

Physicochemical Description of Refinery High Temperature Naphthenic Acid Corrosion

Ishan Patel

Institute for Corrosion & Multiphase Technology
Department of Chemical & Biomolecular
Engineering, Ohio University
342 West State Street
Athens, OH 45701
USA

Gheorghe Bota

Institute for Corrosion & Multiphase Technology
Department of Chemical & Biomolecular
Engineering, Ohio University
342 West State Street
Athens, OH 45701
USA

David Young

Institute for Corrosion & Multiphase Technology
Department of Chemical & Biomolecular
Engineering, Ohio University
342 West State Street
Athens, OH 45701
USA

ABSTRACT

Refinery high temperature naphthenic acid corrosion is known to generate oil soluble iron naphthenates and solid iron oxide as corrosion products. Associated chemical reactions have been written for a long time but are barely sufficient to resolve the comprehensive mechanism necessary to model their kinetics. A mechanism for naphthenic acid corrosion is proposed to be proceeding via formation of active intermediate by adopting the Lindemann-Hinshelwood approach. The rate law for the calculation of pure naphthenic acid corrosion rate was derived using a pseudo steady state hypothesis which could simulate laboratory corrosion data reported in the literature. The rate equation was also validated by experimental corrosion tests conducted in a high temperature flow-through reactors for carbon steel using a model oil solution of petroleum derived acids by manipulating solution concentration and temperature. Also, the formation of the solid iron oxide is proposed to be a result of the decay of active intermediate as an alternative mechanism in contrast with the currently accepted thermal decomposition pathway.

Key words: Naphthenic acid corrosion, Corrosion Mechanism, Kinetics

INTRODUCTION

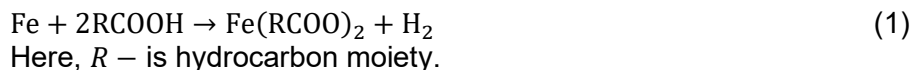
The mechanism of high temperature naphthenic acid corrosion in crude distillation units of oil refineries remains poorly understood despite large-scale collaborative efforts. It has never been more urgent to be able to predict this corrosion due to the economic interest of oil refineries in processing cheaper high acid containing crudes but a lack of confidence in the capability of current prediction models. Moreover, a quite similar trend in corrosion rate is also expected in high temperature conversion of biofuels due to magnitudes of higher concentrations of organic acids therein.¹

The limited success of foregoing investigations can be owed partly to the phenomenological aspects of this corrosion itself. For instance, concentration of naphthenic acids is essential to compute the corrosion rate using a model rate expression. However, thermal decomposition of naphthenic acids, at rates often unknown, makes it difficult to estimate the concentration of remaining acids.²⁻⁶ Both iron and iron oxide catalyze decomposition of these acids⁷ which further compounds analytical challenges. One may consider measuring concentrations of decomposition products with respect to time for the analysis of side reactions, but it is not trivial due to instrumental limitations for *in situ* concentration measurements. Intermittent sampling during the autoclave test would disturb the thermodynamic state of the system. Also, naphthenic acids tend to separate into the vapor phase due to their relatively high vapor pressure.^{8,9} Another important aspect is the variety of molecular structures of organic acids with different reactivities in any crude oil.^{3,6,10} Besides the dissolution of steel, a secondary mechanism of formation of iron oxide near the steel surface has also been observed.^{10,11} In high temperature corrosion tests using a solution of only model acids, iron oxide does not seem to provide much protection against further corrosion. Also, there is no experimental data available on the growth rate of this iron oxide layer since it is difficult to quantify. Finally, naphthenic acid corrosion is always accompanied by sulfidation corrosion which adds further to the analytical complexity. Same as iron oxide, the protectiveness of an iron sulfide layer is also highly debatable.⁹

There are several complexities related to analyses of experimental data. While conducting corrosion experiments in a pilot scale loop or traditional high temperature autoclave, measured corrosion rate results from the contribution of all the aspects stated above. Evaluation of all the associated reactions using measurement of just corrosion rate essentially would involve several hypotheses which cannot be tested easily. In this case, isolated experiments pursuing individual phenomena are most reliable for understanding the mechanism but often not feasible to conduct. The values of reaction rate constants, diffusivities, or similar coefficients for current models estimated by isolated experiments have been unable to predict field corrosion rates with acceptable accuracy. Estimation of model coefficients by regression over field data might seem to be a solution to this problem, but then it defeats the whole purpose of developing a mechanistic prediction model, which demands consistent data to reach a sufficient confidence level. McConomy curves are such regression plots in use for rough estimation of sulfidation corrosion rates, as an integrated part of predicting overall high temperature refinery corrosion.¹² However, data on overall field corrosion rates consisting of naphthenic acid corrosion rates are highly scattered or exhibit a significantly high number of outliers.¹³ Definition of appropriate evaluation metrics might seem a good way to bring scattered corrosion rate data together but it is difficult to define such parameters. In one such attempt, the empirical metric “sulfur/TAN ratio” was investigated pursuing the confluence of corrosion data but with limited success.¹⁴ No other special metrics have been successful in evaluating naphthenic acid corrosion to the best of the authors’ knowledge. Moreover, there is also a paucity of published laboratory corrosion data, especially comprehensive parametric studies. Therefore, a theoretical discussion has been presented here regarding a probable mechanistic pathway which can explain laboratory data on naphthenic acid corrosion.

MECHANISM OF NAPHTHENIC ACID CORROSION

The chemical equation for naphthenic acid corrosion of steel has been formulated as a redox reaction between iron and acids forming iron naphthenates and hydrogen as shown below.¹⁵



From a standpoint of physical chemistry, the above chemical reaction can be described as oxidative dissolution of metal but in non-electrolytic organic solution.¹⁶ From common knowledge about similar other systems of oxidative dissolution, it can be inferred that the mechanism of naphthenic acid corrosion should involve transport of acids towards the steel surface, and redox reaction with steel followed by solvation (mixing/homogenizing) of iron naphthenates in the bulk hydrocarbon mixture.¹⁶

Among these steps, the rate of mass transport of acids towards the steel surface is computable as being proportional to concentration gradient of acids in the mass transport boundary layer.¹⁷ However, molecular mass transport of acids is typically not the rate limiting step since the mass transfer coefficient is at least few orders of magnitude higher than the reaction rate constant in most cases. It is still important to calculate the rate of mass transport of acids in liquid phase for the calculation of near surface concentration of acids.

Elementary steps can be hypothesized for naphthenic acid corrosion reaction (1) by adopting the Lindemann-Hinshelwood approach, according to which the interaction of acids with steel should form an active intermediate $\text{Fe}(\text{RCOOH})^*$.^{18–20} Such an active intermediate can be considered in the pseudo (quasi) steady state.²⁰ Further, surface active intermediate $\text{Fe}(\text{RCOOH})^*$ reacts with another acid molecule to produce iron naphthenate which then dissolves in the bulk fluid mixture. The steps showing formation and further reaction of $\text{Fe}(\text{RCOOH})^*$ are illustrated by Figure 1. The chemical reactions for the mechanism are given by (2) and (3).²⁰

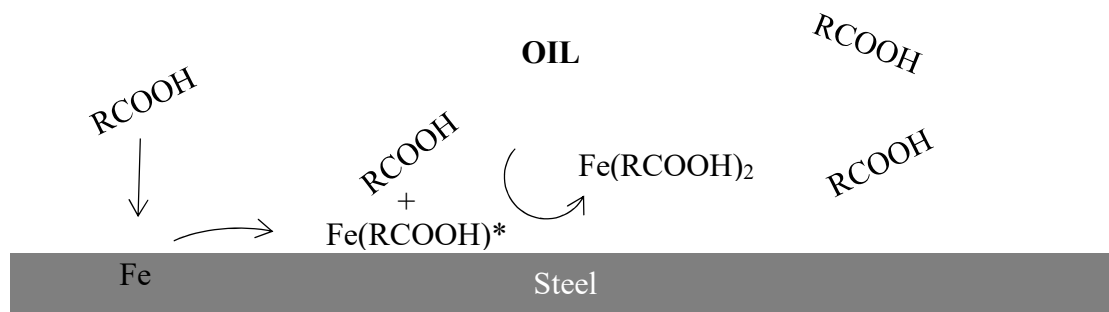
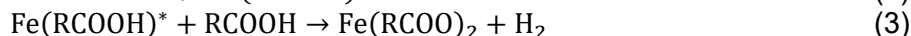


Figure 1: Proposed mechanism of oxidative dissolution of steel by naphthenic acids based on the Lindemann-Hinshelwood approach



Now, the elementary reaction rate law for the first step, reversible reaction (2), can be written as follows.

$$r_{*(2)} = k_1 C - k_{-1} C_* \quad (4)$$

Here, r = rate of formation/consumption of $\text{Fe}(\text{RCOOH})^*$ for the particular reaction in $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$, subscripts indicate the equation number, k_1 = rate constant for the forward reaction in $\text{m}\cdot\text{s}^{-1}$, C = concentration of RCOOH in bulk fluid in $\text{mol}\cdot\text{m}^{-3}$, k_{-1} = rate constant for the backward reaction in equation (2) in s^{-1} , C_* = surface concentration of active intermediate $\text{Fe}(\text{RCOOH})^*$ in $\text{mol}\cdot\text{m}^{-2}$.

For the second step of the mechanism shown by reaction (3), the elementary rate equation can be written as follows.