CHARACTERIZATION OF IRON OXIDE SCALE FORMED IN NAPHTHENIC ACID CORROSION

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Abstract

Naphthenic acid corrosion (NAC) is one of the major concerns for corrosion engineers in refineries. Iron sulfide (FeS) scales, formed from sulfur compound corrosion, are traditionally considered to be semi-protective and lower NAC. However, no relationship has been found between protectiveness and the characteristics of FeS scale. In this study, the corrosive processes of refineries have been probed with laboratory experiments using a model sulfur compound and petroleum-derived naphthenic acids. The morphology and composition of scales were analyzed with a combination of scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), and convergent beam electron diffraction (CBED). These high resolution microscopy techniques revealed the presence of an iron oxide (Fe$_3$O$_4$ or magnetite) layer on metal surfaces under a FeS layer in the scale. The presence of an oxide scale was correlated with the NAP acid activity during the experiments. It is postulated that the formation of the Fe$_3$O$_4$ layer resulted from the decomposition of iron naphthenates at high temperatures.

Introduction

Naphthenic acid corrosion (NAC) is one of the major concerns for corrosion engineers in refineries [1]. With the decreasing supply of light sweet crude oil the increasing prevalence of the heavy crude oil with high naphthenic acid content may lead to severe corrosion of facilities. However, sulfur compounds in crude oils are also corrosive while forming a quasi-protective iron sulfide scale so that interactions between the two components are difficult to predict. Combined sulfur and naphthenic acid (SNAP) corrosion is generally described by the following reactions: [2]

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\begin{align*}
\text{Fe} + 2\text{RCOOH} & \rightarrow \text{Fe}(\text{RCOO})_2 + \text{H}_2 \quad \text{(Reaction 1)} \\
\text{Fe} + \text{H}_2\text{S} & \rightarrow \text{FeS} + \text{H}_2 \quad \text{(Reaction 2)} \\
\text{Fe}(\text{RCOO})_2 + \text{H}_2\text{S} & \leftrightarrow \text{FeS} + 2\text{RCOOH} \quad \text{(Reaction 3)}
\end{align*}
\]

In NAC, naphthenic acid (RCOOH) attacks iron and generates oil-soluble iron naphthenate (Fe(RCOO)$_2$) as shown in Reaction 1. Reactive sulfur compounds in the crude oil also attack the iron (possibly by H$_2$S as an intermediate) and form an insoluble iron sulfide (FeS) scale.
Reaction 2. However, in solution, H₂S reacts rapidly with iron naphthenate and regenerates the naphthenic acid while excess naphthenic acid can, in a slower process, dissolve an iron sulfide scale, Reaction 3. The porous iron sulfide scale can be quasi-protective by limiting diffusion of the reactive species to the surface. However, conditions that promote this protection are ill-defined [3].

Our group has previously reported that NAC not only forms iron naphthenate but also could lead to the formation of a protective scale of magnetite (Fe₃O₄) [5]. This scale was hypothesized to be the product of iron naphthenate decomposition on the surface at high temperatures. To determine the effect of temperature on this magnetite formation, we have extended our pretreatment/challenge protocol to cover a range of temperatures with a model reactive sulfur compound and a petroleum-derived naphthenic acid mixture. To that end, steel rings were subjected to the pretreatment protocol at 450°F, 600°F, or 650°F in an autoclave and then challenged for protectiveness at 650°F in a rotating cylinder flow through reactor. After each corrosion experiment, corrosion rates were determined and surfaces examined by scanning electron microscopy (SEM), focused ion beam/transmission electron microscopy (FIB/TEM), energy dispersive X-ray spectroscopy (EDS), and convergent beam electron diffraction (CBED).

**Experimental**

**Materials**

Two commonly utilized refinery steels, A106 carbon steel (CS) and A182-F5 chrome steel (5Cr), were used in the shape of rings with inner diameter 70.43 mm, outer diameter 81.76 mm, and thickness 5 mm. Before experiments, each ring was polished with 400 and 600-grit silicon-carbide paper (SiC) in succession. Isopropanol was used to flush specimens during polishing to prevent oxidation and overheating. After polishing, specimens were wiped with a paper towel, rinsed with toluene and acetone, dried with N₂, and weighed.

After each experiment, rings were rinsed with toluene and acetone, gently rubbed with a soft plastic brush, treated with “Clarke” solution (ASTM G1 - 03) and reweighed. Corrosion rates were calculated by weight loss.

**Test Solutions**

Recrystallized dodecylsulfide (DDS) and a commercial naphthenic acid mixture (NAP) were used to represent reactive sulfur compounds and naphthenic acids. The DDS and NAP were dissolved in a technical grade white mineral oil to prepare three experimental solutions:

- "NAP only": NAP in mineral oil (TAN = 1.75, S = 0 wt.%),
- "DDS only": DDS in mineral oil (TAN = 0, S = 0.25 wt.%), and
- "DDS + NAP": DDS and NAP in mineral oil (TAN = 1.75, S = 0.25 wt.%).