



Sulfide promoted chronic fouling in a refinery: A broad phenomenon spanning a range of heat transfer surfaces and oil types



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ABSTRACT

Fouling of metal heat-transfer surfaces employed in crude oil refining operations, driven by inorganic corrosion products, is not well understood. Here we employ a range of advanced analytical techniques, including TEM, SEM, FIB and XRD to systematically document the interdependent corrosion – fouling processes of three refinery metallurgies: a carbon steel, a (P91) 9Cr–1Mo steel, and a 347 stainless steel. We utilize two representative crude oil blends, testing at a metal surface temperature of 490 °C and an oil bath temperature of 290 °C. For the three metallurgies there is a mechanistic similarity of the fouling phenomenon, which begins with sulfidic corrosion of the metal surface and progresses to coking. It is observed that after 1 h of testing, carbon steel samples actually fouled somewhat less than the P91, which was initially unexpected since the latter is considered a more sulfidic corrosion resistant alloy. TEM and SEM analyses demonstrate that there is poor adhesion of the sulfide layer on the carbon steel, which we hypothesize results in the metal surface effectively self-cleaning. Despite being the most resistant to sulfidic corrosion and to fouling, the stainless steel nevertheless forms a thin Fe–Cr–Mn rich inner sulfide and a thicker Fe-rich outer sulfide. We also examine the role of volatiles (reactor pressure), and demonstrate that fouling rates drop off with successive tests on the same oil batch. This is attributed to a gradual exhaustion of S-containing species that react at high temperature to sulfide the metal surface, which in turn catalyze the growth of the organic coke.

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1. Introduction

Complex deposits of organic and inorganic material build up and foul the surface of process vessels during crude oil refining operations [1–4]. Wholly described as crude oil fouling [5], the encompassed phenomena distress operations by encumbering efficient heat transfer, increasing hydraulic resistance – reducing throughput, and compromising safety. Consequently, refinery units can realize millions of dollars in incremental expenses due to increased energy consumption and maintenance costs [6]. Opportunity oils are attractive inputs for a refiner, since they can be purchased at a discount, but require complex, deep refining processes to create on-specification products and may present acute challenges related to fouling and corrosion [7]. Accordingly, fouling is an active field of scientific and engineering research [8–12], and improving the quality and knowledge depth of feedstock chemistry

is becoming increasingly essential [13–35]. Crude oil fouling has been described by distinct mechanistic scenarios such as chemical reaction fouling [36], corrosion fouling [37], and particulate fouling [12], which do not manifest with exclusivity in real systems.

Above cracking temperatures or in cases where catastrophic asphaltene flocculation does not occur, chronic fouling has been linked to corrosion, especially from sulfur bearing species and naphthenic acids [37–40]. Wiehe [41] has described the role of iron sulfide towards enhancing wetting behavior of fouling precursor phases on a metallic surface. Furthermore, in catalysis, transition metal sulfides have specific surface chemistry which makes them important compounds for hydrodesulphurization [42]. Wang and Watkinson [8] proposed enhanced adhesion and trapping of fouling precursors due to roughening of a corroding interface. Particulate matter, suspended in crude oils, such as corrosion residuals (iron oxides and sulfides) and various formation minerals (clays and sands), are also contaminants that can influence fouling [12]. In their examination of deposits from an Australian light crude, authors Alem et al. [27] identified suspended particulates as a secondary causation for fouling. More directly, Petkovic and

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Watkinson [43] have investigated particulate fouling in a batch stirred system using a heated carbon steel rod. The same group [44] has recently studied fouling from a sour crude fraction on corroding and non-corroding metallic surfaces, as a function of temperature and shear rate. Mitlin et al. [45] investigated fouling at delayed coking conditions, using 316 stainless steel and iron wires, and emphasized the role of the initiating surface in their analysis.

What remains poorly understood is the degree to which corrosion-fouling is a general phenomenon for different oil types. Moreover, the microstructural details of the hot oil-exposed metal surface for any metallurgy remain elusive, and there are few direct comparisons between different steels found in refining environments. This is the focus of the current study; to provide an in-depth analysis of the metallurgical changes at the wire surface for representative carbon steel, a representative Cr–Mo steel and a representative stainless steel. To make these findings more general, we employ two different oil blends. By providing a detailed analysis on this relatively broad sampling, we are able to draw both the essential commonalities for early stage corrosion – fouling and to highlight the key differences between the metallurgies.

2. Experimental procedure

A stirred 2000 ml autoclave was equipped with a heated wire probe. A detailed schematic is presented as Fig. S1. The reactor assembly allows for the immersion and resistive heating of wire samples in crude oil, under repeatable conditions. The autoclave reactor was designed for batch operation, with a single charge of 1200 ml of crude oil, and is equipped with a magnetically coupled stir bar to provide a degree of fluid flow/agitation. Prior to all tests, the reactor was sealed and sparged for 20 min, with the stir bar set at 300 RPM. The reactor was then pressurized to 0.8 MPa, prior to the start of each fouling run. Pure nitrogen (99.999%) was used for sparging and pressurization of the system. Once the oil bath had reached its temperature set point, the pressure of the reactor was adjusted, through addition of more nitrogen gas, so as to reach the desired working pressure for the fouling run. The crude oil in the autoclave was maintained at a lower constant temperature, using a PID controlled heating element and a thermocouple in a thermowell. Experiments were completed under controlled conditions of bulk oil temperature, stir rate, and pressure.

The wires in the reactor probe were heated resistively to a desired temperature above the bulk oil temperature via a constant current input. The voltage (and thus power output) of the wires increased by approximately 10% from their initial values during the constant current tests, and, to a first approximation, the heat flux across the expanding foulant–oil interface remained (roughly) constant. The temperature of the wire was determined by its resistance. The measured resistance during the fouling run was compared with an ex-situ generated temperature calibration plot for each metallurgy, which was carried out under an inert atmosphere inside a quartz tube furnace. Temperature and resistivity relationships for each wire metallurgy were also verified ex-situ, using temperature indicating liquids purchased from Tempil, and were found to agree within 5–10% of the extrapolated values.

Fouling was monitored via fouling factors, which we calculate and present in two ways. An *in-situ* fouling factor (FF) measurement is obtained directly from wire resistivity data, while assuming a constant heat transfer surface area (A_c). In this case FF is expressed as the following formula;

$$FF = A_c \left[\left(\frac{\Delta T}{P} \right)_{\text{fouled}} - \left(\frac{\Delta T}{P} \right)_{\text{clean}} \right] \quad (1)$$

Additionally, a final fouling factor (FFF) was calculated by taking into account the increase in the heat transfer surface area;

$$FFF = \left[A_f \left(\frac{\Delta T}{P} \right)_{\text{fouled}} - A_c \left(\frac{\Delta T}{P} \right)_{\text{clean}} \right] \quad (2)$$

where ΔT is ($T_{\text{wire}} - T_{\text{oil}}$) and P is the power output across the wire, due to Joule heating ($P = I^2 R_{\text{wire}}$). The area A_c is the initial “clean” surface area of the wire. The fouled surface area (A_f) is calculated using the diameter of the fouled wires (i.e. the clean wire diameter and the observed foulant thickness). This diameter was obtained by SEM analysis of the fouled cross sections, where the foulant includes all inorganic and organic material remaining after cleaning the wires.

After removal from the reactor, the wires were soaked in petroleum ether for approximately 5 min, washed with fresh petroleum ether, and finally rinsed with isopropyl alcohol. This ensured that any pitch (toluene solubles) remained adhered to the sample surface. Generally, petroleum pitch is the nonvolatile product obtained from thermal or catalytic cracking of heavy petroleum residua [46]. Washing/rinsing were done gently in an effort to retain the delicate surface deposits. After cleaning, the wires were dried in an oven at 90 °C for 2 h. All fouled wires were stored in air at room temperature prior to subsequent analysis, which included scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDXS), and X-ray diffraction (XRD), transmission electron microscopy (TEM). SEM and EDXS analysis utilized a Hitachi S-3000N microscope with an Oxford INCA EDXS system. The SEM was operated at an accelerating voltage of 15 kV, and a working distance ranging from 7 to 15 mm, for optimum resolution. EDXS scans were completed at a 15 kV accelerating voltage and a working distance of 15 mm. Cross sections of fouled wires were prepared by mounting a portion of each sample in a metallographic epoxy, to which a finely dispersed nickel powder was added to reduce charging. Subsequent, delicate grinding and polishing produced a cross sectional sample appropriate for imaging and analysis using SEM and EDXS. Thickness measurements of the rough, fouled wire surface were conducted as follows: Using Quartz PCI software the foulant was measured radially at 8 places around the circumference of the wire cross section, in increments of 45°, starting at the 12 o'clock position. The thicknesses reported were the average of these values and utilized for calculation of the FFF data. XRD analysis was performed using a Bruker AXS D8 Discover diffractometer with a HSTAR GADDS area detector. TEM was completed using a JEOL JEM-2100. Selected area electron diffraction patterns were processed using an open source software package that was developed in-house (Diffraction Ring Profiler version 1.7) [47].

We employed three representative refinery metallurgies: The first metallurgy is 347 austenitic stainless steel (max 0.08 wt.% C, 2Mn, 0.045P, 0.03S, 0.75Si, 17–19Cr, 9–13Ni, 1 (Cb + Ta)) (ASTM A240, A580). Alloy 347 is a stabilized stainless steel which offers an excellent resistance to intergranular corrosion, specifically in the range 800–1500 °F (427–816 °C) [48]. Alloy 347 is stabilized by the addition of Cb, Nb and Ta, and utilized in various high temperature refinery processes [49]. Additionally, this material possesses both good ambient and high temperature mechanical properties. The second metallurgy was alloy P91 (9 Cr–1 wt.% Mo steel), which is a power industry standard material for high temperature applications [50,51]. This ferritic alloy is known for its high temperature strength and creep resistance. The third metallurgy was conventional mild carbon steel with up to 0.25 wt.% C and 0.4 wt.% Mn (ASTM A179).

The three metallurgies were tested as 0.2 mm diameter wires. Fig. S2 shows SEM micrographs of the as-received wire cross-sections and surfaces, highlighting their morphology and surface finish. Fig. S3 shows a TEM bright field, indexed SAD (selected area diffraction) and dark field micrographs of cross sections of the as-received carbon steel and P91. The ferrite metallurgy is a standard rolled texture, highlighted in the dark field

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