

AGEING: LOOKING BACK AND LOOKING FORWARD

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ABSTRACT

Ageing is the process of transformation of a fouling layer following its initial formation, whereby the deposit converts to another, usually more cohesive, form. Its importance, and the lack of understanding in this area, was identified by Epstein in a paper published in 1983. A review of subsequent work indicates that the topic has attracted significant attention in some fields since, particularly in the deposition of waxes in crude oil pipelines. A quantitative model of ageing in chemical reaction fouling, linking heat transfer with the evolution of deposit thermal conductivity, is presented here. This model, which is based on simple physical principles, is both plausible and computable, and highlights the importance of timescales, temperature sensitivities and mode of testing on the results obtained from thermal fouling experiments. Support for the modeling approach is given by laboratory measurements of thermal conductivity and data published by Fan and Watkinson (2008). Salient lessons are identified, particularly in relating experimental studies to operating units. The lessons are illustrated with a discussion of the impact of ageing in a heat exchanger on a crude oil preheat train. The need for further quantitative work in this area is highlighted, as well as the scope for exploiting current knowledge.

INTRODUCTION

Ageing (or aging) refers to the transformation of a fouling deposit after it has been formed on a heat transfer surface. In 1981 Epstein (published in 1983) identified ageing as one of the principal mechanistic stages in the process of fouling. In the same paper he described ageing as one of the fields in which the fundamental understanding was most poorly developed. It has attracted significant attention in some applications since, but in others it remains just another unknown factor in heat transfer.

Ageing plays an important role in most of the fouling mechanisms identified by Epstein: corrosion, biofouling, crystallization and chemical reaction. It could be argued that ageing plays a smaller role in particulate fouling, except when this occurs in parallel with another mechanism, or when the presence of a particulate deposit facilitates another mechanism such as the formation of biofouling in the pores of such a layer. Ageing arises because the fouling layer is,

by definition, a static layer of material on the heat transfer surface and is therefore exposed to process conditions over an extended timescale, which promote transformations which would not arise in the moving fluid during its passage through the unit.

Ageing is important because the transformations determine the physical and chemical nature of the deposit, and consequently

- (i) exchanger thermal and hydraulic behaviour;
- (ii) the dynamics of the fouling process;
- (iii) the nature of the material recovered after heat transfer is interrupted: ageing can mask the identity of the material originally deposited;
- (iv) the ease of removal, particularly in cleaning: the symbiotic relationship between fouling, ageing and cleaning was discussed by Wilson (2005).

Figure 1 depicts how wall conditions can differ from those in the bulk fluid in terms of temperature, thereby driving kinetic and thermodynamic changes.

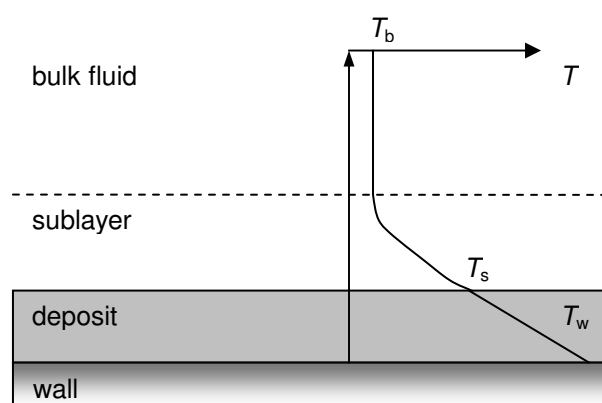


Figure 1 Schematic of temperature distribution in a heat transfer unit subject to fouling, with wall temperature T_w , bulk temperature T_b and deposit-fluid interface temperature T_s .

Other distributed factors include *concentration* (e.g. of oxygen), giving rise to different reaction mechanisms such as anaerobic digestion in biofilms and electrochemical potential, enhancing corrosion; and *shear* imposed by the fluid. Within the stationary deposit there may occur

diffusive mechanisms which have longer timescales than those associated with the flowing fluid. The key condition(s) will depend on the fouling mechanism and associated chemistry.

Furthermore, there often exists a gradient in conditions across the deposit which drives diffusion and structural rearrangement. Local variation is a common factor in reported cases of ageing effects. Examples include:

(a) *Biofouling*: the variation in oxygen and temperature across a biofilm can result in the wall region being dominated by anaerobic processes, which can give rise to deposit sloughing – the rarer example of ageing reducing fouling, but which can also promote corrosion. Biofilms, being composed of cells, are also subject to physiological ageing (Melo, 1999), which adds a layer of complexity to the phenomenon.

(b) *Water scaling*: crystallisation fouling rarely involves direct growth of a surface layer from the fluid, the exception being solidification of ice in water freezing applications (e.g. sea ice, ice cream manufacture). An initially porous crystalline matrix becomes denser over time as secondary crystallisation occurs in the pores (driven by temperature gradients and diffusion). The microstructure and thereby properties (density, strength *etc.*) evolve over time. Bohnet and co-workers (e.g. Brahim *et al.*, 2003) reported quantitative data demonstrating the existence of four different microstructures in calcium sulphate scales. The material next to the wall in their experiments (performed under constant heat flux) was exposed to the highest temperature for long periods, which not only promoted further crystallisation but also transformation of the sulphate crystal to a different polymorph.

The latter illustrates a second ageing effect which may occur in aqueous system fouling, namely the initial deposition of less stable salts which gradually transform to a more stable form. In calcium phosphate scaling, although the thermodynamically stable salt is calcium hydroxyapatite, initial deposits in short (< 100 hour) experiments as reported by Singh and Watkinson (2001) and others, are an amorphous calcium phosphate or octa-calcium phosphate, which age over longer times to hydroxyapatite (Tung, 1998).

(c) *Wax deposition* at a cold wall is another example of crystallisation fouling, and has received considerable attention since Epstein's 1983 paper owing to its importance in subsea and Arctic crude oil production. Although workers disagree on the mechanisms controlling wax deposition (see Bidmus and Mehrotra, 2008; Hoteit *et al.*, 2008), there is widespread agreement that the nascent wax gels formed at the surface harden over time. Tiwary and Mehrotra (2009) reported estimates of deposit thermal conductivity and density over time, which increased asymptotically to limiting values. Toma *et al.* (2006) used a two-zone model to describe the build-up of deposit, where the zone adjacent to the fluid was relatively soft, and subject to deposition and removal, while the layer next to the wall was hard. Hardening has been shown to be due to the increased level of higher carbon number paraffins, which migrate to the wall by diffusion through the pores. The

thermo-diffusive or counter-diffusive mechanism has been investigated in detail by Fogler and co-workers (e.g. Singh *et al.*, 2000; 2001a,b), while Coutinho *et al.* (2003) have suggested that recrystallisation and Ostwald ripening also occur. Tiwary and Mehtora (2009) related their observed changes in deposit properties to a time-dependent shear mechanism, which they quantified in terms of a 1-dimensional structural model. Their 'viscoplastic' model (their label) describes *thixotropy*, and in emphasising that ageing involves microstructural evolutions highlights links to the large body of work on this topic in the rheological literature.

(d) *Molecular transformation*, often observed in chemical reaction fouling whereby the original foulant species undergoes further reaction, promoted by high temperatures in the deposit, to form a more pernicious and adherent product. One of the earliest descriptions of ageing is that in crude oil fouling presented by Nelson in 1934 and elaborated as a two-layer concept (oil and coke) in coker fouling by Atkins in 1962. This two-layer model (tar layer and coke) was formalised in a mathematical model by Crittenden and Kolaczowski in 1979: the field has not advanced much further in chemical reaction fouling owing to the difficulty of quantifying the parameters even for a two-layer model.

Conversion of asphaltenes to coke is illustrated by Dickakian (1990), where at high temperature the first 30 minutes of experiment yielded a deposit consisting of 100% asphaltenes and no coke. At a longer duration, of one hour, analyses of the (more extensive) deposit indicated compositions 95 % asphaltenes-5% coke, and after 2-hours 20% asphaltenes-80% coke. In this meeting, Fan and Watkinson (2009) present isothermal thermogravimetric data for the kinetics of weight loss as heavy oil deposits are aged thermally.

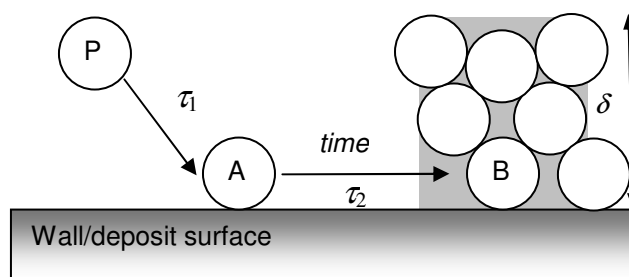


Figure 2 Schematic of ageing: precursor P gives rise to deposit element A which ages to give aged element B in the layer of thickness δ .

Timescales

Ageing is noticed when the properties of aged deposits differ from the original form, and when the timescale associated with the attachment of a precursor P (Figure 2) to form deposit species A, τ_1 , is much shorter than that associated with the timescale required to convert A to the final form, B, labelled τ_2 . If τ_2 is comparable to τ_1 , or smaller, P appears to yield B directly and ageing does not appear to have an impact on the process. It can, however,

still be important as the deposit recovered from the surface, being B, is not the material initially deposited.

Laboratory investigations of fouling, with the exception of wax deposition studies, rarely report deposit ageing. This could be because the timescale of these studies, usually of the order of days, is short compared to τ_2 . One exception is the asphaltene-coke transformation reported by Dickakian (1990) summarized above. Plant timescales, however, are often of the order of years (10^2 - 10^3 days) and ageing can therefore be important. An illustration is given in Figure 3, which demonstrates how ageing should be considered in data reconciliation studies of crude oil fouling. Here, simulation models of a plant heat exchanger incorporating fouling were tuned on the basis of an initial set of operating data. The model incorporating ageing was able to predict the observed behaviour into the future (when time approaches τ_2), whereas the model without ageing could not be made to agree. Extra parameters were required to fit the model, but these were based on a sound ageing concept. Further details are given in Coletti and Macchietto (2009).

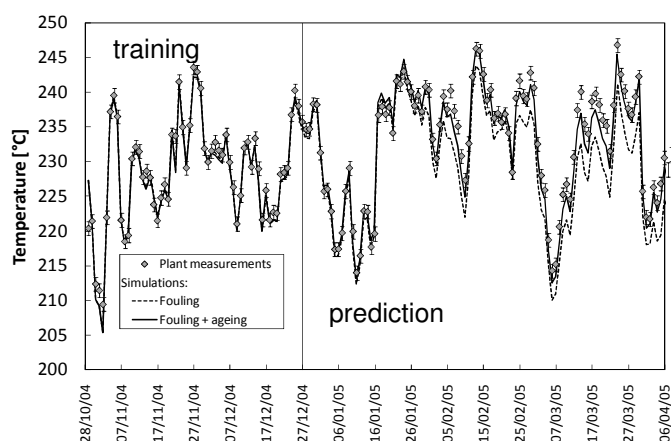


Figure 3 Comparison of plant data with predictions given by heat exchanger simulation models incorporating fouling but no ageing (dashed lines) and fouling with ageing (solid line). The first 100 days were used to estimate the parameters in the models: subsequent calculations are predictive. Data from a refinery preheat train exchanger processing crude oil on the tube-side. After Coletti and Macchietto (2009), reproduced with permission.

Extrapolating results obtained in a laboratory environment to plant operations is therefore subject to these timescale considerations. Some of the particular problems are explored using the quantitative model presented here.

Impact of Ageing

In heat exchanger applications, the deposit properties of interest will be those affecting heat transfer and pressure drop. The thermal impact of fouling is often expressed in terms of the fouling resistance, R_f , which can be approximated by

$$R_f = \delta / \lambda_f \quad (1)$$

where δ is the thickness ($\propto$ volume) of the deposit layer and λ_f its thermal conductivity. Pressure drop is sensitive to thickness and surface roughness: it could be argued that these are less likely to be sensitive to ageing as shrinkage/expansion are not expected over time, and roughness will be dictated by the nature of the fresh deposit.

Thermal conductivity, however, is likely to be affected by ageing as fouling deposits are usually heterogeneous and therefore sensitive to microstructure, particularly porosity (see Wang *et al.*, 2008), and the thermal conductivity of the components. The latter is particularly important in carbonaceous materials, where the difference in thermal conductivity between structures can vary by orders of magnitude. Whereas mineral oils have λ values of ~ 0.1 - 0.2 W/m K, the highly ordered form of carbon, graphite, exhibits values of 25-470 W/m K, depending on orientation. Cokes and related carbonaceous deposits represent intermediate stages in the formation of graphitic materials (Appleby *et al.* 1962). Kern (1988) reported a λ value of 5.8 W/m K for petroleum coke at 100°C: Maksimovskii *et al.* (1990) reported λ values of pyrolysis unit cokes ranging from 1-4 W/m K, with a strong dependence on porosity. This aspect, of thermal change of carbonaceous deposits generated by chemical reaction fouling, is considered further in this paper.

Zhenhua *et al.* (2008) have reported values of 1.7-2.2 W/m K for calcium carbonate scale formed from water in forced convective heat transfer. Their thermal conductivity values were obtained using Eqn. (1), substituting calculated fouling resistance values (obtained through temperature measurements) and average deposit thickness measurements. Singh and Watkinson (2001) reported estimates of λ_f obtained using the same approach for calcium phosphates, of 1.02 ± 0.2 W/m K for scales of densities 1470 ± 370 kg/m³.

Where the thermal conductivity of 'fresh' and 'aged' deposit differ noticeably, Equation (1) shows that the direct impact of ageing, in increasing λ_f , serves to decrease R_f – a thermal measure – but not the hydraulic impact of fouling (as δ does not change). Estimates of λ_f based on pressure drop estimates will therefore vary with time.

Thermal conductivities of fouling layers are seldom reported, partly due to the difficulty in measuring δ in situ. Estimates with δ based on pressure drop (and therefore sensitive to surface roughness) are sometimes reported. Davies *et al.* (1997) reported λ_f values for whey protein deposits obtained by heat transfer tests with clean liquids after fouling, and found that λ_f increased with surface temperature: ageing was also indicated by the change in appearance of the deposit. Tuladhar *et al.* (2002) reported λ_f values for whey protein deposits obtained using their fluid dynamic gauging technique to determine δ directly, but this remains an area where more information is needed.

This paper considers the impact of changing thermal conductivity on the ageing process itself, in the context of chemical reaction fouling. Local temperature is an important factor in most processes associated with ageing: a chemical reaction can be expected, as a first approximation,

to exhibit Arrhenius dependency on temperature, for example. The impact of changing thermal conductivities on the temperature distribution can be illustrated by a simple heat transfer calculation based on Figure 1. Consider heat transfer from a hot wall: equating heat fluxes at the deposit surface, q , gives

$$q = h(T_s - T_b) = \frac{1}{R_f}(T_w - T_s) \quad (2)$$

where h is the film heat transfer coefficient. Rearranging this in terms of the fouling Biot number, $Bi_f \equiv h \cdot R_f$, gives

$$(T_w - T_s) = \frac{Bi_f}{1 + Bi_f}(T_w - T_b) \quad (3a)$$

and

$$(T_w - T_s) = Bi_f(T_s - T_b) \quad (3b)$$

Both equations show that increasing fouling (and Bi_f) results in the temperature difference across the deposit increasing. If ageing causes λ_f to increase, Bi_f decreases, with different consequences depending on the mode of operation:

(a) *Constant temperature driving force, $T_w - T_b$*

This approximates to conditions in non-furnace heat exchangers, where T_w and T_b do not vary markedly over time. Equation 3(a) indicates that a lower value of Bi_f results in T_s being closer to T_w , and therefore more heat is transferred. However, the fouling rate will be sensitive to T_w ; if this is higher, for many chemical reaction fouling mechanisms the rate of fouling is likely to be higher. The layer thickness, δ , however will not decrease and so the deposit will grow at a faster rate, with the change in pressure drop more noticeable than the loss in heat transfer.

(b) *Constant heat flux operation: q constant*

If h remains constant, Eq. 3(b) shows that the temperature difference across the deposit increases with fouling: this is the basis of many fouling measurements in constant heat flux operation. This increase in temperature across the deposit will, however, accelerate any transformations sensitive to local temperature. It is noteworthy that T_s in (a) is bounded between T_w and T_b , whereas here, in the case of a heated wall, there is only a lower limit, of the initial value of T_w . Constant heat flux tests are, therefore, prone to accelerate ageing and this must be considered when translating data from such tests to plant operations. Deposit analysis after different times in such tests is therefore recommended in order to monitor transformation. Under this mode of operation, T_s remains constant so the deposition rate will not change over time. A reduction in Bi_f due to higher λ_f will reduce T_w and therefore retard ageing. This case corresponds to fired heater operation, but at furnace temperatures τ_2 is likely to be small, and the impact of ageing is not likely to be noticeable. Hence many furnace studies report the formation of coke rather than intermediate forms.

REACTION AGEING MODEL

We present a quantitative model describing the thermal effects of ageing based on simple reaction principles. This work was inspired by experimental studies on coker deposits at 550°C by Fan and Watkinson (2006, 2008) which demonstrated that ageing is associated with changes in chemical composition. A detailed description of the model is given in Ishiyama *et al.* (2009), and is supplemented here by simple experiments confirming some of the assumptions. Fan and Watkinson reported a decrease in deposit H/C ratio from 0.6 to 0.26 over three days, following a first order decay. This corresponds in chemical terms to an increase in structural order, interpreted as graphitization in Figure 4.

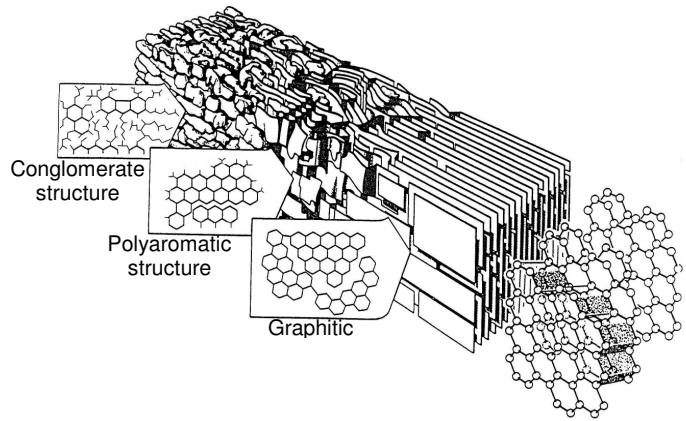


Figure 4 Deposit structural evolution model in high temperature ageing (following Marsh-Griffiths graphitization, 1982: reported by Fan and Watkinson, 2009)

Relating chemical composition to thermo-physical properties is not straightforward. Ishiyama *et al.* propose a simple relationship of the form:

$$\lambda_f = \lambda_{f,\infty} + [\lambda_{f,0} - \lambda_{f,\infty}] \cdot y \quad (4)$$

where $\lambda_{f,0}$ is the thermal conductivity of the initial foulant and $\lambda_{f,\infty}$ that of the final, aged form: y is a 'youth' variable, with initial value 1 and lower limit 0, which can be related to chemical or structural states.

Various models for the thermal conductivity of heterogeneous materials exist, relating the effective thermal conductivity, λ_{eff} , to the volume fraction and λ value of each phase. The effective media model of Wang *et al.* (2008) is used here. Figure 5 shows the λ_{eff} values estimated for a range of compositions of graphite powder ($\lambda = 4.4$ W/m K, density 1.64 g/cm³) and paraffin wax ($\lambda = 0.2$ W/m K, density 0.91 g/cm³), presented in terms of H/C ratio. It can be seen that over the range of H/C values pertinent to Fan and Watkinson's data the relationship is reasonably linear, following Eq. (4).

Also shown on Figure 5 are λ_{eff} data obtained for mixtures of graphite powder and organic fillers, measured with a Hot Disk™ device. Two groups of samples were prepared, accessing different ranges of H/C ratio; known

compositions of graphite dispersed in (i) paraffin wax and (ii) naphthalene. The samples were moulded into cylinders (diameter 3.2 cm and height 3cm). The method employs a thin disk sandwiched between two equal cylindrical samples. The device contains a transducer which sends a heat pulse through the sample and records the temperature transient as the heat dissipates through the sample. All experiments were performed at 16°C. A linear dependency on H/C ratio is again evident, suggesting that this could be mapped directly on to y .

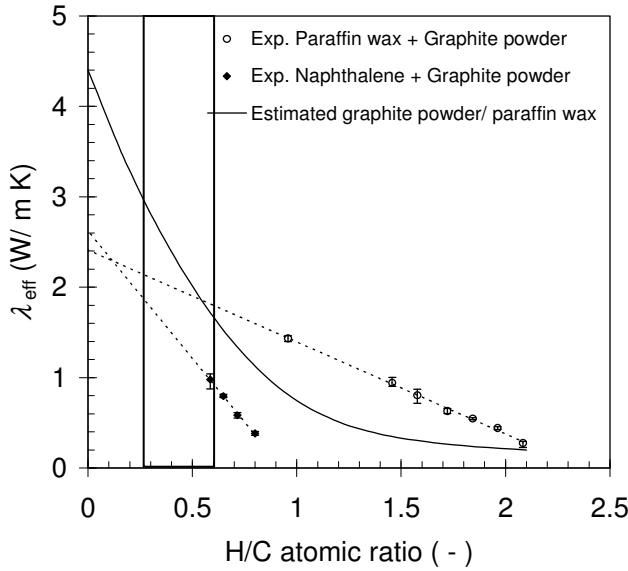


Figure 5 Effective thermal conductivity estimated for graphite powder/paraffin wax mixtures (solid line) and experimental measurements of mixtures of graphite powder and naphthalene (solid symbols) and paraffin wax (open symbols), after Ishiyama (2009). The shaded region indicates the range of H/C ratios reported by Fan and Watkinson (2008).

The youth variable is postulated to undergo a first order decay, mirroring the behaviour in H/C ratio reported by Fan and Watkinson, with a decay constant, k_a , which follows an Arrhenius dependency on local temperature, T :

$$\frac{dy}{dt} = -k_a y \equiv -A_a \exp\left[-\frac{E_a}{RT}\right] y \quad (5)$$

Here, E_a is the activation energy of ageing and A_a the associated prefactor.

The local temperature will vary with time and position within the deposit, which is affected by the continuous addition of new deposit. The resulting model resembles a population balance and is evaluated here by considering incremental sublayers deposited over regular time intervals (see Figure 6). In each time interval, a new layer of deposit is generated with thickness δ_i calculated from Eq. (1) and the fouling rate at the deposit surface evaluated using a model for chemical reaction fouling, *viz.*

$$\delta_i = \frac{d\delta}{dt} \Big|_i \cdot \Delta t = \lambda_{f,0} \cdot \left(\frac{dR_{f,s}}{dt} \right) \cdot \Delta t \quad (6)$$

We employ here a fouling model based on the ‘threshold model’ presented by Polley *et al.* (2002) for tube-side crude oil fouling. Their suppression term is omitted to simplify the calculations, giving

$$\frac{dR_f}{dt} = \alpha \text{Re}^{-0.8} \text{Pr}^{-0.33} \exp\left(-\frac{E_f}{RT_s}\right) \quad (7)$$

Here, E_f is the activation energy associated with fouling and α the rate constant.

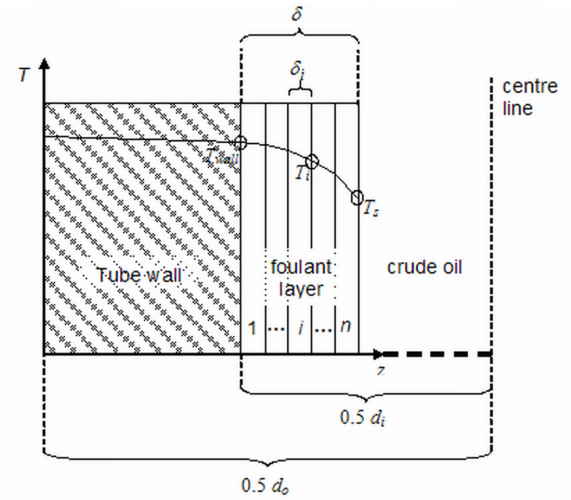


Figure 6 Schematic of deposit ageing model. The curved temperature locus illustrates the variation in T across the deposit as a result of varying λ_f .

The thickness of individual sublayer elements is assumed to remain constant over time (but individual values will vary according to deposition conditions). The overall fouling resistance of the deposit is given by the sum of the sublayer resistances in series, *viz.*

$$R_f = \sum_{i=1}^n \frac{\delta_i}{\lambda_{f,i}} \quad (8)$$

Results are presented for a representative crude oil heat exchanger tube (i.d. 22.9 mm) processing crude with a bulk temperature of 190°C, constant flow rate (corresponding to $Re = 40\,000$), and initial $T_w = 270^\circ\text{C}$. Axial variations in temperature *etc.* are not considered in this lumped parameter form: a model of a distributed system is under development. The deposit thermal conductivities are $\lambda_{f,0} = 0.2 \text{ W/m K}$ and $\lambda_{f,\infty} = 1.0 \text{ W/m K}$, corresponding to an oil and hardened deposits (Watkinson, 1988), respectively. Further details of the calculation procedure and simulation parameters are given in Ishiyama *et al.* (2009). Calculations were performed using Matlab™ on a PC.

It should be noted at this point that the timescales mentioned previously are related to the prefactors A_a (Eq. 5) and $\lambda_{f,0} \propto \alpha \text{Re}^{-0.8} \text{Pr}^{-0.33}$ (Eqs 6,7). Three values of this ratio

are considered, namely 0.1, 1 and 10, which are termed slow, medium and fast. A second, important ratio is the sensitivity to temperature, expressed in the activation energies E_a and E_f . In this work, E_f is kept constant at 50 kJ/mol (representative of values reported from plant data, see Polley *et al.*, 2002) and E_a varied, between 10, 50 and 200 kJ/mol. Where E_a is varied, α is modified to compensate for the different temperature sensitivity by selecting the value that gives the same initial fouling rate at $T_w = 270^\circ\text{C}$.

RESULTS

Constant wall temperature operation

Figure 7 shows the overall deposit thickness and R_f values obtained for simulations with $\alpha = 1 \times 10^5 \text{ m}^2\text{K/kW h}$ for the scenarios of slow, medium and fast ageing.

The base case, of no ageing, exhibits falling rate behaviour owing to the deposit-crude temperature decreasing over time as a result of fouling (Eq. 3a). With ageing, however, the thickness-time profiles are more linear, as ageing serves to increase T_s . The difference is most noticeable when ageing is fast (Figure 7(c,i)). The degree of linearity depends on E_a , as this characterizes the temperature sensitivity. High values of E_a – such as are associated with chemical reaction steps – result in a slow ageing rate as fouling proceeds, effectively suppressing ageing after a short time. Low values of E_a , as expected for diffusion controlled processes or ones subject to mass transfer limitations, are less sensitive to temperature, and age at a nearly constant rate. The difference between temperature sensitivities in ageing is small when ageing is fast (Figure 7(c, i)), and the range of behaviour is widest in the intermediate case (Figure 7(b)). This simple model illustrates how different mechanisms can give rise to an unhelpfully rich range of fouling behaviour.

The deposit thickness and R_f profiles in Figure 7 exhibit markedly different effects of ageing on fouling. Ageing increases the deposit thickness in the tube, and therefore the pressure drop, whereas it decreases the thermal effect. In the fast ageing scenario, the deposit converts to the high thermal conductivity form almost instantaneously (corresponding to $\tau_2 \ll \tau_1$) and the fouling behaviour is almost linear. Falling rate fouling is evident in the slower ageing cases, which could be interpreted as approaching asymptotic fouling (particularly if the suppression term in the fouling model was introduced). Low E_a values, and therefore least change in ageing rate, causes greatest reduction in R_f compared to the base case.

These results have direct consequences for the interpretation of thermal fouling data. Figure 7(ii) presents a caveat, that observations of falling rate and asymptotic fouling in constant wall temperature operations – whether experimental or data reconciliation – may incorporate ageing effects. Furthermore, accelerated laboratory testing tends to use higher wall temperatures than those employed in practice in order to generate data in a convenient time frame. This can accelerate the rate of ageing as well as the fouling rate, represented by moving from Figure 7(a) towards Figure 7(c). Higher temperatures can also facilitate

different chemical mechanisms, such as the transformation to different crystal polymorphs mentioned by Brahim *et al.*, (2003).

Constant heat flux operation

In this mode q is constant and the deposit growth profile is linear, corresponding to the no-ageing case in Figure 8. Fast ageing (Figure 8(c)) also yields linear fouling behaviour, albeit with a deposit of (higher) thermal conductivity $\lambda_{f,\infty}$ rather than $\lambda_{f,0}$. This illustrates the risk in accelerated fouling tests, and the need to compare the structure and composition of deposits with those found in practice. Ageing again reduces the thermal impact of fouling compared to pressure drop. Linear fouling behaviour is also observed in the intermediate case (Figure 8(b)), with little effect of E_a . This is because constant heat flux operation raises the temperature in the deposit (see Eq. 3b) and ageing is accelerated: the corresponding plots of deposit thermal conductivity against time show that most of the sublayers reach $\lambda_{f,\infty}$ rapidly. Differentiation based on temperature sensitivity is only observed in the slow ageing case, and here the low E_a result lies closest to the no-ageing scenario; under these conditions, the rate of ageing responds less to the increase in temperature of the deposit layer.

DISCUSSION

The model presented here is based on simple physical assumptions and evidently would benefit from detailed mechanistic studies and from experimental validation. Experimental reports of ageing in chemical reaction or crude oil systems are, however, sparse. Quantitative studies are rarer still. Asomaning *et al.* (2000) mentioned, briefly, observations of linear and asymptotic $R_f - t$ behaviour as a result of ageing in crude oil fouling. They suggested that the accelerated fouling conditions often employed in laboratory tests may give rise to rapid ageing of deposits and that this ageing could result in a reduction in deposit strength due to rapid thermal degradation, facilitating removal and potentially giving the appearance of asymptotic fouling behaviour. Polymerisation, however, can serve to strengthen deposits. The thermo-mechanical aspects of ageing have not been considered here, but these have been studied in the context of cleaning (e.g. Hooper *et al.*, 2006). These have been studied in the context of wax deposition, where the development of gel strength draws on the work on dense suspensions and soft solids (see Coussot, 2005). Temperature changes in wax systems do not, we offer, change as markedly as in chemical reaction and water scaling applications where the Arrhenius temperature dependency employed here is likely to be relevant.

There is therefore a need for careful experimental investigations.

The model presented here considers ‘point’ conditions, representative of a lumped parameter approach to describing a heat exchanger, or devices with uniform operating conditions across the surface. Many operating units feature varying temperature and flow fields, requiring the model to be evaluated everywhere locally within a distributed model. Coletti *et al.* (2009) report a distributed model simulation.

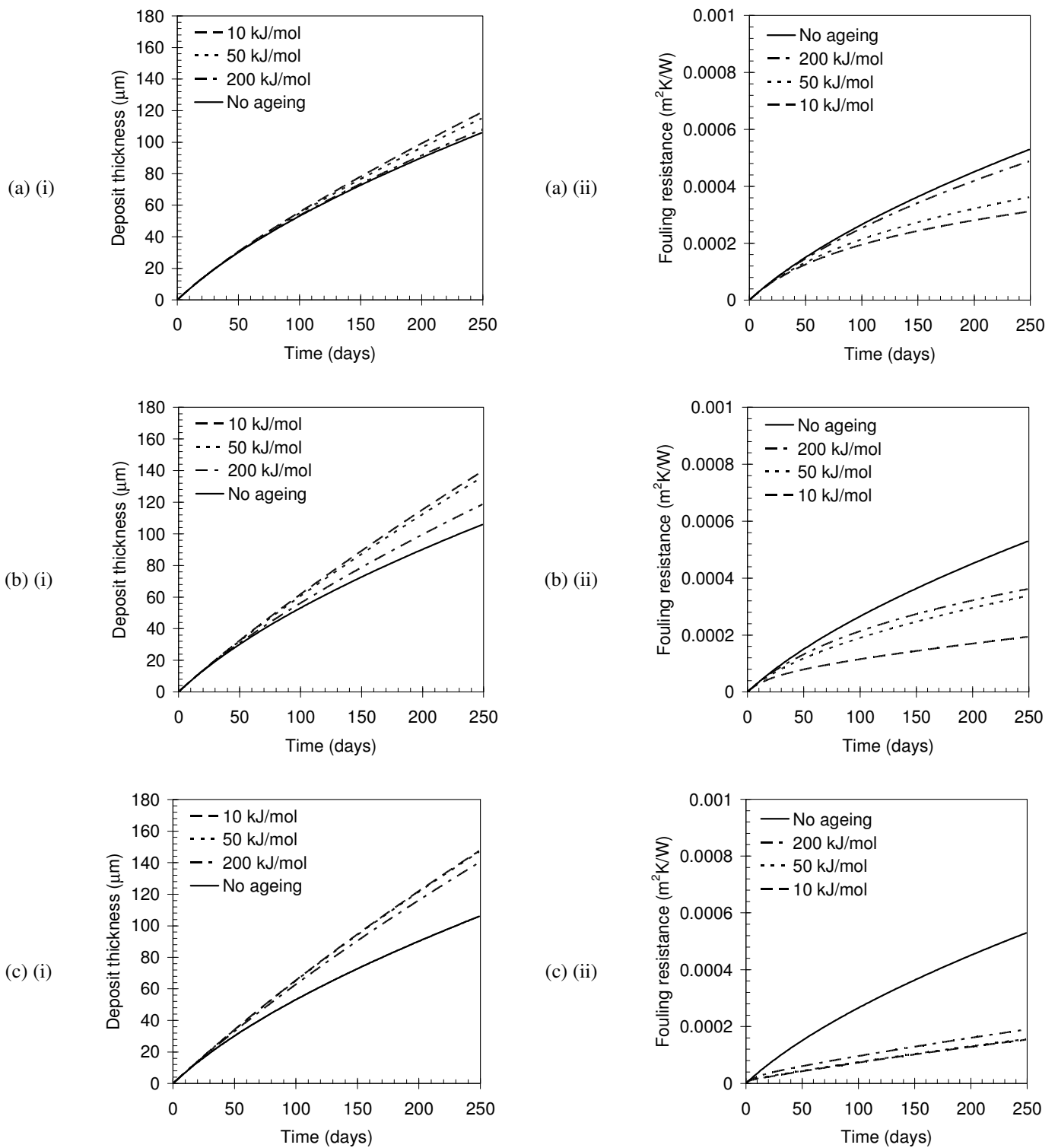


Figure 7 Effect of ageing on fouling behaviour, constant T_{wall} operation; (i) total deposit thickness; (ii) overall R_f . Relative rate of ageing: (a) slow, (b) medium and (c) fast. Solid line in all cases indicates behaviour with no ageing. Reproduced from Ishiyama *et al.* (2009), © American Institute of Chemical Engineers.

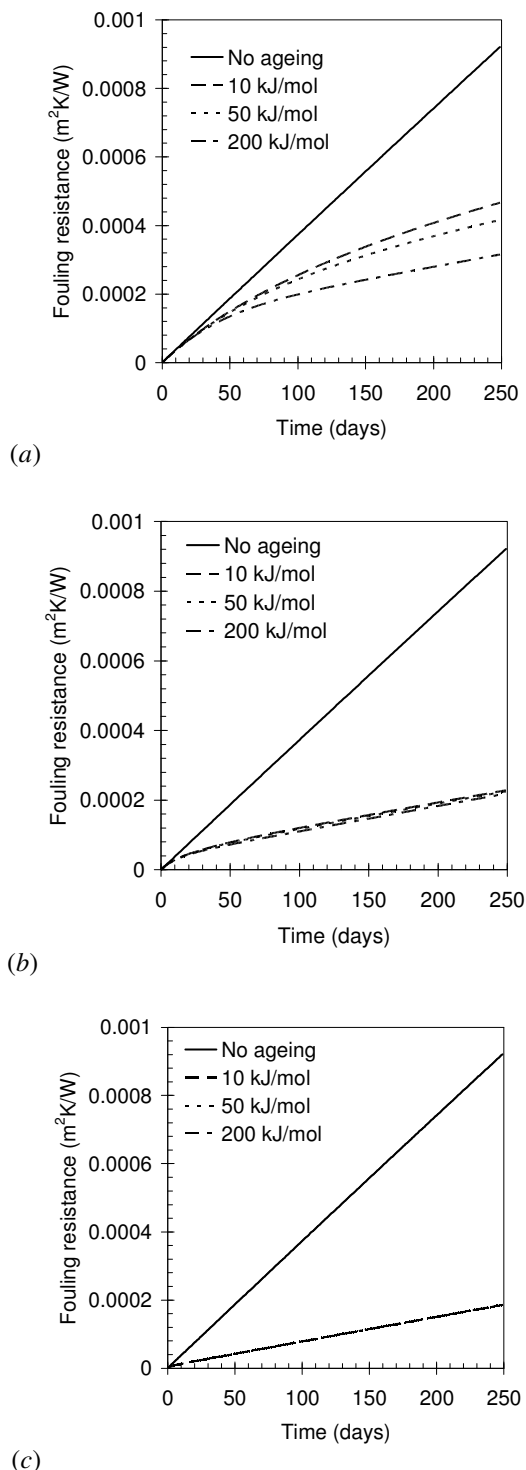


Figure 8 Effect of ageing on thermal fouling behaviour under constant heat flux operation, for (a) slow, (b) medium, and (c) fast ageing. Solid line – no ageing case. After Ishiyama *et al.* (2009), © American Institute of Chemical Engineers.

LOOKING FORWARD

This brief review of reported studies of ageing of fouling deposits has shown that more progress has been made in some areas, driven by the importance of ageing and timescales involved in certain industrial operations. This is

anticipated to continue, particularly when the resources being used (heavy oils, poorer quality or recycled water, *etc.*) introduce components which are likely to promote ageing as well as other effects in fouling.

Ageing studies do, however, require different techniques and more regular testing compared to those performed routinely to date. The quantitative model presented here has demonstrated how ageing can affect R_f -time profiles in different ways, depending on both the effect of ageing and the type of experiment or study. The absence of information on deposit thermal conductivities highlights the need to measure pressure drops, deposit thicknesses and mass, while the need to understand and identify ageing transformations requires systematic chemical analysis to monitor (or infer) reactions or other mechanisms involved. Sampling deposits, as well as interrupted tests, are likely to be needed.

It is unlikely to be possible to estimate thermal conductivities *a priori*, as this property is strongly dependent on the microstructure of the deposit and therefore all operating parameters which affect the evolution of microstructure (and similarly the rheology of the deposit). Direct measurement of thermal conductivities of fouling deposits *in situ* represents a challenge as the fouling layers are frequently thin, fragile and on curved surfaces.

The ageing model presented in this paper is acknowledged to be based on simple assumptions, particularly for the rich reaction and rheological environment involved in chemical reaction fouling. It will require modification in order to describe the particular physical and reaction principles applying to particular cases, but we suggest that it provides a systematic framework for understanding and comparing the effects of fouling, heat transfer and ageing. The numerical formulation could be improved using, for instance, methods employed in population balance modeling.

An immediate area for application of the type of model presented here lies in the interpretation of laboratory data, particularly in linking experimental studies to field measurements. There is a need to revisit existing studies to establish whether ageing could explain some of the reported behaviour, and thereby establish possible timescales for ageing to guide future work: this would serve both the research and industrial communities. Laboratory studies usually have the advantage of ready access to samples of fouling layers for analysis, which we are not the first to suggest should be practiced wherever possible. The fouling fluid should also be monitored and sampled, particularly in laboratory studies with batch systems where depletion of precursors could also give rise to dynamic effects.

The model represents a step forward in completing the replacement of the static response to fouling, as represented by the use of TEMA fouling factors to guide exchanger oversize, with a dynamic, model based approach building on the fundamental understanding identified by Epstein. Incorporating ageing effects into fouling models such as the 'threshold fouling' for chemical reaction fouling allows exchanger performance to be predicted more reliably and designs and operating strategies improved. Reconciliation

of plant operating data, where long timescales apply, can be improved (as reported by Coletti and Macchietto, 2009) thereby supporting operations.

Understanding ageing will also allow the symbiotic relationship between fouling and cleaning identified by Wilson (2005) to be modelled and ‘fouling life cycles’ analysed. The impact on ageing on the cost and effort associated with cleaning fouled heat exchangers varies between applications. In those where units are taken off-line for cleaning, the time and effort spent on cleaning is a fraction of the total downtime, so ageing principally affects process performance over the operating period. Where cleaning-in-place (CIP) operations are conducted regularly, as in the food sector, a resistant, aged deposit will require more aggressive or extended cleaning, directly affecting performance and cleaning costs. Optimisation of fouling life cycles in CIP operations is likely to benefit directly from improved and quantitative understanding of ageing effects.

CONCLUSIONS

1. Progress in the understanding of ageing in fouling mechanisms since Epstein’s landmark paper (1983) have been reviewed briefly. The fundamentals of ageing in crystallisation and wax fouling have received notable attention. The understanding of biofouling has also increased markedly, mainly due to interest in biology (metabolism, *etc.*) rather than in fouling *per se*. Although the impacts of ageing are recognized, quantitative models of these are not well developed. Qualitative models based on reported data exist in several applications. The exception is that of wax deposition, where mechanistic models for the increase in hardness of wax deposits have been developed.
2. A quantitative model for ageing in chemical reaction fouling, formulated for crude oil applications, has been developed based on simple physical assumptions. Ageing is linked to the evolution of deposit thermal conductivity, with a proposed linear mapping supported by laboratory experiments on model mixtures.
3. The quantitative model has been used to illustrate the importance of timescales and temperature sensitivity in fouling situations. A range of thermal fouling behaviours can result, depending not only on the intrinsic properties of the deposition mechanism but also on the mode of heat transfer. The propensity of ageing to confound the interpretation of measured fouling rate data is identified.
4. Key lessons for interpreting plant and laboratory data have been identified and the scope for further work in this area discussed.

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NOMENCLATURE

A_a	ageing prefactor, 1/s
Bi_f	fouling Biot number, -
E_a	ageing activation energy, J/mol
E_f	fouling model activation energy, J/mol
h	film heat transfer coefficient, W/m ² K
k_a	ageing decay constant, 1/s
Pr	Prandtl number, -
q	heat flux, W/m ²
R	gas constant, J/mol K
Re	Reynolds number, -
R_f	fouling resistance, m ² K/W
T	temperature, K
t	time, s
y	youth variable, -
α	deposition model parameter, m ² K/J
δ	fouling layer thickness, m
λ	thermal conductivity, W/m K

Subscript

b	bulk
eff	effective (overall)
f	foulant
i	deposit sub-layer
s	surface
w	wall

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