



High-temperature corrosion of a UNS K03006 steel pipe in a crude oil vacuum residue distillation unit

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ABSTRACT

A carbon steel pipe of ASTM A106 grade B [UNS K03006] specification was in service of vacuum residue in a crude oil vacuum unit at temperatures ranging from 293 to 350 °C. After 20 years of service it failed due to a combination of sulfidic and naphthenic acid corrosion. This failure motivated this work, where the mechanism of corrosion failure mechanism is studied, based on the microstructural characterization of the corroded surfaces of coupons tested in a laboratory simulated vacuum residue environment, with variations in temperature and exposure times. Experimental results showed that at 310 °C, the preferential formation of a homogeneous passive iron sulfide film occurred, which promoted general sulfide corrosion. However, the greatest corrosion rates occurred at 350 °C, due to the generation of sour primary distillates and the fragmentation of the vacuum residue molecule, which triggered a naphthenic acid corrosion mechanism, which caused localized attack corrosion. It is concluded that the most important factor to be monitored in vacuum residue service in crude oil vacuum residue distillation units, in order to predict and prevent corrosion, is the temperature. Specifically, operation temperatures above 310 °C should be avoided, because high corrosion rates and the combination with localized attack in the forms of pitting and grain boundary dissolution. In order to prevent failures in vacuum residue pipes, closed interval thickness surveys and close temperature monitoring are recommended.

1. Introduction

Vacuum residue (VR) from crude oil primary distillation units is composed of a mixture of hydrocarbons that includes polynuclear aromatic compounds, asphaltenes, resins, aromatics, and saturated compounds [1–9]. The aromatic species present in VR contain high concentrations of impurities, such as sulfur, nitrogen, oxygen, and heavy metals (i.e., vanadium, nickel, and iron) which are known to promote high temperature corrosion [1–3]. The API RP 571 indicates that vacuum distillation plants are vulnerable to naphthenic acid corrosion (NAC) and sulfidic corrosion (SC) due to high Total Acid Number (TAN) in the produced fractions [4]. In addition, it has been demonstrated that the vacuum column usually has the highest TAN of the entire refining process [10–14] and therefore has the most corrosive conditions. Crude oil is potentially corrosive if its TAN is greater than 0.5 (1.5 for distillation cuts or fractions). In general, an increase in the TAN is associated with an increase in corrosiveness in the vacuum column, at the boiling

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points of hydrocarbon fractions in the same molar mass range [11].

Laboratory studies have indicated that NAC can occur in different mechanisms depending on the sulfur content and type of crude oil [4,15,16]. Furthermore, sulfur components and naphthenic acid (NA) have been shown to coexist at high temperatures in refinery environments, producing corrosion in the form of tearing, ridges, laminar furrows, rivulets, and, in certain cases, streamlined grooves, sharp-edged holes, craters, or cavities [17–19]. At present, the generally accepted mechanism for NAC of carbon steel involves hydrogen sulfide, and it is described by the following reactions [11,17,20,21]:



Eq. (1) represents the direct attack of NA (COO-) on carbon steel to produce iron naphthenate [17,21,22], and Eq. (2) describes corrosion by hydrogen sulfide (H₂S). Eq. (3) represents the case in which hydrogen sulfide reacts with the soluble iron naphthenate to produce iron sulfide and carboxylic acid [17]. A particularly dangerous situation may occur if the sulfur compound produces water, as in Eq. (4), where hydrogen is produced by the corrosion reaction of the produced sulfoxides (R₂S=O). In such cases, water may act as an additional medium (besides the liquid hydrocarbon itself) where NA can be dissociated [11,21].

Various studies have investigated the chemical characterization of VR [1–9], NAC, and SC [10–30]. The experimental control variables include the temperature, sulfur content, TAN, fluid velocity, and exposure time of metallic test coupons [16,18,23,25,28]. To investigate the reactions in dynamic fluid conditions, the experiments are generally performed in a rotating cell or pipe loops, where one variable is independent; e.g., the fluid temperature while the flow velocity and fluid composition are kept constant [5,7]. Although the corrosion mechanisms related to NA and SC are well known [15,30], there are few studies focused on the VR as the primary corrosive fluid. In the present study, a detailed microstructural and surface analysis was conducted to characterize the morphology of the corrosion attack produced by VR on ASTM A106 grade B [UNS K03006] carbon steel in a laboratory set up in which the temperature, pressure, and fluid velocity were controlled.

The ASTM A106 grade B [UNS K03006] was chosen because it was the fabrication material of a VR pipe circuit that failed by NAC after approximately 20 years of service in a vacuum residue distillation unit of a crude oil refinery. The pipe was 305 mm nominal diameter, and 19 mm nominal thickness, and it was part of a circuit with origin at the distillation tower and discharge at the vacuum processing unit. The pipe suffered severe uniform and localized corrosion, as shown in Fig. 1. The failure initiated at a corrosion pit of

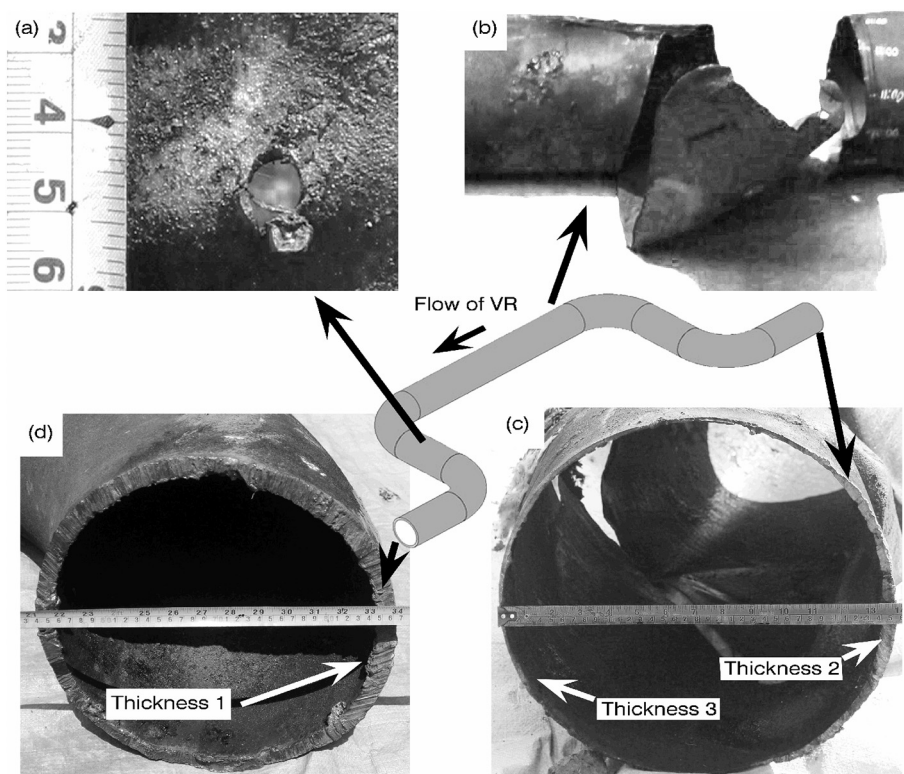


Fig. 1. Failed pipe of a VR circuit in a vacuum residue distillation unit (a) Open corrosion pit identified as the failure initiation site, (b) Pipe rupture near an elbow, (c) upstream segment, (d) downstream segment.

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