PROCESSING LOWER COST CRUDES WITH GREATER CONFIDENCE AND IMPROVED RELIABILITY

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INTRODUCTION

For more than 100 years, it has been understood in the petroleum refining industry that certain crude oils—or, more accurately, crude oil fractions—contain sulfur (S) species and levels of organic acids that may be very corrosive to equipment and piping in crude distillation and downstream units. Economic pressures on the refining industry are forcing many refiners to look at lower-priced high acid or opportunity crudes to improve margins. The challenge for the integrity management community is how to evaluate the effects of a crude on the equipment metallurgy installed and subsequent impact on equipment reliability. The benefits of having a more accurate crude corrosion model are large in that it allows a refinery to potentially process cheaper crudes for increased profitability with greater confidence and better anticipation and understanding of the potential damage to the equipment/piping.

Some operating companies have focused research on this subject individually or through several joint industry programs (JIPs), but current methods available to most refiners still struggle to accurately predict corrosion behavior in refinery streams on a consistent basis.

This article presents a new simultaneous S/TAN model combined with a superior flow model (SNAPS-TAC) to better predict the corrosivity of hot crude oil streams. Fundamentally, the model relies on a thin barrier layer between the iron(Fe)-based metal and the hot oil fluid. The competing reactions of barrier layer formations due to naphthenic acid (forming a magnetite/Fe_3O_4 scale) and S (forming an iron sulfide/FeS scale) and their destruction by turbulence and acid species are at the core of the new model. Thermodynamic and kinetic factors were derived from literature published over the past 60 years.

Common industry rules of thumb are 1 or 1.5 to 1 ratio of S/TAN to minimize acid corrosion. However, the quantities of S (wt%) differ so much from the mg KOH/g used to neutralize the acid (total acid number/TAN) that such values are arbitrary. The new model can explain why two crude oils with similar S/TAN values can corrode quite differently at the same temperature.

The new SNAPS-TAC model, resulting from the combined work and experience of numerous Becht SMEs, can help:

- Set integrity operating windows (e.g., crude and side stream TAN, S/TAN ratio, flow velocity)
- Predict corrosion for RBI
- Evaluate corrosion rate of crude blends
- Address turbulent flow issues
- Estimate time to restore protective barrier layers
- Establish TAN or S processing limits with given equipment
- Estimate optimum aggressive crude slate to reach turnaround (or other controlled shutdown) within remaining life
- Provide guidance on use of commercially available inhibitors to mitigate corrosion when running corrosive crudes
- Prioritize the circuits to upgrade for a stepwise investment strategy
- Identify which circuits or parts of circuits should be monitored more thoroughly
- Identify spot crudes for feed blending for a given period of time
- Determine blend limits on opportunity crudes without excessive upgrading or replacement in kind
- Calculate crude blending requirements to reach non-corrosive levels
- Evaluate alternating high TAN/high S block operations
- Estimate barrier layer persistence
- Compare block operation with blending opportunity crudes
- Provide much needed information for proactive decision making to maintain or improve equipment reliability when running opportunity crudes

In addition to all of these offline uses, the new model can be linked to the refinery's DCS/Historian system and track the expected cumulative metal loss over time depending on actual crudes/blends processed and the operating conditions.

UNDERSTANDING THE SNAPS-TAC MODEL

Without going too deep into scientific detail, the following paragraphs provide an overview of the SNAPS-TAC model that should be sufficient to demonstrate its ability to affect better decisions for refinery operations. This model combines sulfidic and naphthenic acid (NAP) attack and flow effects, based on well-established, published principles that were benchmarked against published lab and plant data. These benchmarking exercises are never easy, because all of the information is rarely provided and test results need to be conditioned for the way the testing was performed.

A. Primary Reactions	
(1) Acidic Corrosion	$RCOOH + Fe \rightarrow Fe(OOCR)2 + 2 H\bullet$
(2) Sulfidation	$R\text{-}S\text{-}R + Fe \rightarrow FeS + R\text{-}R$
B. Corrosion Product Reactions	
(3) Recrystallization	$FeS_a \rightarrow FeS_c$
(4) Magnetite Formation	$Fe(OOCR)_2 \rightarrow Fe_3O_4 + Fe + R\text{-}(C{=}O)\text{-}R + CO_2$
C. Interactions	
(5) Dissolution	$RCOOH + FeS \rightarrow (RCOO)_2Fe + H_2S$

Figure 1. Key Reactions involved in SNAPS Removal of Fe from Metals

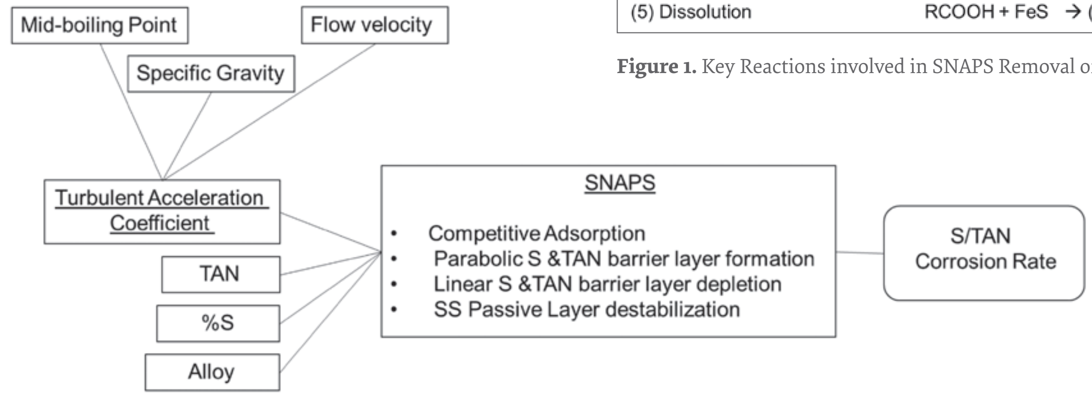


Figure 2. SNAPS Corrosion Model: Simultaneous NAP and Sulfidation (SNAPS) with Turbulent Acceleration Coefficients

In the range of 450-750°F, reactive S compounds cause sulfidic corrosion (sulfidation) of carbon, chrome, or stainless steels in crude distillation units or in the front ends of other downstream units. Sulfidation, in the absence of added hydrogen, is often treated with the modified McConomy curves, which do not explicitly consider flow effects. The original McConomy curves were developed from a broad survey relating corrosion rate with alloys, temperature, and a factor of 0.6%S for concentration of the total sulfur (%S). The original curves were later modified to be less conservative. Although useful for alloy comparisons, scattering in the survey data limits these curves to broad guidelines, as outlined in API RP 939.[1]

Naturally occurring carboxylic acids in crude oils, e.g., NAP, are very corrosive in the same temperature range.[3,4,5,6] However, NAP-containing crudes are not S free and are often co-distilled with S-bearing crudes so that simultaneous naphthenic acid and sulfidation (SNAPS) corrosion is applicable to crude unit operations.[7,8,9] Research and experience yield conflicting observations based on the %S/TAN ratio. In the absence of a generally accepted model, industry practice for SNAPS control relies on rules of thumb or on the %S/TAN tables found in the appendices of API RP 581.[2] No validation data was provided for the API 581 table values and the guidelines advise caution in their application, especially for high-flow locations.

In general, the industry has modeled S and TAN independently and then used proprietary algorithms to combine them with wall shear stress (WSS) to capture the effect of refinery flow turbulence.

The authors have taken an alternate approach that is designed to connect the lab chemistry with refinery flow turbulence that is based upon diffusion mass transport. Research at the Institute for Corrosion and Multiphase Technology (ICMT) at Ohio University has developed a two step "pre-treat and challenge" protocol to follow the formation and depletion of scale formation. The published results show that scale formation and structure are a function of S/TAN ratio and that diffusion (mass transport) through the scale varied in part due to the presence of magnetite in the scale.[10,11,12]

A review of the underlying reactions led to the development of a SNAPS corrosion model. In this model, the primary, product, and interaction reactions are incorporated into the equations (**Figure 1**).

The combined kinetics of these laboratory reactions is linked with refinery application based on turbulence-driven mass transport kinetics (**Figure 2**). As discussed below, the flow factor, or turbulent acceleration coefficient (TAC), is calculated from flow conditions and fluid properties at reaction temperature. In this model, both reactive S and NAP acids react simultaneously, forming and depleting an amorphous nano-porous "barrier layer." Mass transport affects the delivery of reactants to and through the barrier layer by a combination of fluid and solid phase diffusion mechanisms. In the model (which has parallels with an approach taken by the nuclear power industry for flow-assisted corrosion), mass transport characteristics of the fluid are calculated separately and then used as an input in addition to TAN, %S, and alloy. As the kinetics are a function of barrier layer growth over time, the algorithms can rationalize the effect of duration.[13,14,15]

The primary reactions in hot crude corrosion are illustrated in **Figure 1**.

The reactions on and under the amorphous barrier layer and corresponding fluid diffusion barrier layer are keys to the SNAPS model.[16,17] This barrier layer (FeSa) is generated by parabolic reaction of S and NAP after competitive adsorption on the metal

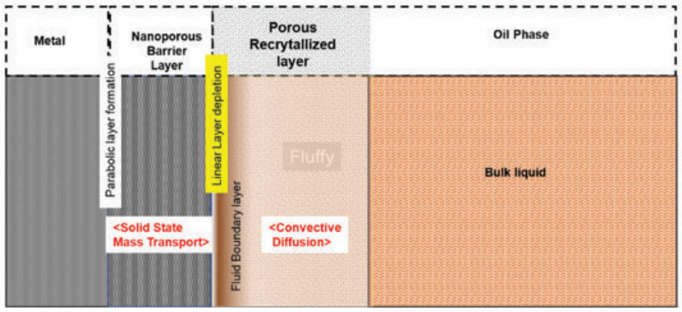


Figure 3. Schematic of SNAPS Reaction Layers (not to scale).

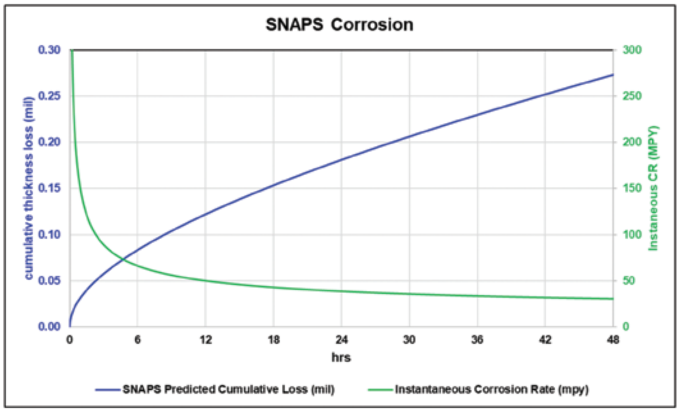
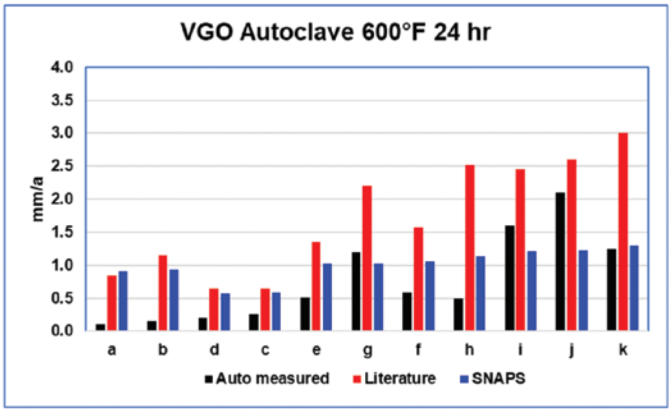


Figure 4. SNAPS Output plot showing sum of cumulative Fe loss curves in mils and the corresponding instantaneous corrosion rate in mpy



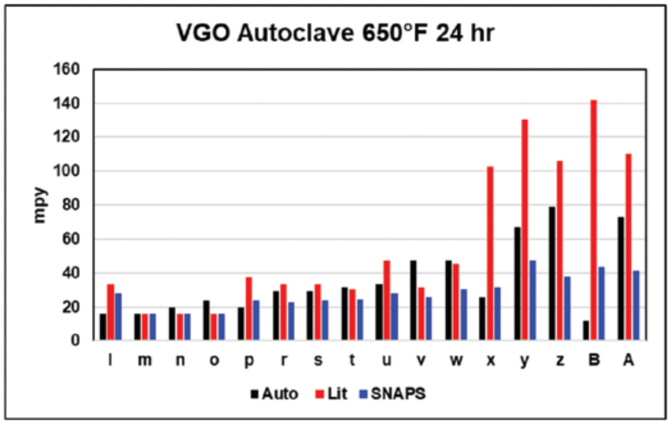


Figure 5. Comparison between Literature model and SNAPS for predicting in 24 hr lab autoclave tests

surface and depleted by recrystallization and acid dissolution on the outer edge of the FeSa barrier layer (see **Figure 3**).

The output from the SNAPS model is an instantaneous corrosion rate and a cumulative metal loss amount in thickness, as shown in **Figure 4**.

In addition to TAN, %S, and temperature, inputs to the SNAPS model are modifiers (coefficients) for flow configuration, corrosion inhibitors, alloy metal, and TAC. Flow configuration (geometry) and inhibitor factors are applied directly to SNAPS equations to obtain overall corrosion rates with the expected effect. Geometric factors increase rates beyond TAC on straight pipe, while corrosion inhibitors suppress corrosion rates by competitive adsorption resulting in surface coverage.

VALIDATION OF %S/TAN & TEMPERATURE PARAMETERS

SNAPS calculated corrosion rates have been demonstrated to agree well with measured values in a wide variety of laboratory tests. In just one example, the measured values and SNAPS results agree as well as or better than those for other models where the data was generated (see **Figure 5**).

INJECTION OF COMMERCIALLY AVAILABLE INHIBITORS

There are several commercially available inhibitors that have demonstrated successful corrosion mitigation when injected while running high TAN crudes. The SNAPS equations incorporate terms that reflect the mitigation achieved by inhibitor injection and check to make sure TAN levels, S levels, and flow conditions are within acceptable limits for inhibitor injection.

ALLOYS

SNAPS equations apply alloy factors similar to those used in other corrosion models. Alloy factors determine the magnitude and equations applied for different steels. Mitigating factors are applied to both equations for carbon steel, ferritic Cr steels, and austenitic stainless steels. The correlations of SNAPS alloy calculations with lab results are as good as those for carbon steel. As with the McConomy curves and API RP 581, the SNAPS alloy factors appear to be independent of temperature.

TURBULENT ACCELERATION COEFFICIENT (TAC) FLOW EFFECTS

Calculated values of TAC demonstrate that the oil matrix, independent of TAN or S, can have substantial effect on predicting corrosion rates. SNAPS-TAC is based on mass transport kinetics that focus on the diffusion of reactive species at a molecular level. In addition to the chemical reactions, fluid physical properties play a big role in the actual corrosivity in regard to the flow effects. TAC only requires readily available assay type fluid analyses and engineering data for unit operations, which include specific gravity, mean average boiling point, and Watson characterization factor (Kw).

Similar S and TAN crudes can have drastically different corrosion behavior due to their differing physical properties and their effects on molecular mass transport. In contrast to flow momentum in WSS, TAC is a function of molecular motion (diffusion),

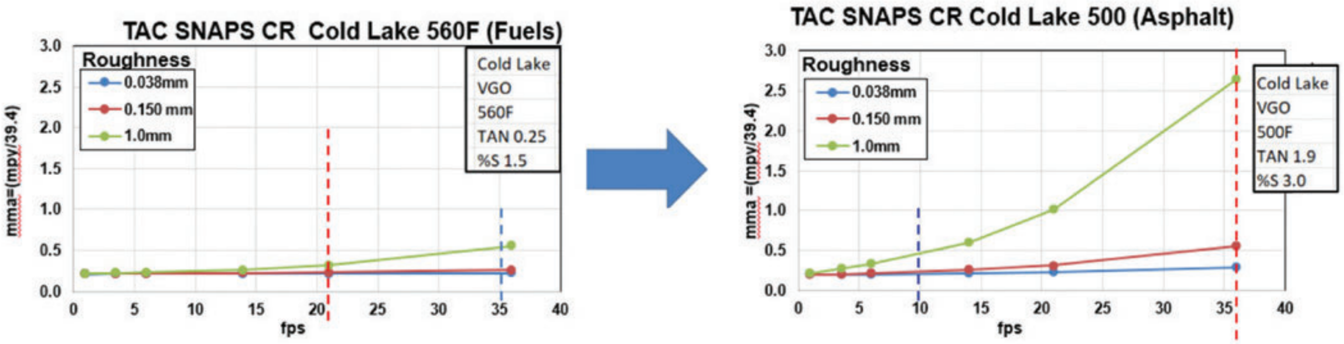


Figure 6. Case Study for Two FCV Pipes in Operation Changes on Cold Lake Crude

i.e., TAC-SNAPS is a form of chemical, rather than mechanical, erosion corrosion. Pipe roughness, pipe diameter, and flow velocity all affect the TAC. When compared to WSS, TAC is observed to be more sensitive to fluid operating conditions than WSS.[18,19, 20, 21, 22]

The calculations predict that lower boiling fractions accelerate SNAPS reactions more than higher boiling fractions. They also suggest that "typical value" for oils distilled to the same cut points leave a large margin of error among oils. Therefore, the calculation of TAC from crude specific assay data (or preferably refinery stream analysis) can increase the precision of SNAPS predictions as a function of flow.

EXAMPLE

SNAPS-TAC calculations also appear to agree with field measurements. In this example, a refinery was switching from fuels to asphalt distillation operations on Cold Lake crude oil. Both operations ran on the same feed, but differences in cut points and operations changed both flow rate and temperatures in small diameter piping around two flow control valves. Corrosion rates increased in both, as determined by long term averaging. In one, the flow rate went from 21 to 36 fps, while in the other, the flow decreased from 35 to 10 fps. Based on available Cold Lake properties and TAN and %S for the streams, the SNAPS-TAC corrosion rates were calculated for both conditions with three roughness values (see **Figure 6**). In these cases, the location of the pipes was sufficiently complex that a 1mm "roughness" (obstruction) would be appropriate. In the first case (red dotted lines), the increased flow increases TAC sufficiently to overcome a decrease in TAN. In the second case (blue lines), the increase in TAN is such that the SNAPS-TAC corrosion rate appears unchanged. However, this evaluation assumes that fluid properties other than TAN and %S are the same in both operations. As shown in **Figure 6**, that is not the case. With more complete properties for the oils under the two conditions, a more definitive case was made for the operating changes.

BLOCKED OPERATIONS

The role of the barrier layer thickness is key to understanding the relationship among different block operations. Fundamental to the SNAPS-TAC equations are the paralinear growth of the barrier layer thickness starting with a bare metal. An overlay of corrosion rates on cumulative thickness of Fe lost and barrier layer growth reveals an inflection point around 48hr. This is a good value to evaluate the corrosion rate as steady state.

Corrosion rates for blocked operation can be calculated to compensate for differences among the barrier layer thickness depending on how the crudes or blends are processed. That is, in the beginning and at the end of each feed block, the thickness of the barrier layer must be calculated so that the effect of its thickness on the diffusion is applied correctly. Because SNAPS calculates cumulative thicknesses of iron (metal) loss and barrier layer thickness for a given TAN, %S, and Temperature, the thickness at end of run of a block operation on one feed can be used as the thickness for the start of run for the next block (with a time adjustment to reach steady state). By keeping a running sum of the durations of each block, an elapsed time for multiple block changes can be recorded. Because this approach occurs in the presence of a developed barrier layer, most of the change is a linear function of time. Consequently, only the start of run and end of run values need to be calculated for each block.

The result of these methods is a corrosion prediction which accounts for new conditions, while also taking into account the past operating conditions effect on development of the barrier layer which affects future corrosion (See **Figure 7**). After the initial establishment of the barrier layer and stabilization of the corrosion rate, a change in conditions causes an increase in the instantaneous corrosion rate due to disruption and

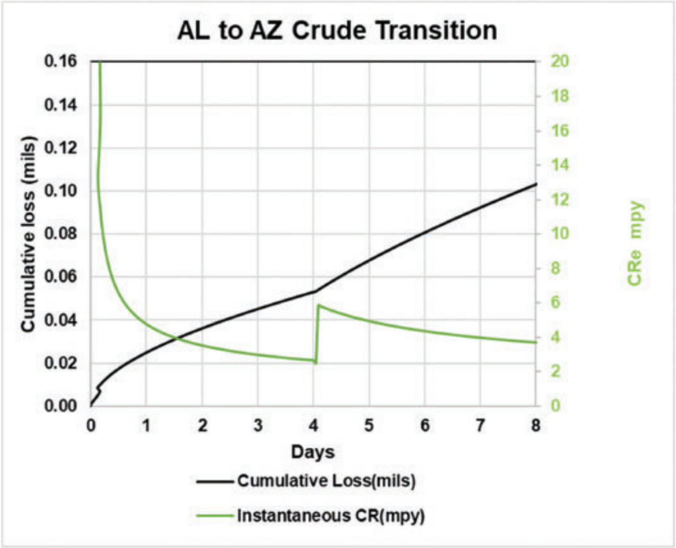
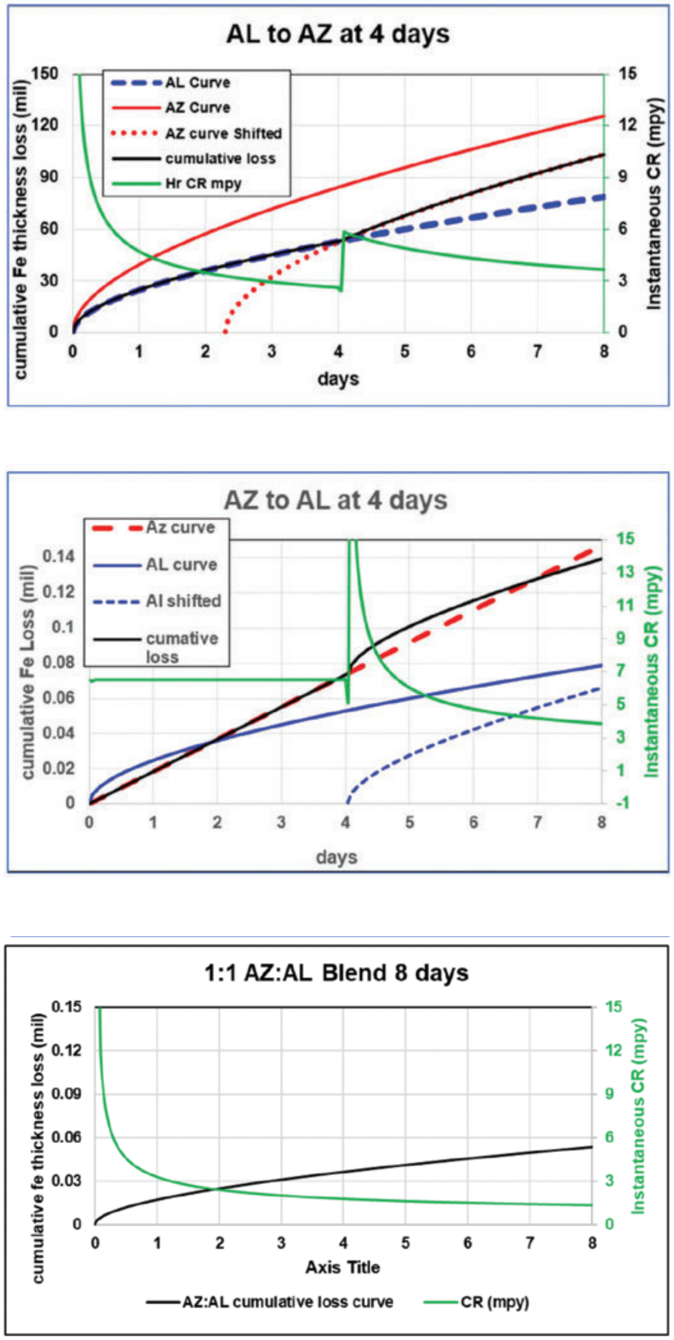


Figure 7. Impact of crude transitions on instantaneous corrosion rate with calculated accumulated loss



SNAPS Transitions estimated 8 Day corrosion rates

Jet Product @ 260C

Arab Light TAN 0.76/ 0.032%S

Azeri Light TAN 0.02/ 2.0%S

4 Days Azeri Light + 4 Days Arab light → 0.141 mil loss
4 Days Arab Light + 4 Days Azeri light → 0.103 mil loss

8 Days 1:1 Blend Arab Light and Azeril Light → 0.055 mil loss

Figure 8. Showing total predicted metal loss ranges from 1.39 to 3.58 microns for an 8 day run of two crudes in block operation (one crude first and the other second and vice versa or blended).

re-establishment of the barrier layer. After the initial increase, the rate then re-stabilizes.

In an example of running two crudes (Arab Light and Azeri), the plots in **Figure 8** show how the staging of the order in which they are processed, or blended, results in 3 different predictions of cumulative metal loss.[23] This illustrates that the effect on equipment is history/path dependent.

OVERALL CRUDE EVALUATION EFFORT

This model can be used as part of an overall crude evaluation effort. It starts with a list of candidate crudes. They are then evaluated for crude compatibility, like asphaltenes and desalting characteristics. Then, the crude business planners evaluate them for what end products can be produced and the yields. At that point, the attention turns to the Mechanical Integrity folks and to estimate the effect on the installed equipment.

The first need is an accurate detailed study/model of the unit and a good understanding of the logistics of crude supply, storage, and how they can be blended. A review of the inspection data to identify the critical components in each circuit, such as reducers, elbows, etc. is also important. Then, the model predictions are applied to those critical components and evaluated.

Using commercial blending software, the critical parameters used in the model are provided; they are S, TAN, Temperature, Boiling Point, specific gravity, and Watson K number. The physical properties of the oil stream are very important in that they affect corrosion. The flow factors, such as surface roughness, viscosity at temperature, and bulk velocities, are also needed to calculate the TAC or effect on any limiting component. Those components are the target for inspections and/or upgrading. The model will also accommodate the use of NAP inhibitors.

To take full advantage of this technology, more frequent sampling may be necessary when changing blends. Permanently mounted

UT sensors are desirable to be able to measure thickness in real time in an attempt to track/trend wall thickness losses and confirm model predictions.

SUMMARY AND CONCLUSIONS

- A need existed for an improved model for predicting SNAPS corrosion. The SNAPS-TAC model was developed based on open literature going back for almost 60 years and incorporates published information from JIPs.
- Refineries often rely on empirical correlations such as McConomy curves or API 581 guidelines. Some lab-based models combine separate rates for sulfidation and NAP corrosion with an interaction term to predict a collective S+TAN corrosion rate, but they have their limitations and have not been adopted widely.
- The SNAPS-TAC model considers NAP and active sulfidic corrosion simultaneously forming and depleting a barrier layer on the steel or alloy surfaces under mass transport control. All of the common materials of construction used for hot oil circuits are covered.
- Turbulent acceleration coefficients (TAC) are calculated from flow velocity, pipe diameter and roughness, and physical properties of the fluid. This can explain how two crudes with similar S and TAN values can have much different corrosion behavior.
- The SNAPS-TAC equations can be used to predict corrosion rates and cumulative metal loss for any fluid and location in the hot oil circuits based on the properties that should be readily available in a refinery.
- This model allows one to calculate path-dependent metal loss and can better predict the actual metal loss based on crudes processed in real time. It can also help answer tough questions, such as blending vs block operations, whether a shutdown can be reached, whether to use an inhibitor or perform selective upgrading.
- When combined with a plant's process model, the SNAPS-TAC model can identify opportunities for processing cheaper crudes. Additional stream sampling and analysis, inspection, or permanent installed measuring systems may be needed to gain the confidence to truly take advantage of the large potential to optimize profitability. ■

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