A DIGITALIZED CORROSION PREDICTION AND QUANTIFICATION FRAMEWORK FOR IMPROVING REFINERY UNIT RELIABILITY AND PROFITABILITY

By

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ABSTRACT

The need to work with opportunity crudes in refinery unit operations, a business imperative of crude blending and crude slate optimization, has meant that operators face substantial risk of corrosion damage in the crude distillation unit (CDU), vacuum distillation unit (VDU), associated equipment and side stream piping. Using Total Acid Number (TAN) and Sulfur content in crudes as proxies for Naphthenic Acid and Sulfidic corrosion in refinery operations has often led to conservative, cost-inefficient decision making in terms of crude selection, crude processing and unit metallurgy specifications. Alongside, the refining industry has consistently sought, for reasons of improved economics and ROI, 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 of low-cost opportunity crudes as an integral part of crude-slate planning has become a business necessity to improve refining margin.

Based on decades of fundamental crude parametric analyses and corrosion research, Becht has developed the industry's first ever simultaneous naphthenic acid and sulfidic corrosion prediction and analysis software framework, CorrExpert®-Crude[1], which is foundational to quantifying naphthenic acid and sulfidic corrosion correlated with unit process data and operating data. The model seamlessly connects unit process / operating data with unit metallurgy to predict metal loss rates and remaining life for critical CDU/VDU piping exposed to hot oil conditions.

This cloud-based application enables realization of the business need to work with opportunity crudes without risking corrosion damage to CDU / VDU equipment. Leveraging crude assay data and information available through process historian, the framework can also facilitate enforcement of appropriate Integrity Operating Windows (IOW) through utilization of corrosion rate as a dynamic IOW parameter alongside other key operating variables such as TAN, Sulfur and Temperature. The system's ability to seamlessly collaborate with other platforms including crude blending and supply chain planning applications such as Haverly®[2] and PIMS®[3] has important implications for creation of a digitalized solution integrating crude assay with automated predictive analytics *en route* to achieving crude processing flexibility, improved reliability and enhanced profitability.

Keywords: corrosion prediction, modeling, reliability, opportunity crudes, crude corrosivity, naphthenic acid, reactive sulfur, optimization, digitalization, software

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[1] Registered Trademark of Becht, Inc.
[2] Registered Trademark of Haverly Systems, Inc.
[3] Registered Trademark of Aspen Corporation

INTRODUCTION

Refinery operations, characterized by significant process complexities, have traditionally remained as a domain where accurate asset integrity and life prediction have been difficult to achieve. Such difficulty stems from the need to characterize and manage corrosion across different critical process units and parameters; quantifying corrosion has thus become a key factor in ensuring asset integrity, and absence of appropriate corrosion management strategies has often been the cause of some of the most destructive and expensive corrosion failures.

Managing corrosion in refineries is a complex task, given the engineering intricacies associated with the processes and operations. Changing feedstock and process chemistry, coupled with the need to constantly meet demanding production targets, exacerbate the challenges with understanding and managing corrosion, a phenomenon defined at the intersection of process thermodynamics and fluid dynamics. 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. [1,2]

Reliable, accurate prediction of corrosion rates due to hot oils containing naphthenic acids and reactive sulfur species has long been a challenge for the refining industry. The past 60 years have yielded a body of literature and research on the topic. Refineries have utilized a wide variety of published references, lab-based models, and proprietary factors to predict corrosion rates, but many of these methods have limitations. Utilizing results, algorithms and factors from these studies, we have derived a mechanistic model for the simultaneous naphthenic acid, sulfidation, and mass transport model for predicting corrosion rates.[3]

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.[4-7] 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.[8-10] 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. Although sulfidation and acid corrosion occur over the same temperature range, they differ in two significant ways. Sulfidation forms of 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.[11-13]

Potential circuits susceptible to Naphthenic Acid and Sulfidic Corrosion in refinery crude processing operations are shown in Figures 1 and 2 below.

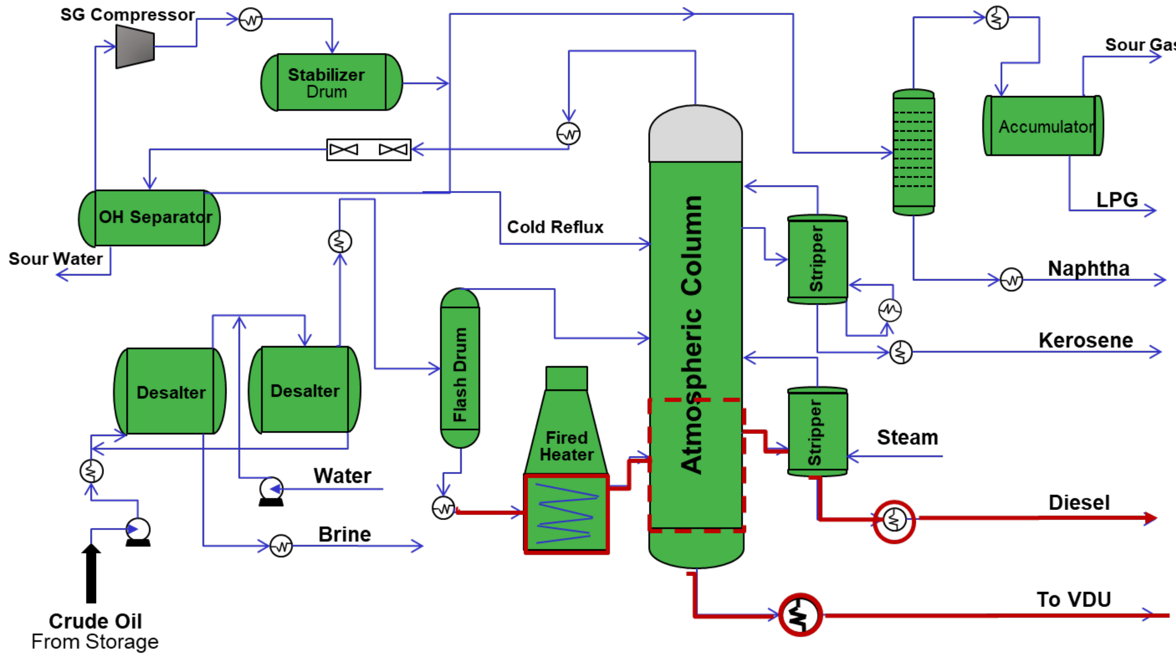

Figure 1: Potential areas of a CDU for occurrence of Naphthenic Acid / Sulfidic Corrosion

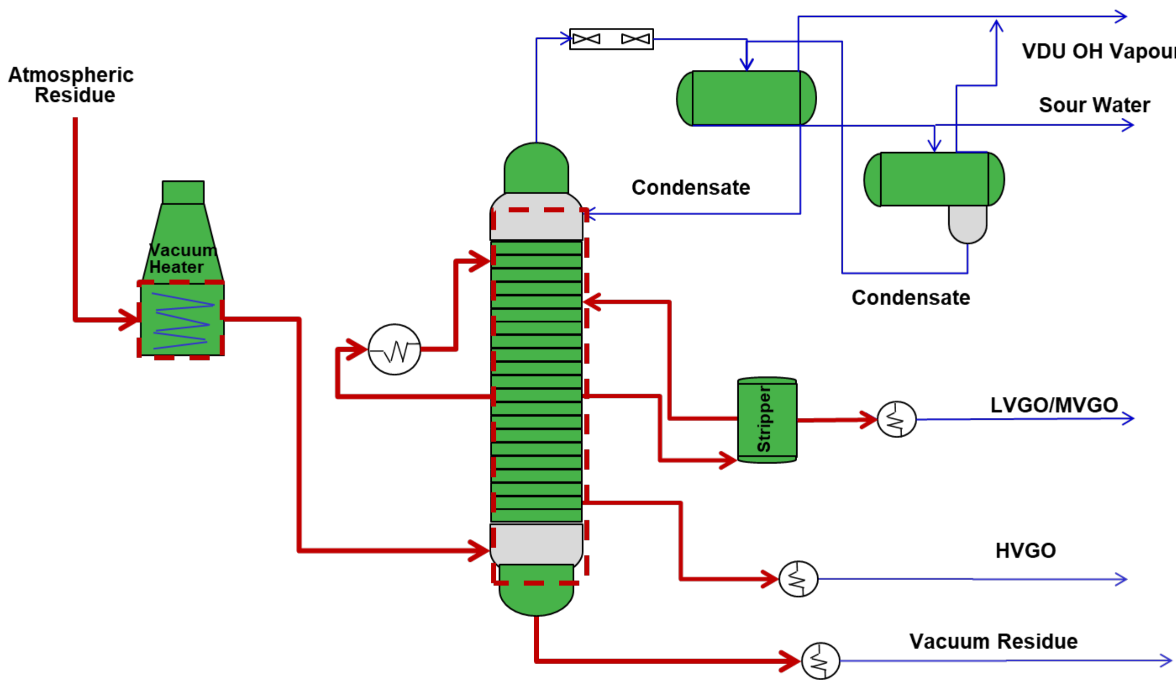

Figure 2: Potential areas of a VDU for occurrence of Naphthenic Acid / Sulfidic Corrosion

TECHNICAL BACKGROUND

As the world's supply of crude oils has become more diverse, the number of sour and acid offerings (opportunity crudes) has been increasing.[14-15] Several industry programs have developed empirical Sulfur/TAN corrosion models for based on statistical correlations of large lab databases. [16, 17] Most of these engineering models are based on parallel independent acid and sulfidic corrosion 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 2021, the authors introduced a corrosion model based on reaction fundamentals in molecular dimensions. 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 3.[3]

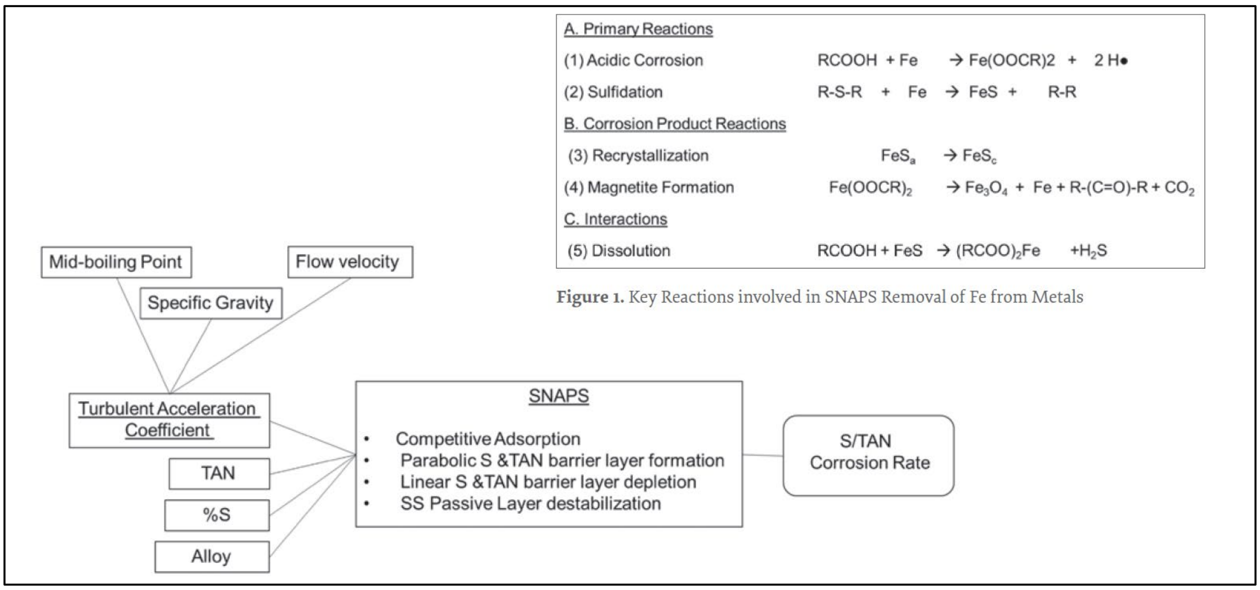

Figure 3. Corrosion Prediction Model Functional Overview

This new model, called CorrExpert®-Crude, 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.

CORREXPERT-CRUDE: MODEL DESCRIPTION

The rate of corrosion (loss of wall thickness) is a function of both reaction and mass transfer kinetics. Alloy corrosion rates due to combinations of Naphthenic Acid (NAP) and Reactive Sulfur (RS) involve simultaneous competitive and interdependent chemical reactions. Here, corrosion is modeled as competitive adsorption between NAP and RS on the metal surface with an accompanying generation of a nano-particulate layer. Central to the model are the reactions simultaneously generating and depleting this iron sulfide (FeS) layer at the metal surface. Combined NAP and RS corrosion products act as a diffusion barrier to further reaction resulting in parabolic decreases in corrosion rates. However, NAP and RS react simultaneously on the exterior of the layer to deplete its thickness linearly by dissolution and recrystallization reactions. Thus, simultaneous naphthenic acid and sulfidation corrosion simultaneously removes Fe from a metal surface into and out of the barrier layer (Figure 4). As indicated in the figure, the nanoparticulate barrier layer allows both molecular diffusion of NAP and RS to the metal surface along with solid-state diffusion of iron away from it.[3]

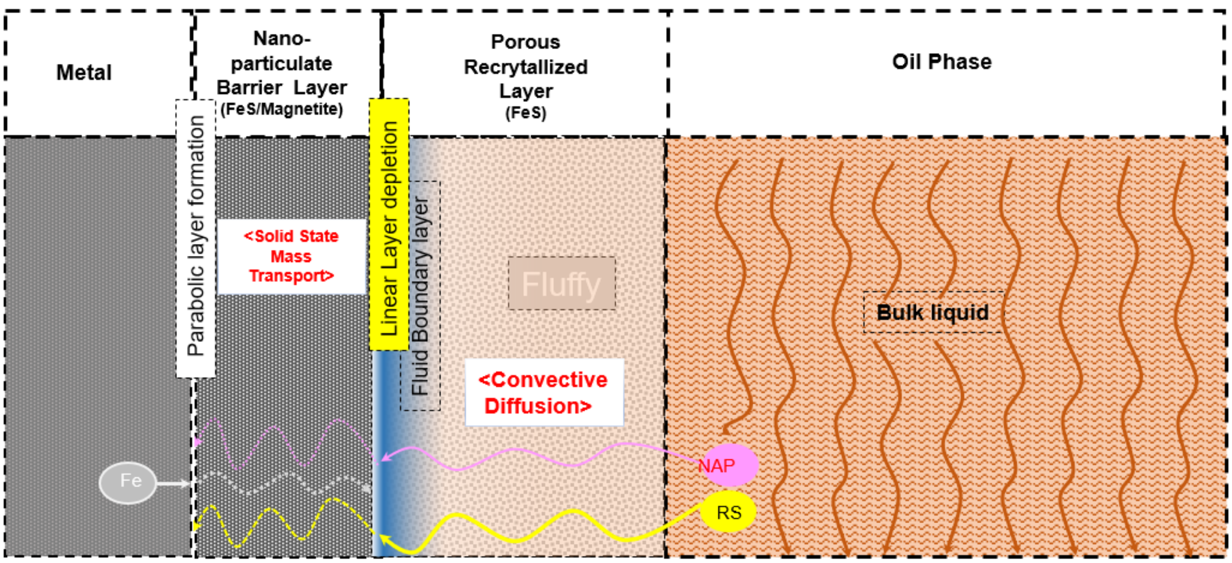

Figure 4: Schematic of Diffusion Pathways in Simultaneous Naphthenic Acid and Sulfidation Corrosion

Based on decades of fundamental crude parametric analyses and corrosion research as well as extensive experimental simulation and data, Becht has developed the industry's first ever simultaneous naphthenic acid and sulfidic corrosion prediction and analysis framework, CorrExpert®-Crude, which is foundational to quantifying naphthenic acid and sulfidic corrosion correlated with unit process data and operating data. The model seamlessly correlates unit process / operating data with unit metallurgy as a means to predict metal loss rates and remaining life for CDU/VDU piping exposed to hot oil conditions.

This cloud-based application enables realization of the business need to work with opportunity crudes without risking corrosion damage to CDU / VDU equipment. Leveraging crude assay data and information available through process historian, the framework can also facilitate enforcement of appropriate dynamic (not fixed) Integrity Operating Windows (IOWs) through utilization of corrosion rate as an IOW parameter alongside other key operating variables, such as TAN, sulfur, and temperature. The system's ability to seamlessly collaborate with other cloud-based process and refinery applications has important implications for the creation of a true digital twin, integrating real-time operating data and automated predictive analytics as a means to achieve crude processing flexibility, improved reliability, and enhanced profitability.

CorrExpert-Crude provides an intuitive, browser-based user interface (Figure 5) designed to quickly capture relevant user inputs to predict / quantify corrosion rates for various metallurgies typically utilized in CDU / VDU unit operations.

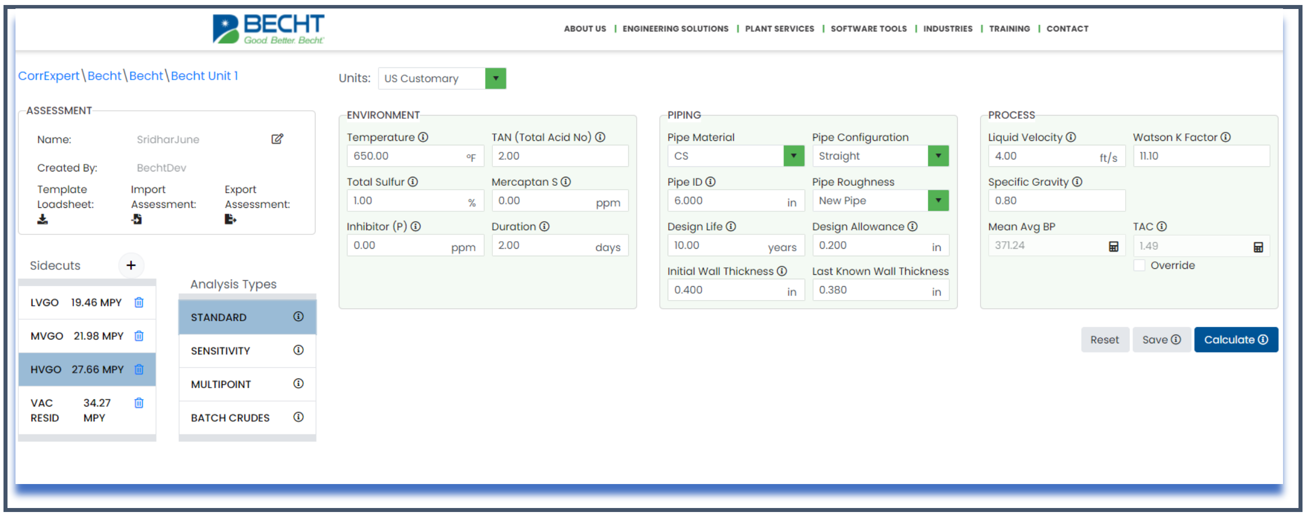

Figure 5: Prediction Model User Interface

Based on the user data for the process environment and piping systems, CorrExpert-Crude will predict corrosion rates and offer a number of corrosivity-related insights, including:

- Comparison of corrosion rates for commonly used materials of construction and with API 581 (Figure 6)

The ability to track cumulative metal loss, instantaneous corrosion rate on a time scale as well as the average corrosion rate (Figure 7)

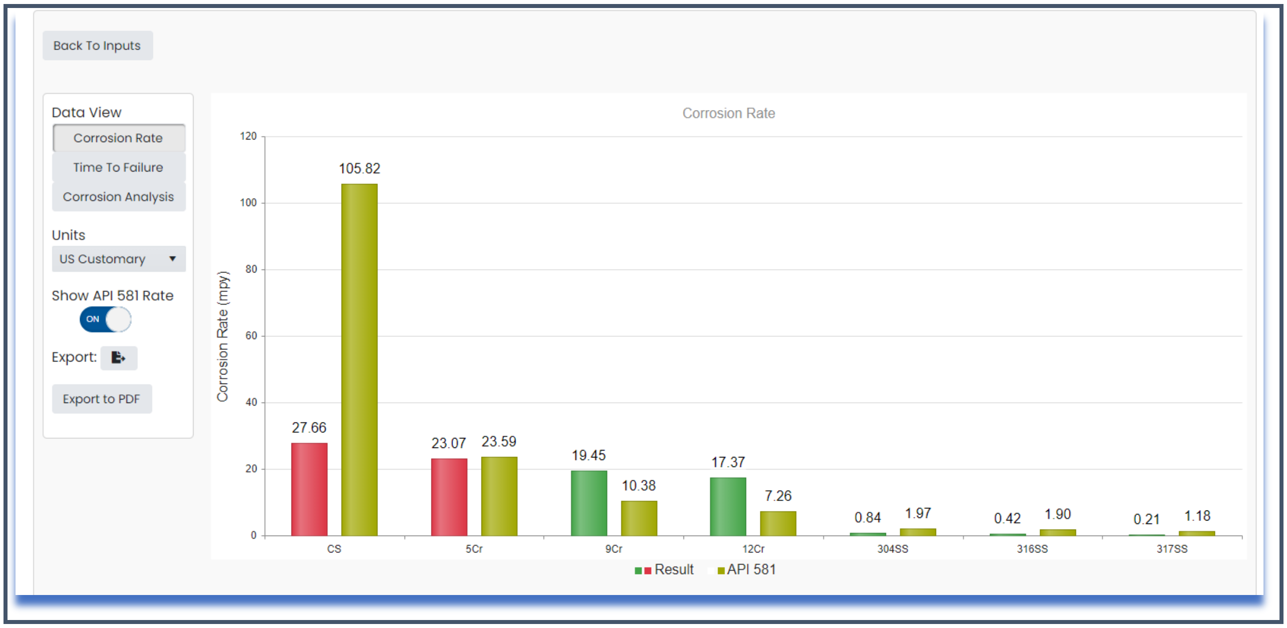

Figure 6: CorrExpert-Crude Corrosion Rate View

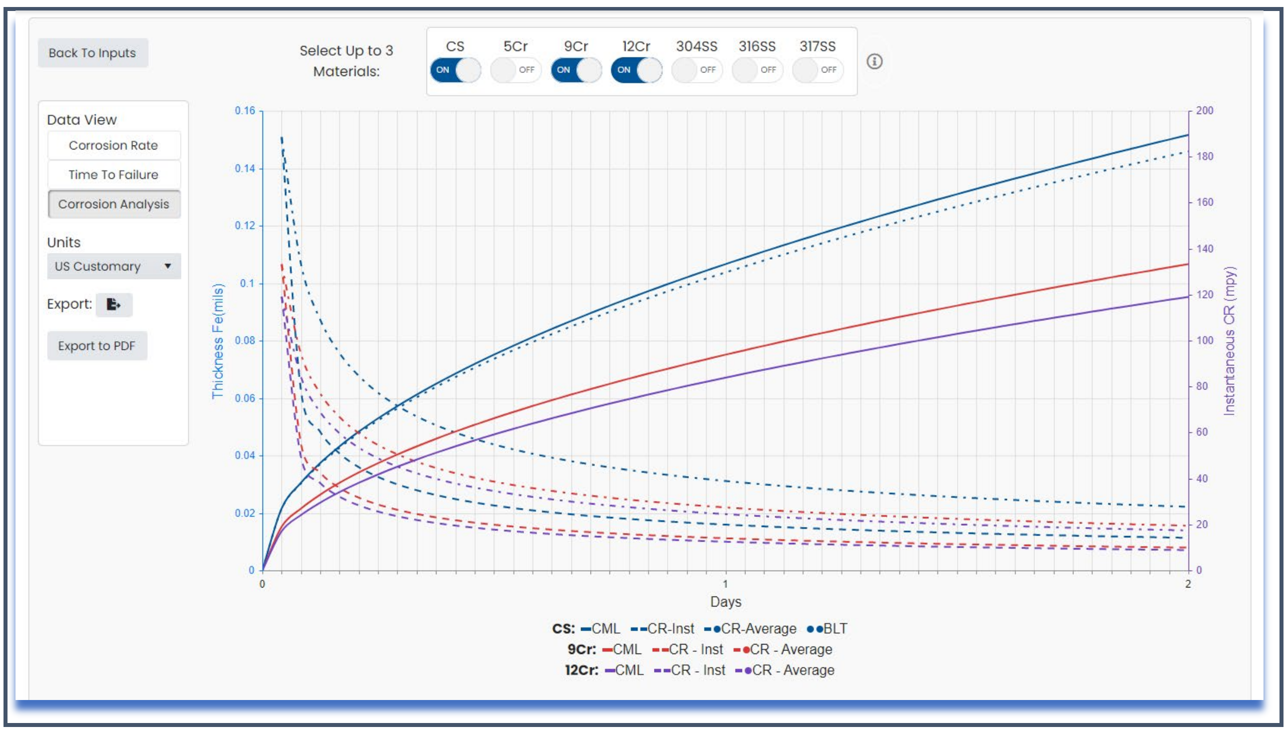

Figure 7: Prediction Model Corrosion Analyses Results

MODEL APPLICATIONS

Because CorrExpert-Crude is a cloud-based model, it can be used as a software sensor to monitor corrosion rates in real time. Because the model can predict corrosion rate (instantaneous and average) as a function of time, it can also be used to assess / optimize sequencing of crudes for processing optimality.

The model calculates combined NAP and RS 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 overall corrosion rates can be calculated for batch crudes of any duration.

For the example shown in Figure 8 with refinery block operations, a change in feed starts with the pre-existing barrier layer and the TAN & %S for the new NAP and RS 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.

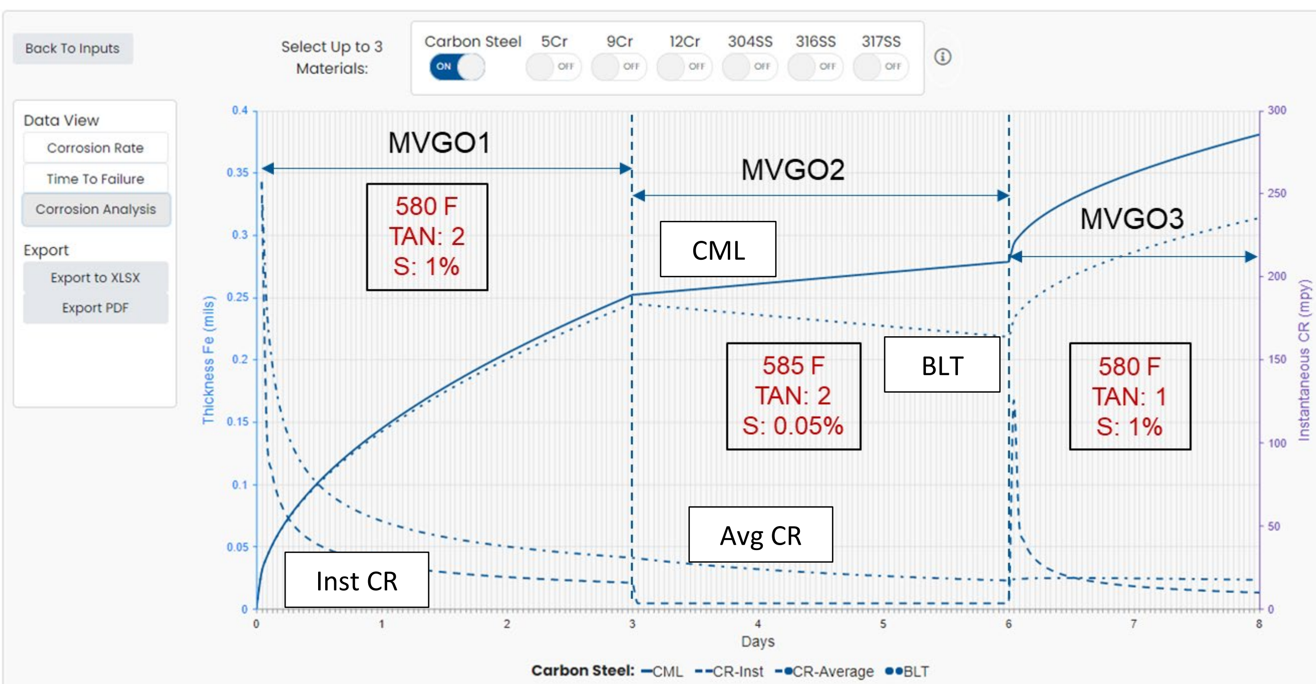

Figure 8: Using the prediction model to optimize crude sequencing

The CorrExpert-Framework may be easily utilized to create an opportunity crude blend optimization system. Using the Application Program Interface (API) made available by CorrExpert-Crude, the system can be integrated with both Assay libraries and plant historians to quantify blends from a Sulfur/TAN corrosion stand point instantaneously. The framework can also be used as synergistic component in the crude planning / scheduling activity through integration with planning tools such as Aspen PIMS or Aveva Spiral as well as Plant IDMS and LIMS systems.

A typical framework utilizing all the components in a crude planning / procurement / blending optimization solution is given in Figure 9.

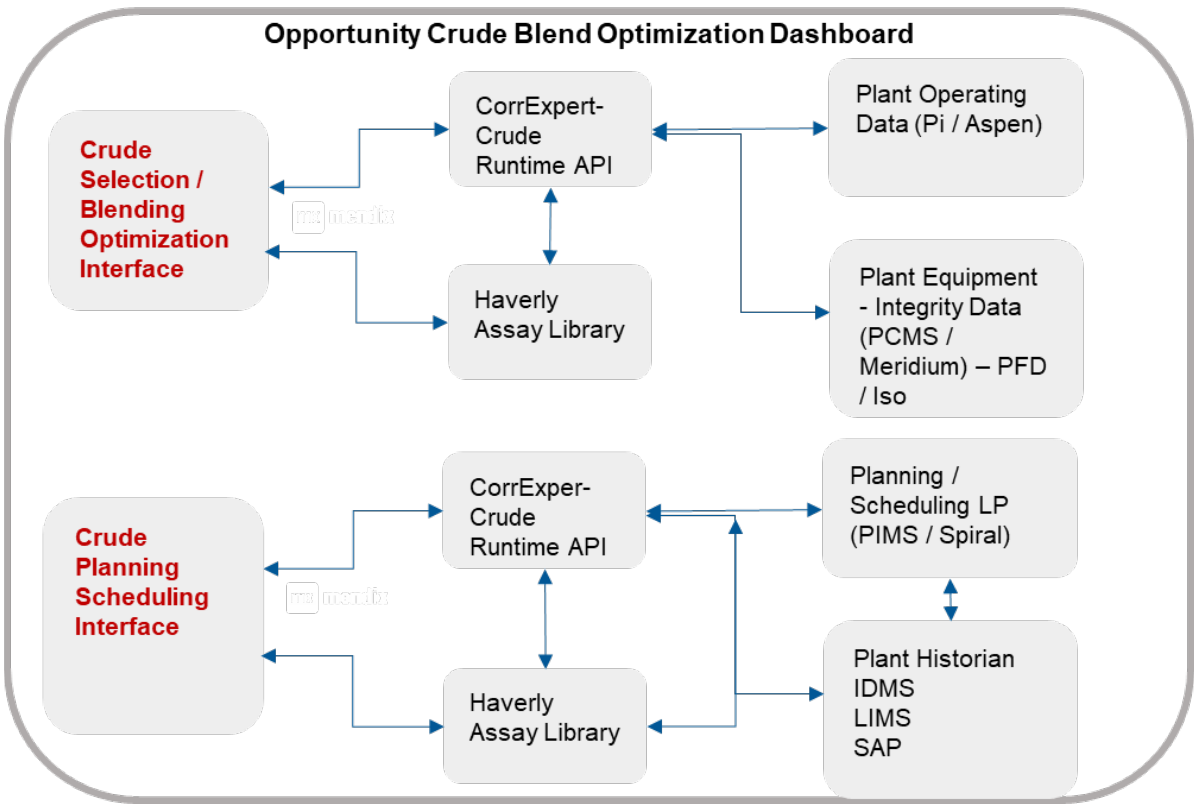

Figure 9: Opportunity Crude Blend Optimization and Planning Dashboard

Benefits For Refinery Operators

The cloud-based CorrExpert-Crude model is designed to provide refinery reliability/corrosion engineers and process managers the ability to see the impact of process transients on corrosion and degradation. The system can be easily configured to correlate with other unit operational data as well as inspection data from Thickness Monitoring Locations (TML) in real time. Such real time prediction technology is designed to support:

- Support flexible and adaptive throughput management in crude unit operations or processing opportunity crudes by leveraging increased corrosion visibility
- Correlate process data to corrosion in real-time, make the right decisions on direction for process changes, and minimize the impact of corrosion
- Maximize throughput while limiting corrosion and operational risk
- Identify critical hot spots (i.e. high corrosion rate locations) to drive optimized inspection
- Identify and extend actual process operating boundaries
- Support optimized planning for turnarounds and upgrades
- Promote collaboration and data sharing between Maintenance and Operations teams
- Extend equipment life, and increase reliability and availability
- Integrate operational data into maintenance and inspection planning
- Implement a dynamic IOW system capturing the interaction between disparate critical parameters to corrosion rates and safe operating limits

CONCLUSIONS

The CorrExpert-Crude cloud-based corrosion prediction model represents a new evolution in corrosion prediction technology, designed to provide refiners enhanced asset integrity, optimized throughput and blend management and flexibility to work with opportunity crudes leading to improved profitability. The framework supports defining meaningful IOWs and deviation management methodologies through articulation of corrosion rate connections to critical process parameters, as well as asset integrity characterization, through its ability to link up to real time data sources. Applications such as a Cloud Historian or other Cloud applications that can serve or utilize corrosion data can communicate and share data with CorrExpert-Crude through a purpose-built API. Successful implementation of this framework is designed to ensure superior mechanical integrity through enforcement of appropriate parametric limits and operation of process units in a proactive mode to drive enhanced refinery safety and profitability.

REFERENCES

1. Srinivasan S., Constantineau P., Yap K M., “Improved Mechanical Integrity Through Real-time Process Monitoring and Predictive Analytics”, Paper No 13286, Corrosion/2019, Nashville, March 2019
2. Srinivasan S., Yap K M., Kane R D., “Role of Sulfur Compounds in Mitigating Naphthenic Acid Corrosion”, EuroCorr/2013, Paper No 1506, Estoril, Portugal, September 2013
3. Wing, Abbey, Winston Robbins, Gerrit Buchheim, and Frank Sapienza. "Introducing an Innovative Simultaneous Naphthenic Acid, Sulfidation and Mass Transport Corrosion Model for Crudes and Sidestreams." In *CORROSION 2021*.
4. Lewis, Keith R., M. L. Daane, and Roy Schelling. "Processing corrosive crude oils." In *CORROSION 99*.
5. Qing, Wu. "Processing high TAN crude: part I." *Petroleum technology quarterly* 4 (2010): 35.
6. Yeung, T.W., *Latest Refinery Advances to Process HAC and BOB.* Crude oil Quality Group Association, 2007. Archives(Chicago, Il June Meeting).
7. Hau, J. "Predicting sulfidic and naphthenic acid corrosion." *Corrosion* 65, no. 12 (2009): 831-844.
8. Rebak, Raul B. "Sulfidic corrosion in refineries–a review." (2011): 123-133.
9. Foroulis, Z. A. "High temperature degradation of structural materials in environments encountered in the petroleum and petrochemical industries: Some mechanistic observations." *Anti-Corrosion Methods and Materials* (1985).
10. API. RP 939-C Guidelines for avoiding sulfidation (sulfidic) corrosion frailures in oil refieries. API Subcommittee on Corrosion & Materials, Version 5.0, February 2008. New Orleans, LA: API, 2008
11. Tebbal, Saadedine. "Critical review of naphthenic acid corrosion." In *CORROSION 99*
12. Kane, Russell D., and Michael S. Cayard. "Roles of H_2S in the behavior of engineering alloys: a review of literature and experience." In *CORROSION 98*..
13. Yoon, Yuhchae, Igor Kosacki, and Sridhar Srinivasan. "Naphthenic Acid and Sulfur Containing Crude Oil Corrosion: A Comparative Review." In *CORROSION 2016*.
14. Johnson, David, and Greg McAteer. "The safe processing of high naphthenic acid content crude oils-refinery experience and mitigation studies." In *CORROSION 2003*. OnePetro, 2003.
15. Kapusta, Sergio D., Alex Ooms, Andrew Smith, and William C. Fort. "Safe Processing of High Acid Crudes." In *CORROSION 2004*.
16. Fort, W.C., “Balanced Approach to Processing High TAN Crudes”, High Tan Crude 2005 Conference, Singapore, 2005.
17. Bota, Gheorghe M., Dingrong Qu, Srdjan Nesic, and H. Alan Wolf. "Naphthenic acid corrosion of mild steel in the presence of sulfide scales formed in crude oil fractions at high temperature" ,In *CORROSION 2010*.

Author Bio

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Sridhar Srinivasan is currently Modeling and Software Leader at Becht Engineering, Inc. In his current role, Mr. Srinivasan is responsible for design, development, and delivery/support of high value engineering software models and modeling tools for various applications related to corrosion, reliability and risk management. With over 30 years of experience in designing and delivering asset integrity solutions for multiple industry verticals (Aerospace, Oil/Gas, Refining, Pipelines), Mr. Srinivasan also functions as an industry expert/consultant on issues related to corrosion, mechanical integrity and risk management.

Mr. Srinivasan is an active member of NACE International / AMPP and has been involved in multiple NACE unit committee activities. He has been a member of the Board of Directors for AFPM as well as chairman for NACE committee on Corrosion Monitoring (STG 62). Mr. Srinivasan obtained his MS degree in Mechanical Engineering from the University of Houston and is Six Sigma Green Belt Certified. He has 100 plus papers, technical articles and book chapters in the areas of corrosion, modeling, materials and software development to his credit. He also has multiple patents (pending) in the areas of predictive analytics and real time corrosion / data management.