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Predicted Influence of Pore Structure Modifications for Catalyst Pellets Deactivated by Fouling

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The theory of foulant deposition by wedge layering has been applied to investigate the influence of pore structure modifications upon the deactivation characteristics of catalyst pellets. Previous experimental measurements of the activity of a commercial hydrodesulphurisation catalyst which had been sequentially fouled with ethylene gave the foulant deposition parameter β which is the ratio of thickening to penetration rate. Using this value of β, pellet activity and productivity behaviour can be predicted as the pore structure is varied. The results show that uniform pores are always more effective than pores of distributed sizes. Also, for the present example, although catalysts with fine pores and high initial activity deactivate more rapidly, their integrated output or productivity is greater than that for a less active catalyst comprised of larger-diameter pores. The theory shows that for coke accumulation, finely structured pellets accumulate coke or foulant at a rapid initial rate, but have lower ultimate coke contents due to pore-mouth plugging. It is also evident that if activity is observed with respect to foulant penetration, nondiffusion-influenced activity loss due to pore-mouth plugging can appear to be disguised as a diffusion-influenced reaction accompanied by pore-mouth poisoning.

INTRODUCTION

When a catalyst is deactivated by a foulant deposition, such that the volume of foulant occupies a significant proportion of catalyst pellet porosity, the available active catalyst surface area can lose its activity by two mechanisms. Firstly, there will be activity loss because of surface coverage of active sites which is analogous to activity loss by poisoning. Secondly, the possibility exists for the foulant to accumulate to such an extent that a pore becomes physically plugged or sealed by the deposit. In this way, any active surface interior to the point of blockage in any closed-end pore will be rendered inaccessible to reagents, and its activity will be accounted for as zero, so long as the pore remains blocked. These mechanisms of activity loss have been appreciated for some time (*1*, *2*), but only recently have structural quantitative efforts been made to define them (*3–6*).

Progress in the quantitative analysis of the general fouling problem is reliant upon the description of both the pore structure and the geometry of the foulant deposit. An adequate description of the complexities of pore structure remains to be resolved, and though some recent work has pointed the way towards a quantitative analysis based upon stochastic interconnected pore networks (*7*), the best currently available pore structure model is the so-called "parallel bundle of tubes." This model continues to find wide application despite the fact that it neglects the physical reality of pore interconnectivity. The model exists in a number of slightly different forms, but in the present approach it will be assumed that the complex pore structure of a catalyst pellet can be represented by a set of parallel-sided nonintersecting cylindrical pores each of a given length L (related to pellet geometry), whose diameters vary according to some definable statistical distribution. In considering the definition of the geometry of the foulant deposit, it will be assumed that

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foulant deposition takes place by the process of wedge layering (*5*), in which a fixed ratio is maintained between the thickness of the deposit at the mouth of a pore and the extent of penetration of the foulant into the pore. Some experimental evidence obtained by electron microprobe techniques has shown that deposits do show greater thickening towards pore mouths (*8*), confirming that the concept of wedge layering may be fairly widely appropriate.

The wedge-layering concept of foulant deposition within a pore incorporates the pure pore-mouth poisoning case as a lower limit of behaviour. It can conveniently accommodate varying degrees of pore-mouth plugging as the thickening rate increases relative to the penetration rate and in the limit can account for deactivation taking place purely by pore-mouth plugging at negligible penetration and coverage of pore surface area.

It is not difficult to visualise a number of ways in which a deposition process of wedge layering can occur. In the simplest case, analogous to the presently considered experimental results (*5*), two reagents A and B are considered to react independently upon the catalyst. Component A is the coke precursor forming the foulant deposit. If this reaction is sufficiently fast to introduce concentration gradients of A within a pellet, then the formation of a wedge of foulant can take place. In practical cases, component A might only be present in a very small amount and might be identified with Conradson carbon having a very high rate of coke formation. Surface covered by such a foulant deposit is considered likely to be inactive. Component B reacts to form some desired product C, viz. B → C, and this reaction takes place on unfouled surface which is interior to the foulant deposit. This second reaction if sufficiently slow will not be influenced by any diffusion restriction anywhere in the pore. In such a circumstance, the rate of this reaction would be dependent upon the extent of unfouled surface remaining accessible in an unplugged pore. It is this simplest case which forms the basis of the present analysis. More complex possibilities are easy to conceive, but more difficult to analyse. These can involve series/parallel kinetics with various degrees of diffusional resistance.

The wedge-layering notion does not necessarily imply that the foulant deposit is formed by a reaction subjected to diffusional resistance. A previous exploratory analysis (*4*) based upon assemblages of randomly variable diameter pores showed how a wedge layer could be formed in the complete absence of diffusional effects. However, this case is more complex (although for different reasons) and must form the basis for a more rigorous future analysis.

The present simple approach does take account of the physical interactions of pore structure and foulant geometry and is intended to be useful in defining optimized pore structures which can mitigate the deactivation. It should also be applicable to instances where the accumulation of foulant can physically destroy the strength of a catalyst pellet (*9*).

NOMENCLATURE

D	pore diameter
$\hat{D}$	median pore diameter in log-normal distribution
F	reduced dimensionless catalyst activity
$f_N(D)$	pore size number frequency distribution
$f_s(D)$	pore size area frequency distribution
$f_v(D)$	pore size volume frequency distribution
h	pore-mouth foulant thickness
L	pore length
N	number of pores per gram of catalyst
P	pellet productivity
q_c	weight percentage of coke on catalyst
S_g	pellet specific surface area

$V_f'(h)$	volume of foulant per gram of catalyst in plugged pores
$V_f''(h)$	volume of foulant per gram of catalyst in unplugged pores
$V_f(h)$	total volume of foulant per gram of catalyst
x	foulant penetration
β	ratio of foulant thickening to penetration rate
σ	pore size variance in log-normal distribution

ANALYSIS AND DISCUSSION

Activity and Foulant Accumulation

The quantitative definition of the relationships between activity loss and the extent of foulant accumulation can be deduced by reference to Fig. 1. As foulant thickens and simultaneously penetrates, the larger pores become progressively sealed off. The smaller-diameter pores become blocked first as shown in Fig. 1a and this happens at relatively modest penetration x, with the result that an extensive loss of activity takes place, since the smaller pores give rise to proportionately more surface area per unit of pore volume. The larger-radius pores can remain unblocked (albeit with restricted entrances) as thickening and penetration proceed, as shown in Fig. 1b. Such unblocked pores retain the intrinsic activity of the unfouled surface, though this might be reduced if the foulant deposit introduces some additional diffusional resistance. By using the wedge-layering model (*5*), the constant ratio of mouth thickness to depth penetration is given by

$$\beta = h/x. \tag{1}$$

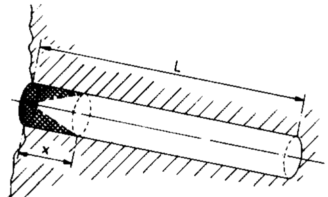
The activity loss which accompanies foulant deposition can be represented by using the reduced dimensionless activity at any given mouth thickness h which is given by

$$F(h) = \left(1 - \frac{x}{L}\right) \int_{2h}^{\infty} \frac{f_s(D)dD}{S_g}. \tag{2}$$

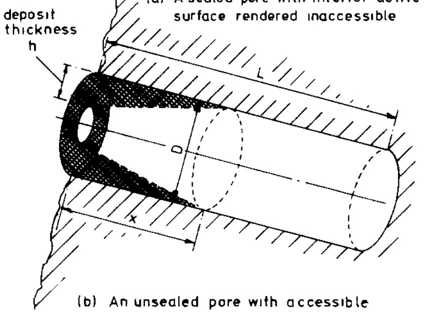
The first term in parentheses accounts for fractional activity loss due to surface coverage and the integration of the surface area distribution function $f_s(D)$ over the restricted range from h to ∞ accounts for the activity lost due to the pore-mouth sealing of all those pores for which $D < 2h$. The use of the fixed relationship between h and x for the wedge-layering model gives

$$F(h) = \left(1 - \frac{h}{\beta L}\right) \int_{2h}^{\infty} \frac{f_s(D)dD}{S_g}. \tag{3}$$

The corresponding amount of foulant accumulated within the parallel bundle of pores at any given foulant thickness h is potentially an important parameter in analysing deactivation by fouling since it can be easily experimentally determined from the weight of foulant simultaneously with the current pellet dimensionless activity. This is not the case for the thickness or the penetration, both of which are difficult to determine. The volume (or weight) of foulant is found by adding together the foulant contained in sealed pores where $D < 2h$ and the foulant in unsealed pores for which $D > 2h$. The volume of foulant contained in a single plugged pore of size D (Fig. 1a) is given by $\frac{1}{6}\pi D^2x$, and using the



(a) A sealed pore with interior active surface rendered inaccessible



(b) An unsealed pore with accessible interior active surface

FIG. 1. Foulant deposition by wedge layering.

wedge-layering factor $\beta = h/x$, the total foulant volume per gram of catalyst is given by integration with $0 < D < 2h$, such that

$$V_f'(h) = \int_0^{2h} \frac{\pi}{12} \frac{D^3}{\beta} N f_N(D) dD, \qquad (4)$$

where N is the total number of pores per gram of catalyst and $f_N(D)$ is the pore diameter frequency distribution function.

The amount of foulant in a single unplugged pore (Fig. 1b) is given by $\pi\beta x^2(D/2 - \beta x/3)$. Again by using the wedge-layering factor β, the total volume of foulant per gram of catalyst in unplugged pores is given by

$$V_f''(h) = \int_{2h}^{\infty} \frac{\pi h^2}{\beta} \left(\frac{D}{2} - \frac{h}{3}\right) N f_N(D) dD. \qquad (5)$$

Equations (4) and (5) show clearly that D varies within the given range, but the value of h is fixed, and this removes the ambiguity on the interrelation of h, x, D, and β within the integrals, which was not made sufficiently clear in a prior presentation (5).

The total volume of foulant accumulated is then found from the summation of Eqs. (4) and (5) so that it is given by

$$V_f(h) = \frac{S_g}{\beta L} \left[\int_0^{2h} \frac{D^2}{12} f_s(D) dD + \int_{2h}^{\infty} h^2 \left(\frac{D}{2} - \frac{h}{3}\right) \frac{f_s(D)}{D} dD \right], \qquad (6)$$

where the number distribution has been replaced by the surface area distribution function $f_s(D)$.

The experimental correlation of $F(h)$ and $V_f(h)$ provides a framework for assessing the relative proportions of deactivation produced by surface coverage and pore-mouth plugging. Figure 2 shows a set of experimental results previously obtained using Comox 1661, which is a commercially available cobalt molybdate hydrodesulphurisation catalyst. The activity of the catalyst was determined with respect to the hydrodesuphurisation of thiophene in a small fixed-bed plug-flow reactor at 300°C and the catalyst was separately fouled using ethylene in nitrogen at 500°C. The extent of coking by ethylene was varied by exposing the catalyst to ethylene at 500°C for periods from 5 min up to 2 hr. These previous measurements indicated that the appropriate value of β for this catalyst (see below for its pore size distribution) was around 4×10^{-5}, which placed the deactivation in the regime dominated by pore-mouth plugging (5). As Ref. (5) makes clear, an activity loss/coke profile can be approximately fitted by two values of β, one in the poisoning-dominated and one in the plugging-dominated region. The inflected shape of the experimental curve indicated that the β value for the regime dominated by pore-mouth plugging was the appropriate one.

Effect of Pore Structure Modifications upon Pellet Activity and Productivity

The manufacturer's published data on the pore volume distribution of Comox[2] catalyst pellets, which were extruded cylinders of dimensions 10 × 1.5 mm, indicates that a satisfactory representation of the pore structure can be obtained by a log-normal distribution with $\hat{D} = 120$ and with a variance $\sigma = 0.30$. The pore size volume frequency distribution is therefore given by

$$f_v(D) = \frac{\exp(-(\log_e (D/2) - \log_e (\hat{D}/2))^2/2\sigma^2)}{\int_0^{\infty} \exp(-(\log_e (D/2) - \log_e (\hat{D}/2))^2/2\sigma^2) dD}.$$

The corresponding cumulative volume curves are presented in Fig. 3.

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[2] Manufactured by Laporte Industries Ltd., General Chemical Div., Widnes, England.

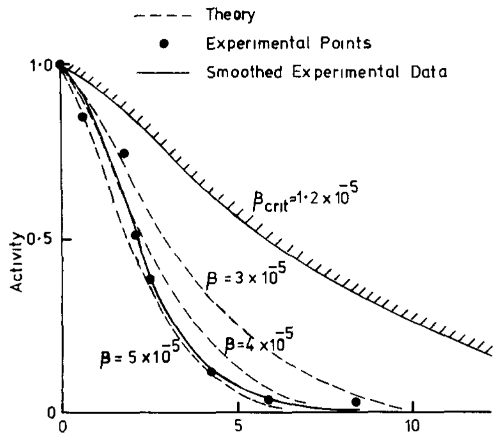

FIG. 2. Experimental fit of the wedge-layering model.

In the absence of a theoretical framework to assess fouling behaviour, the choice of a particular pore structure/surface area distribution is bound to be somewhat arbitrary. The present approach which is based upon a physicochemical structural representation for the location of the foulant and its distribution within the pore structure, enables us to examine the impact of changes of the pore structure upon the chemical performance of a pellet. Any assessment of the consequences of changes in pore structure requires some performance factor. One performance factor which could be used to discriminate amongst different pore structures is the integral of the pellet activity over the period in which fresh, fully active catalyst pellets become completely deactivated by foulant deposition.

To illustrate the determination of this pellet productivity performance factor, it will be assumed that mouth thickening takes place such that a pore of diameter 6000 Å will be sealed in 1 hr. This means that the rate of thickening foulant at the pore mouths is 3000 Å hr^{-1}. If the external conditions for fouling remain constant, the assumption of linear thickening would be reasonable. By taking the initial activity of Comox ($\hat{D}$ = 120 Å, σ = 0.3 with log-normal $f_V(D)$) to be unity at a surface area of 158 m^2 g^{-1}, then the predicted decline in activity is presented in Fig. 4 for a set of variations in the pore size distribution induced by variation of the variance σ. The corresponding pore size distributions are shown in Fig. 5. The activities in Fig. 4 are the accessible interior pore surface area, assuming that diffusional resistances are negligible. This will always be the case if the desired reaction taking place on unfouled surface is sufficiently slow that the accumulating deposit in the pore mouth does not introduce a significant diffusional resistance.

From Fig. 4 it can be seen that the "standard" Comox activity has declined by 90% in 130 sec. The inflected curve indicates the preponderance of pores around 120 Å, which is the log-mean of the pore size distribution. Also shown in Fig. 5 are the curves corresponding to log-normal dis-

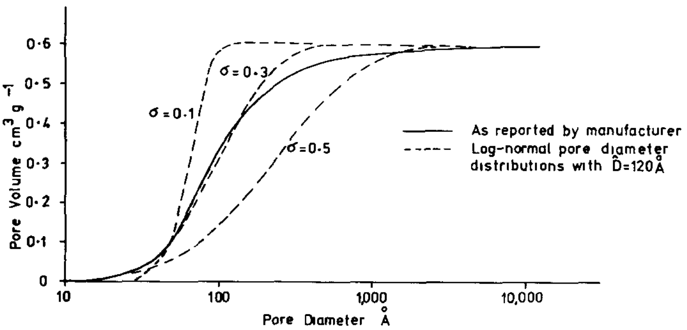

FIG. 3. Cumulative pore volume distributions.

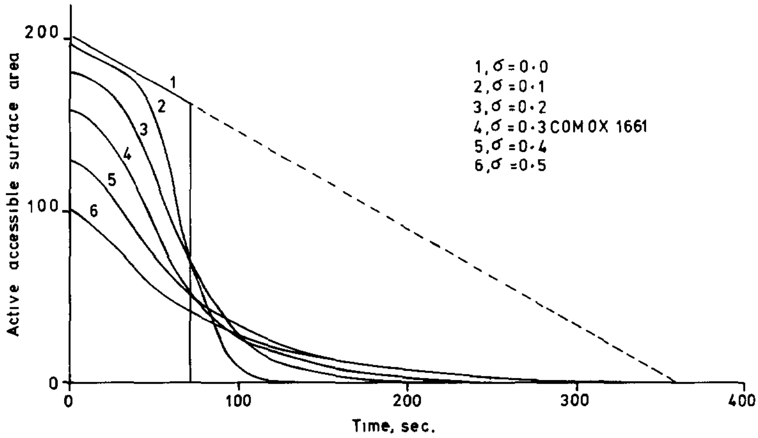

FIG. 4. Deactivation behaviour for modified pore structures with $\hat{D}$ = 120 Å.

tributions each with $\hat{D}$ = 120 Å and variance changing from 0 through to σ = 0.5, with each distribution truncated at D = 6000 Å. As the variance is reduced, the initial activity is greater than that for the standard Comox. The case of σ = 0 corresponds to a pellet composed only of pores of diameter 120 Å with a fresh surface area of 204 m^2 g^{-1}. Such pellets have a fresh activity of 1.29 relative to "standard" Comox. For these uniform pores, deactivation would proceed linearly until the foulant had thickened to 60 Å, at which point the pore mouths would block, and the activity would instantly fall to zero after a time of 72 sec. The predictions show that "hypothetical" pellets with higher initial activities deactivate more rapidly than those pellets which have lower initial activities associated with a wider spread of pore sizes. For pellets with σ = 0.5, the fresh dimensionless activity is just above 0.6, but the activity remains higher over the later stages of deactivation. The pellet productivity in each case is obtained from

$$P = \int_0^\infty F(h)dt,$$

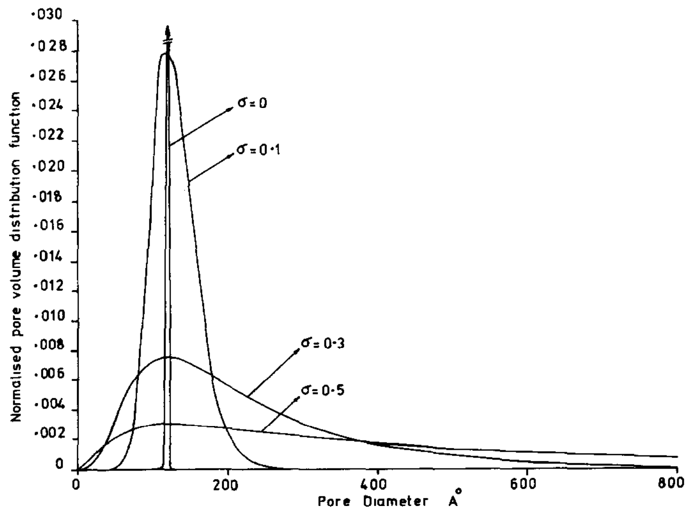

FIG. 5. Log-normal pore volume distribution functions with $\hat{D}$ = 120 Å.

where, effectively, the integration can be terminated at total deactivation, which apart from the uniform case is after 1 hr.

The corresponding pellet productivities are given in Table 1. The integration of the activity—time curves shows clearly that the uniform pores give the greatest pellet output, and that the pellet productivity declines as the variance in pore sizes increases. It would appear then that in the manufacture of catalyst pellets subjected to deactivation of the present type, the pore structure ought to be fabricated so as to have as uniform a pore size as possible in order to maximise pellet productivity with respect to the desired reaction.

TABLE 1

Pellet Productivity with $\hat{D}$ = 120 and σ Varying

Variance of log-normal pore size distribution σ	Initial catalyst activity		Pellet productivity for desired reaction P
	S_g	$F(0)$	
0	204	1.291	1.233
0.1	199	1.241	1.209
0.2	182	1.152	1.162
0.3	158	1.000	1.000
0.4	129	0.816	0.944
0.5	99	0.626	0.781

Having determined that uniform pores give rise to optimal pellet output, the remaining pore structure parameter which can be manipulated to give improvements is the mean of any available distribution. The effect of varying $\hat{D}$ at a fixed σ = 0.3 (corresponding to σ for "standard" Comox) is presented in Fig. 6, with the corresponding normalised pore volume distribution functions given in Fig. 7. The behaviour is similar to that for changes in variance. Thus, reducing the mean pore size gives higher initial fresh activities, but with a rapid deactivation initially. The much lower activity catalyst comprising

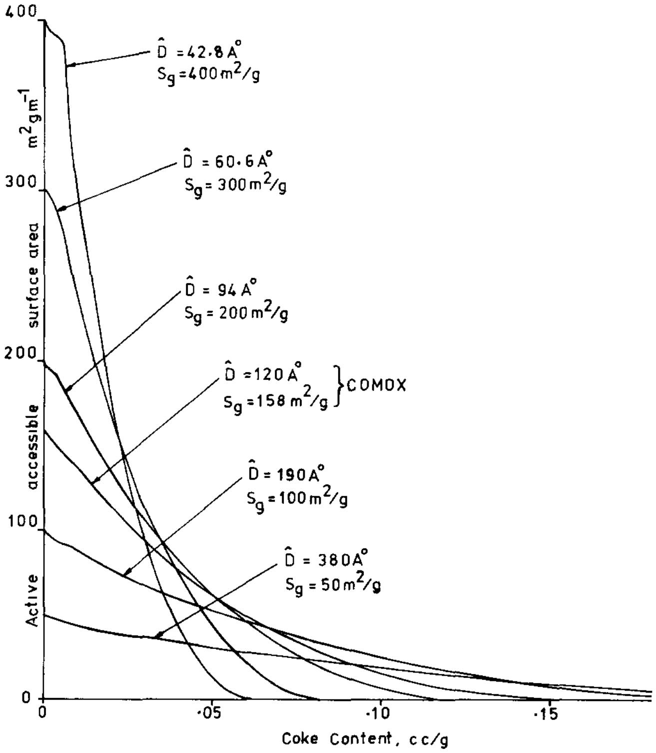

FIG. 6. Deactivation behaviour for modified pore structures with $\hat{D}$ varying and σ = 0.3.

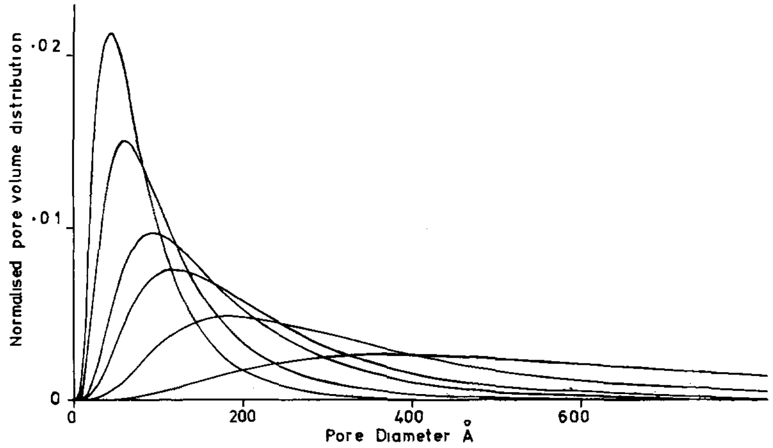

FIG. 7. Log-normal pore volume distribution functions with $\sigma = 0.3$.

larger pores, as before, has a lower initial activity which is, however, sustained over a longer period, in the later stages exceeding the activity of pellets of finer pores. The integral pellet productivities for these cases of variable $\hat{D}$ are presented in Table 2. This table shows clearly that the optimal pellet output performance is the direction of smaller $\hat{D}$, and consequently higher initial fresh catalyst activities.

Concerning the pellet productivities (relative to "standard" Comox) it can be seen that for the smaller pores the increment in productivity is substantially less than the increase in initial catalyst surface area. This trend is reversed for a porosity comprising larger pores, where the pellet output is preserved at a relatively higher value than the corresponding reduction in fresh activity would suggest. This behaviour is a consequence of the complexities of the balance between activity loss by surface coverage and by the pore blocking process.

TABLE 2

Pellet Productivities for $\sigma = 0.3$ with $\hat{D}$ Varying

$\hat{D}$ of log-normal pore size distribution with $\sigma = 0.3$ $\hat{D}$	Initial catalyst activity S_g		Pellet productivity for desired reaction P
	S_g	$F(0)$	
42	400	2.531	1.254
60	300	1.899	1.208
94	200	1.265	1.132
120	158	1.000	1.000
190	100	0.632	0.934
380	50	0.316	0.566

Figure 6 presents a measure of the activity loss as a function of the volume of foulant accumulated in respect to each of gram of catalyst. This form of correlation is preferable to weight percentage used in Fig. 2, since weight percentage is reliant upon specifying a value of the foulant density. This is particularly difficult to establish in practice. The literature contains a diversity of values ranging from 0.5 to 2.0 g cm^{-3} and moreover a particular value of foulant (coke) density is likely to be highly sensitive to both the feedstock and the reaction conditions. Deactivation characteristics in the case of fouling are a result of the volumetric interaction between foulant deposit and pore volume distribution; hence, the present preference for coke volume. In particular instances, experimentalists should attempt to determine a properly valid figure for foulant density in interpreting weights of foulant accumulated. The correspondence of Figs. 2 and 6 implies a coke density of 0.6 g cm^{-3} which is at the lower end of observed values. This value is somewhat lower than a value of 1.0 g cm^{-3}

utilised in the previous analysis (*5*), since in the present paper the value of the overall surface area of Comox has been revised downwards to 158 m^2 gm^{-1}.

The present approach based upon a formalised analysis of the interaction of pore structure and foulant deposit is useful for suggesting improved pore structure configuration. For the present example, where ethylene was deposited as the foulant, the theory predicts that improvements in the amount of thiophene hydrodesulphurised will result by decreasing the pore size and by reducing the spread in the distribution of pore sizes.

It appears that in present practice, catalyst manufacturers strive to maximise the pore volume associated with a given surface area. This maximal pore volume policy represents an attempt to reduce the pore-clogging characteristic of the foulant in order to provide longer uninterrupted production runs, even when this would be at the cost of a higher catalyst inventory. The present analysis could be considered academic in this respect. However, better understanding of the role of pore size distribution at fixed pore volume, notwithstanding the development of hitherto unachieved degrees of pore size distribution control, ought to lead to improved performance of catalysts subjected to fouling.

Predictions of Foulant Accumulation

The theory of foulant deposition by wedge layering in conjunction with the parallel-bundle pore structure model has proved useful in making predictions of the influence of pore structure modifications on an existing catalyst. Since the theory is based upon the interactions of physical and chemical effects, it gives rise automatically to several other predictions of properties which might be useful in analysing observations of catalyst deactivation by fouling. Amongst these properties are fouled-pellet permeability and effective diffusivity, as well as the location and thickness of the foulant within the pellet pore structure. Moreover, the approach can in principle be developed to analyse selectivity behaviour during fouling and has potential for predicting deactivation/reactivation behaviour if, for example, the foulant is burned off to regenerate a deactivated pellet. One other important characteristic that can be immediately predicted is the timewise behaviour of foulant accumulation and the quantitative features of the foulant accumulation trajectory may be useful in discriminating whether the deactivation process is dominated by pore plugging or penetration/coverage of active catalyst surface. This can be seen from Fig. 8 where time-

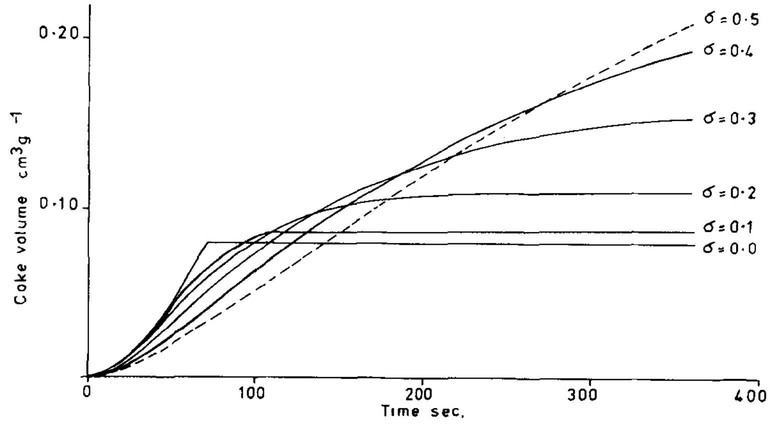

FIG. 8. Timewise coke accumulation behaviour.

wise foulant accumulation is shown for "standard" Comox and pore structure variance changes for log-normal distributions at a fixed mean pore diameter $\hat{D}$ = 120 Å.

The sharply inflected curves for σ = 0, 0.1, and 0.2 are in contrast to the apparent monotonic nature of the curve for σ = 0.5. The low-variance pore size distributions thus give rise to an induction period followed by a period of rapid accumulation after which no further fouling is observed (because all the pore mouths are blocked). For the curve with $\hat{D}$ = 120 Å and σ = 0.5, the induction period is much less distinct and is followed by a slower steady accumulation of foulant, almost linear with time. This less active catalyst pellet which contains larger pores, therefore undergoes a slower initial fouling, but ultimately has a much higher fouling content. This kind of behaviour has been observed by Levintner *et al.* (*2*), whose results are presented in Fig. 9. For their case the foulant is coke and its accumulation characteristics were changed by using a single catalyst (alumina) with different feedstocks having different coking tendencies or coking activities. This would correspond to a variation of β for the present wedge-layering approach. The important point is that the characteristics of coke accumulation with time show the same qualitative features as those in Fig. 8. This would seem to be a possible explanation for the sometimes-surprising observation that catalysts which coke more slowly at first have ultimately a greater capacity for coke accumulation. The converse observation is that pellets with higher initial activities coke-up more quickly, although as we have shown they may be more pro-

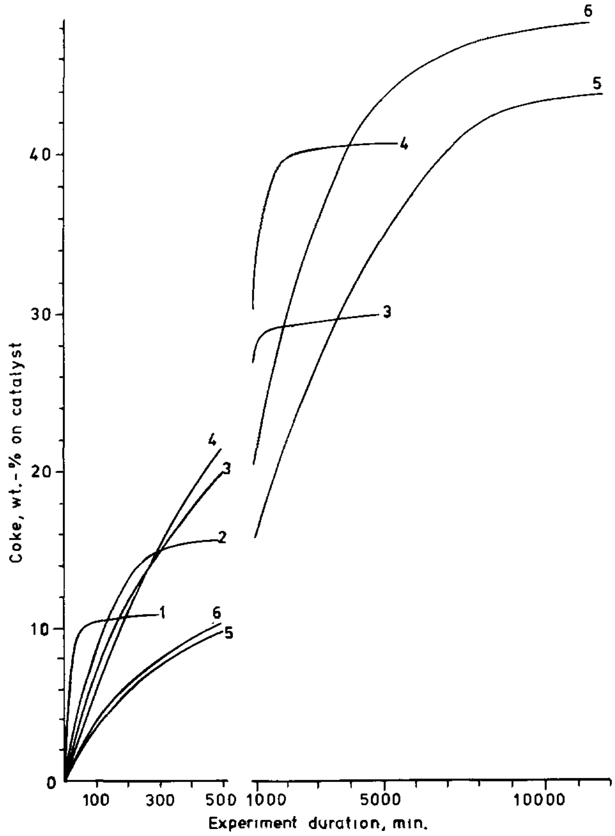

FIG. 9. Coke accumulation results of Levintner *et al.* (*2*).

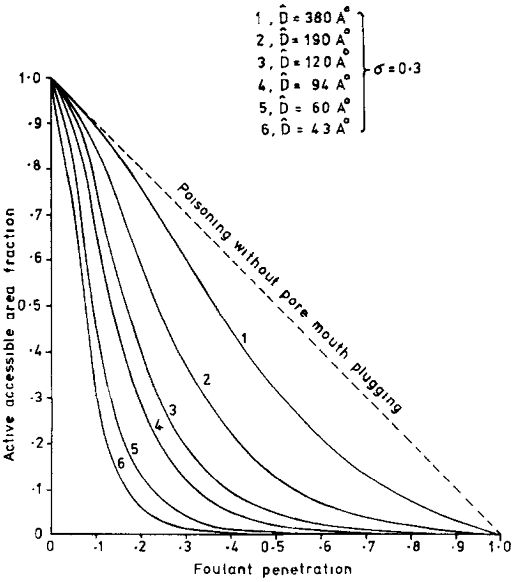

FIG. 10. Activity and foulant penetration characteristics for fouling by wedge layering.

ductive in an integral sense. The present picture of foulant and pore structure interference during fouling is a more secure basis for understanding fouling and is superior to the empirical Voorhies correlation (*10*) for investigating coking and fouling in catalysts.

Finally, it must be emphasised that any analysis of fouling must take account of the fact that the deposit has a finite and measurable volume relative to the pore volume of the pellet. The traditional analysis of deactivation by fouling has relied upon the ideas of poisoning, where the poison does not change the pore geometry. If the present reaction were to be analysed by correlating pellet activity against "poison" penetration (for example, by splitting pellets and measuring the advance of coke if this could be done, or by using more sophisticated microprobe techniques (*11*)) a result as shown in Fig. 10 would be obtained. The process of deactivation by foulant deposition for a nondiffusion-influenced reaction would be wrongly identified as a diffusion-influenced desired reaction accompanied by a pore-mouth poisoning (*12*). It is evident that the effect of pore-mouth closures can be mistakenly interpreted as a diffusion influence upon the main reaction. Any reactor designs or catalyst design strategies based upon such a misconception could not be expected to be particularly successful.

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