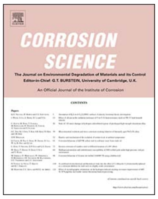
Corrosion Science xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci



Effect of sulfur compounds on formation of protective scales in naphthenic acid corrosion in non-turbulent flow

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ARTICLE INFO

Keywords:
A. Carbon steel
B. SEM
B. TEM
C. Acid corrosion
C. High temperature corrosion

ABSTRACT

Naphthenic acids corrosion is generally considered to leave no corrosion product on steel surface. However, our prior research demonstrates that a protective oxide scale is formed in corrosion with model acids under stagnant conditions. In present study, the corrosion by model acids and a reactive sulfur compound has been investigated alone and in combination in a flow through system. None of the model acids alone forms an oxide scale. However, mixtures of the acid and sulfur compound form a protective scale consisting of an oxygen-containing layer underneath a sulfide layer. A mechanistic model of corrosion and scale formation is proposed.

1. Introduction

Processing low-cost heavy crude oils can be profitable for crude oil refineries world-wide. However, the low cost of many of these oils comes with the presence naphthenic acids (NAP) and reactive sulfur compounds, two species that contribute to high temperature (200–400° C) refinery corrosion [1–4]. NAP are the natural carboxylic acids in petroleum crude oil typically measured by Total Acid Number (TAN, the amount of potassium hydroxide in milligram to neutralize one gram oil). It is widely recognized that both NAP corrosion and sulfidation (corrosion by sulfur compounds) occur simultaneously in the refinery.

The corrosion process can be described by three generic free radical reactions that occur at high temperatures [5]:

$$Fe(s) + 2RCOOH \rightarrow Fe(RCOO)_2 + H_2 \quad (1)$$

$$Fe(s) + H_2S \rightarrow FeS(s) + H_2 \quad (2)$$

$$Fe(RCOO)_2 + H_2S \leftrightarrow FeS(s) + 2RCOOH \quad (3)$$

Thus, a NAP molecule (RCOOH) oxidizes metallic iron to its ferrous state forming iron naphthenate salt ($Fe(RCOO)_2$) and atomic hydrogen (Eq. (1)). In this reaction, R represents the hydrocarbon portion of the NAP molecule and COOH is the corrosive carboxylic acid functional group. Because iron naphthenate is oil soluble, it is assumed that there is no buildup of iron naphthenate or hydrogen on the surface [5–8]. Some of the reactive sulfur compounds found in petroleum may react directly with steel surfaces while others may first decompose to form hydrogen sulfide (H_2S), and this process is known as sulfidation. In either case, insoluble iron sulfide (FeS) and hydrogen (H_2) are formed (Eq. (2)). In sulfidation, the iron sulfide builds up on the steel surface in the form of a scale. Secondary reactions connect the NAP and sulfidation corrosion pathways (Eq. (3)). In the forward direction, hydrogen sulfide reacts iron naphthenate in solution to precipitate iron sulfide and "regenerate" the NAP; conversely, in the reverse direction high-concentration NAP dissolve the iron sulfide scale while releasing oil soluble iron naphthenate. Generally, iron sulfide scales are considered to be partially protective against NAP corrosion by creating a barrier to acid permeation.

Refinery operating conditions (temperature, turbulence, ratio of oil volume/metal surface area, and month long durations) are difficult to reproduce for corrosion studies in a laboratory setting. Some engineering models have been developed that correlate short term laboratory corrosion rates with TAN, total%S, physical parameters [9,10]. Given the multiplicity of reactive sulfur and naphthenic acid species in crude oil, fewer studies have dealt with molecular structure [11–15]. Probably one of the most important factors that have received little attention is the interaction between sulfur compounds and NAP in the formation of scale.

The present authors discovered that the corrosion by combinations of reactive sulfur compounds and naphthenic acids can form thin protective oxygen-containing scales under much thicker sulfide scales in stirred autoclave experiments [16–22]. Although oxygen in corrosion product scale has been detected previously in studies by other groups, its presence was dismissed as experimental artefacts [23–25]. When this stirred autoclave work was extended to corrosion with model acid and sulfur compounds on carbon steel in stirred autoclaves, it was found that some model acids formed protective scales in the absence of any

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https://doi.org/10.1016/j.corsci.2017.11.027
Received 26 January 2017; Received in revised form 19 October 2017; Accepted 27 November 2017

Please cite this article as: Jin, P., Corrosion Science (2017), https://doi.org/10.1016/j.corsci.2017.11.027

Table 1
Chemical composition of A106 carbon steel (CS) specimen (%wt).

C	Si	Mn	P	S	Cr	Ni	Mo	V	Cu	Fe
0.18	0.41	0.8	0.11	0.06	0.02	0.04	0.02	0.03	0.08	Bal

Table 2
Model compounds in experiment.

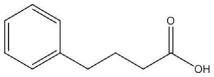
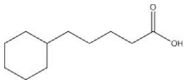
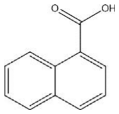
Model compound	Structure
4-Phenyl butyric acid (PBA)	
4-Cyclohexyl pentanoic acid (CxPA)	
1-Naphthoic acid (NA)	
Palmitic acid (PA)	$CH_3(CH_2)_{14}COOH$
NAP acid mixture (TCI): TAN around 220, N0343 from TCI America	–
Tuffo 6056 (obtained from CITGO)	White mineral oil (density 0.876 g/mL)

Table 3
S/TAN ratios for DDS + PA solutions.

Solution No.	Sulfur content (S, %wt)	TAN (mg KOH/g oil)	S/TAN	Sulfur content (mmol/L)	Acid content (mmol/L)
1	0.25	1.75	0.14:1	68	27
2	0.58	1.75	0.33:1	158	27
3	1.16	1.75	0.66:1	315	27
4	1.75	1.75	1:1	476	27

reactive sulfur compounds [26,27]. In our work, formation of protective iron oxide scale depended on the model acid structure. The iron oxide scale can only be formed in the corrosion by the acid with at least one hydrogen atom on the carbon adjacent to the carboxylic group. For example, 4-phenyl butyric acid (PBA) and 4-cyclohexyl pentanoic acid (CxPA) generated an iron oxide scale in a stirred autoclave but naphthoic acid (NA) did not [28]. It was proposed that iron oxide scale was formed by thermal decomposition of iron naphthenates to ketones and wüstite followed by disproportionation of the wüstite to magnetite and α-ferrite (Eqs. (4) and (5)) [28].

$$Fe(RCOO)_2 \rightarrow FeO + CO_2 + RCOR \quad (4)$$

$$4FeO \rightarrow Fe_3O_4 + \alpha\text{-}Fe \quad (5)$$

At the end of the autoclave experiments, ketones corresponding to the model acids were detected in spent solutions and magnetite was found on the specimen surface [20,28]. Historically, decarboxylation of metal carboxylic acid salts has been used for over 100 years for synthesis of ketones [29,30]. In recent years, this reaction has been employed to prepare nano particles of magnetite (Fe_3O_4) extensively applied in the electronic industry [31–33]. Wüstite (FeO), the initial product is thermodynamically unstable and disproportionates to magnetite below 500° C in the absence of oxygen [34–36]. In the autoclave experiments, corrosive fluids were not replenished and corrosion products were accumulated. Hence, interaction of reactive sulfur and carboxylic acid in the mechanism of oxygen-containing scale formation is clouded by prolonged exposure of specimens to secondary reactions. Current research focuses on the mechanism of oxygen-containing scale formation during NAP corrosion experiments in the presence of reactive sulfur compounds under conditions of constant replenishment (non-turbulent flow).

2. Experimental

2.1. Experimental materials

Corrosion experiments were performed on A106 carbon steel (CS) specimens (Table 1 as provided by Alabama Specialty Products).

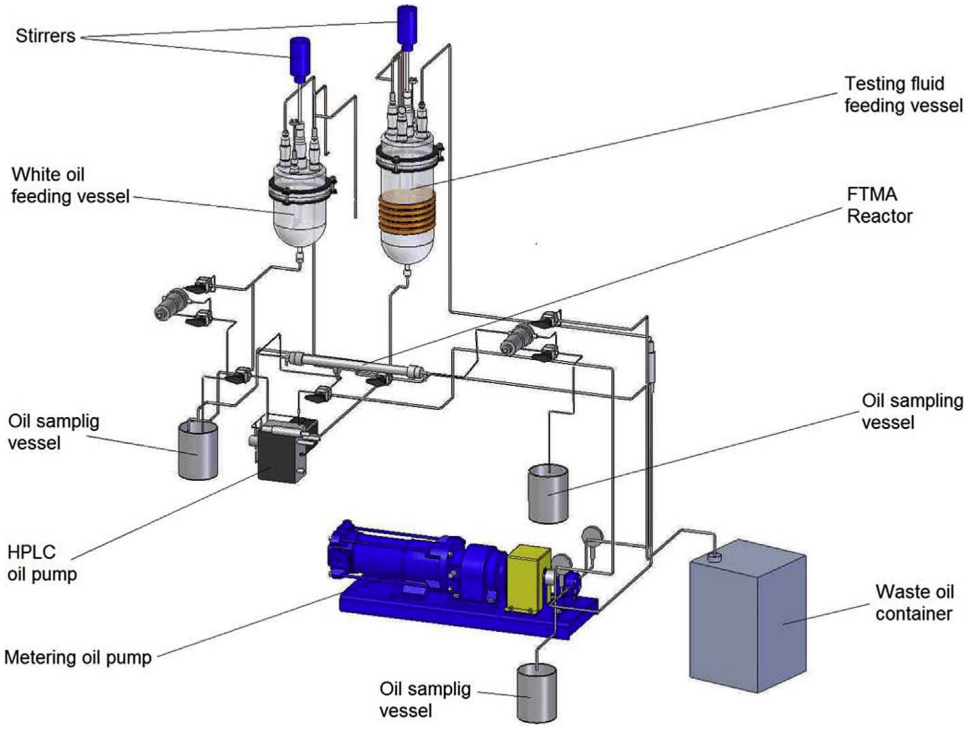


Fig. 1. Schematic rendering of the FTMA.