



## Full Length Article

# A comprehensive investigation of refinery preheaters foulant samples originated by heavy crude oil fractions as heating fluids

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## ABSTRACT

A deep understanding of the mechanisms responsible for fouling from both crude oils and their fractions is paramount to ensure efficient energy recovery in heat exchangers of crude preheat trains. In this work, seven samples of fouling deposits, carefully collected from a number of refinery heat exchangers processing vacuum gas oil (VGO) and vacuum bottom (VB) streams in an atmospheric crude preheat train were investigated using a range of characterization techniques with the aim of identifying the underlying mechanisms that led to deposition. Characterization of the deposits included morphological and physical examination, fractionating solubility test, Scanning Electron Microscopy-Energy Dispersive X-ray, Combustion Analysis and X-ray Diffraction. In all samples examined, more than 75 wt% of the deposits were identified as inorganic, with about 50 wt% being FeS. At 270–300 °C, FeO(OH) was also identified to be deposited on the tube surfaces made in Cr steel alloy, where more fouling and less corrosion were evident compared to carbon steel (CS). These observations were found in agreement with recent laboratory studies aimed at identifying the role of temperature and tube material in petroleum corrosion. Furthermore, sulphur crystals were found in several VGO fouling samples. Based on the experimental results obtained, a mechanism was proposed to explain the corrosion fouling phenomenon, considered to be the underlying mechanism affecting the refinery. The mechanism involves naphthenic acid attack to the tubes' metal surface, decomposition of iron naphthenate, disproportionation of iron oxide and sulphidation reactions. The results highlighted the importance of studying deposits formed under industrial conditions, timescales and variation of the deposition process, evidenced by the deposit characteristics, along extensive heat exchanger networks.

## 1. Introduction

Atmospheric crude distillation is the first process unit in oil refineries. The performance of the distillation columns where oil is fractionated into products affects significantly that of the entire crude oil refining process. The most important factor influencing the column performance is the crude oil inlet temperature, together with the flowrates and temperatures of the recycled fluids. A significant portion of the thermal energy in product streams leaving the distillation column is recovered by a network of heat exchangers, the pre-heat train, in which the inlet crude oil is heated up before entering the furnace. The study of fouling in these exchangers has been the subject of intense interest from both academia and industry and its impact on operations, energy costs and environmental emissions has been well documented

[1,2], however the underlying phenomena are still largely poorly understood.

Many fouling mechanisms have been identified to occur in crude pre-heat trains [3]. These include scaling (salt precipitation), corrosion, precipitation (by cooling, blending or breaking of emulsions), chemical reaction (thermal cracking, polymerisation of conjugated olefins, aromatic growth, oxidation, etc.), and particulate deposition (such as entrained coke, asphaltenes, iron sulphides) which could act individually or in combination with each other. Characterization of fouling deposits is an important first step in understanding the underlying mechanisms. For instance, when 10–15 wt% or more inorganic components are detected in a fouling sample, this could be a good indication that either scaling, corrosion and particulate are the possible mechanisms responsible for deposition [4,5].

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**Table 1**  
The operational information of foulant samples.

Samples	VGTO-1	VGTO-2	VGTO-3	VGTO-4	VGTO-5	VBTI-1	VBTO-2
Origin Fluid	VGO	VGO	VGO	VGO	VGO	VB	VB
Exchanger Name	E1A	E2B	E2A	E3B	E3A	E4	E5
Tube Material	C.S.	C.S.		1¼ Cr-1/2 Mo		C.S.	5Cr-1/2Mo
Max Bulk Temp Range (°C)	180–120	254–200		300–230		230–190	280–250

Several efforts are found in the literature attempting to standardise the generation, collection and analysis of crude oil samples. One such effort is the analytical industrial protocol patented by Brons et al. in 2004 [4]. The protocol details characterization methods for solids collected in refinery heat exchangers, that can be used to identify the mechanism/s involved in their generation. The analysis prescribed included methylene chloride or toluene extraction, Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX), Thermogravimetric Analysis (TGA), Elemental Analysis (EA) and Optical Microscopy (OM) arranged as a sequential diagram. In 2006, an industrial task force published recommended guidelines aimed at facilitating direct comparison between non-proprietary fouling data [5]. Techniques included were Fourier transform infrared spectroscopy (FTIR), X-ray fluorescence (XRF), X-ray diffraction (XRD), X-ray photoelectron spectroscopy and Nuclear magnetic resonance (NMR). In 2009, Venditti et al. [6] applied some of these techniques following solubility tests, size exclusion chromatography and UV-fluorescence to characterize four foulants deposited in a refinery heat exchanger by desalted crude oil, kerosene, vacuum gas oil and crude oil residue. In another work, Young et al. [7] employed the same analysis on deposits generated in a laboratory batch stirred cell. These deposits were then characterised and their thermal data were correlated with oil and deposits taken from various process conditions by measuring deposit thickness along and around the probe using a laser and coherent light scanning procedure. Recently, Joshi in [8], announced that the same simplified analysis proposed by Brons et al. [4] is sufficient for quantification of only a few elements, required to distinguish between the most common mechanisms of crude oil fouling. He also described the concept of setting a mass balance between the measured weight percentages of the identified elements to verify the quality of the results or to specify the necessity of more analysis to recognise the possible missing elements.

Analysis of deposits formed in lab-tests may help improve the fundamental understanding of the processes involved in fouling deposit formation. However, the conditions leading to deposition in industrial systems are very difficult to reproduce in lab-test, as a result of the complexity of crude oil composition, the frequent variation of feedstock and the long times scales for significant fouling build-up (months or years). Obtaining reliable outcomes requires appropriately collecting fouling samples from the heat exchangers in a refinery, while considering systematically their fluid properties and operating conditions. Foulant samples deposited by hydrocarbon fluids are complex materials containing both organics and inorganics. Their low solubility makes them unsuitable for characterization by common analytical techniques [6], and adequate protocols for sample preparation are required prior to the chemical characterization.

Following an uninterrupted 8-year field study on fouling of crude oil preheaters at a refinery in Iran processing the same feedstock [9,10], in this paper, several foulant samples deposited by vacuum gas oil and vacuum bottoms as heating fluids of crude oil were investigated. This was done by recording their general appearance, then carrying out a fractionating solubility test, SEM-EDX, XRD and combustion/CHN analysis. First, sample description, preparation and analysis in the experimental work are described, with results elucidated in three categories of morphology, physical and chemical characteristics. The presence of FeS and FeO(OH) is then discussed, taking into account laboratory case studies and the role of temperature and tube material. A

novel corrosion/deposition mechanism is proposed to explain the observed results. Finally, the presence of sulphur crystals in the maltenes fractions of some vacuum gas oil (VGO) foulant samples is noted and suggested for further investigations.

## 2. Experimental

### 2.1. Samples

Foulant samples were collected during a major shutdown of a crude oil distillation unit following a 4-year period of operation. The collection was performed following water circulation and steam purging, after which the tube bundles were pulled out of their shells. Five samples were taken from foulant deposited by VGO and two from VB as heating fluids (see Table 1). The foulant originated by VGO presented greater volume compared to those of the other heating fluids, included that formed by VB.

In the refining process, VGO (of Specific Gravity SG = 0.9137) leaves the middle of the vacuum distillation column at about 300 °C. It is then cooled in the crude oil preheaters and air coolers and partly recycled back to the column, with the remainder sent to a hydro-cracking unit for conversion into more valuable products. VB (SG = 1.0115), the heaviest material in the distillation columns, is pumped out from the bottom of the vacuum column at about 360 °C to the hot-end preheat exchangers.

Operational information of samples including the fluids from which foulants were originated, the exchangers name, tube material and maximum bulk temperature ranges (input-output) are listed in Table 1. As for the notation used in describing the foulant samples, VG and VB indicate the corresponding fluid, while TO and TI indicate whether the sample was taken from tube outer or inner surface, respectively. The higher the number at the end of the sample names, the higher was the operating temperature for that fluid.

### 2.2. Preparation

The analysis preparation step consisted in removing the free bulk fluid trapped in the foulant contents and converting it into powder for further analysis in the available equipment. Sufficient quantity (in 10 to 1 ratio) of n-heptane was added to 10–25 g of sample in an airtight jar and kept for at least 4 h at room temperature. Using a vacuum pump, the mixture was filtered repeatedly using additional solvent until a colourless filtrate was obtained. This way, it was safe enough to assume that all trapped fluid was removed. The leftover on the filter paper was dried for at least 12 h in an oven at 60–80 °C, grinded with 60 mesh (250 µm) sieves, and mixed thoroughly [8,11].

### 2.3. Analysis

With a view to maintaining a simple strategy to characterize foulant samples and explore the prevailing mechanism/s, a set of analytical tests was carried out on the raw samples and powders prepared as explained above.

The general appearance of the raw samples was first recorded using a digital camera. The sample layer thickness was also measured when possible using a digital calliper with an accuracy of ± 0.01 mm.

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