

BEYOND FOULING FACTORS: A REACTION ENGINEERING APPROACH TO CRUDE OIL FOULING MODELLING

E. Diaz-Bejarano¹, F. Coletti² and S. Macchietto^{1,2}

¹Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, UK

²Hexxcell Ltd., Imperial College Incubator, Bessemer Building Level 2, Imperial College London, London SW7 2AZ, UK,
s.macchietto@imperial.ac.uk

ABSTRACT

Describing crude oil fouling in heat exchangers in terms of a fouling factor has many intrinsic limitations. More sophisticated methods recently developed account for the variation of the fouling deposit thermal conductivity with temperature and time but do not include information on the composition of deposits, which has substantial influence. A more fundamental approach is needed to account for deposition mechanisms, assess the effect on operations, relate cleaning actions to deposit properties, and assist in monitoring, prediction, and design.

Here, a reaction engineering approach to describe the fouling layer is proposed. The analysis is based on a recently developed multi-component model for crude oil fouling deposits, where the deposit is characterized at each point by the composition of deposited species. Fresh deposit composition is determined by the mass fluxes of various fouling species from/to the bulk oil phase, and the composition at each point may vary due to chemical reactions between the species. This determines the physical properties of the layer, such as thermal conductivity.

This improved model of fouling deposits was implemented within a dynamic, distributed, first-principle thermo-hydraulic model for a shell-and-tube heat exchanger. A case study is presented for an industrial multi-pass shell-and-tube heat exchanger operating in typical conditions. Simulations, carried out for several scenarios, illustrate the impact of deposit composition on the thermal-hydraulic resistance of fouling and the importance and advantages of the proposed reaction engineering approach. The ability to describe organic and mixed organic-inorganic fouling and their significant effects on the thermal and hydraulic performance of the exchanger are discussed, showing the inadequacy of, and the need to move beyond the traditional thermal resistance measure of fouling.

INTRODUCTION

The overall effect of fouling is generally represented using a fouling factor or fouling resistance (R_f) which, added to other thermal resistances in a clean heat exchanger, gives the overall heat transfer coefficient under fouled conditions. This thermal performance assessment is typically used in design, fouling monitoring in refinery operations, and the evaluation of mitigation options.

Although fixed fouling factors are typically used, the process by which material builds up on heat exchange surfaces is intrinsically dynamic, with a gradual degradation of thermal performance over time, for which fouling rates are typically defined. In crude oil fouling in refineries, threshold models, first proposed by Ebert and Panchal (1995), are the most common semi-empirical correlations used to fit and predict fouling rates. This approach has serious limitations. First, it is case specific, as it does not directly reflect oil feedstock or type of foulant (this must be done by changing a few adjustable parameters); second, it lumps together many underlying (and some poorly understood) phenomena with distinct and sometimes opposite responses to process conditions. The few adjustable parameters in the model have a tall task indeed, and in most cases the capabilities to fit and, more importantly, to predict fouling behavior are very limited. In spite of this, the success of threshold correlations is explained by the difficulty in studying crude oil fouling using more mechanistic approaches and the poverty of quality fouling data. Generating and replicating such data at conditions close to industrial ones in controlled experimental set-ups is notoriously difficult.

Fouling factors provide limited information about the extent, location and nature of the deposit. First, an increase in fouling resistance does not necessarily correlate to deposit growth, as it could also be due to changes in thermal conductivity of a constant thickness layer (e.g. due to ageing (Coletti and Macchietto 2011)). Second, as deposits build up, the flow area is gradually reduced leading to increased pressure drop, flow imbalance between parallel branches, and difficulties in maintaining throughput (Coletti et al. 2015). Fouling resistance does not provide information on the deposit thickness. Finally, composition of the deposit which determines the relative importance of thermal and hydraulic impact of fouling (Diaz-Bejarano et al. 2015d) is simply ignored.

One way for the R_f -based approach to include an estimate of deposit thickness is to use the thin-slab assumption with some average, constant conductivity (Yeap et al., 2004) and to include ageing of organic deposit by modelling the layer as a number of resistances in series. Each layer then evolves as function of a proposed ageing kinetics, and the thermal conductivity of each layer can be

adjusted accordingly. Such efforts highlight the need for (and potential benefits of) more descriptive models of the deposit, but still rely on a definition of fouling as a lumped thermal fouling resistance, utilize such nomenclature, and carry along all underlying assumptions.

Moving away from a lumped R_f view of fouling requires reformulating the description of the layer and fouling rates with more emphasis on first-principles. Coletti and Macchietto (2011) proposed a model of the fouling layer using dynamic heat balances in a 2D (axial and radial) spatial distributions. This was implemented together with a dynamic and distributed model for heat exchangers and shown to successfully predict refinery data over long periods. The organic ageing model of Ishiyama et al. (2010) was used locally at each point. This enabled to calculate a thermal conductivity at each point in the deposit layer which reflects its full temperature history.

The above modifications deal exclusively with organic fouling, which was considered the main fouling mechanism in the hot end of pre-heat trains. However, inorganic deposits (corrosion products, such as iron sulfide and oxides and inorganic salts) are very often found in heat exchangers together with organic matter (Crittenden et al. 1992; Mozdianfar and Behranvand 2013; Joshi 2014). Diaz-Bejarano et al. (2015d) proposed a modification of the model by Coletti and Macchietto (2011) to account for the presence of inorganic materials considering a composition weighted average between the conductivity of the inorganic and organic portions (with the relative proportions assumed to be in constant and fixed a priori). The presence of inorganics was shown to help interpret and explain operational data in a refinery case study.

In all cases above, the layer properties are only indirectly related to the composition of the deposit layer and to the amount of each species being deposited or removed, as these quantities are not explicitly defined. In order to achieve a much more general representation, it is necessary to reformulate the problem using a more standard reaction engineering approach. This involves additional variables characterizing the state of the deposit and a richer description of its behavior based on mass as well as energy balances, mass fluxes for deposition/removal terms and chemical reactions for internal transformations such as ageing.

A reaction engineering approach to fouling was proposed in the past. For instance, Paterson and Fryer (1988) in the field of milk fouling proposed modelling chemical reaction fouling in a viscous sub-layer as a chemical reactor. However, there have been only few attempts to use the same approach in crude oil fouling. Kinetics (Crittenden et al. 1992) and mass transfer (Epstein 1994) have been proposed as the limiting steps in first-principle models for crude oil chemical reaction fouling. More recently, advanced simulation techniques, such as CFD or DNS (Sileri et al. 2009; Yang et al. 2014), have also been proposed, using powerful capabilities to solve the full momentum, mass and heat balances with phenomena such as diffusion, adhesion, chemical reactions and detailed oil composition. Such solutions are still at preliminary stage,

are very demanding computationally and difficult to incorporate into simulation of multiple heat exchangers.

Here, differently from Paterson and Fryer (1988) and others but consistently with Coletti and Macchietto (2011), the approach is to isolate the deposit layer subsystem from that of other adjoining components (wall, fluid, wall). Here, we focus on a more complete description of the deposit layer and its dynamics, rather than deposition mechanisms (formation of precursors, aggregation, deposition, suppression) or removal mechanisms (as in cleaning) in the other sub-systems. The fouling layer model by Diaz-Bejarano et al. (2015a) is used for this purpose. In that publication, a single tube was considered with oil flowing inside and uniform wall temperature operation.

In this paper, the new fouling layer model is implemented in a shell-and-tube heat exchanger model. First, a brief summary of the key features of that model is presented, highlighting the advantages of a reaction engineering approach. A case study is then presented where the layer model (with composition and reactions) is used within a full multi-pass shell-and-tube heat exchanger model, as schematically shown in Fig. 1, in typical industrial conditions. Simulations carried out for several scenarios illustrate the impact of deposit composition on the thermal-hydraulic resistance of fouling and the importance and advantages of the proposed reaction engineering approach. The ability to describe organic and mixed organic-inorganic fouling and their significant effects on the thermal and hydraulic performance of the exchanger are discussed in the conclusions.

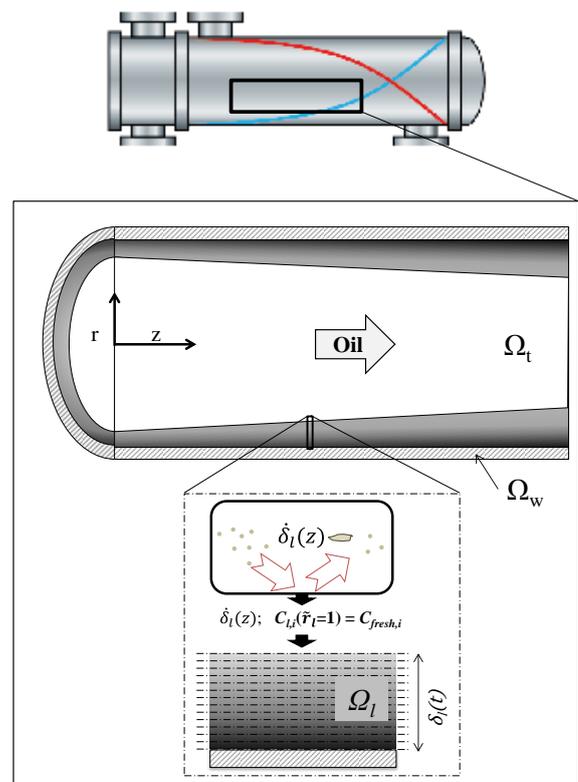


Fig. 1 Schematic representation of a growing fouling layer at a particular location along a heat exchanger tube within a shell-and-tube heat exchanger.

MODEL DESCRIPTION

The model features:

1. Description of the layer state at each point in terms of its composition as well as temperature and physical properties, with multiple reactions occurring at each point.
2. Definition of changes in the layer state in terms of first-principles mass and energy balances in cylindrical coordinates with suitable boundary conditions.
3. Ability to retain time/temperature history at each point under all circumstances.
4. Ability to describe in a single model layer growth, stagnation, reduction and growth resumption after full or partial reduction, through fluxes at the oil/layer boundary.

Deposition and removal mechanisms are considered as local inlet/outlet of chemical species to/from the layer, and define the species' concentration at the surface on the deposit. The local net flux of such material dictates the change in thickness of the deposit. The approach enables capturing the evolution of the properties of the layer due to changes in composition (e.g. due to different foulants being deposited or reactions within the layer), but also to the interactions of fouling/cleaning processes with the deposit.

The new model for the fouling layer and numerical solution aspects are explained in detail in Diaz-Bejarano et al. (2015a). The layer is defined as a multi-component varying-thickness solid deposit undergoing chemical reactions on the inner surface of heat exchangers' tubes. The model is defined in cylindrical coordinates and uses a non-dimensional radial coordinate to permit solution of the moving boundary introduced by the variation of the deposit thickness. The main equations are listed below, while variables are defined in the nomenclature section. It should be noted that the variables and equations below are defined and solved for each pass within the shell-and-tube heat exchanger.

- Mass balance for component i ($i = 1, \dots, N$) considering NR chemical reactions:

$$\frac{\partial c_{l,i}(z, \tilde{r}_i)}{\partial t} - \frac{\tilde{r}_i}{\delta_i(z)} \dot{\delta}_i(z) \frac{\partial c_{l,i}(z, \tilde{r}_i)}{\partial \tilde{r}_i} = \sum_{j=1}^{NR} v_{ij} r_j(z, \tilde{r}_i) \quad (1)$$

- Heat balance:

$$\begin{aligned} \delta_i^2(z) \rho_i(z, \tilde{r}_i) C_{p,i}(z, \tilde{r}_i) \left(\frac{\partial T_i(z, \tilde{r}_i)}{\partial t} - \frac{\tilde{r}_i}{\delta_i(z)} \dot{\delta}_i(z) \frac{\partial T_i(z, \tilde{r}_i)}{\partial \tilde{r}_i} \right) = \\ = \frac{1}{RI - \tilde{r}_i \delta_i(z)} \frac{\partial}{\partial \tilde{r}_i} \left((RI - \tilde{r}_i \delta_i(z)) \lambda_i(z, \tilde{r}_i) \frac{\partial T_i(z, \tilde{r}_i)}{\partial \tilde{r}_i} \right) \end{aligned} \quad (2)$$

- Dimensionless radial coordinate:

$$\tilde{r}_i = \frac{RI - r}{\delta_i(z)} \quad (3)$$

The dimensionless coordinate varies between 0 (at the interface deposit-tube wall, $r = RI$) and 1 (at the moving surface of the deposit, $r = R_{flow}$). The second term on the left

hand side of Eq. (1) is the key feature of the model, since it conveys information on local composition of the deposit along the radial dimensionless coordinate and the deposit thickness changes. This feature, together with appropriate formulation of the boundary condition and discretization strategy (detailed in (Diaz-Bejarano et al. 2015a)), permits simulation of deposit growth, partial removal, fouling re-start after removal, multicomponent systems and changes in fouling behavior with a single model.

The physical properties of the deposit depend on the local composition and are calculated using typical mixing rules. The most relevant property, which determines the resistance to heat transfer, is thermal conductivity. Here, it is assumed that the effective conductivity at a given location is given by the weighted average of those of the single components, on a volume basis:

$$\lambda_i(z, \tilde{r}_i) = \sum_i^N x_{i,i}(z, \tilde{r}_i) \lambda_i \quad (4)$$

Other conductivity models for heterogeneous solids, function of the internal structure (Wang et al. 2008) could be easily used. The time variation of thickness is formulated as the sum of all deposition and removal terms:

$$\dot{\delta}_i(z) = \sum_{i=1}^N \frac{1}{\rho_i} n_{nd,i}(z) - \frac{1}{\rho_i} \sum_{k=1}^{NC} n_{r,k}(z) \quad (5)$$

where n denotes mass flux ($\text{kg/m}^2\text{s}$) at the deposit surface, nd refers to net deposition, r to removal and NC the number of removal processes. The first term in Eq. (5) is a function of the deposition mechanisms. Those could be a surface reaction, or a mass flux of particles or fouling species depositing on the surface. Eq. (5) assumes the various fouling rates to be additive. This first term refers to net deposition and may be given as the difference between two competing mechanism, i.e. deposition and suppression (particle or foulant re-entrainment from the near wall region into the bulk). The second term in Eq. (5) refers to removal processes, which may include removal by shearing or by deliberate operations such as cleaning. Deposition and suppression/removal processes may occur during operation, when oil is flowing through the equipment and being heated. On the other hand, cleaning activities are carried out when the heat exchange equipment is off-line. Mathematically, the choice between these two options is performed by introducing binary variables, as discussed in (Diaz-Bejarano et al. 2015a).

The above fouling layer model was implemented in the Hexxcell Studio™ (Hexxcell Ltd. 2015) shell-and-tube heat exchanger model. The layer model is interfaced with oil flow and tube wall domains models as detailed in Coletti and Macchietto (2011), who also outlined the development of the heat exchanger model.

CASE STUDY

A single-shell heat exchanger operating under typical pre-heat train hot-end conditions is simulated (Coletti and Macchietto 2011). The main geometric parameters and inlet operating conditions are reported Table 1. Two scenarios

are considered: A) Organic matter fouling B) mixed organic/inorganic fouling. These examples show the capability of the model to simulate changes in the layer composition following either chemical reactions or the deposition of different types of foulants, or a mix of both.

Case A. Crude Oil Organic Fouling undergoing Ageing

Previous modelling works (Ishiyama et al. 2010; Coletti et al. 2010) defined ageing as the transformation of organic deposits over time at high temperatures from a fresh, low conductive soft deposit (“gel”) to gradually form a hardened deposit with higher conductivity (coke). As in those works, the thermal-conductivity of gel and coke are assumed to be 0.2 W/mK and 1 W/mK, respectively. As discussed in (Diaz-Bejarano et al. 2015a), the ageing model in (Coletti and Macchietto 2011) can be redefined in terms of concentration of the gel:

$$r_a(z, \tilde{r}_i) = A_a \exp\left(-E_a / R_g T_i(z, \tilde{r}_i)\right) c_{i,gel}(z, \tilde{r}_i) \quad (6)$$

With only organic fouling, the mass balances (Eq. (1)) are reduced to:

$$\frac{\partial c_{i,gel}(z, \tilde{r}_i)}{\partial t} - \frac{\tilde{r}_i}{\delta_i(z)} \dot{\delta}_i(z) \frac{\partial c_{i,gel}(z, \tilde{r}_i)}{\partial \tilde{r}_i} = -r_a(z, \tilde{r}_i) \quad (7)$$

$$\frac{\partial c_{i,coke}(z, \tilde{r}_i)}{\partial t} - \frac{\tilde{r}_i}{\delta_i(z)} \dot{\delta}_i(z) \frac{\partial c_{i,coke}(z, \tilde{r}_i)}{\partial \tilde{r}_i} = r_a(z, \tilde{r}_i) \quad (8)$$

The change in thickness is determined by the mass flux of gel at the oil/deposit boundary. Classic fouling rate equations describing thermal fouling, developed for deposition of organic materials, are typically expressed in terms of thermal resistance. Ideally, mechanistic models would be desirable to evaluate fouling as function of operating conditions and oil composition. However, this is beyond of the scope of this work. Here, the same functional form of the Threshold model by Panchal et al. (1997) is used to describe this deposition (Diaz-Bejarano et al. 2015a). The fresh deposit is assumed to be composed only of gel:

$$n_{gel}(z) = \alpha' \text{Re}(z)^{-0.66} \text{Pr}(z)^{-0.33} \exp\left(-\frac{E_f}{R_g T_{film}(z)}\right) - \gamma' \mathcal{G}_y(z)$$

α' has units of $\text{kg}/\text{m}^2\text{s}$, and thus can be understood as a mass transfer coefficient. Therefore, even though Eq. (9) is simply a re-interpretation of the model by Panchal et al. (1997), the definition of the parameters is more coherent with a reaction engineering description of the deposition process. Coke is assumed to be formed in-situ only within the layer hence:

$$n_{coke} = 0 \quad (10)$$

A simulation was run using typical fouling parameters and assuming fast ageing (Coletti and Macchietto 2011), which are shown in Table 1. These parameters were estimated from historical plant data and, therefore, provide a realistic fouling rate for refinery heat exchangers. The evolution of the deposit thickness over time is shown in Fig. 2(a) at the midpoint of a tube in the first pass. The concentration profile in the same location at times 50, 100 and 200 days is shown in Fig. 2(b). At all times the deposit is composed of gel-like deposit at the surface.

Table 1. Exchanger geometry, inlet conditions and fouling/ageing parameters

Geometry		Fouling/ageing	
Parameter	Value	Parameter	Value
N_t	900	α' ($\text{kg}/\text{m}^2\text{s}$)	0.78
RO (mm)	12.7	E_f (kJ/mol)	28.5
N_p	4	γ' ($\text{kg}/\text{m}^2\text{s Pa}$)	$4.4 \cdot 10^{-10}$
L	6.1	A_a (1/s)	0.01
D_s (m)	1.4	E_a (kJ/mol)	50
Inlet conditions			
Parameter	Shell		Tube
T_{in} ($^{\circ}\text{C}$)	330		204
F (m^3/h)	161		443

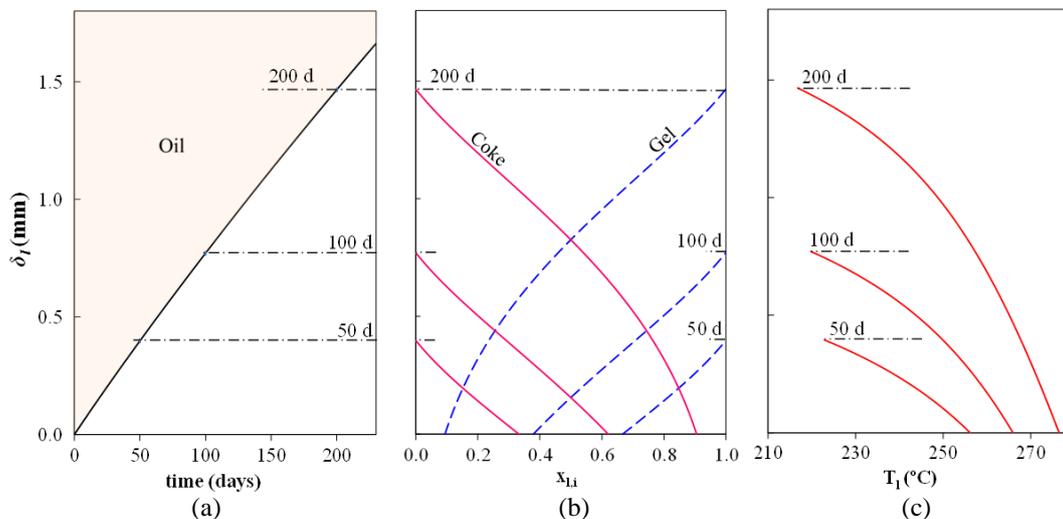


Fig. 2. Deposit thickness over time (a) and deposit mass fraction (b) and temperature (c) radial profile after 50, 100 and 200 days, for organic fouling at the midpoint of a tube in the first pass (Case A).

Once it has deposited, the deposit undergoes ageing, and gel gradually transforms into coke according to Eq. (6). This transformation increases the effective conductivity of the deposit to some intermediate value. The conductivity profile has the same shape as the concentration of coke, and it is not shown here. This leads to the temperature profile in Fig. 2(c). This profile presents a curvature with steep temperature decrease near the surface, as a result of the low conductivity of the fresher deposit. As the deposit grows, the thermal resistance increases, leading to higher temperatures at the wall (as a result of higher shell fluid temperature due to reduced heat exchange) and lower surface temperature. Thus, two opposite effects determine the thermal impact of fouling: deposit build up (negative) and ageing (which lessens the previous one). The effect of ageing rate under various operation modes was explored in detail elsewhere (Coletti et al. 2010).

Case B. Multi-component deposits: Effect of inorganics

As noted in the introduction, the presence of inorganic species in crude oil preheat trains is often reported in field studies. For example, Joshi (2015) notes that corrosion products such as iron sulfide (FeS) and iron oxide (Fe₂O₃) are commonly found in large quantities in refinery heat exchangers. In that work, the analysis of field deposits revealed iron content ranging between 22-24_{wt}% and sulfur content of 13-17_{wt}%. The presence of such species has been reported in other field studies (e.g. Crittenden et al. (1992) reported ash content between 15-40_{wt}%, of which 28.1-42.2_{wt}% was reported to be iron) and laboratory studies (see review by Wang and Watkinson (2011)).

The conductivity of pure salts and corrosion products is generally greater than that of organic deposits. As a result, the heat transfer properties of the layer are expected to deteriorate less rapidly when salts are present together with organics. In the example, it is assumed that Fe₂O₃ and FeS (with conductivity approximately 3 and 5 times that of coke, respectively (Müller-Steinhagen 2000; Wang and Watkinson 2011)) deposit in addition to the organic fouling

in the previous section. The layer is thus characterized by 4 species.

Fe₂O₃ and FeS may be formed by corrosion of the tube metal or formed upstream and deposited following a particulate mechanism. Iron species are likely to increase the fouling (Watkinson et al. 2000) and ageing rate of the organic deposit. In addition, iron sulfide could also age over time if exposed to hydrogen sulfide (Nasr-El-Din and Al-Humaidan 2001). For simplicity, and in order to focus the discussion on the effect of enhanced conductivity due to the presence of the inorganics, here it is assumed that: a) Fe₂O₃ and FeS do not participate in any reaction and do not affect the fouling rate of the organic deposit; b) Fe₂O₃ and FeS are deposited as particles (corrosion mechanism neglected); c) the deposition rates of Fe₂O₃ and FeS are proportional to that of organic gel; d) the deposition rates of gel, Fe₂O₃ and FeS are additive. The mass balances within the layer for these two species are:

$$\frac{\partial c_{l,FeS}(z, \tilde{r}_i)}{\partial t} - \frac{\tilde{r}_i}{\delta_l(z)} \dot{\delta}_l(z) \frac{\partial c_{l,FeS}(z, \tilde{r}_i)}{\partial \tilde{r}_i} = 0 \quad (11)$$

$$\frac{\partial c_{l,Fe_2O_3}(z, \tilde{r}_i)}{\partial t} - \frac{\tilde{r}_i}{\delta_l(z)} \dot{\delta}_l(z) \frac{\partial c_{l,Fe_2O_3}(z, \tilde{r}_i)}{\partial \tilde{r}_i} = 0 \quad (12)$$

Based on the typical compositions previously noted, the deposition rates of Fe₂O₃ and FeS are assumed to be 20% and 30% on volume basis of the deposition rate of gel, respectively (Eq. (13, 14)). As a result, from Eq. (15) the fresh deposit at the oil/deposit interface is composed of a mixture of gel, Fe₂O₃, and FeS, with volume fractions 0.67, 0.13 and 0.2, respectively.

$$n_{FeS} = 0.2n_{gel} \quad (13)$$

$$n_{Fe_2O_3} = 0.3n_{gel} \quad (14)$$

$$x_{fresh,i} = \frac{n_i / \rho_i}{\sum_{i=1}^N n_i / \rho_i} \quad (15)$$

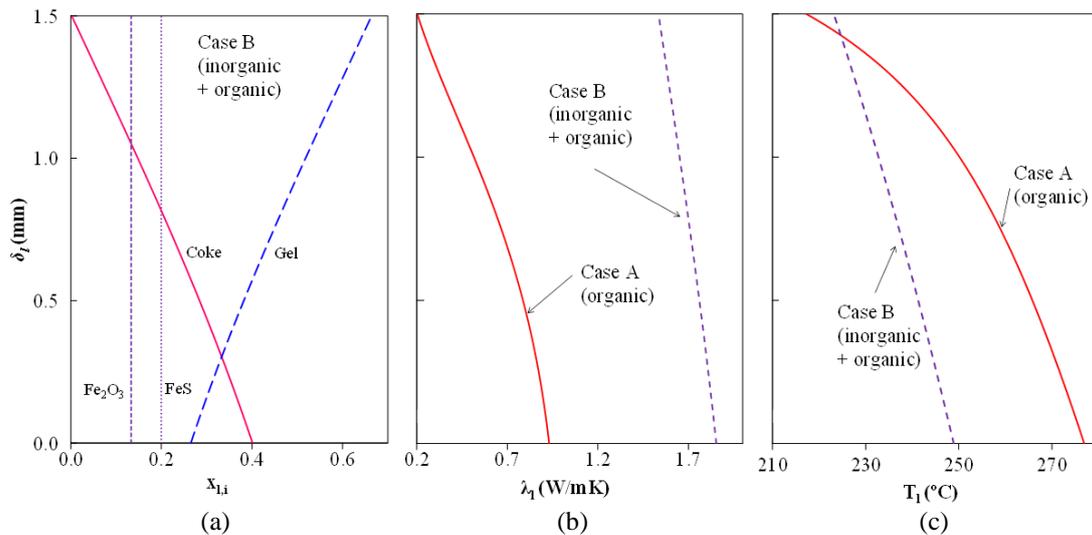


Fig. 3. Volume fraction (a) for an organic/inorganic mixture (Case A). Conductivity (b) and temperature profile (c) for organic (continuous line, A) and organic/inorganic mixture (discontinuous, B). Comparison for a layer thickness of 1.5 mm.

The concentration radial profile of all four species at the midpoint of a tube in the first pass when the layer has reached 1.5 mm of thickness is shown in Fig. 3(a). As before, gel gradually converts into coke, however no such ageing occurs for the inorganic species, which explains their constant concentration throughout the layer. As a result of the presence of inorganic salts, the conductivity of the layer (Case B in Fig. 3(b)) is well above that of the comparable situation with organic deposit only (Case A in Fig. 3(b)).

The total deposition rate is greater with the iron species (fouling rates are assumed to be additive). With organic deposition only (Case A) it takes 206 days for thickness to reach 1.5 mm, and only 130 days when iron salts are also depositing (Case B). Fig. 3(c) compares the temperature radial profile when the deposits have grown to 1.5 mm for the two cases. In Case B, the temperature is almost linear in the radial direction and the wall temperature, 249°C, is much lower than in Case A (277°C). This is result of the greater conductivity with inorganics, which leads to greater heat transfer from shell to tube fluids. As a result, the presence of inorganics masks the reduction in thermal performance caused by the organic deposits.

On the other hand, despite the lower wall temperature, the temperature at the surface at this time is higher when inorganics are present, contributing to even greater fouling rates, according to the temperature dependence in Eq. (9). The increased fouling rate will also increase the deposit thickness and affect the hydraulic performance, leading to greater pressure drops.

Thermo-hydraulic performance

The exchanger thermal-hydraulic performance is visualised using the TH- λ plot (Diaz-Bejarano et al. 2015c). The plot shows the exchanger heat duty and pressure drop relative to the corresponding values in clean conditions on the vertical and horizontal axis, respectively. Periodic (daily, weekly or monthly) data plotted on this graph show the relative evolution of the thermal and hydraulic impacts of the deposit. In addition, reference performance lines for fixed conductivity (λ -lines) give an indication of the nature of the deposit.

The TH- λ plot for the two previous cases is shown in Fig. 4, where the black dots represent monthly data and their label the month number since the start of operations, after a full clean. This Performance line gives an idea of the process dynamics. For organic matter, the Performance line is initially close to the Gel λ -line. As the deposit ages, it gradually moves towards the Coke λ -line. The plot shows that, in Case A, thermal performance decreases faster initially (from $Q/Q_c = 1$ to approximately 0.7 in 3 months). Afterwards, the thermal performance decreases slowly, but the pressure drop starts increasing very fast (the distance between black dots in the horizontal direction is progressively greater). When inorganics are present (Case B), the Performance line is above the Coke λ -line at all times. The rate of growth of the layer is revealed by the fast increase in pressure drop. For instance, the pressure drop becomes twice that in clean conditions in less than 4 months, while in Case A over 6 months are required to reach such value. From Fig. 4, it is obvious that the organic

material on its own leads to thermal performance issues, whilst the presence of inorganic is likely to lead to affect the hydraulic limit.

The exchanger overall fouling resistance for the two cases is plotted in Fig. 5. Such fouling resistance is traditionally used to monitor fouling and fit fouling models. Fig. 5 shows that R_f grows faster in Case A than in Case B. After a year R_f of Case A is double that of Case B. Consideration of Fig. 5 alone (i.e. of R_f , a thermal performance measure), however, can lead to the erroneous conclusion that the deposition rate (hence the deposit's thickness, which determines the hydraulic performance) is also faster in case A than in case B, while the opposite is true.

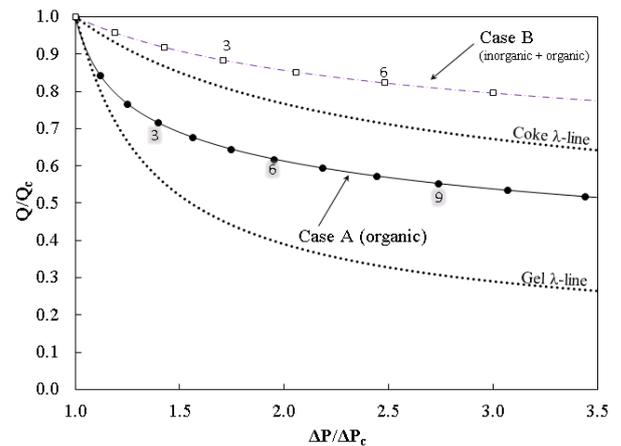


Fig. 4. TH- λ Plot for organic (Case A) vs. inorganic-organic (Case B).

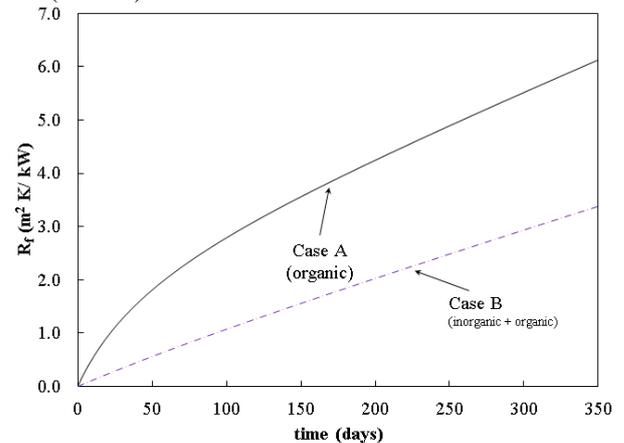


Fig. 5. Fouling resistance for organic (Case A) vs. inorganic-organic (Case B).

These results highlight the importance of moving beyond fouling resistance as traditionally defined and used, when studying fouling. As shown, simultaneous consideration of both thermal and hydraulic performance indicators should be used to monitor the extent of fouling. This can help to identify the nature of the layer, understand the underlying fouling mechanism, and potentially identify the fouling cause (e.g. corrosion or problems in desalting) and the most suitable mitigation option. Study of fouling merely based on fouling resistance does not give adequate insights into hydraulic effects and composition of the

deposit, and may well lead to wrong operation and mitigation decisions.

DISCUSSION AND CONCLUSIONS

A modelling framework was presented for the simulation of heat exchangers undergoing crude oil fouling that uses a reaction engineering approach in the description of the deposit layer. The layer model, summarized in the second section, captures the detailed time-conditions history at each point in the layer by including multicomponent species, multiple reactions and fluxes at a moving oil/deposit boundary. The main differences between the traditional approach and the approach used here are summarized in Table 2. Due to the software organization, the new layer model was easily implemented within a dynamic, distributed model for shell-and-tube heat exchangers. Here, two case studies have been presented, simulating the thermal-hydraulic performance of a typical industrial single-shell heat exchanger over a year with deposits composed of: A) organic matter; B) mixed organic and iron particulates. Results for the concentration radial profiles at the midpoint of the first pass, and the consequent conductivity and temperature profiles have been shown.

The results show how the local conductivity of the deposit, being a function of composition and varying along each tube in a pass and between passes, determines the overall thermal and hydraulic behavior of the heat exchanger. This is well evidenced on a thermo-hydraulic TH- λ Plot. It has also been shown that analysis of the same exchanger operations data using a traditional fouling resistance measure may lead to a misleading interpretation of the heat exchanger conditions and underlying causes of fouling. Validation of some of these results with field data remains a subject for future work, for which thermal and hydraulic measurement and deposit analysis is required.

Table 2. Comparison between traditional and reaction engineering approach to modelling heat exchanger fouling.

Traditional Approach	Reaction Engineering Approach
Fouling rates in terms of thermal resistance	Mass fluxes for deposition and removal, change in thickness
Conductivity, “youth”, ageing	Mass balance, concentration, reactions
Independent fouling rates and ageing models	Interdependent mass balance and fouling rates
A-priori definition of removable/non-removable deposit by cleaning	Definition of cleaning rates as function of deposit characteristics

The capability of this layer model to describe, within a single dynamic model, partial removal of the deposit (either by shear or cleaning), subsequent resumption of fouling, and cleaning cycles was discussed in Diaz-Bejarano et al. (2015a). A second paper (Diaz-Bejarano et al. 2015b) showed its use in exploring vexed questions and hypotheses regarding the mechanisms limiting fouling deposition, such as suppression and/or removal, and their effects on

measurable variables. This should be useful to guide the design of laboratory experiments aimed at providing the required empirical evidence.

The framework presented offers excellent new possibilities for incorporating these more advanced thermo-hydraulic analysis in the design, monitoring, cleaning and generally operations support and optimization of industrial heat exchangers, and in particular refinery preheat trains. Results in this direction will be presented in future publications.

ACKNOWLEDGMENTS

This research was partially performed under the UNIHEAT project for which EDB and SM wish to acknowledge the Skolkovo Foundation and BP for financial support. The support of Hexxcell Ltd, through provision of Hexxcell Studio™, is also acknowledged.

NOMENCLATURE

A_a	Ageing activation energy, 1/s
C_{fresh}	Concentration of fresh deposit, kg/ m ³
C_p	Specific heat capacity, J/kg
$c_{i,i}$	Concentration of component i in the layer, kg/m ³
D_s	Shell Diameter, m
E_a	Ageing activation energy, J/mol
E_f	Fouling activation energy, J/mol
F	Volumetric flowrate, m ³ /h
L	Tube length, m
n	Mass flux, kg/m ² s
N	Number of components in the layer
NC	Number of removal processes
N_p	Number of passes
N_t	Number of tubes
NR	Number of reactions
Pr	Prandtl number, $C_p\mu/\lambda$, dimensionless
RI	Inner Radius, m
RO	Outer Radius
R_f	Fouling resistance, m ² K/W
R_{flow}	Radius at the fouling layer-fluid interface, m
R_g	Ideal gas constant, 8.314 J/molK
r_j	Rate of reaction j, kg/ m ³ s
r	Radial coordinate, m
\tilde{r}_j	Dimensionless radial coordinate, dimensionless
Re	Reynolds number, $\rho u_o/\mu$, dimensionless
R_f	Fouling resistance, m ² K/kW
t	Time, s
T	Temperature, K
T_{film}	Film Temperature, K
$x_{i,i}$	Volume fraction of component i in the layer, -
z	Axial coordinate, m
α'	Modified Deposition constant, kg/ m ² s
γ'	Modified suppression constant, kg/ m ² s Pa
δ_l	Deposit thickness, m
δ_f	Rate of change of fouling layer thickness, m/ s
ΔP	Pressure drop, Pa
λ	Thermal-conductivity, W/mK
ρ	Density, kg/m ³
v_{ij}	Stoichiometric coefficient for component i in reaction j
τ_w	Shear stress, N/m ²

Ω Heat exchanger domain

Subscript

c Clean conditions
 coke Aged organic deposit
 Fe_2O_3 Iron oxide
 FeS Iron sulfide
 gel Fresh organic deposit
 i Component number
 in Inlet
 j Reaction number
 l Layer
 nd Net deposition
 r Removal
 t Tube
 w Wall

REFERENCES

- Coletti, F. et al., Ishiyama, E.M., Paterson, W.R., Wilson, D.I. and Macchietto, S., 2010. Impact of Deposit Aging and Surface Roughness on Thermal Fouling: Distributed Model. *AIChE J*, 56(12), pp.3257–3273.
- Coletti, F., Joshi, H.M., Macchietto, S. and Hewitt, G.F., 2015. Introduction to Crude Oil Fouling. In F. Coletti and G. F. Hewitt, eds. *Crude Oil Fouling: Deposit Characterization, Measurements, and Modeling*. Boston, US: Gulf Professional Publishing.
- Coletti, F. and Macchietto, S., 2011. A Dynamic, Distributed Model of Shell-and-Tube Heat Exchangers Undergoing Crude Oil Fouling. *Industrial and Engineering Chemistry Research*, 50(8), pp.4515–4533.
- Crittenden, B.D., Kolaczowski, S.T. and Downey, I.L., 1992. Fouling of Crude Oil Preheat Exchangers. *Trans IChemE, Part A, Chem Eng Res Des*, 70, pp.547–557.
- Diaz-Bejarano, E., Coletti, F. and Macchietto, S., 2015a. A new dynamic model of crude oil fouling deposits and its application to the simulation of fouling-cleaning cycles. *in press: AIChE J*. DOI: 10.1002/aic.15036.
- Diaz-Bejarano, E., Coletti, F. and Macchietto, S., 2015b. Crude oil fouling deposition, suppression, removal - and how to tell the difference. In *Heat Exchanger Fouling and Cleaning XI*. Enfield (Ireland).
- Diaz-Bejarano, E., Coletti, F. and Macchietto, S., 2015c. Detection of changes in fouling behaviour by simultaneous monitoring of thermal and hydraulic performance of refinery heat exchangers. *Comp Aided Chem Eng*, 37, pp.1649 – 1654.
- Diaz-Bejarano, E., Coletti, F. and Macchietto, S., 2015d. Impact of Crude Oil Fouling Composition on the Thermo-Hydraulic Performance of Refinery Heat Exchangers. In *11th Int Conf on Heat Transfer, Fluid Mechanics and Thermodynamics*. Kruger National Park, South Africa.
- Ebert, W.A. and Panchal, C.B., 1995. Analysis of Exxon crude-oil-slip stream coking data. In C. B. Panchal, ed. *Fouling Mitigation of Industrial Heat-Exchange Equipment*. San Luis Obispo, California (USA): Begell House, pp. 451–460.
- Epstein, N., 1994. A model for the initial chemical reaction fouling rate for flow within a heated tube, and its verification. In G. F. Hewitt, ed. *10th Int. Heat Transfer Conf*. Rugby: IChemE, pp. 225–229.
- Hexxcell Ltd., 2015. Hexxcell Studio. Available at: <http://www.hexxcell.com>.
- Ishiyama, E.M., Coletti, F., Macchietto, S., Paterson, W.R. and Wilson, D.I., 2010. Impact of Deposit Ageing on Thermal Fouling: Lumped Parameter Model. *AIChE J*, 56(2), pp.531–545.
- Joshi, H.M., 2015. Analysis of Field Fouling Deposits from Crude Heat Exchangers. In F. Coletti and G. F. Hewitt, eds. *Crude Oil Fouling: Deposit Characterization, Measurements, and Modeling*. Boston, US: Gulf Professional Publishing.
- Mozdianfard, M.R. and Behranvand, E., 2013. A field study of fouling in CDU preheaters at Esfahan refinery. *Applied Thermal Engineering*, 50(1), pp.908–917.
- Müller-Steinhagen, H., 2000. *Handbook of Heat Exchanger Fouling: Mitigation and Cleaning Technologies*, Essen, Germany: Publico Publications.
- Nasr-El-Din, H.A. and Al-Humaidan, A.Y., 2001. Iron Sulfide Scale: Formation, Removal and Prevention. In *SPE Int Symposium on Oilfield Scale*. Aberdeen, UK.
- Panchal, C.B., Kuru, W.C., Liao, C.F., Ebert, W. A. and Palen, J.W., 1997. Threshold conditions for crude oil fouling. In T. R. Bott, ed. *Understanding Heat Exchanger Fouling and its Mitigation*. Lucca, Italy: Begell House, pp. 273–281.
- Paterson, W.R. and Fryer, P.J., 1988. A reaction engineering approach to the analysis of fouling. *Chem Eng Sci*, 43(7), pp.1714–1717.
- Sileri, D., Sahu, K., Ding, H and Matar, O K, 2009. Mathematical modelling of asphatenes deposition and removal in crude distillation units. In H. Müller-Steinhagen, M. R. Malayeri, and A. P. Watkinson, eds. *Int. conf. on heat exchanger fouling and cleaning VIII*. Schladming, Austria, pp. 245–251.
- Wang, J., Carson, J. K., North, M. F., Cleland, D. J., 2008. A new structural model of effective thermal conductivity for heterogeneous materials with co-continuous phases. *Int Journal of Heat and Mass Transfer*, 51(9-10), pp.2389–2397.
- Wang, W. and Watkinson, A.P., 2011. Iron Sulphide and coke fouling from sour oils: review and initial experiments. In M. R. Malayeri, H. Müller-Steinhagen, and A. P. Watkinson, eds. *Int conf on heat exchanger fouling and cleaning 2011*. Crete Island, Greece, pp. 23–30.
- Watkinson, A.P., Navaneetha-Sundaram, B. and Posarac, D., 2000. Fouling of a sweet crude oil under inert and oxygenated conditions. *Energy and Fuels*, 14(11), pp.64–69.
- Yang, J., Matar, O. K., Hewitt, G. F., Zheng, W. and Manchanda, P., 2014. Modelling of fundamental transfer processes in crude-oil fouling. In *15th Int Heat Transfer Conference, IHTC-15*. Kyoto, Japan.
- Yeap, B.L., Wilson, D. I., Polley, G. T. and Pugh, S. J., 2004. Mitigation of crude oil refinery heat exchanger fouling through retrofits based on thermo-hydraulic fouling models. *Chem Eng Res and des*, 82(1), pp.53–71.