DEMETALLATION, DEACTIVATION AND BEDPLUGGING IN RESIDUUM HYDRODESULFURISATION

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The reduction of sulfur oxide emissions resulting from the use of high-sulfur crudes has recently become of increasing importance. High sulfur petroleum fuel oils contribute to the problems of air pollution. The conversion of high sulfur crudes to synthetic crudes low in sulfur, would increase the supply of limited natural resources.

One method of reducing the sulfur content in crude oils and residua is residuum hydrodesulfurisation in trickle-bed reactors. Total operating costs for this process can be divided into three components i.e. catalyst costs, hydrogen consumption costs and utilities plus investment charges. Catalyst costs represent a significant fraction of the total operating costs and also control the hydrogen and investment costs.

The factors contributing to catalyst utilisation will be the subject of this paper. These factors are classified broadly into two categories. Intraparticle diffusion leading to pore plugging and rapid catalyst deactivation. Secondly, interparticle reaction leading to bed-plugging. The possibilities for increasing catalyst utilisation in these two respects will also be considered.

PORE DIFFUSION IN RESIDUUM DESULFURISATION-DEMETALLATION

From recent papers[1-5] on residuum hydrodesulfurisation, the major conclusion is that metals contents of the feeds essentially control catalyst utilisation. Analysis of pore diffusion problems will therefore be limited to a pore plugging deactivation mechanism which progressively retards mass transfer of the sulfur-containing molecules to the interior portion of the catalyst pellet. This mechanism has been recognised for some time [6-8] but little quantitative information is available from journals or patent literature.

Effectiveness factors for demetallation of vanadium compounds are significantly less than 1.o.[3] Assuming typical values of liquid hourly space velocity (1.o) and desulfurisation conversion (75%), a corresponding demetallation conversion results (75%).[1] Catalyst particle size can now be plotted against the effective diffusivity for demetallation with effectiveness factor as a parameter. In Figure 1, for an effectiveness factor of o.75, with a catalyst particle size of 1/16 inch diameter, a minimum diffusivity of $5 \cdot 1o^{-7}$ $cm^2/sec.$ is required. An effectiveness factor of o.5 allows the minimum diffusivity to be as low as $2 \cdot 1o^{-7}$ $cm^2/sec.$ A first order reaction has been assumed together with a spherical particle shape.

Figure 2 shows estimates for values of the effective diffusivity as a function of molecular weight. The Stokes-Einstein equation was used to estimate liquid diffusivities for large molecules[9] together with a catalyst porosity of o.5. The parameter in Figure 2 is the tortuosity factor with values of 2, 5, 1o and 2o. The initial value is close to that for loosely packed beds and probably represents a minimum for a formed catalyst particle such as an extrudate. The final value of 2o may reflect the accumulation of metal sulfides and coke in pores of the catalyst particularly in an outer anulus of the pellet. From Figure 2, using a tortuosity factor of 5, an effective diffusivity of $3.5 \cdot 1o^{-7}$ $cm^2/sec.$ is estimated for a compound of molecular weight 4ooo. The latter value is towards the lower end of the spectrum of asphaltene molecular weights for Arabian Heavy atmospheric residuum.[1,3] A preliminary conclusion from figures 1 and 2 based on pore diffusion theory and an oversimplified molecular picture is that effectiveness factors of about o.6 are probably attainable in demetallation of a feed such as Safaniya to 1 weight per cent product sulfur.

It can be estimated however that the effective diffusivity for demetallation is substantially lower than $3 \cdot 10^{-7}$ $cm^2/sec.$ for a Safaniya feed being reduced to 1% product sulfur. This may be the result of adsorption phenomena particularly for vanadium compounds.[6] Other data for the desulfurisation reaction[10,11] provide upper bounds to the estimates for effective diffusivity for metal containing compounds within the catalyst particle.

Effective Diffusivity for Desulfurisation

Kinetic data for the desulfurisation of Kuwait VGO is available at two different particle sizes of the same catalyst.[12] An effective diffusivity of $8 \cdot 10^{-7}$ $cm^2/sec.$ was estimated. It is plotted on figure 1 and provides a useful upper limit for subsequent estimates. This value would probably be reduced at reaction rates more typical of current VGO practice. In the test data, the conversion (75%) and the liquid hourly space velocity (1.3) were modest by VGO standards. The above diffusivity means a tortuosity of 5.

Residuum desulfurisation data[10] together with information from the patent literature[11] allows an estimate to be made for the effective diffusivity of a Safaniya feedstock. A value of about $2 \cdot 10^{-7}$ $cm^2/sec.$ was calculated for assumed process conditions of one liquid hourly space velocity and 60% desulfurisation conversion. This provides an upper limit to the value of the effective diffusivity for demetallation when desulfurising a Safaniya feed to 1% product sulfur. The precision of the estimates is contingent upon a number of assumptions so that only order of magnitude values are possible at this time.

The effective diffusivity for demetallation will be less than the corresponding value for desulfurisation since much of the desulfurisation takes place from that fraction of the feed boiling between 650-1000°F. Demetallation takes place from feed boiling above 1000°F.

Effective Diffusivity for Demetallation

Some data for demetallation[6] in the form of concentration profiles in the pellet is available for an Iranian topped residue, 21° API gravity. The vanadium concentration in the regenerated catalyst

pellet was extremely steep but the pellet diameter was 5 mm. An effective diffusivity for vanadium of $2 \cdot 10^{-7}$ cm^2/sec. was estimated. This value is also plotted on Figure 1.

More recent data is available by means of electron micro-probe profiles in a spent catalyst pellet[3]. An effective diffusivity of $1 \cdot 10^{-7}$ cm^2/sec. was estimated for vanadium during the desulfurisation of an Arabian Light feedstock, 17.5°API. Correlating the above estimates for effective diffusivity with feed gravity suggests an order of magnitude value of $3 \cdot 10^{-8}$ cm^2/sec. for vanadium when desulfurising Safaniya to 75% conversion at a space velocity of 1.0. This value is indeed lower than the upper bound of $2 \cdot 10^{-7}$ cm^2/sec. suggested from desulfurisation data.

Referring to the minimum diffusivity plot for demetallation, Figure 1, an effectiveness factor of about 0.1 is obtained for a Safaniya feed. In the same way, an effectiveness factor of 0.3 is obtained for an Arabian Light feed.

Catalyst Utilisation

The only aspect of catalyst life that is being considered is the ability of the catalyst to accept metals within its pores yet maintain desulfurisation conversions of approximately 75%. This degree of desulfurisation corresponds to approximately 75% demetallation[1].

The catalyst metals loading at end-of-run is determined by the effectiveness factor for demetallation associated with a particular feedstock. A pore plugging mechanism combined with effectiveness factors less than 1.0 means that the catalyst pore volume available for deposition of metal sulfides is reduced from the fresh catalyst value. For example, an effectiveness factor for demetallation of 0.1 means that a catalyst whose pore volume is 0.5 cc/gram will only provide 0.05 cc/gram of pore volume for deposition of metal sulfides and coke in the part of the catalyst where the pore-plugging mechanism is critical. Coke is considered to deposit uniformly throughout the particle but will play a minor role in the pore plugging mechanism. A value of 10 weight per cent coke has been assumed deposited on the spent catalyst together with a coke density of 1 gm/cc. This is about one-half the ideal value since the coke formed on a heterogeneous catalyst surface is unlikely to occur in its ideal state. Similar reasoning allows the use of 3 gm/cc as the nickel and vanadium sulfides density.

With these considerations, it becomes possible to estimate the catalyst life in residuum desulfurisation as a function of metals removed from the feed. The effectiveness factor (η) for demetallation is the important parameter. Figure (3) shows estimates for catalyst life as a function of feed metals deposited inside the catalyst pellet. These metals may well be derived from the asphaltene fraction of the crude oil and represent about 70% of the total metals in the residuum.(13)

Residua from Middle East crudes are in general predicted to have longer catalyst lives than Venezuelan stocks. Differences within Middle East stocks are also considerable. An Arabian Light feed for example with an effectiveness factor of 0.3 is predicted to have a catalyst life of about 7000 hours. A Safaniya feed was estimated to have an effectiveness factor of 0.1 so that the predicted catalyst life is about 1000 hours. This can be improved to 3000 hours by increasing the effective diffusivity threefold to about $9 \cdot 10^{-8}$ cm^2/sec. The introduction of macropores could achieve this but the original activity and stability of the catalyst must be retained.

A similar comparison between Kuwait and Gach Saran residua gives a predicted life of about 3000 hours for Kuwait and 1000 hours for Gach Saran. This is not quite the factor of (x2) based on Gulf RDS life estimates(2) but shows the correct trend.

The parameter that obviously must be checked by experimental observations with different feeds and catalyst is the effectiveness factor for demetallation at a given desulfurisation reaction rate. If product sulfurs less than 1 weight per cent are desired when processing Middle East residua such as Kuwait and Safaniya, then a 1/16 inch catalyst particle size imposes severe limitations on process conditions. Liquid hourly space velocities of about 0.5 and catalyst lives of about 6 months or less are envisaged.

Methods of increasing catalyst utilisation

Particle Shape

The effectiveness factor for demetallation essentially controls catalyst utilisation when the pore plugging model applies. With effectiveness factors for demetallation less than 0.5, the length dimension in the Thiele modulus is apparently the most important of the catalyst properties that constitute the modulus. The volume to surface ratio of the particles is the most general definition of the length dimension. For the same nominal particle size e.g. 1/16 inch diameter, the value of the length dimension is substantially influenced by the shape of the catalyst particle.

Figure (4) shows the influence of particle shape on effectiveness factor in the strongly diffusion influenced regime. The sphere was taken as a standard. Cylinders of length to diameter ratio equal to 3/1 and 10/1 were considered. Crushed particles were also included using volume and surface shape factors from a micromeritics text.[14]

It is interesting that cylinders are apparently the least desirable catalyst shape for a given nominal diameter. Particles in the form of "flakes" or "poker chips" are predicted to be the most effective. Ring-shaped catalysts are another alternative and have provided benefits in activity and stability for methanol oxidation.[16] Decreased reactor pressure drop was an additional bonus.

A frequent counter-argument to the use of crushed catalyst particles is that an increased reactor pressure drop will result when using the catalyst in its crushed form rather than cylindrical form. Using the Ergun equation[15] for flow through packed beds, a decrease in the equivalent particle diameter of a factor of (x2) may be compensated by a 30% reduction in gas rate. This trade off may be attractive with a feed such as Safaniya when catalyst costs due to low effectiveness factors for demetallation, approach 20 c/Bbl.

Pore Structure

The effective diffusivity and hence the effectiveness factor for metals can be increased by increasing the pore diameter.[9] The simplest expression relating the effective diffusivity to catalyst physical properties suggests that the diffusivity is directly proportional to pore diameter. At low effectiveness factors, the Weisz number criterion at constant observed reaction rate and particle size (1/16"), shows that the effectiveness factor for metals capacity is

directly proportional to pore diameter.

A pore plugging model would predict a greater dependence of effectiveness factor on pore diameter. The essential difference between the conventional pore mouth poisoning phenomena and pore-plugging is that the access of sulfur-bearing molecules to the interior of the catalyst particle is prevented when the diameter of the partially blocked pore approaches the size of the asphaltene and metal-containing molecules. This simple picture suggest that the effectiveness factor for demetallation is proportional to the square power on pore diameter based on estimates for the size of asphaltene molecules.[17]

Data is available[10] to test this relationship but the method of preparation of the catalyst suggests that an increase in the macropore volume was probably the way the diffusivity was increased. This suggestion is consistent with the relatively large decrease in pellet density resulting from a modest increase in pore volume. When macropores (greater than 600Å diameter) are present in the pore structure, the concept of volume-average pore diameter is a better correlating parameter than surface average pore diameter.[18] A relationship can be suggested between volume average pore diameter and fraction macropore volume. Desulfurisation effectivenes factors[10] now correlate well with volume average pore diameter raised to the square power. This relationship would also hold approximately for demetallation and is close to the value required by a simple pore-plugging model. Obviously, more data needs to be considered for better evaluation of the effect of pore structure on the effectiveness factors for desulfurisation and demetallation.

Catalyst preparation techniques can be modified to significantly improve the micropore volume and pore diameter. Reduction of surface tension during drying is shown to increase the micropore volume of an extruded alumina.[19] Calcination in wet air has a similar effect. For a given boehmite crystallite size, a compromise is necessary between pore volume and pore diameter of the extruded alumina.

BED-PLUGGING IN RESIDUUM DESULFURISATION

In addition to catalyst deactivation by the metals a second major problem in residuum processing is bed-plugging.[1,3] Desalting alone is not enough to prevent the build-up of interstitial material. This material reduces bed voidage, especially at the top of a trickle-bed reactor, and causes a significant increase in overall reactor pressure drop. The interstitial deposits are composed mainly of the sulfides of iron, nickel and vanadium.[3] They are contained in residuum stocks in organo-metallic compounds and in the case of iron, its feed concentration may obviously be supplemented by corrosion processes in lines ahead of the reactor. Nickel and vanadium sulfides depositing on the external surface of the catalyst pellet are probably held only weakly as nickel and vanadium in micelle-type structures. Their rate of reaction is probably greater than the nickel and vanadium deposited within the catalyst pellet. Coke deposits will also occur both inside the particle and interstitially.

Prediction of Bed-plugging

Estimation of plugging lives in trickle-bed-reactors can be made as a function of feed metals concentration reacting externally, with rate constant as a parameter. A first order reaction has been assumed. Interstitial deposits are considered to occur in the top 2o% of the trickle-bed-reactor.[3] Using the Ergun equation,[15] pressure drop increase against decreasing bed voidage can be plotted in a dimensionless form Figure (5). Taking a factor of 5-1o increase in overall pressure drop as a criterion for the plugging life (θ_{PLUG}) the corresponding volume of interstitial deposits can then be calculated. This is translated to grams of interstitial metal sulfides per cc of reactor if a metal sulfide density of 3 gm/cc is assumed. This value is abouth one-half the ideal crystalline sulfide densities but in a trickle bed reactor metal sulfides formed are unlikely to occur in their well-ordered, ideal states. Assuming for example, first order rate constants from 1-1o, plugging lives may be estimated, Figure 6.

Once again, the problems of processing Mid-East residua are

ignificantly less than Venezuelan residua due to the higher metal content of the latter. Within the crudes of the Mid-East, some distinctions may be drawn since demetallation rates decrease as molecular weight increases.[13] This implies that interstitial rates of reaction for Arabian Heavy feeds are less than for Arabian Light feedstocks. If it is considered that interstitially deposited metals are derived mainly from the maltene fraction of crude oils then about 30 % of the total nickel plus vanadium metals will be available for interstitial reaction requiring essentially little catalyst surface. In addition, the presence of 5-10 ppm of iron[3] in the residuum will also be available for interstitial reaction and subsequent deposition as iron sulfides. For an Arabian Light feed, using a rate-constant between 5 and 10 hr^{-1} and an entering feed metals concentration of 20 ppm, a plugging-life of about 7000 hours is predicted from Figure (6). With a Safaniya feed, a rate constant of about 2-5 hr^{-1}, an entering feed metals concentration of 40 ppm, a plugging life of about 6000 hours is predicted from Figure (6). Venezuelan residua would have very short plugging lives of about 1000 hours. In the comparison between Arabian Light and Safaniya feeds, the decreased rate of reaction has eased the plugging problem for the Safaniya feed.

The assumed value of the metal sulfides density would strongly affect the predictions in Figure 6 and the slope of the curves. The presence of salt and particulate iron has been found[1,2] to substantially decrease plugging lives. For accurate predictions the interstitial rate constants and metal sulfides density should obviously be determined experimentally.

Methods of increasing plugging lives

The methods available depend on whether the fixed bed concept of operation is retained or the flexibility of an ebullating bed system is considered. The latter system will be considered first since one of the primary advantages of the ebullated bed is the lack of pressure drop buildup with time on-stream.[5]

Moving Beds: The advantages of the H-oil process have frequently been described and are generally associated with uniform distribu-

tion of reactants, isothermal operation, lack of bed plugging and continuous catalyst withdrawal and replacement. The formation of coke-catalyst agglomerates in the reactor is avoided if recyle of a gas-oil fraction is practised.[19] However, there are disadvantages associated with the use of this reactor design if hydrodesulfurisation is of primary importance. Staging of the reactors becomes necessary to achieve the desired conversion levels.[20] This means that the flow through the reactor does not approach the plug flow of the trickle-bed operation. A completely mixed system probably defines the ebullating bed better and is consistent with the strong claims made for isothermal operation. This conclusion is also consistent with values for the height of a mixing unit (H.M.U) obtained in three phase fluidisation studies.[21] These studies showed that the H.M.U. for an air-water-ballotini system with 6 m.m. spheres was of the order of 4-10 cm i.e. approaches plug-flow. The column diameter was 9 inches, the bed height 14 feet. If the particle size was decreased to 1 m.m.(~ 1/32 inch) the value of the H.M.U. increased signigicantly to 40-100 cm. The change was attributed to bubble disintegration with the larger particles and bubble coalescence with the smaller particles. Using 0.1 m.m. particles (~ 200 mesh) it is thought that the value of the HMU may increase by another order of magnitude to 10^3 cm. The deviation from plug flow is considerable.

In summary, pore diffusion arguments dictate a small catalyst particle size of about 200 mesh, but mixing problems require a large particle size, about 6 mm., to approach plug flow. A compromise of 1/32 inch catalyst size seems to be suggested particularly if the problem of separating the fine catalyst from the oil is important. A completely mixed system would also result in higher hydrogen consumptions due to increased hydrocracking. The ebullated bed reactor volume must also be significantly greater than the plug-flow case. Bed expansions of the order of 50 %[20,21] are used and with a 75 % conversion, the volume of a completely mixed reactor system would be at least twice the volume of a plug flow reactor. Indeed, the bed-plugging problem is eliminated but deviation from plug flow and its associated disadvantages are to be expected.

Fixed Beds: If the fixed bed concept of operation is retained, then graded catalyst beds can be used to relieve the interstitial bed-plugging problem. Graded catalyst beds are already being used[3] in deasphalted oil Isomax.

Graded catalyst beds incorporate the principles associated with the specific surface of variously sized particles and particle shapes with low pressure drop characteristics. Ringshaped catalysts have been used in methanol oxidation[16] to decrease the pressure drop across the reactor. The presence of interstitial deposits reacting from the feed makes this approach particularly useful.since the void volume per unit volume of reactor has been increased in comparison to cylindrical particles. The surface area of a catalyst particle per unit volume of reactor is inversely proportional to the diameter so that large particles at the top of a trickle-bed reactor will reduce the available surface for the interstitial reaction and spread the metals further down the bed.

CONCLUSIONS

Approximate methods have been outlined for the prediction of catalyst lives in fixed bed residuum desulfurisation. Predicted catalyst lives were consistent with trends in current RDS literature. A pore-plugging mechanism due to metals deposition was assumed to be the cause of catalyst deactivation for desulfurisation. Demetallation effectiveness factors less than o.5 are considered typical for Middle East residua. Methods of decreasing the pore diffusion problem are related to special catalyst preparations and the use of unusual catalyst shapes.

Approximate methods have also been outlined for the prediction of fixed bed plugging in RDS. Plugging lives less than 8ooo hours are considered likely for Middle East residua. For Venezuelan stocks 1ooo hours may be typical. Novel catalyst shapes could again be useful. Deviation from plug-flow is expected with ebullating catalyst beds particularly with 2oo mesh size particles.

More experimental data and more rigorous theoretical treatments are required to improve predictions.

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FIGURE 1 : CATALYST PARTICLE SIZE vs. EFFECTIVE DIFFUSIVITY.

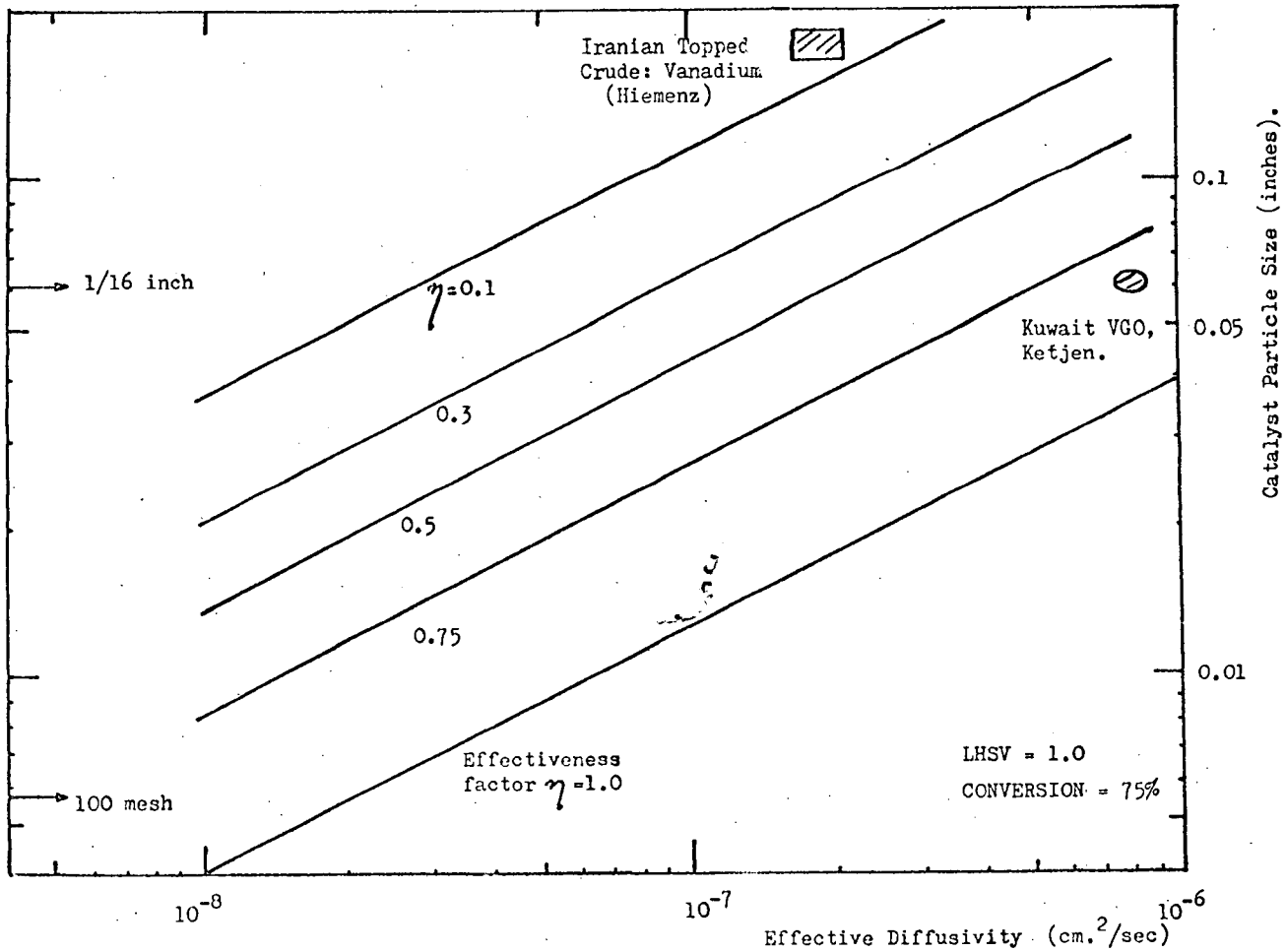

FIGURE 2 : EFFECTIVE DIFFUSIVITY vs. MOLECULAR WEIGHT.

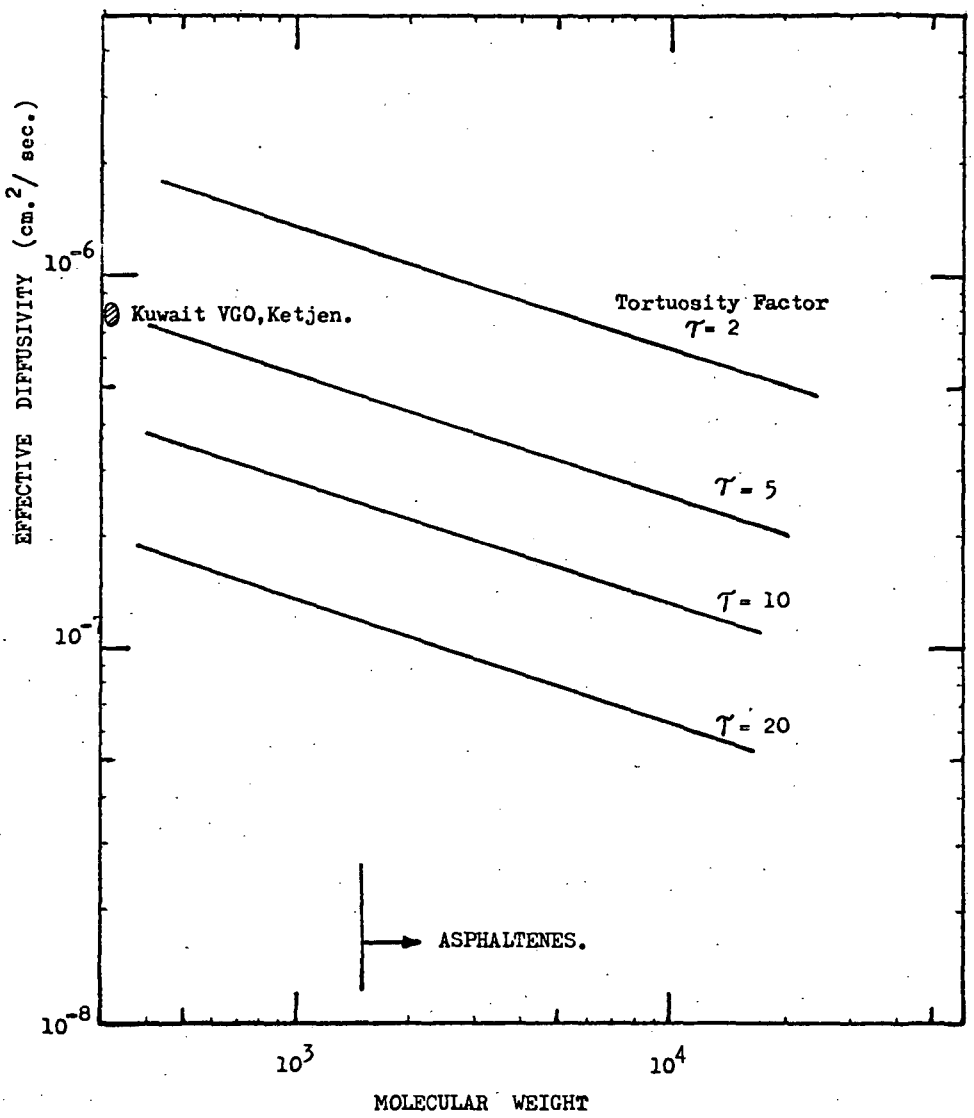

FIGURE 3 : CATALYST LIFE vs. METALS DEPOSITION IN RESIDUUM DESULFURISATION.

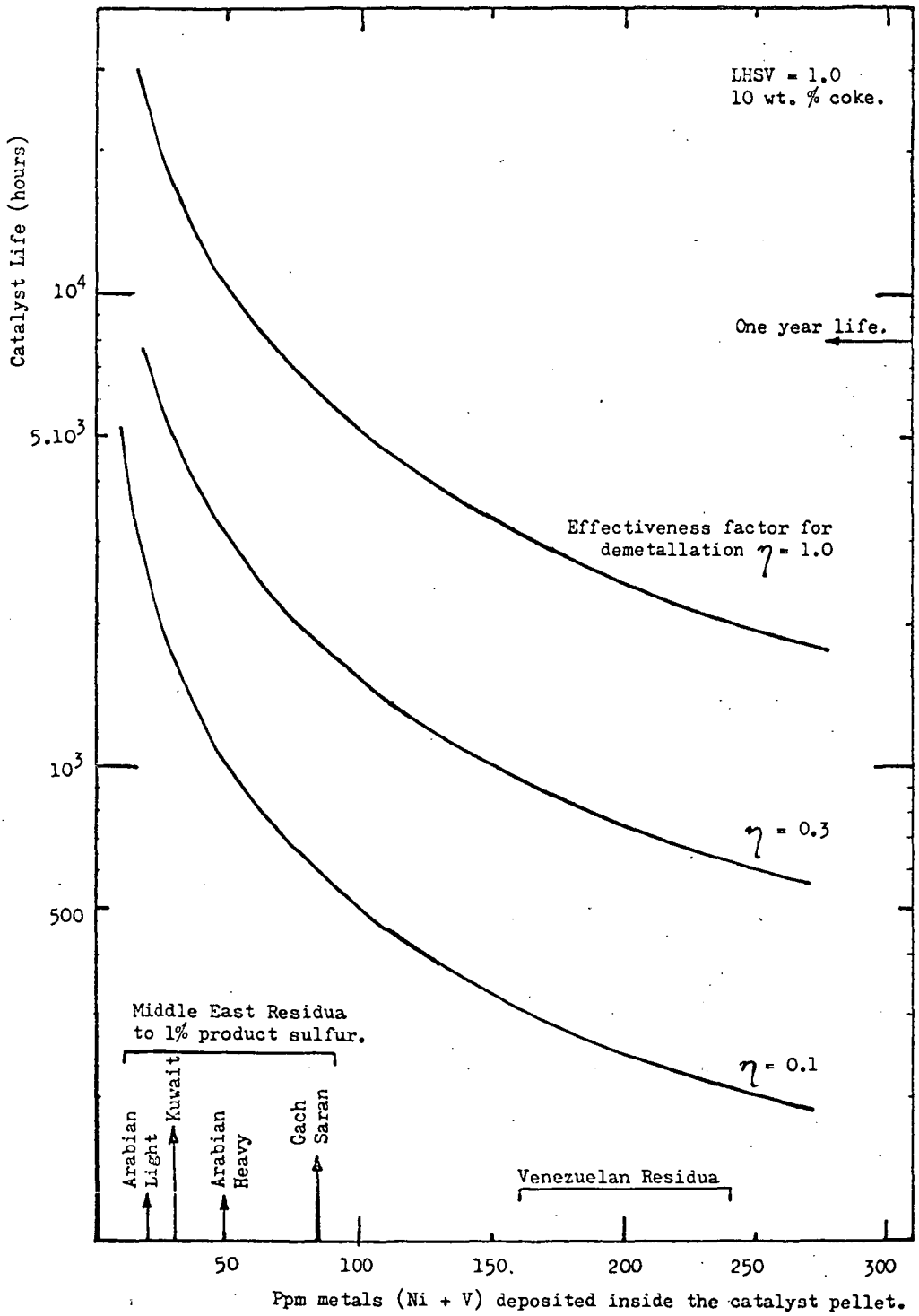

FIGURE 4 : EFFECT OF PARTICLE SHAPE ON EFFECTIVENESS FACTOR

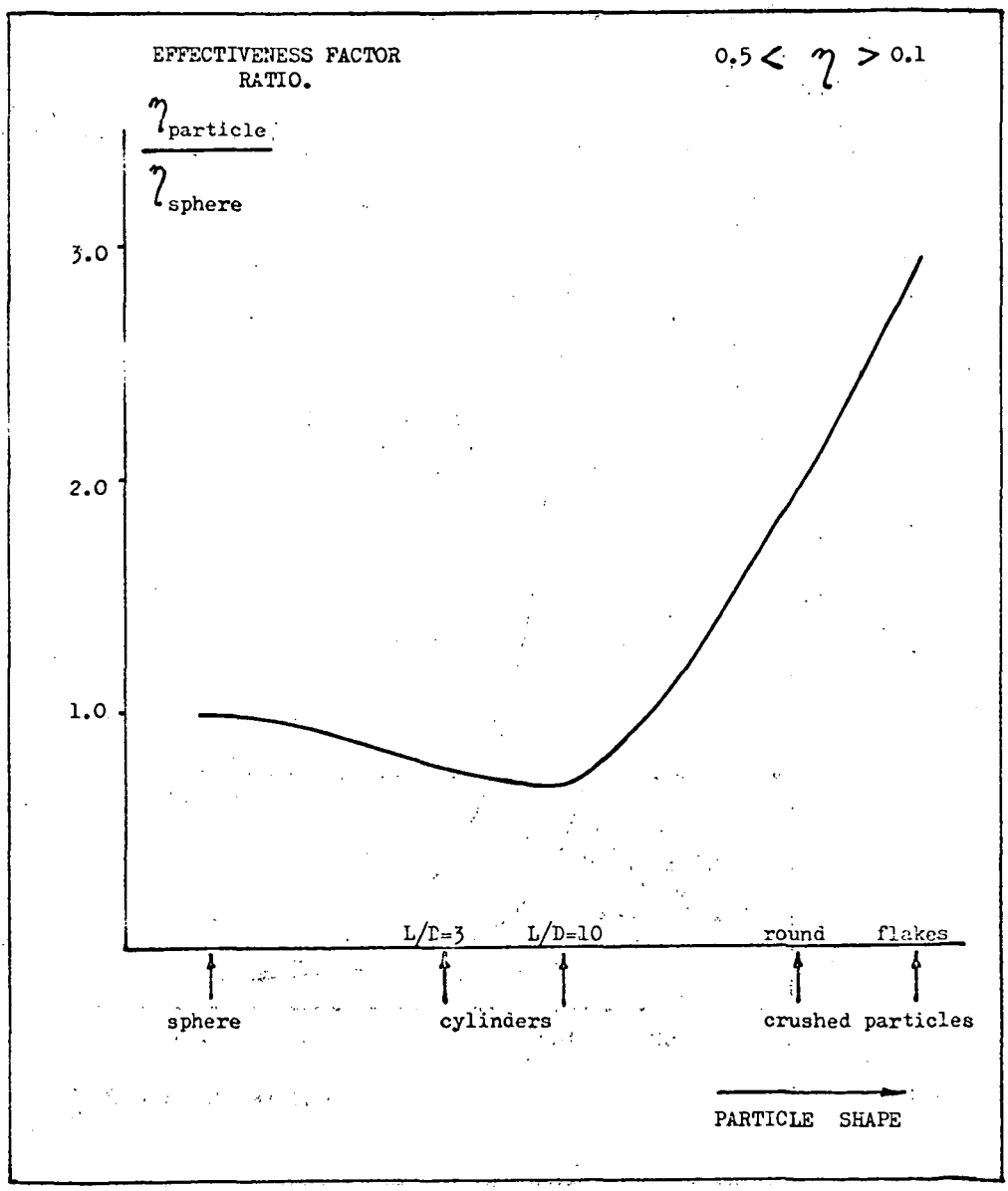

FIGURE 5 : EFFECT OF DECREASING BED VOIDAGE ON FIXED BED PRESSURE DROP.

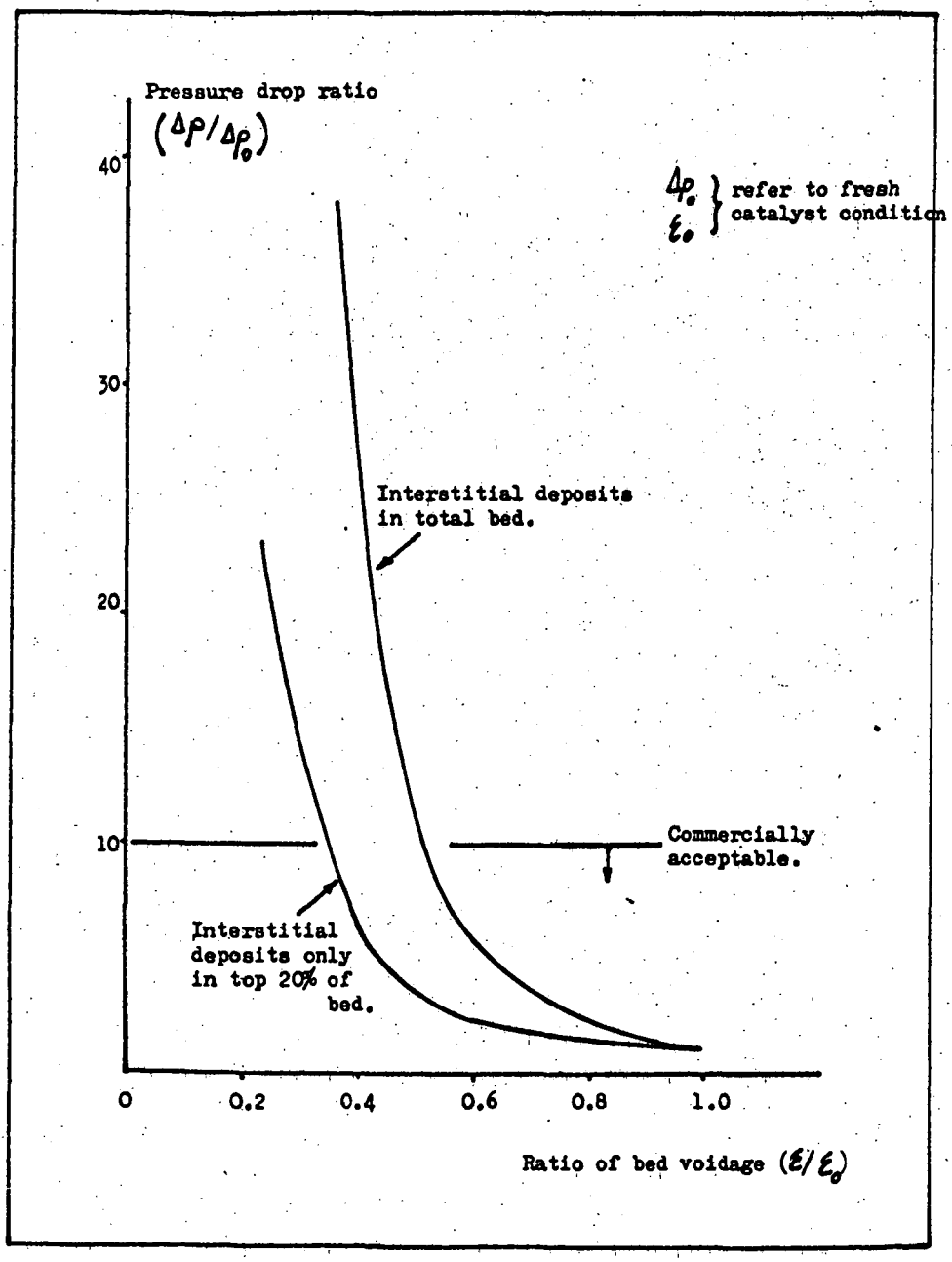
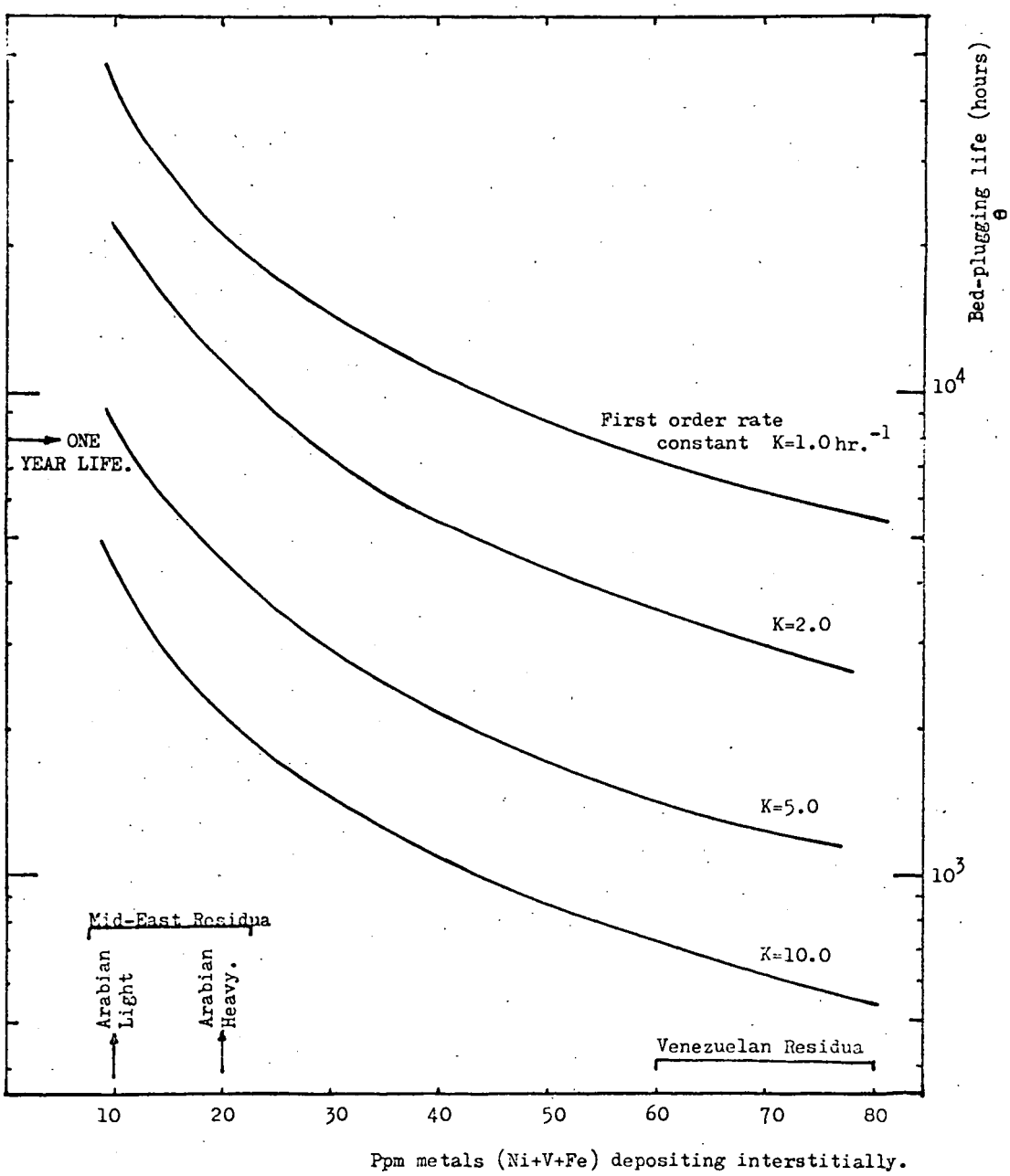
FIGURE 6 : BED-PLUGGING LIVES vs. INTERSTITIAL METALS DEPOSITION