate for the reduction of iron surface availability from alloys. Inputs include typical refinery operating / process parameters, oil composition and properties commonly available in a refinery. The model predicts instantaneous and average corrosion rates as well as cumulative metal loss while incorporating reactions simultaneously generating and depleting a “barrier layer”. This is accomplished by including additional steps in the NAP and OSC reaction mechanisms. The effect of flow conditions on corrosion kinetics is determined in terms of mass transport or accelerated mass transport of reactive species toward the vessel walls.

Key words: Corrosion rate, Corrosion science and technology, Naphthenic acid, Sulfidation, Prediction, Sulfur, Simulation, Modeling

INTRODUCTION

Sulfur and acidic impurities in crude oils pose serious hot oil corrosion problems in crude distillation units (CDU) and associated vacuum distillation units (VDU), especially with the increase in processing of low-quality, opportunity crudes.¹⁻⁴ In the range of 200-400°C, reactive sulfur compounds cause sulfidation corrosion of ferritic carbon and chrome steels in CDU, VDU, and front ends of downstream units operating at hot oil temperatures.⁵⁻⁷ Over the same temperature range, naturally occurring carboxylic acids in

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crudes can be so aggressive that higher alloy, austenitic stainless steels containing >2.5% Mo are required for processing high acid oils.⁸⁻¹¹ Although sulfidation and acid corrosion occur over the same temperature range, they differ in two significant ways. Sulfidation forms an iron sulfide solid that is semi-resistant to further corrosion and relatively insensitive to flow velocity. Acids form oil soluble organic salts that can be washed away especially in areas of high turbulence.¹²⁻¹⁴

Refiners have traditionally relied on industry surveys to develop rough, rule-of-thumb guidelines for safe operations and material selection.¹⁵⁻¹⁷ Oils with S >0.5% considered “sour” and potential sources of sulfidation. Oils with acid concentrations >0.50 TAN (TAN = mg KOH/g, measured by titration) are considered corrosive. Because sulfidation yields a somewhat corrosion resistant solid scale, one rule of thumb suggests that acid and sour crudes could be blended to some %S/TAN to minimize the effect of acids, but the optimum value for such a ratio varies among refiners.¹⁷

As the world’s supply of crude oils has become more diverse, the number of sour and acid offerings (opportunity crudes) has been increasing.^{3,18,19} Several industry programs have developed empirical S/TAN corrosion models for based on statistical correlations of large lab databases.^{11,14, 20,21} Most of these engineering models are based on parallel independent acid and sulfidation reactions that are combined with refinery fluid dynamics based on either mass transport or wall shear stress. While the proprietary engineering models have been applied somewhat successfully, their predictive capabilities are limited because they lack a fundamental description and understanding of the underlying reaction chemistry at the molecular level. In Corrosion/2021, we introduced a ‘SNAPS’ corrosion model based on reaction fundamentals in molecular dimensions, and included supporting data showing close correlation between model predictions and field measurement and lab-measured rates. In addition to the critical factors of Arrhenius temperature and kinetic dependence of duration (time), other parametric aspects of the model are schematically shown in Figure 1.²²

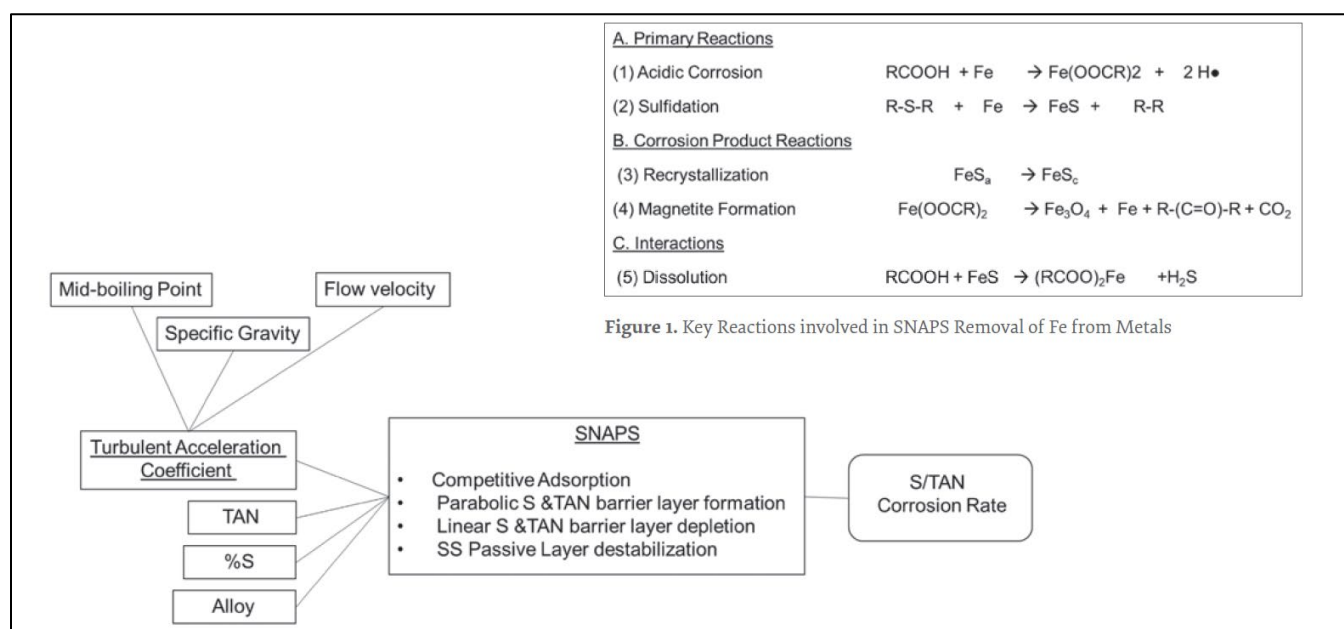


Figure 1. Corrosion Prediction Model Functional Overview

The new model, called CorrExpert[®]-Crude¹, calculates the instantaneous and average corrosion rates for simultaneous molecular reactions of acids and reactive sulfur compounds based on surface coverage; hence, duration of exposure has a key role in computation of both cumulative corrosion and average corrosion rates. Cumulative thickness of Fe removed from carbon steel surfaces is determined and divided by exposure duration to obtain corrosion rates. Alloy factors reduce calculated Fe thickness loss on the basis of Fe surface availability. A turbulent acceleration coefficient (TAC), determined by fluid and operation conditions, is applied for increased mass transport at refinery flow rates.

A molecular model of hot oil corrosion differs in terms of space and time scales from commonly used refinery engineering correlations. (The molecular model quantifies ‘nano scale’ dimensional interactions whereas engineering calculations are significantly more macro - Figure 2).

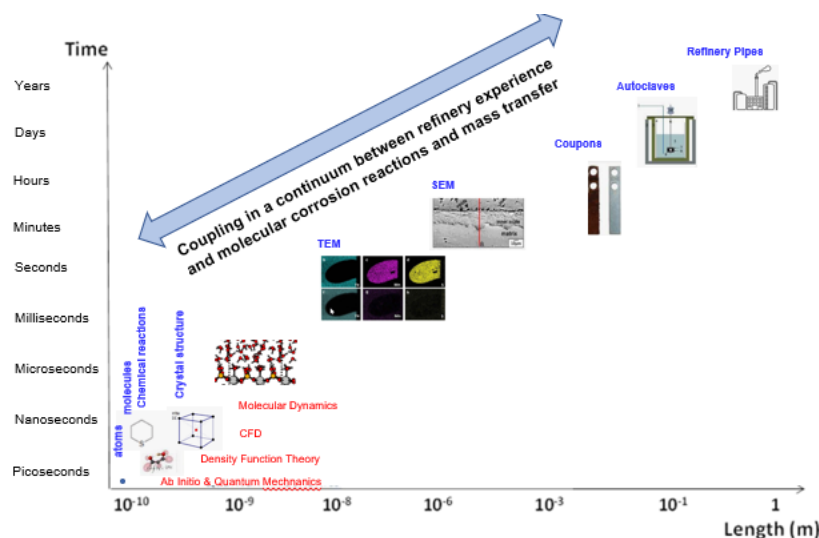


Figure 2. Time and Dimension Corrosion Continuum

Hot Oil Corrosion is a chemical process. Molecular reactions between iron atoms and corrosive molecules occur at 10^{-10} m in 10^{-10} sec time scales while refinery flows occur in pipes with about 10^{-1} to 10^0 m diameters over periods of days (8.6×10^4 sec) or longer. Historically, the effects of corrosive impurities have been followed down corrosion in terms of mils per year on refinery scale pipes through autoclave testing on coupons followed by inspection with sophisticated surface characterization methods that reach down into the nanometer (10^{-9}). These surface techniques, however, are applied to “frozen samples”. Hot oil chemistry occurs within 10^{-12} to 10^{-5} seconds at elevated temperatures while the SEM & TEM images are recorded after hours of preparation at room temperature²¹. On the other hand, on-line monitoring can follow the reduction in wall thickness at temperature but lacks instantaneous compositional data on the corrosives.²³

The new model takes a radically different view of hot oil corrosion and begins by examining corrosion reactions at a molecular time and distances dimensions. Thus, the motion of molecules toward a reactive surface is coupled with the reactions at that surface, a combination of mass transport and reaction kinetics that was called at one point “chemo-mechanical erosion corrosion”.²⁴ This approach draws from a wide range of chemistry and physics, building from a theoretical basis of corrosion chemical reactions involves quantum electron transfers. This molecular approach has evolved from extensive analytical and corrosion testing in the past 25 years.^{14,25,26, 27,28}

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Reactive Species – Understanding the Molecules

One of the hot corrosion mechanisms of greatest concern to refineries is that due simultaneous sulfidation and naphthenic acid (SNAPS) thinning. Hot oil chemistry is often discussed in refineries in terms of “TAN” and “H₂S” because their measurement is associated with acidic (NAP) and sulfidation corrosion respectively. However, in many models these values fail to adequately predict corrosion behavior, and alternate analytical methods have been explored, and this paper is building on the past data.^{18,29,30}

Total Acid Number (TAN)

Total Acid Number (TAN = mg KOH/g oil) is a measure of all the acids in a petroleum sample as determined by titration of an oil sample.³¹ Many alternative acid measurements in crudes and distillates have been proposed due to poor correlation with corrosion rates.³² Generally, correlations with TAN are adequate for sulfur free systems. At very low levels or no Sulfur, corrosion rates remain constant with time, follow Arrhenius behavior, and increase linearly with TAN up to about TAN of 10.¹⁴ The model attributes the historically poor correlations for crude oil TAN to an under-appreciation of the effects of concurrent NAP volatilization, thermal decomposition, and competitive concurrent sulfidation.^{33, 34, 35} The historically poor TAN/corrosion correlations led to the development of many alternative methods for measuring, isolating and characterizing naphthenic acids.²⁵

Collectively, petroleum carboxylic acids are called “naphthenic acids” (NAP) after the first type of carboxylic acid isolated.³⁶ The acid functionality carried on some type of ring or branched hydrocarbon skeleton is >85% -CH₂-COOH.³⁷ Typically, carboxylic acids attached to a ring are identified as naphthenic acids.

NAP in crude have been extensively characterized with > 3000 individual species detected in a single crude.³⁸ Although NAP with different molecular weights or structures differ in boiling point, there is no evidence of a difference in the reactivity of the -CH₂COOH functional group as measured by TAN. For the purposes of the model, “Naphthenic Acids” (NAP) will mean all carboxylic acids in a petroleum sample. Although much has been learned about the origin and complexity of NAP mixtures in crude, currently no acid measure has been found to correlate better with corrosion rates than TAN though there is evidence to show that NAP molecular structure complexity and acid boiling point have a role. Therefore, TAN is used as the acid concentration in the model.

OSC, Sulfur and Thiols (R-SH)

Unlike NAP, there are several reactive organic sulfur functional groups within the organic sulfur compounds (OSC) along with some unreactive sulfur compounds in crude oils.³⁹ Much of the difficulty in using total %S for corrosion prediction arise from this multiplicity of S functional groups. Industry-wide API projects developed methods for predicting corrosivity. McConomy curves, which use S/temperature correlations with a S modifier, were one of the results of this effort.¹⁵ Later, recommended practices for thinning included tables for combinations of TAN and total S, but these very conservative estimates were for setting inspection priorities, and not true predictions of thinning rates (this statement has been made by the document authors at numerous conferences).¹⁷ Another early method that showed promise was H₂S evolution.^{40,41} Geo-chemical and hydroprocessing studies generated a rule of thumb that 2/3rd of the S in crude oil is thiophenic, the dominant form of “non-reactive S”, multi- ring compounds with the S incorporated into aromatic rings.^{42,43,44} The model uses the total S value and applies a “1/3 rule”, meaning 1/3rd of total S is assumed to be reactive OSC. Since 2000, extensive characterization studies of crude oils in have demonstrated that prevalent reactive S OSC are aliphatic mercaptans and alicyclic S compounds. As in the case of NAP, crudes oils contain a plethora of closely related OSC species; characteristic of reactive OSC is a single C-S bonds and H₂S is a by-product of OSC thermal dissociation. For the model, %S and mercaptan concentrations are used as inputs.

Surface Coverage

On a molecular scale, all corrosion is local. That is, NAP or OSC must contact the reactive surface. When both are present, the surface concentration of the corrosion-driving species is determined by competitive adsorption. Because the reactions are a function of the relative number of each type of molecule, concentrations are converted to molar units: TAN and %S are significantly different units of concentration. When converted to moles, a 1:1 ratio of %S/TAN means that there are 17.5 moles of total S or 8.5 moles of reactive S molecules for each acid molecule competing for each Fe atom on a metal surface.

CORROSION CHEMISTRY

In quantum terms, the outer electrons of metallic iron (Fe^0) are so weakly bound to metal atoms that they are free to act as a swarm of electrons in an array Fe^{+2} . (Figure 3)

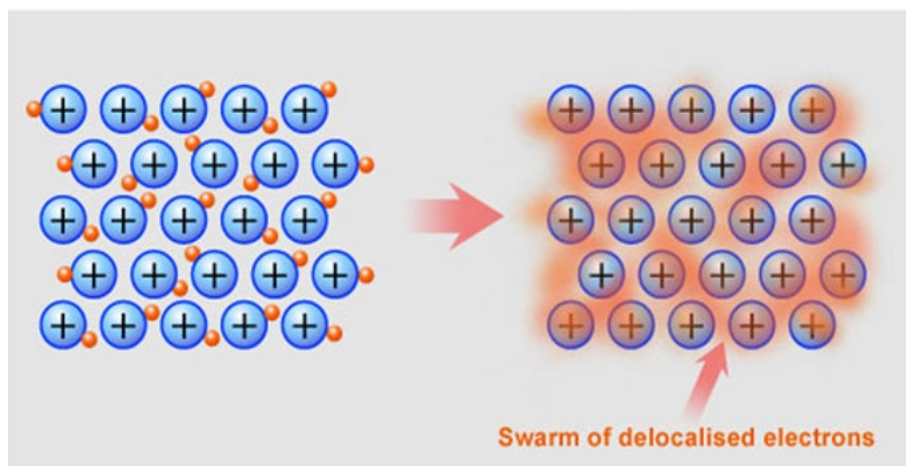


Figure 3. Metallic Iron as a source of delocalized electrons

Metallic iron reacts by giving its electrons to attacking moieties to achieve a more stable permanent Fe^{+2} state. Thus, a molecular view of the SNAPS reactions sees hot oil corrosion as an atom of iron in a metal releasing an electron to an approaching NAP or OSC molecule. Thus, the metal is oxidized (loss of an electron) and the corrosive species reduced on an atomistic/molecular level. In this 'radical' view of SNAPS corrosion driven by free radicals, hot oil corrosion involves quantum electron transfer reactions with free radical intermediates with none of the proton driven electrolytic or ionic processes typical of aqueous corrosion at lower temperatures. Density function theory (DFT) can rationalize the location of nuclei and electrons in orbital that overlap in reactions. Molecular dynamics (MD) can model the molecular collisions. Concepts from both were used to model NAP and OSC reactions alone before addressing interactions in simultaneous reactions.

NAP Reactions

The NAP reaction commonly written in Figure 1, is an unlikely three body reaction. More properly, NAP corrosion chemistry is the sum of two sequential non-ionic reactions in an inert matrix. In the first, one NAP molecule chemisorbs onto an edge Fe atom on the metal surface through the carbonyl oxygen while ejecting a hydrogen atom ($\text{H}\cdot$). Density Function Theory (DFT) predicts that carboxylic acids adsorb dissociatively by homolytic O-H cleavage on the metal surface.^{45,46} Then another NAP repeats the process forming oil soluble iron naphthenate and a second hydrogen atom