PACIFYING POTENTIAL CORROSION

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discuss how to enable enhanced refinery reliability and economics through optimised blending and corrosion management.

Refinery crude unit operations, characterised by significant process complexities and crude blend/fraction assay properties, have traditionally remained an area where accurate asset integrity and life prediction have been difficult to achieve. Such difficulty stems from the need to characterise and correlate corrosion across widely varying unit operating scenarios and process conditions. Quantifying corrosion has thus become a key factor in ensuring asset integrity, and the absence of appropriate corrosion management strategies has often been the cause of some of the most destructive and expensive corrosion failures.

Changing feedstock and process chemistry, coupled with the need to constantly meet demanding production targets, exacerbates the challenges associated with understanding and managing corrosion, a phenomenon defined at the intersection of process phase behaviour and thermodynamics, multiphase fluid dynamics, and metallurgy. One of the primary impediments to overcoming this complexity has been the absence of quantified corrosion data that can be correlated to unit operating/process conditions.

Naphthenic acid and sulfidic corrosion in refinery crude unit operations have often led to conservative decision making in terms of crude selection, crude processing, and unit metallurgy specifications. Additionally, the refining industry has constantly sought, for reasons of improved economics and return on investment, to move in the direction of processing heavier, high-sulfur, high-acid opportunity crudes. Such a directional shift has been a consequence of depleting reserves and declining sweet crudes. Processing low-cost opportunity crudes available in the market has become imperative to improving refining margin. 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 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 nano layer that is

semi-resistant to further corrosion and relatively insensitive to flow velocity. Naphthenic acids form oil-soluble naphthenates that are quickly removed from the corroding surface due to fluid flow.[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% are 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 barrier FeS layer inhibiting acid corrosion, one rule-of-thumb suggests that acid and sour crudes could be blended to some %S/TAN to minimise 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 programmes have developed empirical S/TAN corrosion models 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. This Simultaneous Nap Acid Sulfidation (SNAPS) corrosion model is based on reaction fundamentals representing naphthenic acid and reactive sulfur interactions.

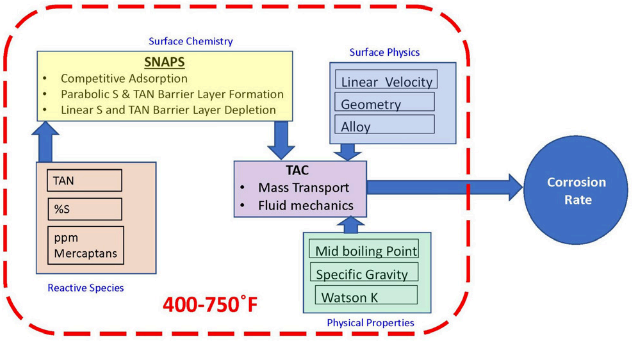

Figure 1. Corrosion prediction model functional overview.

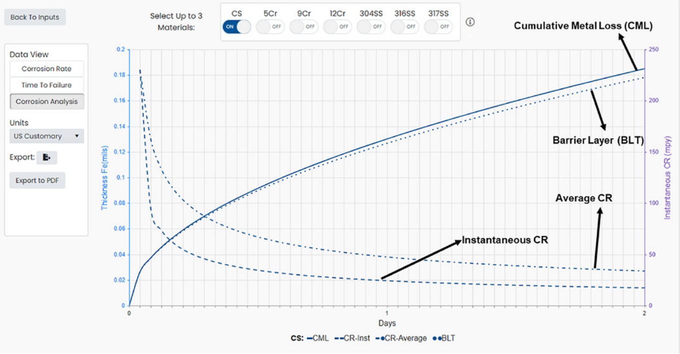

Figure 2. Model results for cumulative metal loss over time (CML), barrier layer thickness (BLT), instantaneous, and average corrosion rates (CR).

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]

The SNAPS model 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 iron (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.

Hot oil corrosion is a chemical process. Molecular reactions between iron atoms and corrosive molecules occur at 10^{-10} m in 10^{-10} sec. timescales while refinery flows occur in pipes with about 10^{-1} - 100 m dia. 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 characterisation 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} sec. at elevated temperatures while the SEM and TEM images are recorded after hours of preparation at room temperature.[21] 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 SNAPS model takes a radically different view of hot oil corrosion and begins by examining corrosion reactions at molecular time and distance scales. 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 that involve quantum electron transfers. This molecular approach has evolved from extensive analytical and corrosion testing in the past 25 years.[14,25-28]

Reactive species: understanding the molecules

One of the hot oil corrosion mechanisms of greatest concern to refineries is that due to simultaneous sulfidation and naphthenic acid thinning. Hot oil chemistry is often discussed in refineries in terms of TAN and H_2S because their measurement is associated with naphthenic acids (NAP) and sulfidation corrosion respectively. However, in many models these values fail to adequately predict corrosion behaviour and alternate analytical methods have been explored.[18,29,30]

Total acid number

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 behaviour, 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 volatilisation, thermal decomposition, and competitive concurrent sulfidation.[33-35] The historically poor TAN/corrosion correlations led to the development of many alternative methods for measuring, isolating, and characterising naphthenic acids.[25]

Collectively, petroleum carboxylic acids are called 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% $-CH_2-COOH$.[37] NAP in crude have been extensively characterised 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 $-CH_2COOH$ functional group as measured by TAN. For the purposes of the model, NAP will mean all carboxylic acids in a petroleum sample. Although much has been learned about the origin and complexity of nap acid 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 arises from this multiplicity of S functional groups. Industry-wide API projects developed methods for predicting corrosivity. McConomy curves, which use S/temperature correlations with an 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.[17] Another early method that showed promise was H_2S evolution.[40,41] Geo-chemical and hydroprocessing studies generated a rule-of-thumb that two-thirds of the S in crude oil is thiophenic, the dominant form of 'non-reactive S', consisting of multi-ring compounds with the S incorporated into aromatic rings.[42-44] The model uses the total S value and applies a 'one-third rule', meaning one-third of total S is assumed to be reactive OSC. Since 2000, extensive characterisation studies of crude oils have demonstrated that prevalent reactive S OSC are aliphatic mercaptans and alicyclic S compounds. As in the case of NAP, crude oils contain a plethora of closely related OSC species; characteristic of reactive OSC is a single C-S bond and H_2S 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.

Reaction kinetics

In the model algorithms, cumulative Fe thickness loss from carbon steel is calculated as a function of kinetic rate constants, NAP and OSC concentrations, and duration. It is the sum of parabolic generation and linear depletion reactions forming the barrier layer, i.e., the sum of the thickness of Fe lost to and through the barrier layer.

Although the depletion reactions do not directly remove Fe from the metal, they do reduce the thickness of the barrier layer to enable higher rates of convective diffusion, increasing the total rate above pure parabolic. Over time, the parabolic generation rate is asymptotic with respect to the linear depletion rate so that rates become linear. Hence, the kinetics are para-linear (Figure 2).

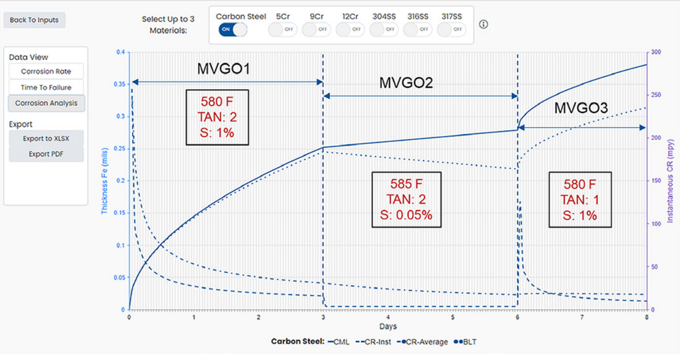

Figure 3. Using a SNAPS-type model to optimise crude blend sequencing.

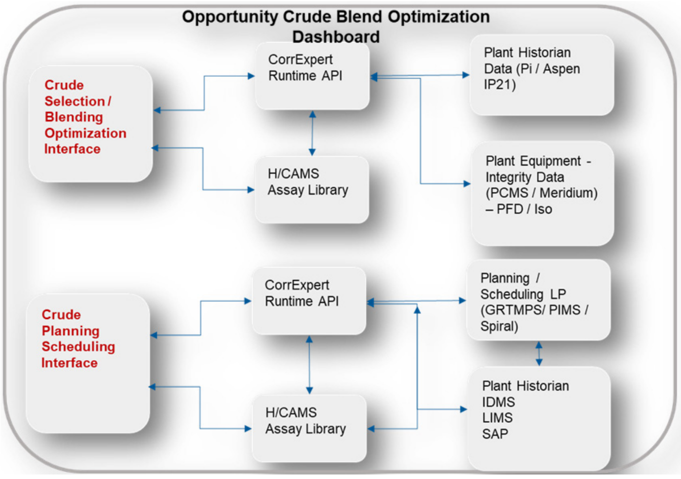

Figure 4. Framework for correlating crude fraction data from blends.

The model calculates combined NAP and OSC para-linear corrosion rates for carbon steel instantaneously and reports the results as the cumulative Fe thickness loss. Using, for convenience, the cumulative Fe loss thickness = CML and barrier layer thickness = BLT, cumulative results can be used to calculate CR for different time intervals, i.e., both instantaneous and average corrosion rates can be calculated for blocks of any duration. The calculation assumes a short duration of oil but long duration of metal at temperature, i.e., in metal that is constantly exposed to steady-state reactive concentrations. The initial parabolic rate approaches linearity with the first day (1440 min). The para-linear kinetics connects short-term (<2 days) lab autoclave corrosion rates with long-term refinery operating (>2 days) experience. However, lab testing includes any loss of TAN or H_2S generation during the 2-day exposure of an oil to temperature. That is, oil time at temperature is one key to understanding hot oil corrosion.

For the example with refinery block operations shown in Figure 3, a change in feed starts with the pre-existing barrier layer, and the TAN and %S for the new NAP and OSC drive the kinetics toward a new steady-state corrosion rate, i.e., the barrier layer is consumed in the second blend due to a highly naphthenic, low S blend but does not result in a high corrosion rate due to the presence of the barrier layer from the first MVGO blend. This shows how the model can be used to sequence 'opportunity' crudes to benefit from the presence of a previously built up FeS layer.

Optimised crude blending and optionality

One of the key enhancements to using a SNAPS-type model is facilitation of a time-based prediction of both instantaneous and cumulative corrosion to help manage opportunity crude blends, thereby enabling optimised blend identification and processing. Through linkage of crude assay data and blend properties available through assay applications, the model provides an easy framework to integrate data from assay libraries as well as a process historian to enable identification and selection of appropriate, profitable crude blends for processing. A schematic showing the interaction between a SNAPS corrosion model and other cloud applications is shown in Figure 4.

Key benefits of the model include:

- Optimise blend management (through appropriate integration with assay data and fraction properties).
- Use as a rolling TAN solution (mix and match high-corrosivity opportunity crudes with low-corrosivity crudes from inventory).
- Process on-the-fly selected blends.
- Create linkage to KPI dashboard to showcase economic value.
- Gain predictive insights to drive proactive safety and reliability.
- Gain real-time insights to support corrosion and maintenance management (when linked to historian).

Through linkage of crude assay data and blend properties available from other assay applications, the model provides an easy framework to integrate data from assay libraries as well as a process historian to enable identification and selection of appropriate, profitable crude blends for processing. A schematic showing the integration of the Haverly® H/COMET application with CorrExpert-Crude is shown in Figure 5 and demonstrates the workflow of how data between CorrExpert-Crude and other cloud applications may be shared and analysed.[45]

Summary

A mechanistic corrosion prediction model for refinery hot oil corrosion has been developed. The framework of the model has been described in terms of molecular functional groups. All carboxylic acids measured by TAN are treated as naphthenic acids. Corrosive, reactive sulfur compounds, approximated as one-third total %S and mercaptans, are treated as organic sulfur compounds. NAP and OSC react directly with the metal by quantum electron transfer with solid state and molecular diffusion. Linear and parabolic kinetic parameters have been determined for independent NAP and OSC reactions, reactions of the corrosion products, and secondary reactions.

Using a cloud-based predictive application enables realisation of the business need to work with opportunity crudes while minimising damage to CDU/VDU equipment. Integrating crude assay data and information available through crude assay libraries and a cloud-based process historian, the framework facilitates enforcement of appropriate integrity operating windows (IOW) through utilisation of corrosion rate as a dynamic IOW parameter alongside other key operating variables such as TAN, sulfur, fluid turbulence, and temperature. The system's ability to seamlessly collaborate with other platforms, including crude blending and supply chain planning applications, has real-time benefits in providing a digitalised solution integrating crude assay with automated predictive analytics to achieve crude processing flexibility and enhanced unit economics.

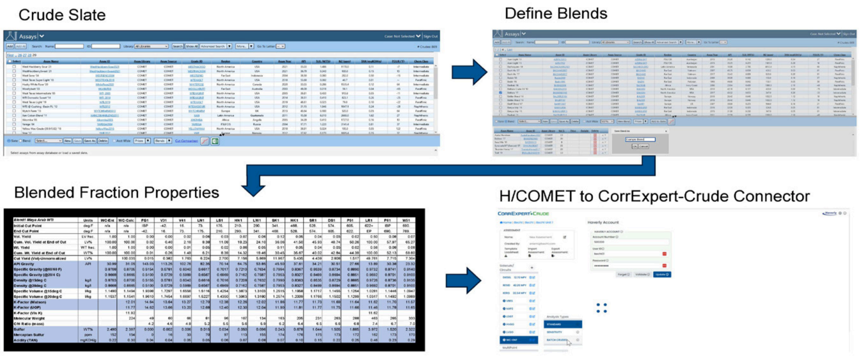

Figure 5. Enabling on-the-fly blend analyses through integration with other cloud applications.

References

For a full list of references, please visit: https://www.hydrocarbonengineering.com/refining/01072025/pacifying-potential-corrosion--references/