

Naphthenic Acid Corrosion and Sulfidic Corrosion in Crude Oil Fractions

Yuhchae Yoon, Hui Li, and Kwei Meng Yap

Honeywell Process Solutions

11201 Greens Crossing Blvd. Suite 700 Houston, TX 77067

ABSTRACT

Crude Corrosivity issues manifest themselves at locations where fluid flow rates and velocities are relatively high in atmospheric distillation units, vacuum distillation units, transfer lines, valves, baffles, heat exchangers, and side cut piping in refinery systems. The heavy vacuum gas oil fraction of the vacuum distillation plant is the crude fraction which usually has the highest total acid number (TAN) due to high concentration of naphthenic acids close to their boiling points. This mechanism of non-aqueous corrosion in the presence of crude oil or oil fractions with high quantities of organic acids and sulfur compounds is termed as high-temperature naphthenic acid and sulfidic corrosion.

This paper will describe naphthenic acid corrosion behavior and corrosion rates of multiple alloys (C1018 carbon steel, A182-F5 5Cr-0.5Mo low alloy steel, A182-F9 9Cr-1Mo alloy steel, AISI 410 stainless steel, and AISI 304L stainless steel) stemming from a comprehensive Joint Industry Program (JIP) conducted to quantify influence of crude oil chemistry on naphthenic acid corrosion, contributions of reactive sulfur chemistry to protectiveness and FeS scale formation, and the ability to resist naphthenic acid corrosion utilizing beneficial sulfur speciation within the context of operational parameters of temperature and wall shear stress.

Key words: Crude Corrosivity, Naphthenic Acid Corrosion, Sulfidic Corrosion, Corrosion Prediction Model

INTRODUCTION

In the petroleum industry, much greater attention has been focused on more highly sour and acidic oil resources due to the gradual depletion of conventional sweet oil resources. In addition, reducing crude oil costs have forced to look for opportunity (alternate) crudes, usually low-quality corrosive crude oils with high concentrations of naphthenic acids and sulfur compounds.¹ The main constituents in the crude that cause corrosion are sulfur compounds, organic and inorganic chlorides, salt water, organic and inorganic acids. Processing of these highly acidic and sulfur-containing crudes at high temperatures in refineries has promoted significant corrosion problem in hot oil distillation units and associated piping systems.¹⁻⁸

Crude Corrosivity issues occur at relatively high fluid velocity regions in refineries. The heavy vacuum gas oil of the vacuum distillation plant is the crude fraction which usually has the highest total acid number (TAN) due to high concentration of naphthenic acids at boiling points of the hydrocarbon fractions. This

crude corrosivity mechanism is non-aqueous corrosion in a temperature range of approximately 400 F (204°C) to 700 F (371°C), in the presence of crude oil or oil fractions with high quantities of organic acids and sulfur compounds and is mainly impacted by high-temperature naphthenic acid corrosion (NAC) and sulfidic corrosion (SC).

Naphthenic acids in the refining industry often include many organic acids with thermal stability relevant to crude oil distillation.¹⁻⁸ Naphthenic acid corrosion was dependent on the concentration of the naphthenic acids in the crude oils, operation temperature, fluid velocity and activity of the naphthenic acids.² The number of naphthenic acid species in the refining industry is large for any given crude oil fraction and can differ between different crude oils. These organic naphthenic acids have complex compositions and cannot be easily characterized due to their complexity and a variable range of concentrations, and according to geographical location. Pure naphthenic acids were more corrosive than light aliphatic organic acids and less corrosive than aromatic organic acids at boiling temperature.⁶ Some naphthenic acids can undergo thermal decomposition to produce lower molecular weight naphthenic acids.⁶ The physical and chemical properties of naphthenic acids depend on the nature and source of the individual crude oil.⁶ Generally, organic acids with lower molecular weight are more corrosive, naphthenic acids are most corrosive at boiling temperature, and organic acids with multiple ring structures tended to have lower corrosivity.^{3,6,7,9}

Naphthenic acid distributions change in oil fractions for different crude oil sources and there is also speculation that organo-sulfur compounds with naphthenic acids in crude oil fractions may inhibit the naphthenic acid corrosion.¹⁰ The total organo-sulfur compounds in crude oils vary from 0.2 to 2.5 wt%, but some crude oils have as high as 6 wt%.¹¹ However, the total sulfur content in crude oil is not a true indication of the corrosivity of the crude oil, which is dependent on the thermal decomposition of the several organo-sulfur compounds as active sulfur species by liberating hydrogen sulfide.^{1,7,11} There are a wide variety of organo-sulfur compounds found in crude oils and oil fractions and number more than 10,000. Sulfidic corrosion in refinery distillation units is at least in part due to the presence of hydrogen sulfide (H₂S) evolved from the thermal decomposition of organo-sulfur compounds to corrosive hydrogen sulfide.¹² The activity of organo-sulfur compounds to decompose to corrosive species is based on several factors including the class of sulfur compound, molecular weight, organic acid contents, and temperature.^{8,13} Each organo-sulfur compound has a different thermal stability in crude oil.

This paper presents the finding of project deliverables from a joint industry program (JIP) conducted by Honeywell entitled “Prediction and Assessment of Hot Oil Corrosion in Crude Oil Refining” to focus on the assessment and prediction of corrosion associated with high temperature corrosion in refineries.

MATERIALS AND EXPERIMENTAL PROCEDURES

Materials

Corrosion rates of multiple alloys, UNS G10180 (C1018 carbon steel), UNS K41545 (A182-F5 5Cr-0.5Mo low alloy steel), UNS K90941(A182-F9 9Cr-1Mo alloy steel), UNS S41000 (AISI 410 stainless steel), UNS S30403 (304L stainless steel), UNS S31603 (316L stainless steel), UNS S31700 (317L stainless steel) and UNS N08904 (904L stainless steel) were evaluated under stirred conditions in autoclaves. Carbon steel and alloy steels are the typical materials of construction in side-cut piping and hot oil distillation circuits. The nominal compositions for the alloy coupons are presented in Table 1.

Table 1. Nominal Alloy Compositions

	Alloy Composition [wt %] (balance Fe and trace elements)							
	Cr	Mo	Ni	C ($\leq$)	Mn	P ($\leq$)	S ($\leq$)	Si ($\leq$)
C1018	N/A	N/A	N/A	0.20	0.60-0.90	0.04	0.05	N/A
A182-F5	4.00-6.00	0.44-0.65	0.50 (max)	0.15	0.30-0.60	0.03	0.03	1.00
A182-F9	8.00-10.0	0.90-1.10	N/A	0.15	0.30-0.60	0.03	0.03	0.50
AISI 410	11.5-13.5	N/A	0.75	0.15	1.00 (max)	0.04	0.03	1.00
AISI 304L	17.5-19.5	N/A	8.00-11.0	0.03	2.00 (max)	0.05	0.02	1.00

Chemicals

Synthetic oil fraction of Process Oil was utilized throughout the experiment for preparation of base test oil. As a base test oil for developing oils with specific corrosive chemical content, Process Oil was required to contain low amounts of acid and sulfur species. A naphthenic acid blend was added to the Process Oil to result in target TAN values for the experiment from low, medium, and high TAN values. The sulfur-containing tests were conducted using H₂S mixed gas. The active sulfur level of experiments was determined by measurement of H₂S partial pressure in the autoclave. So certain partial pressures of H₂S in the autoclave were corresponded with levels of active sulfur.

Experiments

Corrosion evaluation for multiple alloys was determined using oil autoclaves. These specially designed and operated autoclaves can maintain target temperature and pressure, allow stirring of the oil to apply wall shear stress (WSS) to coupon surfaces and transfer the deaerated oil into and out of the autoclave. Stirring of oil was necessary in hot oil experiments to maintain a homogeneous liquid phase and to apply wall shear stress to alloy coupon surfaces.

Flow parameters are critical to corrosion rates and mechanisms in crude corrosivity. WSS has been used as a flow parameter for capturing the effects of flow conditions to corresponding amplification of crude corrosivity.^{7,12} WSS includes the impact of multiple parameters (oil viscosity, density, velocity, volumetric flow rate, pipe size and configuration, and friction factor). Computational fluid dynamic (CFD) simulations were performed for geometries, fluid, and flow conditions relevant to the autoclaves. The results of the CFD simulations for these autoclaves were used to define the average WSS exerted by flowing fluid on the coupon surface from low, medium, and high WSS.

Following an autoclave test, the coupons were removed from the autoclave, cleaned with toluene, and allowed to air dry. The coupons would then be weighed to the nearest 0.1 mg; this weight was considered the after test – before cleaning weight and was used in part to determine the scale weight of the coupon. Next, each coupon was subjected to a light bead blast to remove sulfide scales on the coupon surface. Following the bead blast, the coupons were rinsed with acetone, allowed to air dry, and then weighed to the nearest 0.1 mg; this weight was considered the after test – after cleaning weight and was used in part to determine both the scale weight and weight loss of the coupon. To correct for non-corrosion related metal loss during the bead blast cleaning step, coupons of each alloy were subjected to several rounds of bead blast and weighing to determine the metal loss from bead blasting. The average weight loss for each alloy was determined and employed as a ‘weight-loss correction factor’.