

**EVALUATION OF REACTIVE SULFUR FOR IMPROVED CORROSION PREDICTIONS IN
OIL REFINERIES**

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ABSTRACT

Refinery operators rely on total sulfur (TS) content (wt. % S) and total acid number (TAN), reported in crude oil assays, to predict high temperature corrosion rates by organosulfur species and naphthenic acids. The sulfur exists in a variety of forms in crude oil, associated with particular molecular moieties; from the standpoint of corrosion, these are grouped into reactive (sulfide and mercaptan) and non-reactive (thiophenic) species. According to an industrial rule-of-thumb, only 1/3 of the TS is considered as reactive sulfur (RS) and, hence, this value, together with TAN, is typically used as input in corrosion models for prediction of corrosion rates. It was hypothesized in this research work that the prediction of a corrosion model should improve if experimentally measured reactive sulfur values were used as an input in modeling instead of employing the 1/3 rule-of-thumb. To measure the percentage of reactive sulfur in a given crude oil, sulfur species were separated into reactive and non-reactive fractions, for 10 vacuum gas oils (VGOs), by an Ag⁺-ligand exchange chromatography method. The concentrations of separated reactive and non-reactive sulfur fractions were measured by X-ray fluorescence spectroscopy (XRF). The sulfur separation method was validated beforehand, using model oil solutions of known concentration of corrosive and non-corrosive model sulfur compounds. Model corrosion rate simulations for the VGOs were performed using as input the experimentally determined reactive sulfur values and the 1/3 rule of thumb for the reported total sulfur content. The comparison of experimental data with model simulations showed the predictions improved for 5 out of the 10 VGOs when experimental values of RS were used as input.

Keywords: corrosion model, high temperature corrosion, sulfidation, naphthenic acids, oil refineries

INTRODUCTION

Naphthenic acids and sulfur species in crude oil cause severe corrosion of the steel equipment of crude distillation units in oil refineries.^{1–3} Because of rapidly changing oil economics, the refineries have inclined towards cheaper “opportunity crudes”, but the high levels of corrosive species, mainly naphthenic acids and organosulfur compounds, in these crudes would reduce the life of the equipment, and also increase the risk of catastrophic failure.³ So the opportunity crudes are often blended with the crudes containing lower levels of corrosive species; this decreases overall concentration of corrosive species and the corrosion rates.^{4,5} However, corrosion rates are not simply proportional to the concentrations of naphthenic acids and sulfur species that are present in the crude oil.^{4,5} Without accurate estimation of corrosion rates by crude oils or their “blends”, carbon steel equipment needs to be constructed with higher wall thickness for safety; if still insufficient, high alloy steels are required. In either case, refinery upgrades significantly increase the capital expenditure.⁶ Currently, refinery operators rely on survey data and empirical

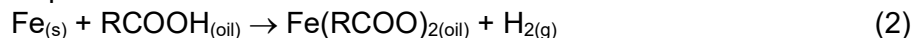
models for the estimation of corrosion rates,^{1,7-11} but due to the limited accuracy of available corrosion models, confidence on estimation of corrosion rates has not been achieved yet.

Naphthenic acids and reactive sulfur species react concurrently with the steel surface in the temperature range of 220°C (428°F) to 400°C (752°F) as described below.¹⁰

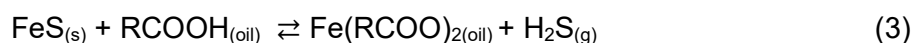
Sulfidation corrosion:



Naphthenic acid corrosion:



Sulfide-naphthenate displacement reaction:



Where, R represents organic moieties bearing the corrosive functional groups in crude oil.

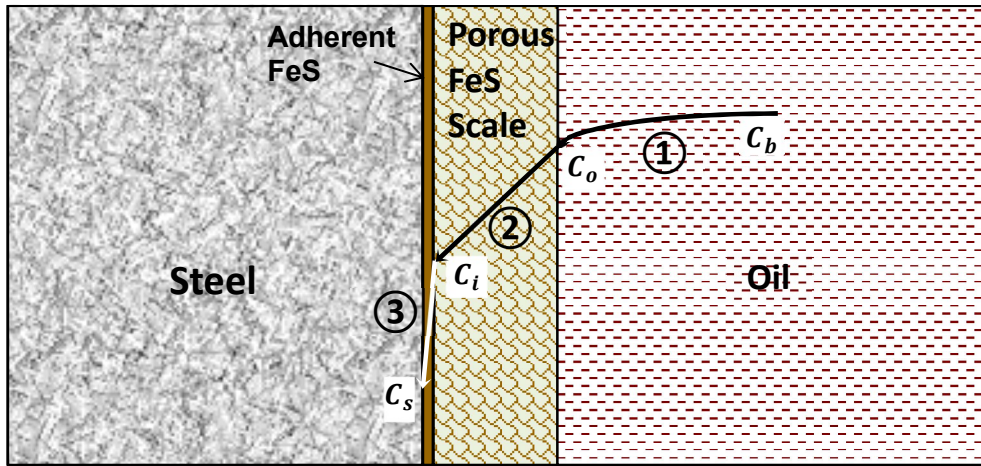
Historically, organosulfur species were considered to react with steel after thermally decomposing to hydrogen sulfide (H_2S) and, hence, reaction (1) has been cited using H_2S in the literature.^{4,9,10} However, Foroulis demonstrated that the “direct reaction of organosulfur species with steel”¹² was more dominant as the reaction pathway, which has also been confirmed by our research group and is shown by reaction (1).¹² In general, reaction of steel with sulfur species produces iron sulfide (FeS) scale which retards mass transport of corrosive species during the reaction. Naphthenic acids are known to dissolve steel “chemically” as described by reaction (2). They are also considered to be responsible for the removal of FeS scale at high velocity of crude oils, most probably according to reaction (3) which has been written usually in the reverse direction by other authors.^{10,13} However, the present work aims to improve the prediction of overall corrosion rates by focusing on the reactivity of sulfur species in crude oil.

Based on the nature of chemical bonding of sulfur with organic moieties, sulfur species in crude oil can be classified into three general categories from the corrosion point of view: sulfides, mercaptans and thiophenes.¹⁴ Sulfide and mercaptans are corrosive or reactive, whereas thiophenes are hypothesized to be non-corrosive and even inhibitive.¹⁵ However, crude oil assays report weight percentage of total sulfur without making any distinction between reactive or non-reactive functional groups. Historically, geochemical and hydroprocessing surveys of the world’s crudes observed that, on average, two thirds of the total sulfur was thiophenic.¹⁶ From this estimation, corrosion engineers derived the popular rule-of-thumb in the refinery industry that the fraction of corrosive sulfur is one third of the total sulfur (TS) in the boiling temperature range.^{13,17} Recently, a convenient method was developed for separation of reactive sulfur (RS) and non-reactive sulfur (NRS) species of crude oil based on ligand exchange chromatography using solid phase extraction cartridges.^{14,18} Further, it was postulated that instead of using the reactive sulfur value by “1/3 rule-of-thumb”, experimentally determined concentration of reactive sulfur should improve the prediction of corrosion rates.

CORROSION MODEL

The corrosion model applied in this work, developed by our research group for the ongoing joint industrial project, was used to check if the true RS values determined after sulfur separations can improve the prediction of corrosion rates. Based on the experimental results, a reaction pathway for naphthenic acid and sulfidation corrosion has been postulated to consist of transport of

corrosive species through the iron sulfide scale, followed by the direct reaction with steel.¹⁹ Iron sulfide corrosion products can be classified into two parts, an outer porous scale and inner adherent layer.¹⁹ Corrosive species pass the mass transport boundary layer over the outer scale by convective and diffusive modes, a porous part of the scale by molecular diffusion and adherent layer by an activation type of process as illustrated in Figure 1.¹⁹ A mass transfer based corrosion prediction model is presented here by hypothesizing that the reaction rate is significantly higher than the flux of corrosive species.¹⁹ This hypothesis is reasonable since the solid corrosion product of iron sulfide significantly retards the flux of corrosive species.



① Convective mass transport, ② Molecular diffusion and ③ Activated process

Figure 1 Schematic representation of the mass transport of corrosive species to the steel surface by different modes

Transport of the species in the bulk fluid towards the steel surface is via convection and diffusion which can be represented using mass transport coefficients of corrosive species as shown below.^{19,20}

$$Flux_{R_2S} = \kappa_{R_2S} (C_{b,R_2S} - C_{o,R_2S}) \quad (4)$$

and

$$Flux_{RCOOH} = \kappa_{RCOOH} (C_{b,RCOOH} - C_{o,RCOOH}) \quad (5)$$

The iron sulfide scale is porous and the transport of corrosive species through the porous corrosion product scale occurs by diffusion which can be written as follows.^{19,20}

$$Flux_{R_2S} = \frac{(D_{R_2S})(\epsilon_{FeS})(\Psi_{FeS})}{\delta_{FeS}} (C_{o,R_2S} - C_{i,R_2S}) \quad (6)$$

and

$$Flux_{RCOOH} = \frac{(D_{RCOOH})(\epsilon_{FeS})(\Psi_{FeS})}{\delta_{FeS}} (C_{o,RCOOH} - C_{i,RCOOH}) \quad (7)$$

An activation type of a process is assumed at the metal-scale interface which can be represented in terms of flux of species as below.^{19,20}

$$Flux_{R_2S} = Ae^{\frac{-B_{R_2S}}{RT}} \ln \left(\frac{C_{i,R_2S}}{C_{s,R_2S}} \right) \quad (8)$$

And

$$Flux_{RCOOH} = Ae^{\frac{-B_{RCOOH}}{RT}} \ln \left(\frac{C_{i,RCOOH}}{C_{s,RCOOH}} \right) \quad (9)$$

Where¹⁹,

$Flux_{R_2S}$ and $Flux_{RCOOH}$ are mass fluxes of R_2S and $RCOOH$, expressed in mol/(m²-s),
 κ_{R_2S} and κ_{RCOOH} are the mass transfer coefficients for R_2S and $RCOOH$ in the hydrodynamic boundary layer,

C_{b,R_2S} and $C_{b,RCOOH}$ are bulk concentrations of R_2S and $RCOOH$ in the liquid phase in mol/m³,
 C_{o,R_2S} and $C_{o,RCOOH}$ are the interfacial concentrations of R_2S and $RCOOH$ at the outer scale/solution interface in mol/m³,

D_{R_2S} and D_{RCOOH} are the diffusion coefficients for R_2S and $RCOOH$ in m²/s,

ε_{FeS} is the outer scale porosity,

Ψ_{FeS} is the outer scale tortuosity factor,

C_{i,R_2S} and $C_{i,RCOOH}$ are the interfacial concentrations of R_2S and $RCOOH$ at the inner scale/film interface in mol/m³,

δ_{FeS} is the thickness of the scale in m,

A and B are the Arrhenius constants, in mol/(m²-s) and J/mol,

T is the temperature in Kelvin and,

C_{s,R_2S} and $C_{s,RCOOH}$ are the concentrations of R_2S and $RCOOH$ on the steel surface and are set to 1.00×10^{-7} in mol/m³.

The corrosion rate (CR) by sulfur species can be obtained by equating the fluxes expressed by using equations (4), (6) and (8) as shown below.

$$CR_{R_2S} = Ae^{\frac{-B_{R_2S}}{RT}} \cdot \ln \left[\frac{1}{C_{s,R_2S}} \left\{ C_{b,R_2S} - CR_{R_2S} \left(\frac{\delta_{FeS}}{(D_{R_2S})(\varepsilon_{FeS})(\Psi_{FeS})} - \frac{1}{\kappa_{R_2S}} \right) \right\} \right] \quad (10)$$

Similarly, corrosion rate by naphthenic acids can be obtained by equating (5), (7) and (9).

$$CR_{RCOOH} = Ae^{\frac{-B_{RCOOH}}{RT}} \cdot \ln \left[\frac{1}{C_{s,RCOOH}} \left\{ C_{b,RCOOH} - CR_{RCOOH} \left(\frac{\delta_{FeS}}{(D_{RCOOH})(\varepsilon_{FeS})(\Psi_{FeS})} - \frac{1}{\kappa_{RCOOH}} \right) \right\} \right] \quad (11)$$

Equations (10) and (11) are implicit equations that can be solved by numerical methods. Total corrosion rate can be given by summing up individual corrosion rates presented by equations (10) and (11).

$$CR_{Total} = CR_{R_2S} + CR_{RCOOH} \quad (12)$$

The corrosion rate values obtained by equation (12) can be converted to required units of mpy or mm/y using density and atomic mass of iron.