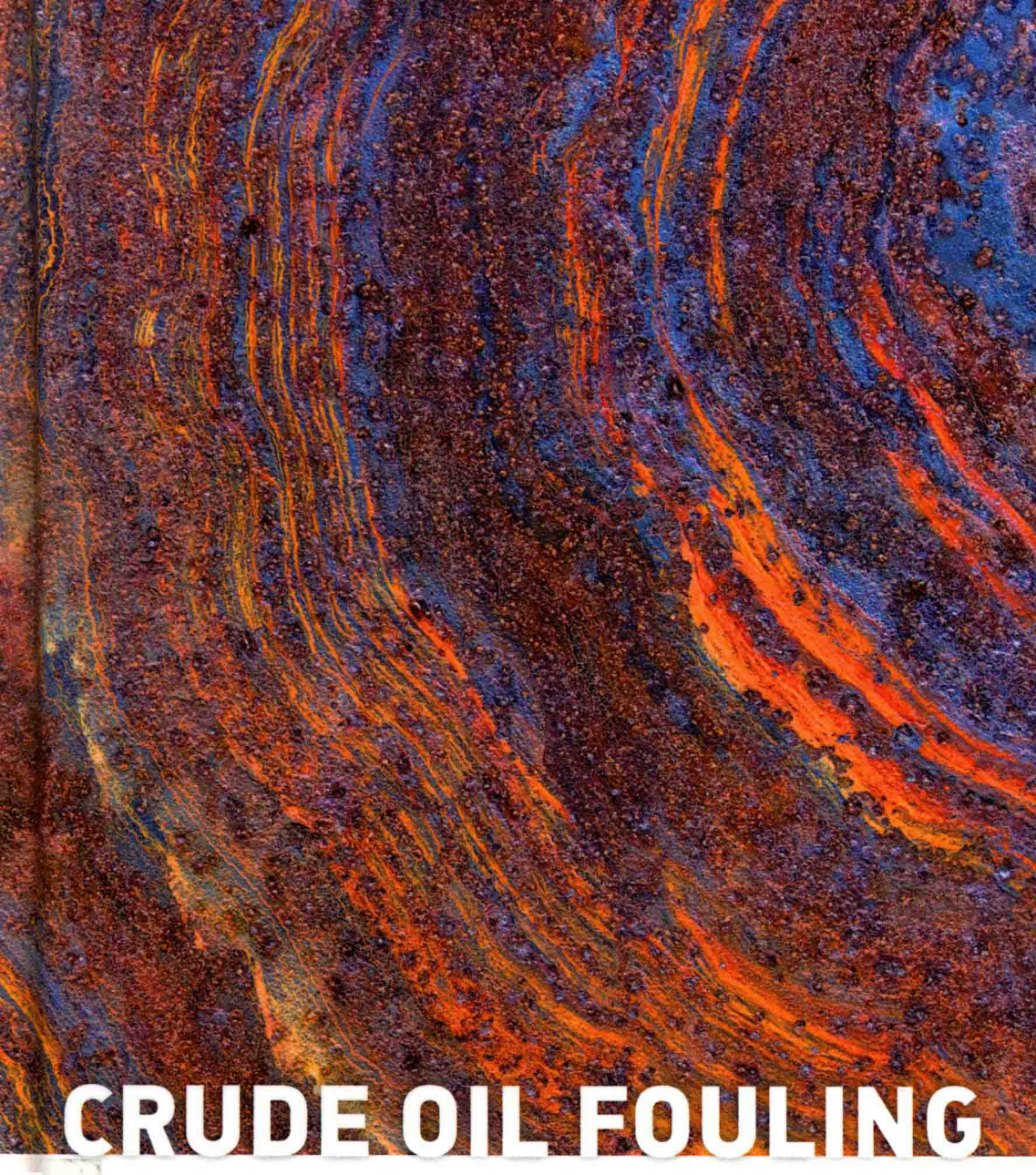

CRUDE OIL FOULING

DEPOSIT CHARACTERIZATION, MEASUREMENTS, AND MODELING

Edited by

Francesco Coletti, PhD
Geoffrey F. Hewitt, PhD

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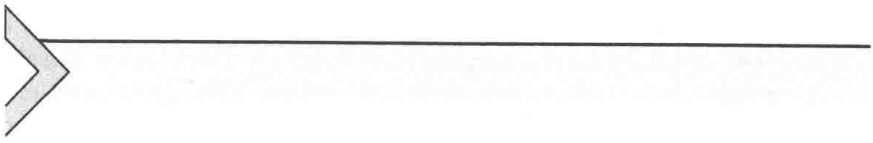

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PREFACE

Nearly every gallon (or liter!) of fuel, which is used in transport vehicles (cars, trucks, trains, airplanes, etc.), is derived from oil that is extracted in the crude state from oil wells and is then processed in an oil refinery to yield the required transport fuel (gasoline, diesel, kerosene, etc.). The first task in the refinery is to separate these useful fuels from the crude oil by the process of *distillation* in which the components of the oil are separated on the basis of their volatility. Of course, the components of crude oil, which are of volatility too low to allow them to be used as fuels, are also separated in the distillation process and can be either directly used (for example, as lubricating or fuel oils) or can be chemically converted to more volatile materials.

In the distillation of crude oils, the separated components are hot and it is important to use this heat in a series of heat exchangers (the "crude preheat train") in which heat is transferred from the separated streams into the incoming crude oil. Unfortunately, these heat exchangers are subject to *fouling*, which reduces the amount of heat they exchange and increases the amount of extra heat that needs to be added (usually through an oil-fired furnace immediately preceding the distillation column). Fouling the exchangers also leads to higher pressure losses (and hence an increased pumping power requirement) and, of course, the exchangers need to be periodically cleaned. Altogether, fouling in the crude preheat train leads to an enormous cost penalty (of the order of 1 billion dollars per annum in the United States alone).

The economic penalties associated with crude oil fouling led the UK Engineering and Physical Sciences Research Council (EPSRC) to finance a research program on crude oil fouling (CROF), which was started in 2006. This three-year program was carried out as a collaboration among Imperial College (London), Bath University, and Cambridge University. Industrial companies representing about 70% of the world's refining capacity also participated through a special Working Party. The work comprised experimental measurements of fouling, analytical modeling, and the development of techniques for the analysis and characterization of crude oils and deposits.

As a result of this research project, a step change has been possible in the characterization and modeling of crude oil fouling and it is clearly important to capture the impact of the work in a published form. Although a number

of articles have been published on various aspects of the work, it was considered important to create a unified and structured presentation of the subject, and this is the objective of the present book.

Although the work described here is focused on crude oil fouling in refinery heat exchangers, most of the experimental and modeling techniques can be either directly applied or readily adapted to address to other types of crude oil fouling. We believe that engineers and researchers involved with waxing in pipelines, fouling of offshore equipment or other downstream units will also find the science and applications contained in the book useful.

Though considerable progress has been made in the work summarized here, it seems safe to predict that crude oil fouling will remain an important focus for research for many years to come!

G.F. Hewitt & F. Coletti

NOMENCLATURE

ROMANS

a	Curvature of annulus (m)
a	Material-specific constant (–)
$a_1,..a_n$	Various fouling model constants
A	Area (m^2)
A	Pre-exponential factor for chemical reaction fouling ($m^2\ K\ J^{-1}$)
A_a	Pre-exponential factor for aging model (s^{-1})
A_{flow}	Cross-sectional area for flow (m^2)
B_c	Baffle cut (%)
Bi_f	Biot number for fouling (–)
C	Phase volume fraction or species concentration (–)
Ca	Capillary number (–)
C_d	Discharge coefficient (–)
C_f	Friction factor (–)
c	Constant of integration (–)
c_b	Concentration in the bulk ($kg\ m^{-3}$)
c_f	Foulant concentration ($kg\ m^{-3}$)
c_p	Concentration of precursors ($kg\ m^{-3}$)
c_p	Specific heat capacity at constant pressure ($J\ kg^{-1}\ K^{-1}$)
c_s	Concentration at the surface ($kg\ m^{-3}$)
c_r	Concentration of reactants ($kg\ m^{-3}$)
D	Diameter (m)
D_d	Deposit diffusion coefficient ($m^2\ s^{-1}$)
D_H	Hydraulic diameter of annulus (m)
D_i	Inner diameter (m)
D_o	Outer diameter (m)
D_{otl}	Tube bundle diameter (m)
D_S	Shell inner diameter (m)
D_s	Inverse of diffusion coefficient ($s\ m^{-2}$)
d	Asphaltene phase mole fraction (–)
d_t	Inner diameter of nozzle throat (m)
d_{tube}	Inner diameter of tube connected to nozzle (m)
dir	Direction of flow (–)
E_a	Activation energy ageing reaction ($J\ mol^{-1}$)
E_f	Activation energy fouling reaction ($J\ mol^{-1}$)
e	Roughness (m)
e	Mathematical constant 2.71828 (–)
e^0	Initial roughness value (m)
e^∞	Final roughness value (m)
G	Free energy ($kJ\ mol^{-1}$)

H	Enthalpy (kJ mol^{-1})
H	Channel height (m)
H_D	Heptane dilution value (–)
ΔH_p	Precipitation enthalpy (kJ mol^{-1})
h	Distance between nozzle and deposit (m)
h_0	Distance between nozzle and substrate (m)
h_{id}	Heat transfer coefficient for ideal cross-flow (W m^{-2} K^{-1})
I_N	Insolubility number (–)
J	Heat transfer coefficient correction factor (–)
J	Mass flux from the oil phase to fouling phase (kg m^{-2})
K	Equilibrium coefficient (–)
K_0	Equilibrium constant at precipitation temperature (–)
k	Order of reaction
k_1	Growth rate constant (s^{-1})
k_2	Removal rate constant (s^{-1})
k_a	Roughness dynamics model constant (–)
k_f	Thermal conductivity of deposit (W m^{-1} K^{-1})
k_m	Mass transfer coefficient (m s^{-1})
k_r	Rate constant of energy barrier (m s^{-1})
k_t	Ageing rate (s^{-1})
l_e	Length of element (m)
l_{eff}	Effective length of tube connect to nozzle (m)
L	Tube length (m)
L_{bc}	Central baffle spacing (m)
L_{bi}	Inlet baffle spacing (m)
L_{bo}	Outlet baffle spacing (m)
L_{tp}	Tube pitch (m)
L_X	Number of moles present for each phase (mol)
M	Mass (kg)
$\dot{M}$	Mass flow rate (kg s^{-1})
$\dot{M}_d$	Mass rate of deposition (kg s^{-1})
$\dot{M}_r$	Mass rate of fouling removal (kg s^{-1})
MW	Molecular weight (kg mol^{-1})
M_c	Characteristic value of mobility (s kg^{-1})
$\dot{m}$	Mass flux (kg m^{-2} s^{-1})
m_g	Measured gauging mass flow rate (kg s^{-1})
$\mathbf{n}$	Normal vector (–)
N	Total number of measurements (–)
N_b	Number of baffles (–)
N_p	Number of tube–side pass per shell (–)
N_S	Number of shells per unit (–)
N_{SS}	Number of sealing strip pairs (–)
N_t	Total number of tubes (–)
$\mathbf{Nu}$	Nusselt number (–)
NV	Number of measurements (–)
P, p	Pressure (Pa)
P	Wetted perimeter (m)

P	Probability (–)
$\mathbf{Pe}$	Peclet number (–)
ΔP_{ij}	Pressure drop between station i and j (Pa)
$\mathbf{Pr}$	Prandtl number (–)
P_t	Tube-side inner perimeter (m)
P_x	Pitch ratio (–)
q''	Heat flux (W m^{-2})
Q	Heat duty (W)
r	Radial coordinate (m)
r	Reaction rate (mol m^{-3} s^{-1})
$\tilde{r}$	Dimensionless radial coordinate (–)
r_d	Density ratio (–)
r_k	Conductivity ratio (–)
r_i	Reaction i (–)
r_v	Viscosity ratio (–)
R	Radius (m)
R_f	Fouling resistance (m^2 K W^{-1})
$\overline{R}_f$	Average fouling resistance (m^2 K W^{-1})
R_g	Universal gas constant (J kg^{-1} mol^{-1})
$\mathbf{Re}$	Reynolds number (–)
$\mathbf{Re}_a$	Reynolds number in the annulus (–)
S	Heat transfer surface (m^2)
S	Entropy (kJ mol^{-1} K^{-1})
S_{BN}	Solubility blending number (–)
T	Temperature (K)
T_b	Bulk temperature (K)
T_f	Film temperature (K)
$\widehat{T}_f$	Modified film temperature (K)
T_{in}	Inlet flow temperature (K)
T_p	Precipitation temperature (K)
T_r	Reduced temperature (–)
T_s	Surface temperature (K)
T_{s0}	Initial surface temperature (K)
T_{st}	Surface temperature at time t (K)
T_w	Wall surface temperature (K)
T_{wb}	Thermocouple temperature (K)
T_{wm}	Thermocouple temperature (K)
T_{ws}	Thermocouple temperature (K)
ΔT_e	Temperature increase of element (K)
t	Time (s)
$t_{0.5}$	Time when θ is half its maximum value (s)
t_{age}	Ageing time (s)
U	Overall heat transfer coefficient (W m^{-2} K^{-1})
u	Velocity vector (–)
u	Mean fluid velocity in the tube (m s^{-1})
$\overline{V}_{bulk}$	Average mean velocity in the bulk (m s^{-1})
V	Volume (m^3)

$\dot{V}$	Volumetric flow rate ($m^3\ h^{-1}$)
V_A	Molar volumes of asphaltenes in the asphaltene phase ($m^3\ mol^{-1}$)
V_d	Volume of deposit (m^3)
V_L	Molar volumes of asphaltenes in the liquid phase ($m^3\ mol^{-1}$)
V_t	Volume of channel (m^3)
v	Velocity ($m\ s^{-1}$)
w	Width of nozzle rim (m)
W	Power (W)
X_{A_i}	Fraction of non-associated molecules (–)
x	Horizontal coordinate (–)
x	Simulated value
$\tilde{x}$	Measured value
x_e	Distance expanded by element (m)
y	Youth variable (–)
y_0	Initial value of youth variable (–)
z	Axial coordinate (m)
z	Vertical coordinate (–)

GREEK

α	Local heat transfer coefficient ($W\ m^{-2}\ K^{-1}$)
α	Angle of nozzle entry (°)
α_{id}	Heat transfer coefficient for ideal cross–flow ($W\ m^{-2}\ K^{-1}$)
α_t^0	Tube–side heat transfer coefficient in clean conditions ($W\ m^{-2}\ K^{-1}$)
β	Linear expansion coefficient (K^{-1})
β	Constant in Ebert and Panchal model (–)
β	Thermocapillarity term (K^{-1})
γ	Suppression parameter ($m^4\ K\ N^{-1}\ J^{-1}$)
$\dot{\gamma}$	Local shear rate (s^{-1})
δ	Thickness of deposit (m)
δ_A	Average solubility parameters in the asphaltene phase ($Pa^{1/2}$)
δ_L	Average solubility parameters in the liquid phase ($Pa^{1/2}$)
ε	Temperature percentage residuals (–)
ζ	Data filtering procedure parameter (%)
η	Dimensionless function (–)
η_{mech}	Mechanical efficiency (–)
Θ	Non-dimensional parameter that depends on L_X (–)
θ	Characteristic formation time of polyaromatic structure in fouling layer (s)
θ	Fractional surface coverage (–)
θ_{tp}	Tube pitch angle (°)
λ	Thermal conductivity ($W\ m^{-1}\ K^{-1}$)
λ	Length of nozzle entry (m)
λ^0	Thermal conductivity for freshly deposit material ($W\ m^{-1}\ K^{-1}$)
λ^∞	The maximum value of thermal conductivity ($W\ m^{-1}\ K^{-1}$)
λ_f	Thermal conductivity of foulant layer ($W\ m^{-1}\ K^{-1}$)

μ	Dynamic viscosity (Pa s)
μ_0	Viscosity of fresh foulant material (Pa s)
ν	Kinematic viscosity (St)
ξ	Structure parameter (–)
ρ	Density (kg m^{-3})
ρ	Molar density in Section 5.2 (mol m^{-3})
σ	Interfacial tension between oil phase and asphaltene phase (N m^{-1})
σ	Measurement variance (K)
τ	Surface shear stress (Pa)
τ_{ya}	Surface shear stress along the arc of inner annulus (Pa)
ϕ_c	Characteristic value of chemical potential (kg m^2 s^{-2})
ϕ_{cr}	Fouling rate decrease by conversion of tarry layer to coke (m^2 K W^{-1} s^{-1})
ϕ_d	Fouling deposition term (m^2 K W^{-1} s^{-1})
ϕ_r	Fouling removal term (m^2 K W^{-1} s^{-1})
ϕ_{tr}	Fouling rate decrease by mass transfer of tars to the bulk fluid (m^2 K W^{-1} s^{-1})
φ	Heat balance closure parameter (%)
χ_i	Weight fraction for component i (–)
Ω	Model domain (–)

SUBSCRIPTS

0	Initial
b	Bulk
c	Cold
cr	Conversion to coke
d	Deposit
f	Fouling, film
h	Hot
i	Inner, i-th component, interface
in	Inlet
L	Fouling layer
n	Pass number
o	Outer
out	Outlet
p	Precursor
s	Shell-side
T	Tube-side
T	Total
tr	Tar layer
W	Wall

SUPERSCRIPTS

0	Initial state of deposit
∞	Final state of deposit
*	Asymptotic value
m	Reaction order for reactant one
n	Reaction order for reactant two
n	Fluid parameter for aging model
l	Reaction order for precursor

ABBREVIATIONS

2D	Two-dimensional
3D	Three-dimensional
AFM	Atomic force microscopy
ATR	Attenuated total reflection
CDU	Crude distillation unit
CFD	Computational fluid dynamics
CG	Coarse grained
C–H	Cahn–Hilliard
CII	Colloidal instability index
CIT	Coil Inlet Temperature
CLSM	Confocal laser scanning microscopy
COT	Coil Outlet Temperature
CV	Control valve
DFT	Density functional theory
DIM	Diffuse interface method
DNS	Direct numerical simulation
DPD	Dissipative particle dynamics
EOS	Equation of State
ETS	Emissions Trading Scheme
FDG	Fluid dynamic gauging
FTIR	Fourier transform infrared spectroscopy
HEN	Heat exchanger network
HEX	Heat exchanger
HiPOR	High Pressure Oil Rig
HTRI	Heat Transfer Research Incorporated
LES	Large eddy simulation
LLE	Liquid–liquid equilibria
LMTD	Logarithmic mean temperature difference
LVDT	Linear variable displacement transducer
N–S	Navier–Stokes
NRV	Nonreturn valve
PHT	Pre heat train

RANS	Reynolds-averaged Navier–Stokes
SAFT	Statistical associating fluid theory
SARA	Saturate, Aromatic, Resin and Asphaltene
SEC	Size-exclusion chromatography
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
UV-F	Ultraviolet fluorescence
VdW	Van der Waals
VGO	Virgin gas oil
VLE	Vapor–liquid equilibria
VLLE	Vapor–liquid–liquid equilibria
VOF	Volume of fluid
XRD	X-ray diffraction

CONTENTS