Crude oil Fouling Deposition, Suppression, Removal and Consolidation - and how to tell the difference

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ABSTRACT

Crude oil fouling on heat transfer surfaces is often described as the result of two competing mechanisms: a deposition and a deposition-offsetting mechanism. There is uncertainty whether the offsetting mechanism is suppression (due inhibition of attachment or back-diffusion of foulant from near the wall into the bulk) or removal of foulant already deposited, due to i) difficulties in experimentally identifying and isolating the key phenomena; ii) the cumulative measurement of deposition rates by monitoring thermal exchange rates (or resistance) alone.

Here, the question is addressed of whether it is conceptually possible to distinguish such phenomena, and if so, in which conditions. A recently developed 2D deposit model and a thermo-hydraulic model of a heat exchanger tube are used to assess the system response to removal, suppression, ageing and consolidation (for which a new model is proposed). It is shown that whilst suppression or removal lead to undistinguishable behavior during overall deposit growth, thermal and hydraulic responses will differ in certain conditions, for which an experimental procedure is suggested. Simultaneous consideration of thermal and hydraulic effects and accurate characterization of the deposit ageing and consolidation processes are suggested as a way to allow the unambiguous identification of the dominant deposition-offsetting mechanism.

INTRODUCTION

Crude oil fouling in the preheat train of refineries leads to significant costs, increased fuel consumption and greenhouse gas emissions [1]. The complexity of crude oil composition, the frequent variation of feedstock, and the long times scales for significant fouling build-up under industrially relevant conditions (typically months or years) make it difficult to study fouling from a fully mechanistic approach. The main dependences of organic matter deposition on operating conditions are well known: fouling rate increases with temperature (thermal fouling) and decreases with flow velocity (or shear stress). The latter suggests the existence of a deposition-limiting mechanism related to mass transfer, shear forces or turbulence.

A general approach, first introduced by Kern and Seaton [2] is to quantify fouling rate as a competition between deposition and removal. The 'removal' term was initially introduced to explain the falling rate of fouling resistance (R_f) with time. Kern and Seaton assumed that the deposit is removed in chunks by effect of the shear action of the fluid (also called spalling or tearing off). Other removal mechanisms are thought to exist including dissolution or erosion (deposit finely removed by shear action) [3]–[5]. The dominant mechanism depends on the specific system under study. Significant progress on understanding particle re-suspension, both theoretical and experimental, has been achieved over the last years in colloidal particulate fouling, as reviewed by Henry and Minier [6]. In those systems detachment and re-suspension of particles (or clusters) depends on particle-fluid, particle-surface, and particle-particle interactions. Deposit removal has been proven experimentally and is relevant, for example, in combustion systems [7], spray driers in the food [8] and detergent industries [9], filtration systems [10] and nuclear reactors [11].

Epstein [12] noted that asymptotic or falling fouling rate data does not necessarily imply a partial removal of the deposit. He listed alternative mechanisms including the suppression of attachment by increasing flow velocity as a result of flow area blockage, the reduced transport due to formation of a thicker viscous sub-layer due to smoothing of the deposit surface, or the gradual weakening of wall catalysis effect as the deposit builds up. Epstein cites instances of fouling studies in different systems where it was shown that no deposit removal occurred using, for instance, radioactive tracer techniques [13].

In crude oil fouling, two main deposition-offsetting mechanisms are generally acknowledged to be possible:

1. Suppression: the inhibition of deposition by back diffusion of foulant, formed in the boundary by chemical reaction, to the bulk (Figure 1a) or inhibition of deposition of particles by fluid dynamics or shear (Figure 1b). The dashed line in the figures indicates the limit of the thermal boundary layer (as in [14]).
2. Removal: the erosion/tearing off of (some) deposit by action of the shear stress, if the deposit is weak (Figure 1c).

The complexity in separately characterizing deposition and deposition-offsetting mechanisms led to the development of simplified, semi-empirical models to quantify thermal fouling rate. The most popular type is the so called ‘threshold’ model, first proposed by Ebert and Panchal [15]:

$$\frac{dR_f}{dt} = \alpha Re^{\beta} \exp\left(-\frac{E_f}{RT_{film}}\right) - \gamma\tau_w \qquad (1)$$

This semi-empirical approach lumps together physical and chemical phenomena involved in deposition using Re, Pr (in following modifications of the same equation) and some adjustable parameters (α, β, γ and activation energy, E_f). The deposition-offsetting term (the negative term on the right-hand side of Eq. (1)) is assumed proportional to the wall shear stress (τ_w). Ebert and Panchal [15] defined it as the removal of foulant by diffusion or turbulent eddies from the thermal boundary layer to the bulk, therefore, as a suppression mechanism. These semi-empirical models are used to: a) fit initial fouling rates to experimental data; and b) fit historical plant data and predict future fouling, in support of operations. In exchanger design, the objective is to find operating conditions that prevent fouling and the above models are used for this purpose. The existence of this threshold was proved experimentally [16].

The debate regarding the mechanism offsetting deposition in crude oil thermal fouling remains open. This is mainly a consequence of the lack of conclusive experimental proof. Crittenden et al. [17] referred to trends in plant data and in situ observations that might suggest a removal mechanism: i) saw-tooth pattern of measured fouling resistance over time; ii) scatter in R_f versus time graphs potentially due to removal and re-deposition; and iii) observation of deposits accumulated at locations apart from the inside of the tube by visual inspection of heat exchangers open for cleaning. More recently Crittenden and collaborators reported negative fouling rates observed in a Batch Stirred Cell System [18, 19] in experiments alternating low stirrer speed with high speed periods. This has been interpreted by the authors as experimental evidence of partial removal of the fouling deposit. The authors acknowledge that a slower mass transfer mechanism might still exist, although shear removal would be dominant.

According to Watkinson and Wilson [20] removal is usually less significant in organic systems than in other types of fouling. Wilson *et al.* [21] referred to the lack of "evidence of deposit removal in crude oil fouling systems" to support suppression as the deposition-offsetting mechanism, although the authors acknowledge that the mechanisms are not well understood and emphasize the importance of considering ageing [22]. The ageing process is considered to gradually change the initial fouling deposit (tarry or gel-like in consistency) to coke at high temperature. Ageing in crude oil fouling is believed to strengthen the deposits, as happens in polymerization systems, leading to the implicit conclusion that removal becomes more difficult, thus suppression is the more likely deposition-offsetting mechanism.

A kinetic model of the thermal effect of ageing was postulated and implemented into lumped [23] and distributed [24] layer models and used to test the effect of ageing under industrially relevant conditions. This showed that ageing improves the thermal conductivity of the layer and contributes to an “apparent” falling rate and asymptotic time profile of the fouling thermal resistance. Consequently, both ageing and deposition-offsetting (suppression and/or removal) mechanisms should be considered when studying crude oil fouling. However, ageing is often ignored in most fouling studies, which tend to focus on fitting threshold models to temperature and flow data. Estimation of fouling parameters considering ageing is limited to the work by Coletti and Macchietto [25].

Diaz-Bejarano *et al.* [26] presented an extended representation and dynamic model of a fouling layer characterized by a single, continuous 2D distribution of compositions and other properties, and showed how it could be used to model deposition, cleaning (including condition-based cleaning) and any transitions between them with a single model. The model permits capturing the simultaneous thermal effects from changes in the deposit thickness and composition, and hydraulic effects resulting from flow area restriction. Here, the above models are used to investigate the effects previously described (suppression, removal and ageing) on the thermal-hydraulic response of a tube undergoing fouling, focusing on developed fouling layers rather than initial rates. Industrially relevant conditions and time scales are considered. The objective is to investigate whether it is conceptually possible to observe, measure and distinguish such phenomena, and if so, in which conditions. An earlier version of this paper was presented at the International Conference on Heat Exchanger Fouling and Cleaning – 2015 in Enfield (Dublin, Ireland) [27].

APPROACH

A single heat exchanger tube is considered. The model comprises three domains: Tube-side, tube wall and fouling deposit layer. The models and solution method are given elsewhere [26] and are not reported here. The model is dynamic and distributed in space and evaluates fouling as function of local conditions.

This paper focuses on thermal fouling of organic materials, with the layer modelled as a two pseudo-components system: fresh material, or 'gel', and aged deposit, or 'coke'. The fresh deposit is assumed to be entirely composed of gel while coke is exclusively formed in-situ from the gel following a first order kinetic model. The thermal conductivity at each point in the layer is affected by the transformation of gel to coke (hence by the composition/temperature history at each point).

In a general formulation, the change in thickness is given by the contribution of deposition, suppression and removal, if all of them are well defined. Here we are interested in testing the deposition-offsetting processes independently (assuming that one of them is clearly dominant).

First, we need to define the situation we wish to represent. It is assumed that a suppression mechanism occurs in the oil phase, before the foulant has settled on the surface, hence it does not interact with the deposit itself. If deposition exceeds suppression, material builds up on the surface contributing to the layer growth. Once deposited, the matter remains undisturbed by the fluid flow. If suppression equals or exceeds deposition, the layer stops growing (all approaching foulant is repelled to the bulk before attaching). The properties of the layer (even at the surface) are then only affected by thermal processes or reactions such as ageing. The local change in deposit thickness due to suppression (with no removal) is:

$$\rho_l \frac{d\delta_l}{dt} = \max(0, n_{d,gel} - n_{s,gel}) \qquad (2)$$

where $n_{d,gel}$ and n_s are the deposition and suppression rates (mass fluxes) of gel, δ_l is the deposit thickness and ρ_{gel} is the density of gel. Negative fouling rates are not allowed.

A removal mechanism disrupts the deposit to a certain depth of the layer, depending on the shear forces, the properties of the layer and type of removal (e.g. a tearing off mechanism may affect greater portions of the layer than erosion, which would be rather superficial). As a result of the continuous deposition-removal, that portion of the layer is continuously renewed. Here, it is assumed that the depth of influence is small, i.e. the effect of removal is superficial (erosion), and removal can be captured as a boundary condition for the deposit layer. The local change in thickness due to removal (with no suppression) is:

$$\rho_l \frac{d\delta_l}{dt} = n_{d,gel} - n_r \tag{3}$$

where n_r is the removal rate (mass flux) and ρ_l is the density of the layer at the surface. The thickness of the layer may increase or decrease. If the thickness decreases, the net effect is that the top layer disappears and the underlying matter (with its own concentration-temperature history) is exposed to the removal mechanism.

If the depth affected by removal is significant compared to the total thickness of the layer, the single layer approach discussed may not be valid. A suitable model for this part of the layer should be defined (not considered here).

An overall model, including deposition, suppression and removal is therefore:

$$\rho_l \frac{d\delta_l}{dt} = \max\left(0, n_{d,gel} - n_{s,gel}\right) - n_r \tag{4}$$

CASE STUDY: SUPPRESSION VS. REMOVAL

The objective of this case study is to investigate, using the model discussed, the phenomena offsetting deposition (removal and suppression) and link them to measurable performance indicators, such as deposit thickness (hydraulic) and temperature (thermal). Deposit thickness, however, is difficult to measure directly. For a tube, pressure drop is taken as an indicator of fouling layer thickness. It should be noted that variations in deposit's roughness have been neglected. This assumption is a good approximation for the deposition-offsetting mechanism here considered (suppression and removal by superficial erosion). However, the variation of this quantity may be important in other cases.

The base case considers a single tube in an oil refinery heat exchanger. Geometric parameters of the tube, physical and fouling properties of the crude oil and operating conditions representative of typical values in oil refineries, are selected (Table 1). Uniform wall temperature (UWT) at the tube wall is assumed. The impact of other wall boundary conditions, such as uniform heat flux, is discussed elsewhere [24]. For UWT, the thermal impact of fouling is observed in the outlet oil temperature and heat duty. For alternative operation modes, such as uniform heat flux, the thermal impact would be observed in the wall temperature.

The deposition and deposition-offsetting rates are calculated as a function of the local conditions based on an adaptation of the Ebert–Panchal threshold model [26], where:

$$n_{d,gel} = \alpha' Re^{-0.66} Pr^{-0.33} exp\left(-\frac{E_f}{R_g T_{film}}\right) \tag{5}$$

$$n_{s,gel} = \gamma_s' \tau_w \tag{6}$$

$$n_r = \gamma_r' \tau_w \tag{7}$$

This correlation was chosen for coherence with previous works [25]. In the original correlation a single deposition-offsetting term (with a single parameter γ) is defined, leading to the vexed question approached in this paper. Values of the three adjustable parameters are reported in various studies fitted to lab or plant data [25, 28, 29]. In order to study the two mechanisms independently, two limit scenarios are considered:

- Suppression is the dominant offsetting mechanism and removal is negligible: $\gamma_s' = \gamma'$, $\gamma_r' = 0$, and Eq. (4) is simplified to Eq. (2).
- Removal is the dominant mechanism and suppression is negligible: $\gamma_r' = \gamma'$, $\gamma_s' = 0$, and Eq. (4) is simplified to Eq. (3).

As a result, three parameters are required as in the original correlation. Here, representative values for the three parameters were chosen (reported in their modified form in Table 1). A sufficiently high value of γ' was chosen to permit moving to non-fouling conditions within the typical allowable velocity range in heat exchangers (up to 3-3.5 m/s).

Threshold conditions are identified by solving the fouling equation (Eq. (2) or (3)) for change in thickness equal to zero. The case considered is of constant mass flowrate of oil, i.e. where flow velocity changes due to change in flow radius as a result of fouling build up or depletion. It is noted that the location of the threshold changes with flowrate.

The threshold curve is represented in terms of film temperature (T_{film}) versus average velocity (u). For the fouling parameters and inlet conditions in Table 1, the threshold loci are shown in Figure 2 (dashed line). The variation of film temperature and velocity as a result of fouling (here referred to as T_{film}-u path) and the deposit thickness at the tube midpoint are also shown in Figure 2 for the *no ageing* case. Starting with a clean tube, the tube operates on the fouling side of the Threshold (point A in Figure 2). As a result of fouling build-up, T_{film} drops quickly initially, more slowly at long times. The velocity, on the other hand, increases at a greater rate at later stages (as flow radius decreases). The line gradually approaches the threshold but still does not reach it after 1 year (point B in Figure 2).

The form of Eq. (2) and (3) suggests that suppression and removal lead to the same behavior when the net deposition rate is positive. The behavior is expected to be different when moving to conditions on the no-fouling side of the threshold. In order to investigate this point, the following operation schedule is considered, consisting of three periods in sequence:

Period 1, of fouling build up for 150 days at constant mass flowrate M=0.3 kg/s starting from a clean tube; Period 2, a high velocity period (M=0.6 kg/s) for 80 days, in order to move to the no-fouling side of the threshold; and Period 3, when the velocity returns to fouling conditions (M=0.3 kg/s) for 50 days. This is similar to the experiments carried out in the Batch Stirred Cell system cited in the introduction [18], but is applied here to a heat exchanger tube under operation conditions and time scales relevant to fouling in PHT heat exchangers. Ageing is expected to affect the thermal and rheological properties of the layer. Three cases are considered: a) No ageing; b) Fast ageing; c) Fast ageing with consolidation (hardening of the deposit).

No Ageing

During Period 1, the behavior of the system follows the one shown in Figure 2 for the first 150 days. Once the flowrate increases to 0.6 kg/s, operating conditions move over the threshold to no-fouling conditions (Figure 3). The increase in flowrate moves the threshold line to the left, as also shown in Figure 3, increasing the distance between the new operating conditions and the threshold loci. Figure 3 also shows in the inset the velocity profile over time for the three periods. Key times at the beginning and end of each period are indicated: end of Period 1 (i), Period 2 (ii to iii) and Period 3 (iv to v). The paths followed by the two models with suppression only (Eq. (2)) and removal only (Eq. (3)) are overlaid in Figure 3. With the suppression model, the deposit layer remains undisturbed during the no-fouling Period 2 (from ii to iii). When the velocity is decreased, the system returns to the same T_{film}-u conditions (point i) as applied prior to the high velocity period (i.e., points i and iv overlap) and fouling is resumed from there in Period 3. With the removal model, T_{film} increases during Period 2 due to partial removal of the layer; as a result, the system resumes from a less fouled situation at the beginning of Period 3, and the T_{film}-u path shows a hysteresis cycle due to the decrease in thickness.

The impact of the two deposition-offsetting mechanisms on the primary measurable variables (oil outlet temperature and pressured drop) is shown in Figure 4. Also shown in Figure 4 are the profiles of a derived quantity (fouling resistance) and a usually unmeasured quantity, deposit thickness, as well as all profiles for the reference base case (fouling at constant initial conditions). After the threshold is crossed, with suppression the layer stops growing and the thickness is constant in Period 2 (Figure 4a). With removal, the layer thickness decreases approximately 0.34 mm during the high flowrate period. There is a sudden decrease in outlet temperature in both cases as a larger amount of oil is heated (Figure 4b). With suppression the outlet temperature remains constant, whilst with removal there is a 3.3ºC increase, as consequence of the reduction in thickness. As discussed, the impact of fouling on the thermal behavior is less significant at later stages; hence the effect on the outlet temperature is relatively small, but still noticeable.

The impact on pressure drop (Figure 4c) is clearly distinguishable between the two cases: pressure drop stays constant with suppression and gradually decreases (about 4.3 kPa) with removal during the high flow period. Opposite to thermal effect, the effect on pressure is more significant at a late stage.

For comparison with traditional methodologies, the tube-average fouling resistance (referred to the outer tube area) is also calculated as an indicator of the change in thermal performance. The fouling resistance, shown in Figure 4(d), follows the same pattern as the thickness, which is expected in this case since no ageing is taking place and the conductivity is radially uniform throughout the deposit.

In conclusion, if no ageing occurs, the nature of deposition-offsetting mechanism could be identified from measurement of either thermal (temperature, resistance) or hydraulic (ΔP) effects in the experiment proposed.

Fast Ageing

Organic matter is likely to undergo ageing under the operating conditions considered here. The previous numerical experiment is repeated with a fast ageing deposit (Table 1). The T_{film}-u path for this case is shown in Figure 5. The ageing process introduces hysteresis in the T_{film}-u path during the high flow Period 2 even with suppression and this effect is amplified with removal. The increase in T_{film} during the high flow period is due to the improved heat transfer properties of the deposit (conductivity) as a result of the partial conversion of gel to coke. This effect is explained in detail below.

The gel-coke concentration radial profiles (and consequent conductivity profiles) at the midpoint of the tube at key times are shown in Figure 6. With suppression, during Period 2 (ii→iii) the thickness of fouling layer does not change, but the deposit undergoes ageing (even at the layer surface) of gel to coke (Figure 6a). This coking of the layer entails an increase in conductivity (Figure 6c, ii→iii), hence an enhancement of heat transfer and higher T_{film}. With removal, a reduction of the deposit thickness occurs in addition to ageing causing a reduction in velocity, a further reduction in thermal resistance and an increase in T_{film}. The corresponding concentration and conductivity profiles are shown in Figure 6d and Figure 6f, respectively (ii→iii).

Once the flowrate returns to the initial value (point iv), the concentration at the layer boundary returns to that of fresh deposit. In Period 3, the deposit layer grows again, but starting from different thickness in the cases of suppression (Figure 6b) and removal (Figure 6e), hence leading to different velocities and surface temperatures. With removal, the lower velocity and higher surface temperature also causes a slightly higher deposition rate. As a result, the thickness growth in Period 3 (iv-v) is (slightly) larger with removal. During Period 3, Figure 6 (b, e) shows a step in the concentration profile which separates the material built-up during Period 1 (older, close to the wall) and that built-up during Period 3 (newer, close to the surface). This step in concentration entails a corresponding step in thermal-conductivity (Figure 6c, f).

The thickness at the tube midpoint, outlet temperature, R_f and pressure drop are shown in Figure 7. The thickness and, hence, pressure drop profiles over time are very similar to those in the no-ageing case. The final thickness is slightly larger than in the no ageing case as a result of the higher conductivity and fouling rate.

Regarding the thermal effect, the profiles of outlet temperature (Figure 7b) and fouling resistance (Figure 7d) with suppression and removal are similar in shape, with a more acute variation during Period 2 for removal. If fouling resistance is taken as indicator, apparent negative fouling rates would be observed during Period 2 (high velocity). The time profile of the fouling resistance presents a saw-tooth shape in both suppression and removal cases, and therefore this kind of response cannot be used in isolation as an indicator of removal, as suggested by Crittenden *et al.* [17]. Unless very precise characterization of the ageing rate is available in advance, so as to accurately characterize the thermal behavior, the use of pressure drop measurements is necessary (and sufficient) to unmask the dominant process offsetting deposition.

Fast Ageing: two high-flow periods

The results presented above show that a reduction in fouling resistance does not necessarily imply removal of part of the deposit. That conclusion is only valid if the conductivity is uniform throughout the fouling deposit, which in the system studied here implies negligible ageing. Under industrial operating conditions ageing is thought to be relevant for long time scales [24]. On the other hand, as discussed by Wilson *et al.* [22], laboratory experiments are usually carried out under conditions that accelerate fouling. These conditions may also accelerate ageing, especially if high temperatures and uniform heat flux (which may lead to deposit overheating) are used. As a result, the negative fouling rates experimentally observed by Young et al. [18], although likely to be due to removal, cannot be taken as unequivocal proof of such mechanism.

Yang *et al.* [19] in a follow-up work seem to provide a more solid evidence of removal. An experiment with two high-speed periods (the first at 390 rpm, and then at 300 rpm) was carried out in a rotating fouling cell. The results showed a gradual decrease of fouling resistance over time in both periods, with the gradient being smaller in the second (300 rpm). Here, a mathematical simulation with an equivalent operations schedule was performed on the tube model by splitting the high speed period (Period 2) described in the previous section in two periods of equal duration with mass flowrates of: a) 0.6 kg/s in the first sub-period; b) 0.5 kg/s in the second one. The thermal resistances over time achieved with suppression and removal are shown in Figure 8. With removal, an abrupt change in the slope of the fouling resistance is observed. In the case of suppression, the fouling resistance shows a continuous profile with gradual change in slope (curvature).

In the experimental data presented by Yang *et al.* [19] it is difficult to appreciate how the transition between high-speed periods occurs because of the discontinuities introduced (the long-duration experiments were interrupted at night and restarted the following day). As a result, it is difficult to distinguish whether the change is slope is abrupt, which would support a removal effect, or gradual, which would not. Therefore, those experimental results may be explained by either a removal mechanism or a suppression mechanism with fast ageing, and cannot be considered an unequivocal proof of removal. Still, to our knowledge these results represent the most solid indication supporting the removal mechanism.

An experiment inverting the high-speed sub-periods, i.e. running the first period at 300 rpm and the second at 390 rpm, is suggested. If the slopes in each period remain the same as in the original experiment (i.e. faster decrease in fouling resistance for higher speed), the partial removal would be proved. An increase in the rate of decrease of fouling resistance after increasing flow speed could only be explained by that mechanism.

Removal with Consolidation by Ageing

So far it has been assumed that the mechanical strength (i.e. resistance to removal) of the deposit layer is unaffected by ageing. However, ageing is believed to harden the organic deposit, as discussed in the introduction. Fouling models exist that consider the resistance of the deposit to shear, although they were developed for systems different from refinery heat exchangers. Most models feature an inverse dependence of the removal term on the shear strength of the material (σ_f) and a direct proportionality to the shear stress, e.g. Bohnet *et al.* [5] for crystallization fouling of calcium sulfate. A similar approach is often used to describe soil erosion by water [30]. These models usually consider two parameters: “erodibility”, related to the strength of the soil (often considered inversely proportional to shear strength); and critical shear stress (τ_c), the minimum shear stress required to start eroding the soil:

$$n_r = \frac{K}{\sigma_f}(\tau_w - \tau_c) \qquad (8)$$

where *K* is a constant. In the case of crude oil fouling, there is no reported data for any of the above parameters to characterize the strength of the deposit and the resistance to shear forces. For simplicity, a critical shear stress is considered and assumed to depend on the composition of the layer at the surface. A removal model alternative to Eq. (8) is obtained by assuming a removal rate proportional to the difference between shear stress and this critical value:

$$n_r = \gamma_r'\left(\tau_w - \left(x_{gel}\big|_{r=R_{flow}}\tau_{c,gel} + x_{coke}\big|_{r=R_{flow}}\tau_{c,coke}\right)\right) \tag{9}$$

This formulation assumes a constant σ_f (in reality it would also depend on the deposit's composition), a substitution of the quotient K/σ_f by a constant γ', and a linear variation of the critical shear stress with the deposit composition. Here, values of $\tau_{c,i}$ equal to 0 (no resistance to removal) and 20 kPa are assumed for gel and coke, respectively. Representative values of τ_c were arbitrarily chosen within a reasonable range [30], to provide negligible resistance to removal of gel, significant resistance to removal of coke and show the effect of consolidation. Experimental characterization of deposits is required to find the actual dependence on concentration and characteristic values for fresh and aged deposit.

In order to explain the implications of the new removal model, the reader is referred to the evolution of the concentration profiles when ageing is significant and removal is the main deposition-offsetting mechanism (Figure 6d, e). During growth, the deposit at the boundary is entirely composed of gel. In that case, τ_c = 0 and Eq. (9) reverts to the original expression for removal (Eq. (7)). For net removal conditions (i.e. high velocity and conditions on the right of the threshold line in the T_{film}-u plot), the superficial part of the deposit is removed and the concentration at the deposit boundary gradually becomes that of older, inner layers, characterized by gradually higher coke content (Figure 6d). As the superficial layers are removed the value of τ_c increases accordingly to the degree of coking, reducing the removal rate.

The same three-periods simulation schedule proposed initially in this paper, with a single high-flow intermediate period, was again run with the removal and ageing-consolidation model. The gradual reduction in removal rate (as the critical shear stress increases) results in a displacement of the location of the threshold due to consolidation, shown in Figure 9. During the high flowrate Period 2 (ii → iii), as the concentration of gel at the surface becomes gradually lower (here only a few snapshots are shown), the deposit becomes harder and more difficult to remove. The result is that higher velocity is required to reach the threshold where, by definition, deposition rate = removal rate.

The impact of this consolidation on the deposit thickness, outlet temperature, pressure drop and fouling resistance is shown in Figure 10. The results (dashed line) are compared to those in Figure 7. The deposit thickness and pressure drop show an initial reduction at gradually decreasing rates, finally reaching a plateau. Whilst the first layer is easy to remove, the layers below present increasingly higher resistance to shear forces. At some point (with removal rate still far from a zero) the removal rate equals the deposition rate and the deposit thickness stabilizes. The thermal effect (outlet temperature and fouling resistance) is intermediate between those with suppression and removal but no consolidation. As in the previous case, thermal resistance alone is not sufficient but measurement of thickness (or pressure drop) changes in addition to outlet temperature allows distinguishing suppression from removal.

With severe consolidation, the reduction in pressure drop (or thickness) produced could be small and difficult to measure, and again it may not be possible to distinguish between suppression and removal based on hydraulic responses alone. Characterization of the ageing process and its effect on the properties of the deposit would be, again, required to decouple effects and a pre-requisite in understanding the dominant deposition-offsetting mechanism. Deposit tracer techniques have been used in other fouling systems to prove [9] and disprove [13] removal of the deposit, and therefore such techniques could also be used in combination with thermo-hydraulic measurements to resolve the question. Hardening of the deposit due to ageing does not necessarily imply the deposition-offsetting mechanism to be suppression, since removal could be still possible if there is a superficial (erosion type) process.

CONCLUSIONS

The phenomena potentially offsetting deposition in crude oil thermal fouling have been considered. A dynamic, distributed first-principles deposit layer model [26] was used to simulate the independent impact of suppression and removal on measurable thermal and hydraulic performance of a heat exchanger tube. Removal was assumed to be of superficial type (erosion). An operating sequence of three periods was considered: 1) deposit build up; 2) increase in flowrate moving to the no-fouling side of the threshold; 3) flowrate reduction to the original value with resumption of fouling. The simulations were performed for three cases: no ageing, ageing, and ageing with deposit consolidation.

It was shown that during a deposit layer growth phase, removal and suppression have the same effect and are therefore indistinguishable by thermo-hydraulic measurements alone. However, removal and suppression mechanisms give different responses during the high velocity period when velocity is increased to cross the threshold curve *after some initial fouling build up*. The results show that thermal effects may be unequivocally taken as an indicator of the dominant deposition-offsetting mechanism only when the deposit *does not age*. When ageing takes place, however, it contributes to the change in the observed thermal behavior. As a result, trends in temperature and fouling resistance for suppression and removal show similar shapes during the high speed period, with the changes being more pronounced in case of removal. Measurement of thermal effects alone is not sufficient to unequivocally resolve the dominant deposition offsetting mechanism. However, the results show that the simultaneous consideration of thermal *and pressure drop* effects in such an experiment would permit to correctly interpret the data and, subject to the required experimental sensitivity, would be sufficient to resolve the vexed suppression vs. removal question.

The conclusions above are valid for a schedule with two high flow periods as in the experiment by Yang *et al.* [19]: a first period at very high speed and a second period at (still high but) lower velocity. It was shown that the results reported from the experiments are not a conclusive evidence of removal. It was also suggested that inverting the order of the high flow periods (with two steps up in the velocity) would lead to more conclusive results in support of the removal hypothesis.

Finally, a modification of the removal term in the traditional Ebert-Panchal model was proposed to include a *critical shear stress*, formulated as a function of the composition of the deposit at the deposit surface. This was used to incorporate mechanical resistance properties of the deposit layer, and in particular to investigate the impact of ageing on the mechanical resistance of the deposit to shear. It was shown that mechanical consolidation by ageing, if acute, may hinder the ability to resolve deposition-offsetting mechanism even when hydraulic effects are measured.

From this analysis, it follows that the typical arguments used in literature to support one or other of the deposition-offsetting hypotheses are not sufficiently conclusive. The work presented here shows the risks of studying fouling merely based on thermal effects, and particularly on thermal resistance alone. To unambiguously distinguish the underlying phenomena, the following is required:

1. Accurate measurement over time of thermal performance and deposit thickness (directly or by measuring pressure drop in the case of a tube).
2. Characterization of ageing and its impact on the properties of the deposit, with special attention to its thermal conductivity and mechanical properties (i.e. strength).
3. Combination of thermo-hydraulic measurements with other experimental techniques, such as deposit tracers.

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NOMENCLATURE

A_a Ageing pre-exponential factor, 1/s

C_p Specific heat capacity, J/kgK

d Diameter, m

E_a Ageing activation energy, J/mol

E_f Fouling activation energy, J/mol

K Removal proportionality constant, kg/ m^2 s

L Tube length, m

M Mass flowrate, kg/s

n Mass flux, kg/m^2 s

Pr Prandtl number, $C_p\mu/\lambda$, dimensionless

R Radius, m

R_f Fouling resistance referred to outer tube area, m^2K/W

R_{flow} Radius at the fouling layer-fluid interface, m

R_g Ideal gas constant, 8.314J/molK

r Radial coordinate, m

Re Reynolds number, $\rho u d_o/\mu$, dimensionless

t Time, s

T Temperature, K

T_{film} FilmTemperature, K

u Linear velocity, m/s

UWT Uniform wall temperature, K

x Volume fraction, -

z Axial coordinate, m

Greek symbols

α, β, γ Constants in Eq. (1)., m^2 K/J, - , m^2 K/J Pa

α' Modified deposition constant, kg/ m^2 s

γ' Modified deposition offsetting constant, kg/ m^2 s Pa

δ_l Deposit thickness, m

ΔP Pressure drop, Pa

λ Thermal-conductivity, W/mK

μ Dynamic viscosity, Pa s

ρ Density, kg/m^2

σ_f Shear Strength, N/m^2

τ_c Critical Shear stress, N/m^2

τ_w Shear stress, N/m^2

Subscripts

i Inner

coke Aged organic deposit

gel Fresh organic deposit

l Layer

d Deposition

o Outer

r Removal

s Suppression

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Table 1. Parameters for single tube model test

Parameter	**Value**	**Parameter**	**Value**
R_i(mm)	9.93	UWT (ºC)	270
R_o(mm)	12.70	Inlet T (ºC)	200
L(m)	6.1	M (kg/s)	0.3
α' (kg/m^2 s)	0.94	E_f (kJ/mol)	30
γ (kg/m^2 s Pa)	$1.2\cdot10^{-8}$	E_a (kJ/mol)	50
A_a (no ageing)(s^{-1})	0	A_a (fast) (s^{-1})	0.01
λ_{gel} (W/m K)	0.2	λ_{coke} (W/m K)	1.0

List of Figure Captions

Figure 1 Schematic representation of suppression (deposition by chemical reaction (a) and particles (b)) and removal (c). Ageing is shown as a gradual darkening. The dashed line indicates the limit of the thermal boundary layer.

Figure 2 Threshold loci for constant mass flowrate (0.3 kg/s) (dashed line) and T_{film}-u path for growing fouling layer (no ageing) over a year at midpoint of the tube (z = 3.05 m). The inset shows the time profile of the deposit layer thickness at the same point.

Figure 3 Threshold (dashed) and T_{film}-u path and velocity over time at midpoint of tube (z = 3.05 m) for no ageing. In the inset, velocity profile over time.

Figure 4 Time profiles of (a) thickness at midpoint of tube (z = 3.05 m), (b) outlet temperature, (c) pressure drop, (d) fouling resistance, during Periods 1 to 3 for a deposit without ageing, for suppression and removal.

Figure 5 Threshold (dashed) and T_{film}-u path and velocity over time at midpoint of tube (z = 3.05 m) for fast ageing. In the inset, velocity profile over time.

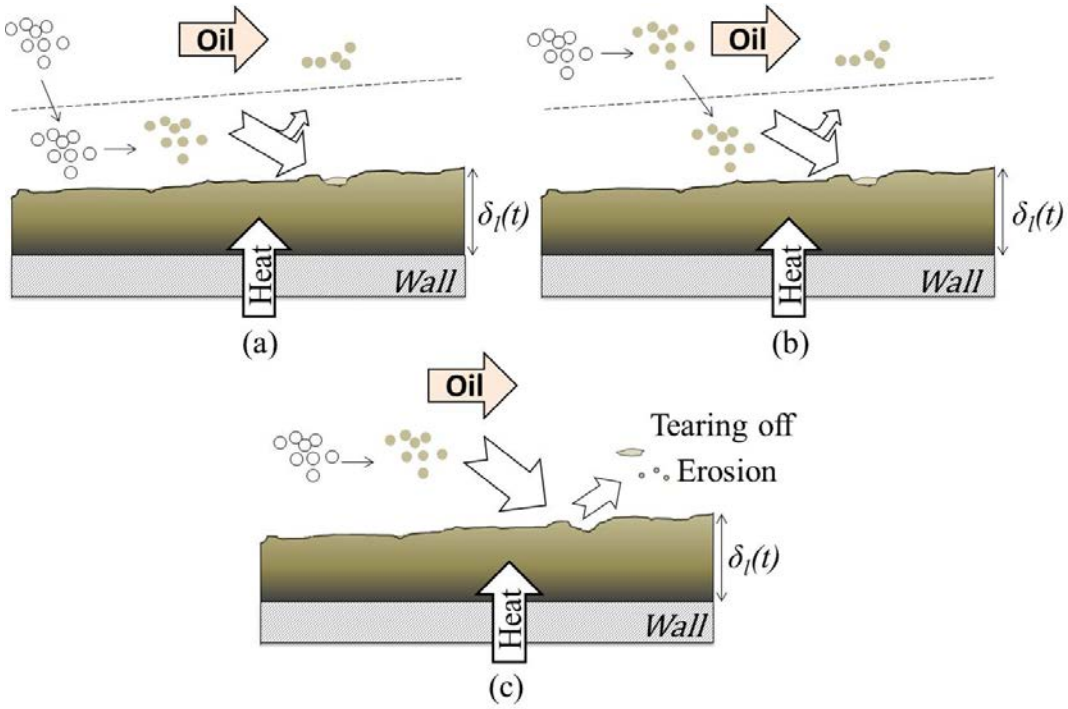
Figure 6 Thickness vs. radial volume fraction profile with suppression (a, b) and removal (d, e) and associated conductivity profile (suppression (c) and removal (f)) at tube midpoint (z = 3.05 m), at key times in Period 2 and 3 for fast ageing.

Figure 7 Time profiles of (a) thickness at midpoint of tube (z = 3.05 m), (b) outlet temperature, (c) pressure drop, (d) fouling resistance, during Periods 1 to 3 for a deposit with fast ageing, for suppression and removal.

Figure 8 Fouling resistance over time for two high-speed sub-periods considering removal and suppression mechanisms

Figure 9 Threshold displacement at the midpoint of the tube (z = 3.05 m) due to consolidation

Figure 10 Time profiles of (a) thickness at midpoint of tube (z = 3.05 m), (b) outlet temperature, (c) pressure drop, (d) fouling resistance during Periods 1 to 3 for a deposit with fast ageing, with suppression, removal and removal with consolidation by ageing.



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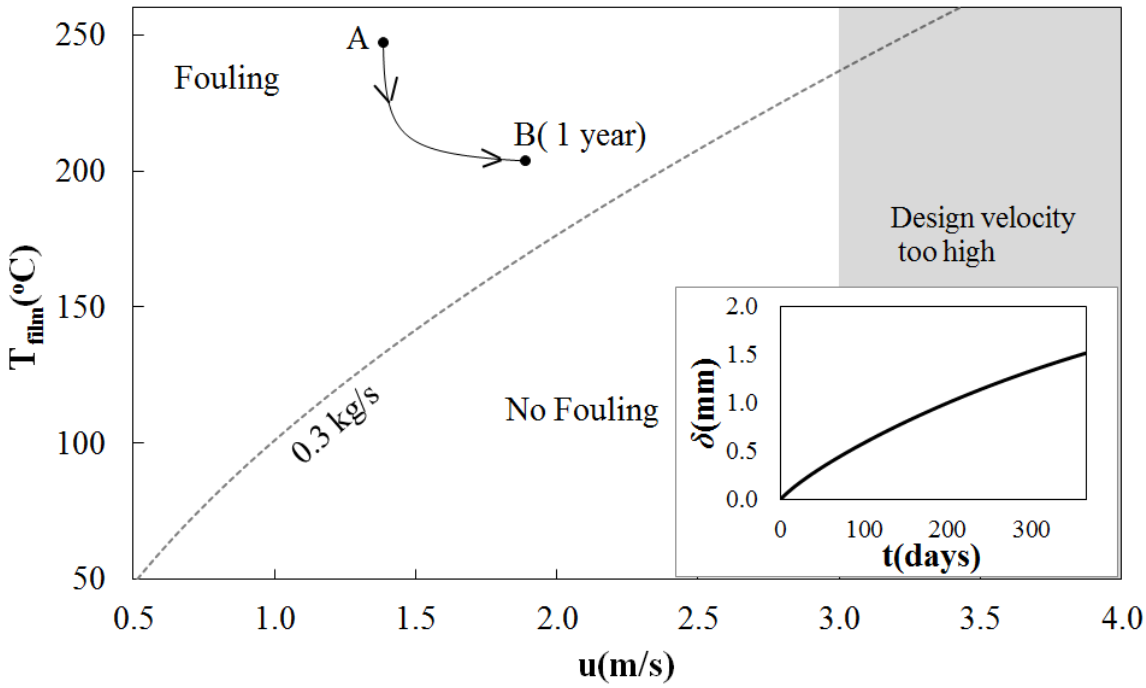

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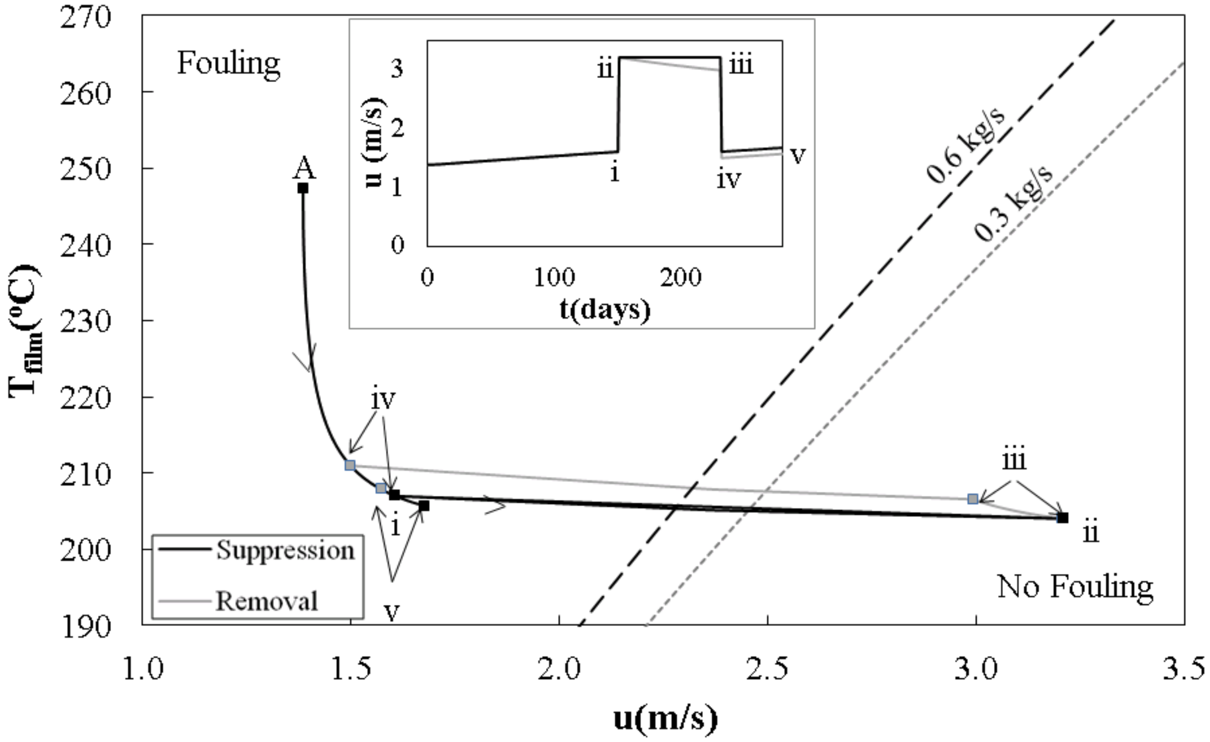

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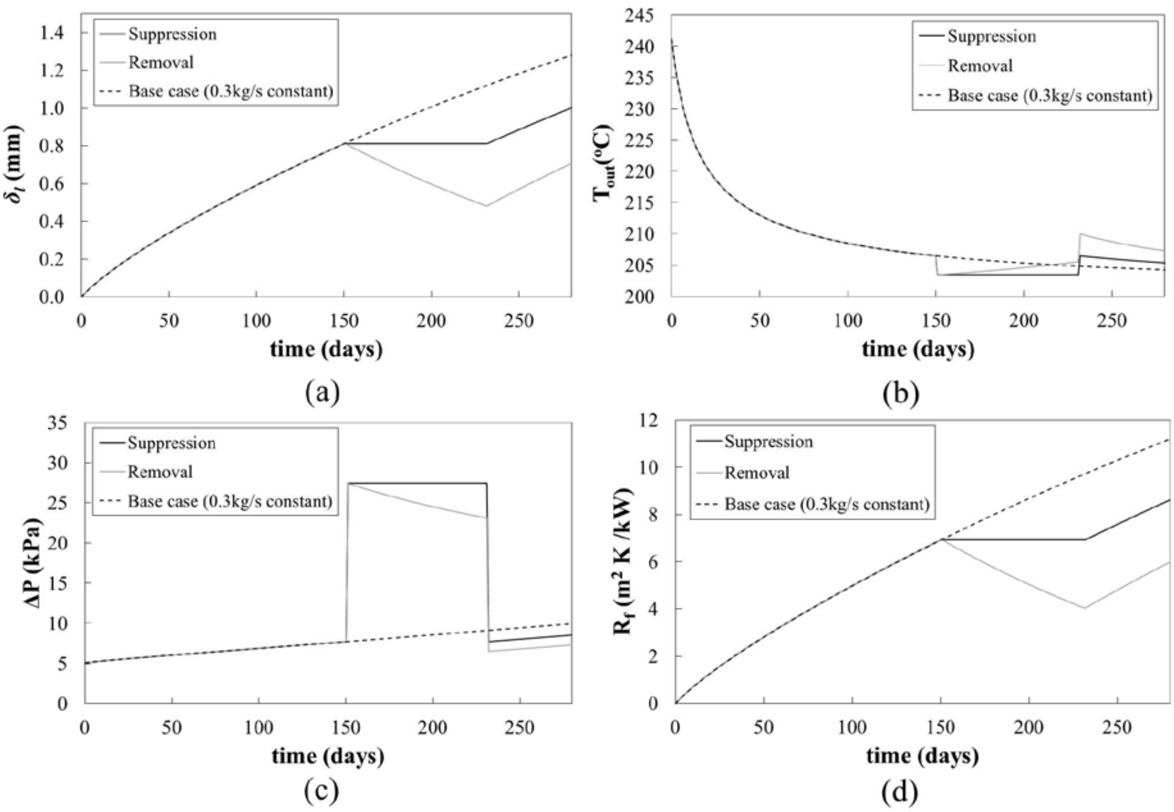

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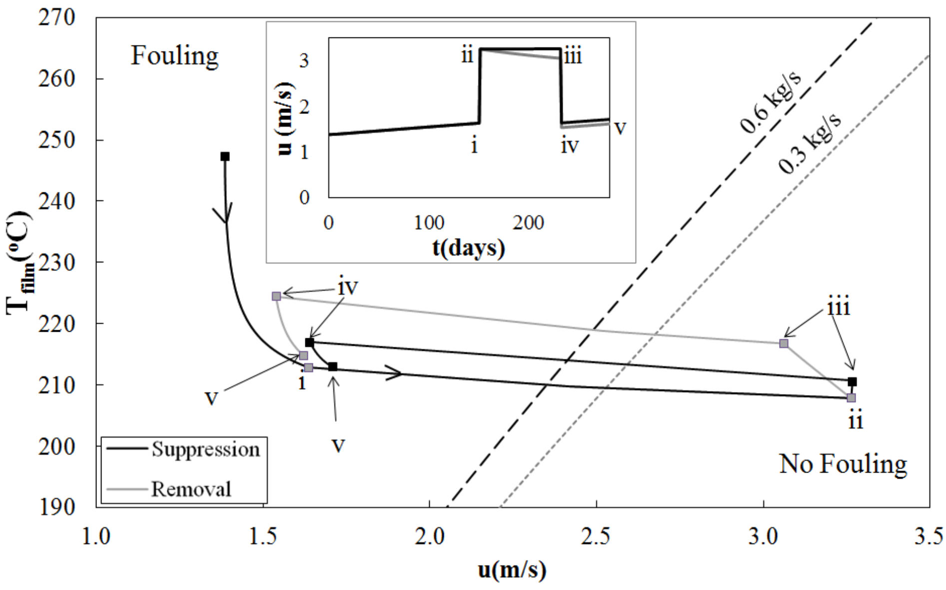

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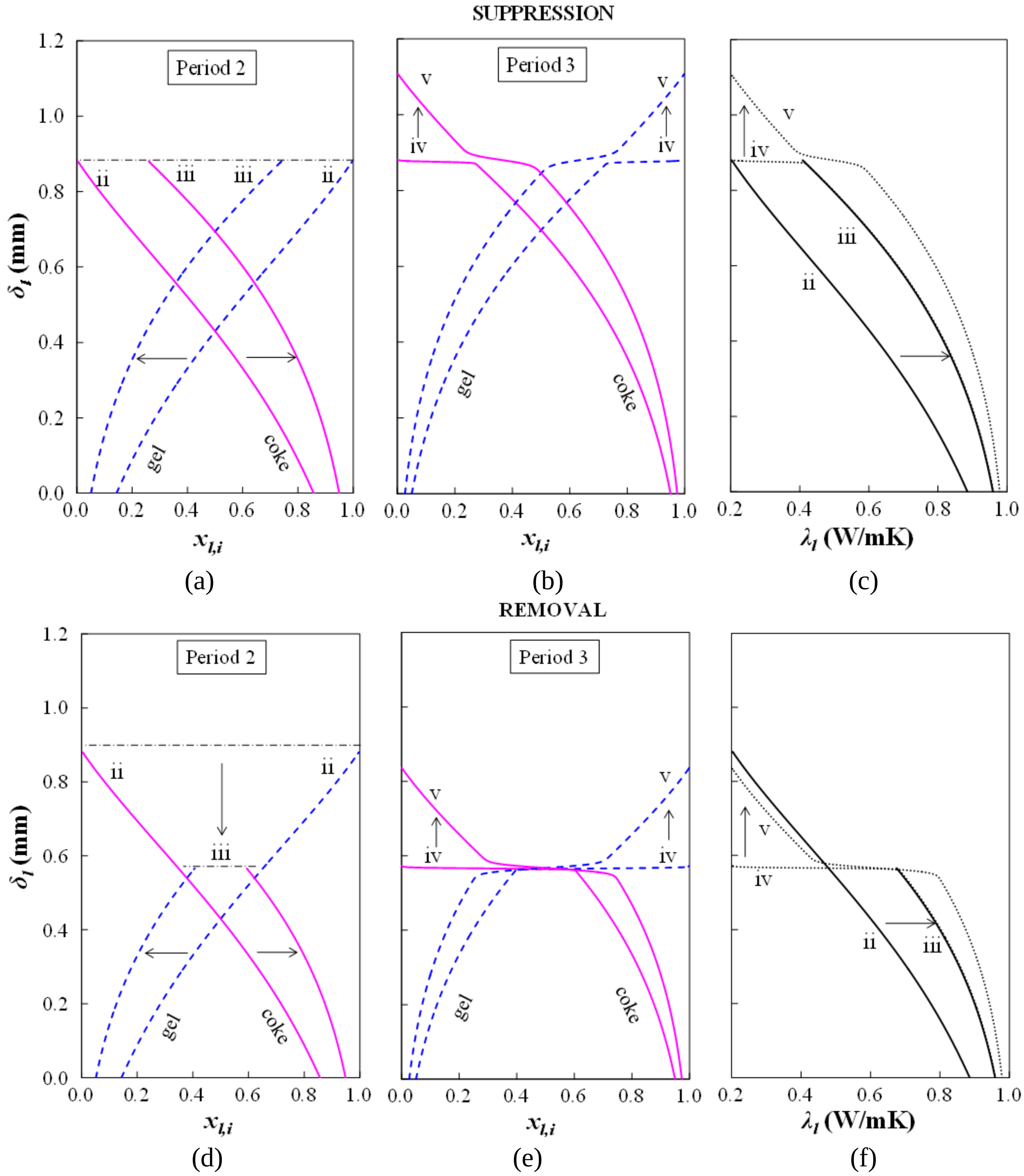

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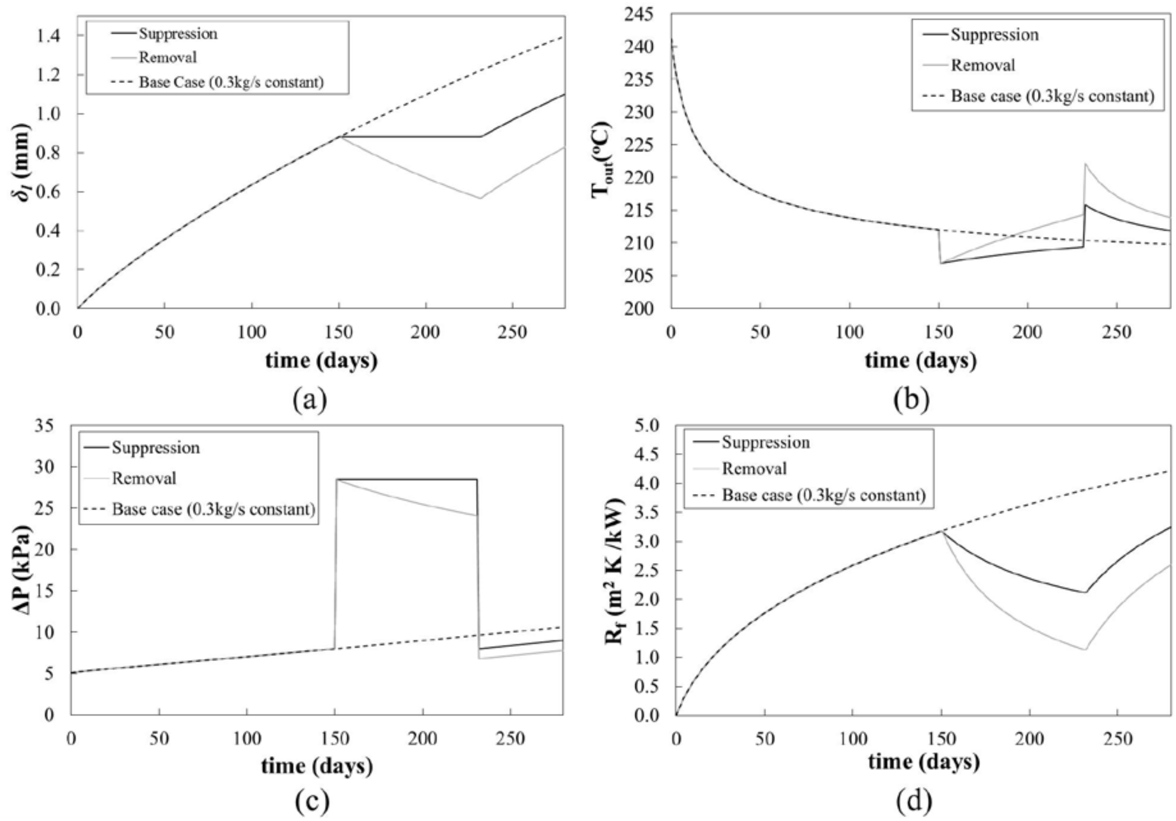

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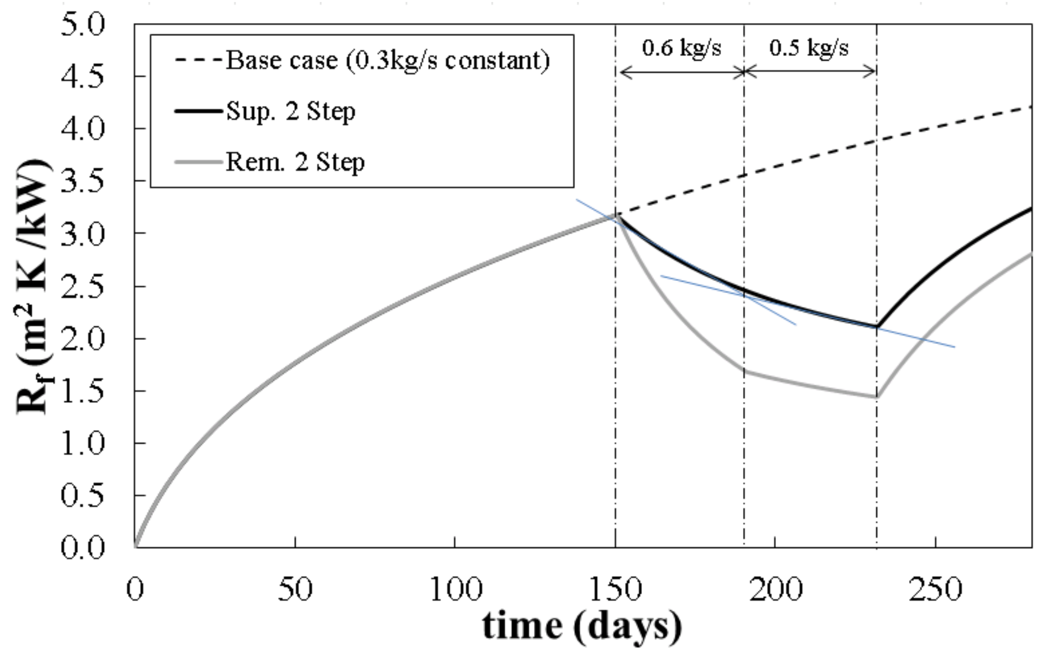

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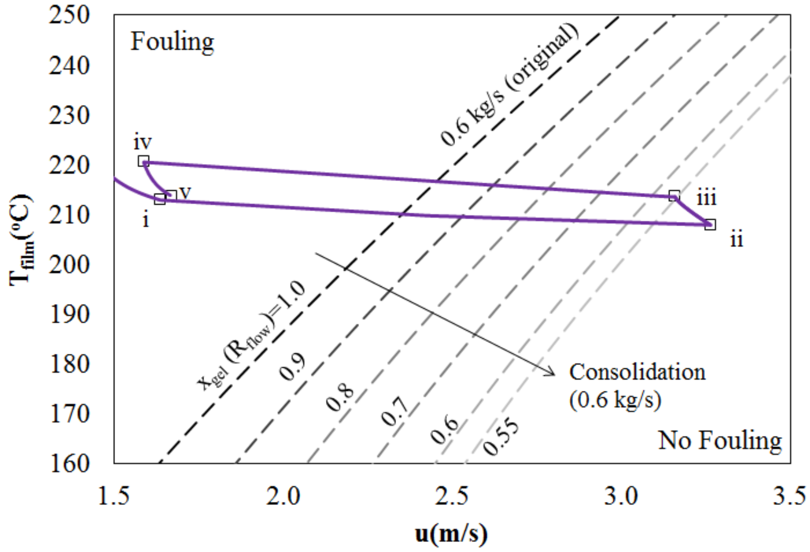

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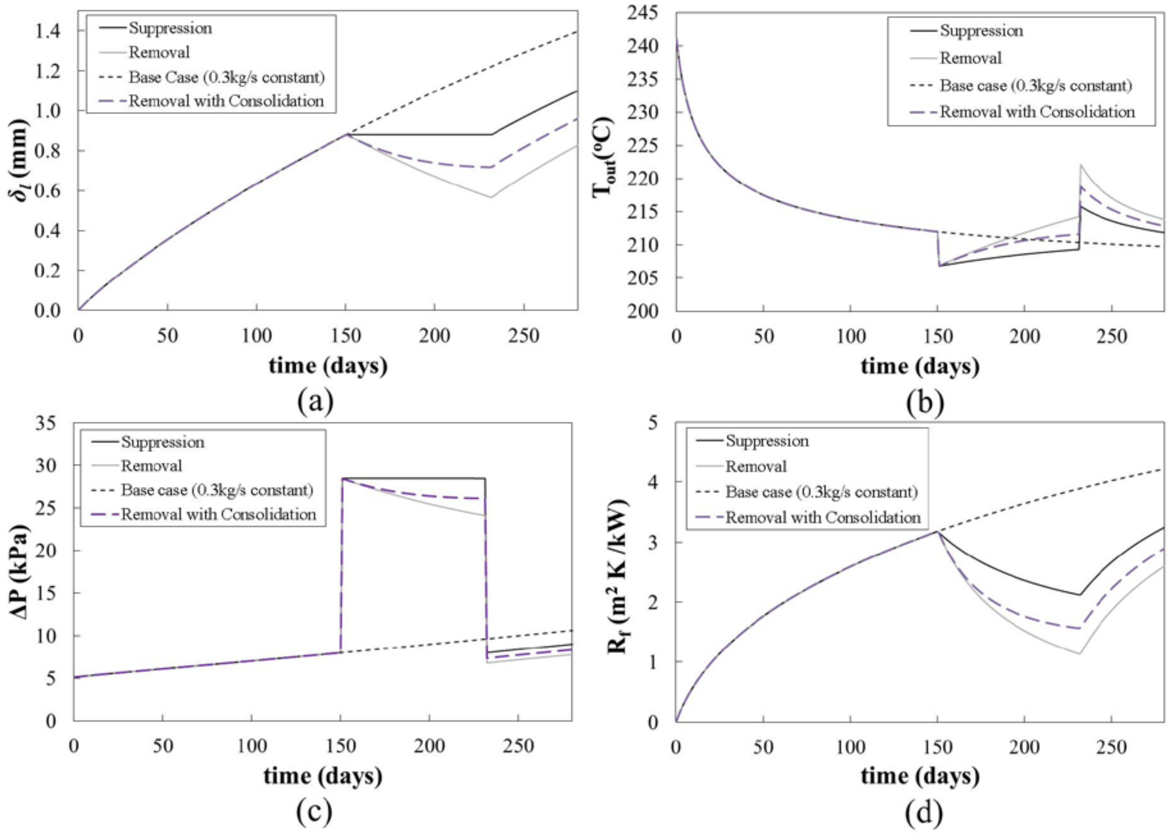

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