ABSTRACT

The production and transportation of petroleum fluids could be severely affected by flocculation and deposition of heavy organics (i.e. asphaltene, paraffin/wax, sand, and/or diamondoid) in the reservoir matrix; production wells; surface equipment; storage vessels, processing facilities; and/or transfer pipelines. This is, in many instances, of devastating consequences if the amount of precipitation is rather large. Therefore, it is important to understand the multi-phase and flow behavior of heavy organic species contained in crude oil.

It is important to be able to predict any potential deposition, "When" and "How much" heavy organics will flocculate out of solution and deposit? as well as "What are" the economic implications? are questions of major interest to the petroleum industry. Since a petroleum crude generally consists of a complex mixture of hydrocarbons and heavy organics it has become necessary to look at this problem from a more fundamental point of view than it had been the practice in the past.

In this paper we present an overview of the heavy organic deposition problem and the causes and effects of such depositions. We present predictive schemes to be used for preventive measures to fight such a problem. Further research on these subjects is going on in our laboratory.

INTRODUCTION

Over the last five decades a number of investigators have conducted research on the nature of heavy organics and the mechanisms of heavy organic deposition. One important conclusion evolved from experimental work is that heavy organic compounds (asphaltene) which deposit possess a wide range of polarities and molecular weights (1-3). Dispersed asphaltenes are sterically stabilized by neutral resins, they are electrically charged (4), and have a diameter of 30-40 Å (5). The stability of these particles can be disrupted by addition of solvents (e.g. n-hydrocarbons), it could also be disrupted during flow conditions due to shear stresses, or by counterbalancing the weak asphaltene particle charge. The latter is an important phenomenon since during crude oil production a streaming potential is generated which has been found to lead to asphaltene aggregation (6). When solvents are used to precipitate asphaltenes, the resulting aggregates may have a diameter as large as 300 µ (7). In addition to asphaltenes there may be other types of particles suspended in the crude oil as well. For instance, sand particles swept from the reservoir matrix, paraffin crystals if the temperature falls below the cloud point of the crude, and/or diamondoids.

In the petroleum reservoir, asphaltene particles have been considered as colloidal particles, or micelles, being comprised of clusters of heavy particles associated principally via π-π interactions. Also, it may be assumed that the repulsive forces between resin molecules and the adsorbed resins on the macromolecular (asphaltene) surfaces keep clusters of asphaltene particles from aggregating. Introduction of a miscible solvent into the oil mixture will cause the resin concentration to vary accordingly. A decrease in resin concentration may be followed by desorption of the resin molecules from the asphaltene-particle surface, and therefore allow the clusters of asphaltene particles to be subject to mutual interactions. This may result in a situation in which clusters of asphaltene particles contact each other on resin-uncovered sites, aggregate (irreversible aggregation), and flocculate out of solution (1-3). During the flocculation process, the clusters of heavy particles are assumed to remain suspended in the solution randomly and independent of one another as Brownian particles due to the molecularly induced thermal motion. Van der Waals attractive forces, and electrical (electrostatic or electrokinetic) repulsive (or attractive) forces would be the factors causing the aggregation and flocculation of heavy organic particles. The peptizing properties of the resin molecules in the solution are closely related to surface characteristics of asphaltene particles. Because of the surface

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characteristics of asphaltene particles, an attempt to increase the surface area will require energy to be spent. The energy to increase the surface area is called surface free energy. Because the surface of asphaltene particles is in a higher free energy state than the bulk solution (oil) a spontaneous tendency exists for the surface area of asphaltene particles to achieve a minimum value. Therefore, all colloidal systems have a built-in tendency to spontaneously flocculate and precipitate unless prevented by other stabilizing factors. The flocculation process, affected by the collision between particles, is assisted by thermal motions of molecules of the dispersion medium. In order to formulate the necessary model(s) for the prediction of the multiphase and flow behavior of heavy organics, extensive research has been performed in our laboratory for over thirteen years. We present next the causes and effects of heavy organic deposition as well as predictive schemes. Case histories are presented to exemplify the deposition problem and the approach that can be undertaken to prevent deposition. Recent developments in the modeling mentioned above are also presented.

HEAVY ORGANIC DEPOSITION (CAUSES, EFFECTS, AND PREVENTIVE TECHNIQUES)

The parameters that govern the precipitation of heavy organics from petroleum fluids appear to be composition of crude and injection fluid (if any), pressure, temperature, flow characteristics, and the properties of the conduit (pipeline, well, etc.) in which the reservoir fluid is flowing. With alterations in these parameters the nature of organic substances which precipitate will vary. Also, precipitation of some of the families of organic compounds (asphaltenes/resins) is generally followed with polymerization or flocculation of the resulting precipitate, which produces an insoluble material in the original reservoir fluid. Because of the complexity of the nature of heavy organics in petroleum fluids the phenomena of precipitation and flocculation of these substances are not well understood. Also in view of the complexity of the petroleum reservoirs, study and understanding of the in situ precipitation of heavy organics seems to be a challenging and timely task. Such an understanding will help to design a more profitable route for petroleum production and processing systems.

In order to model the phenomena of organic deposition from petroleum fluids under the influence of a miscible solvent, or in the process of its blending with another petroleum fluid one has to consider the following: (i) The nature of organic compounds being deposited.; (ii) The nature of the petroleum fluid as a whole.; (iii) The role of temperature, pressure, and composition.; (iv) The role of flow regime and the structure of the conduit (pipeline, well, etc.) through which the flow is underway.

Miscible flooding of Petroleum Reservoirs (8)

Secondary recovery practices usually involve injection of either water or gas into the reservoir to increase the insufficient pressure and keep the reservoir fluids flowing. Oftentimes the injection of miscible solvents is preferred because significantly less residual oil is left in the swept reservoir. Miscible flooding may be divided into three major categories:

First-Contact Miscible Drive: The basis of this process is the injection of hydrocarbons which are completely soluble in residual oil. A typical fluid used for this purpose is propane/butane (or a mixture of both).

Condensing Gas Drive (Enriched gas drive): In this process a miscible fluid is used as well. A typical fluid used is natural gas with a relatively high concentration of ethane, propane, and butane.

Vaporizing Gas Drive (High pressure gas drive): This process involves the injection of a high density fluid such as carbon dioxide or nitrogen at high pressure.

All of the miscible fluids used in secondary recovery (with the exception of nitrogen) have been found to induce the precipitation of heavy organics. Therefore, deposition of heavy organics may be expected to occur at some point during the injection process. Thus, the conditions (if known) at the onset of precipitation should be avoided (3).

Heavy Organic Deposition in the Campeche Sound Marine Platform in Mexico (1)

Heavy organic deposition has been observed in the process of blending crude oil with other petroleum fluids. Especially when the compositional difference among the fluids being blended is appreciable (e.g. the blending of heavy and light crude oils).

This phenomenon is best illustrated with the case history of heavy organic deposition in the Campeche Sound Marine Platform.

Several crude oils of varying compositions and heavy-organic contents are produced in the Campeche Marine area. These various streams are generally mixed together in the platform and then sent to the refinery (or storage). According to Chavez et al. (9) there is no precipitation during production operations. However, heavy organic deposition is observed almost everywhere in the facilities of this platform. One example was the deposit found in the separator of the first stage of the Akkatan-1 production platform. Initially, the deposits were tried to be removed utilizing steam, diesel oil and heavy aromatics without satisfactory results.
The severity of the deposition phenomenon urged the need for a detailed analysis of the organic deposits and samples of the crude oils produced in the area. Table 1 contains the characterization data of some of the crude oils produced in Campeche Marine zone.

<table>
<thead>
<tr>
<th></th>
<th>ABKATUN-93</th>
<th>CHUC</th>
<th>POL-73</th>
<th>MIXT. A*</th>
<th>MIXT. B**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spec. Gravity 20/4°C</td>
<td>0.8933</td>
<td>0.847</td>
<td>0.8694</td>
<td>0.8736</td>
<td>0.8644</td>
</tr>
<tr>
<td>API Gravity</td>
<td>26.38</td>
<td>35.1</td>
<td>31.65</td>
<td>29.94</td>
<td>31.6</td>
</tr>
<tr>
<td>Pour Point, °C</td>
<td>-33</td>
<td>-33</td>
<td>-39</td>
<td>-33</td>
<td>na</td>
</tr>
<tr>
<td>Paraffin, wt%</td>
<td>na</td>
<td>na</td>
<td>4.62</td>
<td>5.11</td>
<td>na</td>
</tr>
<tr>
<td>Cloud Point, °C</td>
<td>45</td>
<td>na</td>
<td>44</td>
<td>46</td>
<td>na</td>
</tr>
<tr>
<td>n-C7 asphaltenes, wt%</td>
<td>5.02</td>
<td>0.5</td>
<td>0.85</td>
<td>2.29</td>
<td>1.1</td>
</tr>
</tbody>
</table>

(*) Mixture A: 50 vol% of Pol-73 and 50 vol% of Abkatun-73; (**) Mixture B: 63 vol% of Pol-73, 20 vol% of Chuc, and 17 vol% of Abkatun-93; (na) not available

Laboratory analyses revealed that the crude oils produced in this marine zone generated large amounts of asphaltic sludges upon contact with hydrochloric acid. Thus, a different well-stimulation technique was developed in order to prevent the formation of asphaltic sludges. Nonetheless, the problem persisted and organic deposits were again detected. A chemical analysis of the heavy organic material encountered in the separation equipment revealed they were comprised mainly of asphaltites, neutral resins, asphaltogenic acids and carbenes (asphaltogenic acids and carbenes were present in small proportions). This suggested that somehow the blending of different crude oils resulted in asphaltene flocculation and deposition. Therefore, each of the crude oil streams arriving at the Campeche marine platform were submitted to "electrodeposition", "deposition due to temperature drop", and "settling by centrifuge" tests.

The "electrodeposition" tests performed were intended to qualitatively simulate the tendency of the crude oils to deposit due to streaming potentials. A streaming potential is generated when a fluid containing charged species (e.g. asphaltites) flows through a channel. However, negligible amounts of deposition were found in these "electrodeposition tests" from all the samples analyzed. Thus concluding that a streaming potential was not a cause for the deposits observed.

The "deposition-due-to-temperature-drop" tests revealed that the samples showed a negligible tendency to form paraffin/wax deposits. All the crude oil samples deposited less than 0.2 wt% of paraffin due to temperature drop. Even this small percentage could cause serious problems if the operating temperature falls below the cloud point.

The "settling-by-centrifuge" tests were intended to simulate the heavy organic deposition due to gravitational forces. In these tests the samples were centrifuged at high (2400 rpm) and moderate (1200 rpm) velocities. The experiments were carried out at 0, 10, 20, 30, 40, 50 °C, and test durations of 10 & 30 minutes. The cloud point of the samples was generally below 50°C (see Table 1).

Figure 1 shows the results for crude oil Abkatun-93. This crude oil has an API gravity of 26.38 with a n-C7 asphaltene content of 5.02 wt%. The cloud point of this crude oil is 45°C. From this figure we observe negligible amounts of deposition at 50°C. This is hardly surprising since this temperature is above the cloud point of the crude. The sediments detected from this sample at 50°C were found to be insoluble in aromatic solvents. At lower temperatures the amount of sedimentation observed is due to paraffin/wax liquid-solid phase transition.

Figure 2 contains the results obtained for Pol-73. This crude oil has an API gravity of 31.65 and a n-C7 asphaltene content of 0.85 wt%. The cloud point for this crude oil was found to be 44°C. Again, negligible sedimentation is observed at 50°C which is insoluble in aromatic solvents. The sediments at lower temperatures are due to paraffin/wax.

The crude oil Chuc was also submitted to this test and showed negligible amounts of sedimentations at all test conditions. This is a light crude oil with an API gravity of 35.1 and its n-C7 asphaltene content is only 0.50 wt%.

Figures 3 depicts the results obtained for a 50/50 volume% mixture of Abkatun-93 and Pol-73 crude oils. This mixture has an API gravity of 29.94 and a n-C7 asphaltene content of 2.29 wt%. The cloud point of this mixture was found to be 46°C. It is observed, from Figure 3, that this mixture presents an appreciable percentage of deposition at 50°C. The amounts of sediments here are higher than those for the pure crude oils, especially for duration times of 30 minutes for all the temperature range. At 50°C the sediment from this mixture ranges from 1 to 1.2 vol%, whereas the pure crude oils showed less than 0.3 vol% of sediments at this temperature. This indicates that flocculation and precipitation of asphaltites has occurred upon mixing of these two crude resulting in a larger amount of deposition even at a high temperature (50°C).

Figure 4 contains the results for a mixture comprised of 63/20/17 volume% of the crude oils Pol-73/Chuc/Abkatun-93. This mixture has an API gravity of 31.6 and a asphaltene content of 1.1 wt%. The cloud point for this mixture was not determined. However it is expected to be below 50°C (see Table 1). From Figure 4 it can be seen that the amounts of sedimentation from this mixture are enormous both at high (50°C) and low temperatures. These results also indicate that the blending of light and heavy crude oils produced in the Campeche Marine zone render in asphaltene flocculation and deposition. Further analysis of the sediments from this mixture revealed that in fact asphaltene had been flocculated out of solution.

In order to prevent asphaltene deposition in the process of blending large amounts of light crude oils with heavier ones.
it is necessary to study the phenomenon from fundamental principles. This will enable the development of predicting techniques for the optimum conditions at which light and heavy crudes can be mixed together without getting to the onset of asphaltene flocculation. Asphaltene deposition can thus be prevented by avoiding the conditions at the onset of flocculation. Several models have been reported in the literature (3, 10, 11, 18-21) which successfully predict the onset and amounts of asphaltene precipitation. These models predict the phase behavior of heavy organics, contained in crude oils, under the influence of a miscible solvent as in the case of miscible flooding or the blending of crude oils with other reservoir fluids. A brief description of each model is given below.

Continuous Thermodynamic (CT) Model (3, 10, 11)

The degree of dispersion of heavy organics in petroleum oils depends upon the chemical composition of the petroleum (12-14). Deposition of such compounds can be explained by an upset in the balance of oil composition. The ratio of polar to non-polar molecules and the ratio of high to low molecular weight molecules in a complex mixture such as petroleum are the two factors primarily responsible for maintaining mutual solubility. The addition of miscible solvents will alter these ratios. Then the heavy and/or polar molecules separate from the mixture either in the form of another liquid phase, or to a solid precipitate. Hydrogen bonding and the sulfur- and/or nitrogen-containing segments of the separated molecules could start to aggregate (or polymerize) and, as a result, produce the irreversible heavy organic deposits which are insoluble in the liquid phase (oil).

Inasmuch as heavy organics have a wide range of size, or molecular weight distribution, one may consider such compounds as heterogeneous polydisperse polymers. Then, in order to predict the phase behavior of heavy organics one can assume that the properties of heavy organic fractions depend on their molecular weights. To perform phase equilibrium calculations, the necessary condition for chemical equilibrium must be satisfied. This is, the chemical potential of every heavy organic fraction in the liquid phase, \( \mu_i^L \), has to be equal to its chemical potential in the solid phase, \( \mu_i^S \):

\[
\mu_i^S = \mu_i^L; \quad i = 1, 2, 3, ... \tag{1}
\]

In this model, the Scott and Magatt theory of heterogeneous polydisperse polymer solutions (15) is employed for calculation of the chemical potentials of heavy organic fractions. Because organic substances such as asphaltenes consist of mixtures of molecules with virtually continuous molecular weight distributions; one can utilize the continuous mixture theory (16, 17), joined with the thermodynamic theory of heterogeneous polymer solutions. Introduction of the continuous mixture theory results in a model that contributes to better characterization of heavy organics and prediction of the onset of deposition and phase behavior under the influence of a miscible solvent. Figure 5 shows the comparison of molecular weight of asphaltenes from petroleum crude oil before and after flocculation, as predicted by the model. According to this figure, the fractions of asphaltene with high molecular weights tend to deposit earlier than the fractions of asphaltene with lower molecular weight.

Steric Colloidal (SC) Model (18, 19)

This model is based upon the assumption that heavy organics (asphaltenes) exist in oil as suspended particles. Their suspension is assumed to be caused by resins (heavy and mostly aromatic molecules) which are adsorbed to the surface of heavy organic particles and keep them afloat because of the repulsive forces between resin molecules in the solution and the adsorbed resins on the macromolecular (asphaltene) surface (see Figure 6). Stability of such a suspension is considered to be a function of the concentration of resins in the solution, the fraction of asphaltene surface sites occupied by resin molecules, and the equilibrium conditions between the resins in solution and on the asphaltene surface. According to thermodynamics, a necessary condition for chemical equilibrium between two phases is that the chemical potential of each component in one phase is equal to its chemical potential in the other phase. Writing this condition for the resins in the asphaltene and oil phase one will obtain:

\[
\mu_{\text{asphaltene phase}}^\text{resin} = \mu_{\text{oil}}^\text{resin} \tag{2}
\]

The significance of the SC model is that the asphaltene particles will remain completely covered regardless of how the nature of the liquid mixture (i.e. add or remove miscible solvent) is changed. So long as the calculated chemical potential remains equal to (or above) the critical chemical potential. Calculation of the chemical potential of the resins in the solid phase would require utilizing small-system thermodynamic techniques. This model, however, requires only one calculation of the chemical potential of the macroscopic asphaltene-free oil phase. and as a result, macroscopic chemical potential calculations are adequate.

The amount of resins adsorbed is primarily a function of the of their concentration in the liquid state (the oil). So, for a given system (i.e. fixed type, amount of oil and asphaltenes) changing the concentration of resins in the oil will cause the amount of resins adsorbed on the surface to change accordingly. This means that we may drop the concentration of resins.
in the oil to a point at which the amount of resins adsorbed is not high enough to cover the entire surface of asphaltenes. This may then permit the asphaltene particles to come together (irreversible aggregation), grow in size, and flocculate.

Fractal Aggregation (FA) Model (20, 21)

The FA is a realistic model for the interaction of heavy and light components of crude oils and accounts for both the solubility and colloidal effects. It is constructed by joining the concepts of continuous thermodynamic theory of solid-liquid phase transition, Fractal aggregation theory of colloidal growth, and steric colloidal collapse and deposition models. This model is capable of predicting the onset and amounts of asphaltene deposition from petroleum crudes under the influence of miscible solvents. This model is based on the fact that resins play a key role in the solubilization of asphaltenes because they reduce asphaltene aggregation. Therefore, the degree of solubility of asphaltenes in the oil depends on the peptizing effect of resins with respect to asphaltenes, as well as on the resin concentration in the solution (i.e. the change of resin concentration in the oil due to the addition of a miscible solvent).

The peptizing properties of the resin molecules in the solution are closely related to surface characteristics of asphaltene particles (22, 23). Because of the surface characteristics of asphaltene particles, an attempt to increase the surface area will require energy to be spent. Because the surface of asphaltene particles is in a higher free energy state than the bulk solution (oil) a spontaneous tendency exists for the surface area of asphaltene particles to achieve a minimum value. Therefore, there exists a built-in tendency to spontaneously flocculate and precipitate unless prevented by other stabilizing factors. The flocculation process, affected by the collision between particles, is assisted by thermal motions of molecules of the dispersion medium. In order to account properly for the phenomenon of asphaltene deposition a model must incorporate the following:

1. The role of resin concentration in such a deposition mechanism and its effect on the colloidal aggregation process of heavy-organic particles under the influence of miscible solvents.
2. The growing size distribution of clusters of heavy-organic particles by introducing the irreversible kinetics of aggregation.
3. Determination of the onset of heavy organic deposition, solubility of heavy organics, the size distributions of heavy organic deposits in the precipitated phase and of heavy organics remaining soluble upon changes in pressure, temperature and composition.

There have been numerous attempts to understand the mechanism and kinetics of aggregation of clusters of heavy particles. Up to now, most of the studies on the cluster-cluster aggregation were concerned with the geometrical aspects of the aggregates which include the Euclidian dimension (d), the fractal dimension of clusters (D), and the average radius of clusters (R). It has been noted that in addition to the geometrical aspects another important characteristic of the colloidal aggregation model is the existence of a given function for the size distribution of the clusters of heavy particles (24). This size distribution may be derived using the kinetic theory of fractal aggregation along with the theory of heterogeneous polymer solutions.

One may consider a system consisting of\(N_C\) clusters of \(N_0\) asphaltene particles (identical particles of radius \(R_0\) and unit mass \(m\)) which are suspended randomly in an oil and stabilized by resin molecules adsorbed on the surfaces of asphaltene particles. The clusters of asphaltene particles act as Brownian particles which are suspended due to the thermal motions of molecules of the dispersion medium. Introduction of a miscible solvent into this system may result in a new condition in which the clusters of asphaltene particles would rigidly stick to each other. That is, a cluster of mass \(m_i\) colliding with a cluster of mass \(m_j\) would form a single new cluster of a mass \(m_{i+j}\). This process is then repeated.

The kinetics of such an aggregation are assumed to obey the following mechanism.

\[
A_i + A_j \xrightarrow{K_{ij}} A_{i+j}
\]

where \(A_i\) is the cluster of mass \(m_i\), and \(K_{ij}\) is a concentration-independent kinetic (or collision) kernel which describes the aggregation mechanism.

This mechanism was originally proposed by Smoluchowski (25) for coagulation and by Flory (26) for branched polymerization. It is extensively studied in the theory of aggregation, as well as in the theory of colloidal suspension. The rate of aggregation, \(R_{ij}\), at which an \(i\)-cluster of a given mass \(m_i\) and a \(j\)-cluster of a given mass \(m_j\) may come into contact with each other and form an \((i+j)\) cluster is given by

\[
R_{ij} = K_{ij}C_iC_j = n_i/n_0 \quad (3)
\]

where \(C_i\) is the number of clusters of mass \(m_i\) (containing \(i\) asphaltene particles of unit mass \(m\)) and \(N_0\) is the total number of particles. Because the population of the resulting \(k\)-cluster (\(k=i+j\)) increases by all collisions between \(i\)-clusters and \(j\)-clusters and decreases when a \(k\)-cluster combines with another cluster, then \(C_k(t)\) will satisfy:

\[
\frac{dC_k(t)}{dt} = \frac{1}{2} \sum_{j=1}^{k-1} K_{k-j,j} C_{k-j}(t) C_j(t) - C_k(t) \sum_{j=1}^{k-1} K_{k,j} C_j(t)
\]

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Eq. 4 is known as the Smoluchowski's coagulation equation. This irreversible growth mechanism of asphaltene particles implies that the tendency of asphaltene particles to aggregate depends on their mass and the concentration of resin in the solution. A major advantage of Smoluchowski's coagulation equation is that many analytic results can be obtained from it. For some forms of $K_{ij}$ (i.e., $K_{ij}=1$, $i+j$, or $iXj$), analytic solutions to Smoluchowski's equation can be obtained. Different investigators have tried to improve this aggregation mechanism by considering the reactivity of a $k$-cluster to be proportional to its effective surface area, $s_k$. A characteristic radius, $R_k$ (for cluster of size $k$), will be proportional to the size of the cluster. The fractal dimension, $D$, of a given cluster is defined through the following expression:

$$R_k \sim k^{1/D} \quad ; \quad D < d$$

(5)

it follows then that $s_k \sim k^w$; $w$ is an exponent (positive or negative) characterizing the effective surface area. Thus, the kinetic (or collision) kernel adopts the forms:

$$K_{ij} \sim (i X j)^w \quad \text{(product kernel)}$$

(6)

$$K_{ij} \sim (i^w + j^w) \quad \text{(sum kernel)}$$

(7)

In order to apply this aggregation mechanism of clusters to the phenomena of aggregation and deposition of asphaltene from petroleum crudes, one is interested in these two kinetic kernels which are proportional to the effective surface area of clusters. Therefore, one must account for the geometrical aspects of clusters in the expression of these kinetic kernels. Consider a system composed of a number of kinetically growing clusters, in which a cluster of size $k$, before sticking to another cluster, diffuses randomly in space of Euclidian dimension, $d$, along a trajectory of the dimension of diffusion walk $d_w$ (where $d \geq d_w$). The volume, $V_0$, of a system can be defined as $V_0 = t_0^d$; $t_0$ is the length of the lattice. Let us also assume that the kinetically growing cluster of size $k$ has a surface diffusion velocity given by: $v_k = t^d / t$; $t$ is the "walk-length" (average distance between clusters); $t$ is the walk time. It can also be assumed that this diffusion velocity is inversely proportional to the diffusing cluster size, $v_k \sim k^{-\alpha}$; $\alpha$ is a negative exponent. If a cluster of size $k$ is assumed to contain $k$ identical particles of unit mass it follows that: $v_k \sim m^\alpha$. It is possible to show how the exponent $w$, characterizing the surface area in the expression of the kinetic kernel, can be expressed in terms of other characteristic constants of the system ($d$, $d_w$, $\alpha$, and $D$) [28]. The time (t) needed by a cluster of size $k$ having a walk-length $t$ is given by $t \sim t^\alpha R_k^{-\alpha}$ or (in terms of the characteristic radius) $t \sim t^{d_w} R_k^{-\alpha}$. Because Eq. (4) is invariant under a semi-group of similarity transformation a change of length scale in the whole system can be performed such that each length is rescaled by a factor of $b$:

$$t \sim \frac{t_0}{b^d} \quad \text{for all clusters}$$

(8)

The corresponding rescaling of time (from $t$ to $t'$) will be $t' \sim b^{d - d_w} \alpha t$. Considering that Smoluchowski's equation, Eq. (4), is scale-invariant, the $K_{ij}$, which has the dimensions of a volume divided by time, must be rescaled as:

$$\frac{K_{ij}}{t^d / t} \sim \frac{V_0}{V_0'} = \frac{t_0^d t'}{(t_0')^d t'} \sim b^{d - d_w + D \alpha}$$

(9)

One may redefine (for convenience) a parameter $b=\lambda^{1/D}$. Thus, the general scaling relation of coagulation kernels, can be written as $K_{ij;ij} = \lambda^{n} K_{ij}$; $K_{ij;ij}$ is the new notation for the transformed coagulation kernel $K_{ij}$ and $n = (d - d_w)/D + \alpha$. It can be concluded that when $n=2w$ the product kernel is used and when $n=w$ the sum kernel is used (27):

$$w = \alpha + (d - d_w)/D \quad \text{for the sum kernel}$$

$$w = (\alpha + (d - d_w)/D)/2 \quad \text{for the product kernel}$$

(10)

Because the nature of the growing clusters is fractal, their fractal dimension must be determined. The fractal dimension $D$, as defined by Eq. (5) for a kinetic clustering phenomenon can be obtained through numerical simulations [28, 29, 32, 33]. In the numerical simulations it is considered that clusters are placed randomly on the $L^d$ lattice sites. By performing numerical simulation assuming cluster aggregation in the square ($d=2$) or a hypercubic lattice model in $d$-dimensions ($d>2$) and periodically bounded in all directions Meakin [32] and Jullien et al. [29] predicted the fractal dimension, $D$, of the growing clusters in different Euclidean dimensions, $d$, as reported in Table 2.
Table 2. Fractal dimension of a growing cluster as a function of its Euclidian dimension $d$

<table>
<thead>
<tr>
<th>$d$</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.38±0.03</td>
</tr>
<tr>
<td>3</td>
<td>1.72±0.11</td>
</tr>
<tr>
<td>4</td>
<td>2.02±0.11</td>
</tr>
<tr>
<td>5</td>
<td>2.30±0.15</td>
</tr>
<tr>
<td>6</td>
<td>2.60±0.15</td>
</tr>
</tbody>
</table>

The fractal dimension, $D$, is determined for $d_w = 2$ (random walk).

Because resin molecules are responsible for asphaltene particle peptization, one must consider, also, the effect of resin concentration on the kinetics of growing asphaltene clusters. Thus, the exponent $w$ which characterizes the effective asphaltene-cluster surface area that is available for interaction with other clusters in aggregation and growth process, should depend on the concentration of resin, $C_R$, in a mixture of stock tank oil and a miscible solvent as in the functional form $w = w(C_R)$. This functionality of $w$ will be utilized in the expressions of the growing average mass of clusters of asphaltene particles and the analytical expression of a "reduced" size distribution of clusters of asphaltene particles. Because the asphaltene cluster of size $k$ can be assumed to contain $k$ identical particles of unit mass, one can see that

$$t \sim t^{d_w} m^{-a}.$$

From this expression, the dynamical behavior with respect to time for the asphaltene cluster of mass $m$ can be written in the power law form $m(t) \sim t^\gamma$. The dynamical behavior of average mass of clusters of asphaltene particles with respect to time can be expressed in terms of the fractal dimension $D$ as follows (28):

$$<m(t)> \sim t^\gamma; \quad \gamma = 1/(1-\alpha -(d - d_w)/D) \quad (11)$$

It can be shown that $\gamma = \gamma(w; C_R)$, thus, the kinetic theory of fractal aggregation process can be utilized to describe properly the growing size distribution of clusters of asphaltene particles due to the influence of miscible solvents. For the mechanism of irreversible kinetic aggregation of diffusive clusters, Botet and Jullien (28) have derived the size distribution of clusters which gives us the analytical expression of a "reduced" size distribution of clusters at a given step of the growing aggregation mechanism. The analytic equation for the "reduced" size distribution of clusters of asphaltene molecules can be shown as follows:

$$F(y; C_R) = (1-2w)^{1-2w} y^{-2w} \exp\{- (1-2w)y\} / \Gamma(1-2w) \quad (12)$$

where $y = m/<m>$ and $w = w(C_R)$. Eq. 12 has the following characteristics:

(i) For $w < 0$, the size distribution exhibits a maximum.
(ii) For $0 < w < 1/2$, the size distribution is always decreasing.
(iii) For $w > 1/2$, the shape of the size distribution function inverts at a finite time, which is known as the signature of the gelation phenomenon (28).

By using the above equations and the principle of phase equilibria, one can derive the expressions for predicting the phase behavior of asphaltene particles under the influence of miscible solvents.

In a heterogeneous polymer mixture, one can specify different fractions of polymers based on their molecular weight. Assuming that a heavy organic behaves as a heterogeneous polymer, one can equate chemical potentials in the oil phase, $\mu^L_y$, and the precipitated phase, $\mu^S_y$. This corresponds to the heavy organics remaining soluble in an oil phase in equilibrium with the heavy organic content of a precipitate:

$$\mu^S_y = \mu^L_y; \quad y = m/<m>, \quad 0 < y < \infty \quad (13)$$

The Scott and Magat statistical mechanical theory of heterogeneous polymer solutions permits calculation of chemical potentials of asphaltene fractions through the equation:

$$\Delta \mu_y /RT = \ln \phi_y + 1 - (m_y/<m>)(1 - \phi_y) - m_y \phi_y + f m_y \phi_y^2 \quad (14)$$
Subscripts $y$ and $B$ in Eq. 14 refer to the $y$th fraction of asphaltene and solvent, respectively. The volume fraction, $\phi$, is defined by the volume, $V$, of a component divided by the total volume, $V_{\text{mix}}$, of a mixture. Therefore,

$$\phi_y = \frac{V_y}{V_{\text{mix}}} \quad ; \quad \phi_B = \frac{V_B}{V_{\text{mix}}} \quad \text{and} \quad (\sum \phi_y) + \phi_B = 1 \quad (15)$$

The segment number of the $y$th fraction of asphaltene, $m_y$, is defined by the ratio of molar volume, $v_y$, of the $y$th fraction of asphaltene over the molar volume, $v_B$, of a solvent, $m_y = v_y/v_B = M_y / \langle \rho_A^{\text{mass}} \rangle v_B$; $\langle \rho_A^{\text{mass}} \rangle$ is the average mass density of the $y$th fraction. The segment number of the solvent is unity. The average segment number, $<m_y>$, of asphaltene may be defined by $<m_y> = \sum x_y m_y$ where $x_y$ is the mole fraction of the $y$th fraction of asphaltene with respect to the total asphaltene (i.e., $\sum x_y = 1$). The parameter $f$ in Eq. (14) is defined as:

$$f = 1/r + v_B((\delta_A - \delta_B)^2 + 2 \delta_A \delta_B) / RT \quad (16)$$

where $r$ is the coordination number between two successive segments in asphaltene molecules ($r$ has a value between 3 and 4 [30]), $K_{AB}$ is the interaction parameter between asphaltene and asphaltene-free oil, given by $K_{AB} = a + b <M_B>$ (It is assumed to be linearly proportional to the average molecular weight of asphaltene-free oil, $<M_B>$); $\delta_A$ is the average solubility parameter of asphaltene, and $\delta_B$ is the solubility parameter of asphaltene-free oil. Solubility parameter $\delta$ is defined by the square root of the molar internal energy change of vaporization, $\Delta u^{\text{vap}}$, over the molar volume:

$$\delta = (\Delta u^{\text{vap}}/v)^{1/2} \quad (17)$$

By utilizing Eq.'s (13) and (14), after simple mathematical manipulations, the following equation can be obtained:

$$\phi_{y}^{k_b} / \phi_{y}^{\delta} = \exp\{ m_y [(1/<m_{y}^{\delta}> - 1/<m_{y}>) + (1-1/<m_{y}>) \phi_{B}^{b} - \phi_{B}^{\delta} ] \} \quad (18)$$

The "reduced" growing size distribution, Eq. 12, of clusters of asphaltene molecules must be joined with Eq. (18) for calculation of the total volume fraction of asphaltene remaining soluble in a mixture in equilibrium with a precipitated asphaltene phase. Thus, this model can predict the solubility of heavy organics in the solution, the size distributions of heavy organics in the precipitated phase and heavy organics remaining soluble in an oil mixture upon changes in pressure, temperature, and composition under the influence of miscible solvents. This may contribute significantly toward better prediction of the phase behavior of the heavy organic deposition mechanism under the influence of miscible solvents.

The FA model could very well be applied to the prediction of the pressure/composition region of asphaltene deposition at high pressures under the influence of a miscible gas. Figure 6 shows a phase diagram for mixtures of Brookhaven stock-tank oil and carbon dioxide at 317°C. From this figure we can see a good agreement between predicted and experimental data (34).

The three models (CT, SC, and FA) for heavy organic deposition from petroleum crudes are based on two different facts. In the CT model the heavy organics are considered to be dissolved in an oil which may or may not form a solid phase depending on the thermodynamic conditions of temperature, pressure, and composition. In the SC model heavy organics are considered as solid particles of different sizes suspended collooidally in the oil and stabilized by large polymeric molecules (i.e. resins) adsorbed on their surface. In the FA model incorporation of the CT and SC models is made and the fractal aggregation theory of colloidal growth is employed. This model considers the asphaltenes to be partly dissolved and partly in the colloidal state, thus it accounts for both the solubility and colloidal effect of heavy organics in light components. The proposed CT, SC and FA models can provide the tool for making satisfactory prediction of the phase behavior of heavy organic deposition.

One experimental measurement of the onset of heavy organic flocculation is needed to tune the above models. Therefore, it is of extreme importance to measure with high accuracy this onset point. Several methods are available for determining the onset of asphaltene flocculation and deposition with various degrees of accuracy and difficulty (35-40). All of these techniques do not possess the desired accuracy and/or are not applicable for all types of crude oils. For this reason a new technique was developed (40,41) which is more accurate than any of the above. A brief description of this new technique is given below.

**Determination of the Onset of Asphaltene Flocculation [40, 41]**

The method presented here is based on the fact that for most pure liquids and for many suspensions viscosity is independent of shear stress and velocity gradient, provided the flow is in the laminar regime and the fluid is Newtonian. However, for other solutions and suspensions deviations from the Newtonian behavior are observed. The main causes of non-Newtonian viscosities are, in many instances, the inter-particle interactions, asymmetry and orientation of the suspended...
particles. Fluid-particle and particle-particle interactions depend largely on the particle size, shape, concentration and surface characteristics. Particle size determines to a large extent the nature and relative significance of the forces governing suspension rheology and hydrodynamic behavior, while concentration determines the level of interparticle interactions. Non-Newtonian effects are important even at low concentrations for suspensions of rigid non-spherical particles. For the case in which the suspended particles are spherical the non-Newtonian behavior becomes important at higher concentrations (interparticle interactions are more intense).

In general, suspended particles affect the flow characteristics of the host fluid resulting in an increased viscosity. The problem of relating viscosities of colloidal suspensions to the properties of dispersed particles has been the subject of numerous experimental and theoretical considerations (42-50).

Einstein (42) concluded that the effect of dispersed particles on the viscosity of a suspension depends only on the total volume they occupy and is independent of their size. However, this is valid only for highly dilute suspensions of rigid, spherical, unisize, and non-interacting particles.

Sherman (43) and Rutgers (47) found that at moderate concentrations, the disturbances in the regions of flow around the particles are sizable, and they become more important for non-spherical and/or deformable particles. Although these findings are applicable to moderately concentrated suspensions, and account, to some extent, for non-rigidity: they consider only particle-solvent interactions but not particle-particle interactions (i.e., aggregation).

For the case in which particles interact to form aggregates of different sizes and shapes, Gillespie (45) studied the effect of particle aggregation and particle size distribution on the viscosity of Newtonian suspensions arriving at the conclusion that these effects resulted in an increase in the relative viscosity of the suspension.

Figures 8, 9 and 10, taken from reference 40, show the viscosity curves for the Mexican Maya and Isthmus crude oils with their respective onsets of flocculation as detected by the new method. These two crude oils were selected for this analysis because Maya is heavy with a density of 0.9164 g/cc at 25°C and an asphaltene content of 12.38 wt%, and Isthmus is light with a density of 0.8357 g/cc at 26.5°C and an asphaltene content of 1.9 wt%. For the Maya crude oil three different precipitating agents were used, n-pentane, n-heptane, and n-nonane. Whereas for the Isthmus crude oil only n-heptane was used. For both crude oil samples two reference systems were considered using non-precipitating solvents such as toluene and THF-S for comparison purposes (THF-S is a 64.333% solution of toluene in THF, this solution has approximately the same kinematic viscosity as that of n-heptane). As can be seen from these figures the onset of flocculation is detected by observation of a strong deviation in the viscosity curve as compared with the reference system (Toluene and THF-S curves). The main goals here is to explain the mixture-viscosity trends and to validate the proposed technique from a theoretical standpoint.

**Theoretical analysis for the proposed new method**

The new methodology proposed by the authors (40) to determine the onset of asphaltene deposition has proven to be equally successful for both heavy and light crude oils. This is an advantage since the previous techniques have the limitation of being applicable only to either heavy or light crude oils but not to both. Therefore, it is worthwhile to perform a theoretical analysis to explain the role of viscosity in the determination of the onset of asphaltene flocculation. In order to do so, we need to further examine the experimental data to see whether more information could be extracted.

Looking at the definitions for viscosity presented in the literature, one definition which is important indeed is the specific viscosity (or specific increase on the relative viscosity) defined as:

\[
\eta_{\text{specific}} = \frac{(\eta - \eta_0)}{\eta_0}
\]

where \(\eta\) is the viscosity of the suspension; \(\eta_0\) is the viscosity of the suspending medium. The specific viscosity is of extreme importance for it provides information about the effect of the presence of the particles on the viscosity of the suspension. Therefore, by plotting specific viscosity versus particle volume fraction one can see the net effect exerted by the suspended particles. These types of plots may also allow the determination of the intrinsic viscosity (characteristic for all colloidal systems) by extrapolating to zero-particle-volume-fraction. The relative viscosity \((\eta/\eta_0)\) can also be utilized for the analysis of the effect of particle concentration on the behavior of the suspension.

In order to perform the data analyses mentioned above, either through the use of specific or relative viscosity, one must know the viscosity of the suspending medium. In the case of crude oil-precipitant mixtures, the suspending medium would be the asphaltene-free liquid phase. Therefore, one must find ways to measure or determine the viscosity of the crude oil-precipitant mixtures in the absence of the asphaltene particles. This can be done if the asphaltene fraction of the crude oil is separated as a preliminary step and then measure the viscosity of the resulting filtrate. It should be pointed out that the separation of asphaltenes must be accomplished without altering the nature of the liquid phase. Unfortunately, given the complexity of the mixture and the difficulty of the separation step this protocol is highly unlikely to be reliable. Therefore, a different way of estimating the viscosity of the suspending medium must be followed.

In the development of the new technique for the onset of asphaltene flocculation (40) toluene and THF-S were used as

**EXITEP96**

INTERNATIONAL PETROLEUM TECHNOLOGY EXHIBITION
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Prediction of the background viscosity

Prediction of liquid viscosities is a major challenge for there is no accurate correlation reported in the literature which can successfully be used for the estimation of this physical property. Given the great complexity of crude oil as a mixture it is very unlikely that prediction of viscosities will be accomplished with success. Nevertheless, a number of correlations proposed in the literature were employed for the prediction of crude oil-polar (or aromatic) solvent mixtures. Acceptable viscosity prediction were obtained using the equation proposed by Lobe (55). This is a correlation for prediction of kinematic viscosities of multicomponent mixtures:

\[ \eta_m = \sum_{i=1}^{n} \phi_i \eta_i \exp \left( \sum_{j=1}^{n} \frac{\alpha_j \phi_j}{RT} \right) ; j \neq i \]  

(20)

In Eq. 20, \( \alpha_j \) is a characteristic viscosity parameter for the \( j \)th component in the mixture, \( \phi_i \) is the volume fraction of the \( i \)th component in the mixture, \( \eta_m \) and \( \eta_i \) are the mixture and \( i \)th component kinematic viscosities, respectively. Given the complexity of crude oil mixtures and the lack of characterization data, we consider the system to be comprised of a solvent and crude oil (as a pseudo component), then the above equation reduces to:

\[ \eta_m = \phi_A \eta_A \exp(\eta_B \phi_B + \eta_B \phi_B \exp(\eta_A \phi_A)) \]  

(21)

where subscript \( A \) denotes the component with the lower viscosity, and subscript \( B \) the one with higher viscosity, and \( \alpha_j^* = \frac{\alpha_j}{RT} \). Lobe (55) proposed that if the mixture kinematic viscosity varies monotonically with composition the parameter \( \alpha_j^* \) could be obtained using expressions:

\[ \alpha_A^* = -1.7 \ln \left( \frac{\eta_A}{\eta_B} \right) \]  

(22)

\[ \alpha_B^* = 0.27 \ln \left( \frac{\eta_B}{\eta_A} \right) + \left[ 1.3 \ln \left( \frac{\eta_B}{\eta_A} \right) \right]^{1/2} \]  

(23)

The coefficients in Eqs. 22 and 23 were obtained by fitting experimental kinematic viscosity data for many Newtonian binary mixtures (55). In the case of crude oil mixtures the parameters \( \alpha_A \) and \( \alpha_B \) were obtained by fitting the experimental data (40) to Eq. 21. Thus, from pure-component kinematic viscosities, it is possible to estimate the crude oil - solvent binary mixture viscosity. At first it may cause hesitation in utilizing this empirical expression because of its simplicity. However, it turns out to be a correlation which could give a good prediction as depicted in Figures 11 and 12. Figure 11 shows the predicted viscosities for mixtures of THF-S - Maya-crude-oil mixtures. THF-S is a 64.33 vol% solution of THF in toluene with approximately the same kinematic viscosity as that of n-heptane. It may be noticed from Figure 11 that the predicted viscosities are in good agreement with the experimental data (40) except at low dilution ratios. This could be due to the fact that at high concentrations asphaltenes tend to self-associate into larger aggregates. Therefore, to find a better viscosity prediction one must incorporate the effects of asphaltene self-association on the mixture viscosity. However, for the purpose of the present analysis we may assume the currently employed correlation is valid. Figure 12 shows the results obtained for mixtures of THF-S - Isthmus-crude-oil mixtures. From this figure we can see a better agreement with the experimental data. The asphaltene content in this crude oil is quite low (1.9 wt%) and hence the effect of asphaltene self-association is not as important as in the case of Maya crude oil.

Now, if n-heptane behaved as a very good solvent for asphaltenes then the solutions it would form with crude oils may be expected to be Newtonian as in the previous cases. Thus, Eq. 21 may be used to predict the viscosity of the n-heptane - crude oil mixtures. Since the kinematic viscosity of THF-S is very similar to that of n-heptane then the parameters \( \alpha_A \) and \( \alpha_B \), in Eq. 21, are expected to be nearly the same for these two solvents. Therefore, the “background viscosity” for n-heptane - crude oil mixtures has been predicted using the parameters \( \alpha_A \) and \( \alpha_B \) previously obtained for THF-S - crude oil mixtures.

Figures 13 and 14 show plots of the specific viscosity versus volume fraction of precipitating solvent in the mixture for the Maya and Isthmus crude oils, respectively. As we can see from these figures, there is a point after which the effect of the suspended particles increases more rapidly. This point coincides with the previously determined onsets of asphaltene flocculation. The rapid increase in the specific viscosity may be explained considering the fact that at the onset there is no solid-phase separation at all. Whereas after this point the amount of asphaltene flocculated out of the solution increases with increasing solvent concentration reaching a limiting value. It may also be explained considering that as precipitating solvent in the mixture increases, the diameter of the asphaltene aggregates increases as well. This has experimentally been reported...
by Ferwom, et al. (7) as depicted in Figure 3 of their paper. At high dilution ratios, fluctuations in the specific viscosity are observed. These fluctuations may be explained based on the fact that the large aggregates produced at high dilution ratios are not rigid structures and they may break easily upon shaking or due to shear stresses experienced by the aggregates during viscosity measurements. Also, at these high dilution ratios the Brownian motion and interparticle interactions are dominated by hydrodynamic effects.

Effect of precipitating solvent concentration on asphaltene particle size and shape

In the previous section it has been demonstrated that the onset of asphaltene flocculation can be accurately determined by plotting the specific viscosity versus volume fraction of solvent in the mixture. As mentioned earlier, a plot of this type show explicitly the net effect of the suspended particles on the viscosity of the suspension. Therefore, it is important to know the concentration of the particles responsible for the increase in the specific viscosity. It is highly unlikely, however, that the concentration of asphaltene particles effecting the changes in viscosity observed in Figures 11 and 12 could be measured accurately. This is due to several reasons: (i) the crude oils is a very complex mixture; (ii) the mechanism of asphaltene aggregation is very complicated and fractal in nature; (iii) Asphaltene aggregates show a high degree of polydispersity; (iv) the diameter of these aggregates and the degree of polydispersity are both function of solvent concentration (i.e. resin content); (v) the resin-asphaltene interaction are not well understood. Nevertheless, we may use an alternate way of estimating the effective volume fraction of asphaltene particles in suspension.

Gillespie (45) proposed the following expression for the relative viscosity of a suspension:

\[
\eta_r = \frac{1 + \varnothing_{\text{eff}}/2}{(1 - \varnothing_{\text{eff}})^2}
\]

where \( \eta_r \) is the relative viscosity of the suspension (ratio of dynamic viscosities); \( \varnothing_{\text{eff}} \) is the effective volume fraction of particles in suspension. This expression was proposed to account for the effect of aggregation and particle size distribution on the viscosity of suspensions.

In the derivation of Eq. 24 dynamic viscosity was employed, therefore, we must transform this equation to be applicable for kinematic viscosity data. The transformed equation reads as follows:

\[
v_r = \frac{\rho_0}{\rho} \left( \frac{1 + \varnothing_{\text{eff}}/2}{(1 - \varnothing_{\text{eff}})^2} \right)
\]

where \( v_r \) is the relative kinematic viscosity of the suspension; \( \varnothing_{\text{eff}} \) is the effective volume fraction of particles in suspension.

The viscosity of the suspending medium ("background viscosity) was calculated assuming that the precipitant (i.e. n-heptane) behaves as a very good solvent for asphaltenes. Thus, we may assume that the density of the suspending medium would be approximately the same as that of the suspension. Therefore equation (25) can be written as:

\[
v_r = \frac{1 + \varnothing_{\text{eff}}/2}{(1 - \varnothing_{\text{eff}})^2}
\]

Using equation (26) we can obtain expressions for the specific viscosity \( (v_r - 1) \) as:

\[
v_{\text{specific}} = \frac{5/2 \varnothing_{\text{eff}} - \varnothing_{\text{eff}}^2}{(1 - \varnothing_{\text{eff}})^2}
\]

Eq. (27) may be compared to Einstein's expression (42) for the specific viscosity defined as: \( v_{\text{specific}} = 5/2 \varnothing \), to see that the Einstein's coefficient \( 5/2 \) is indeed contained in Eq. 27 and that there is in fact correction for non-sphericity and particle size distribution in the squared terms. From this equation and the specific viscosity estimated previously we may find the theoretical effective volume fraction of the particles responsible for the increase in the specific viscosity of crude oil - n-heptane mixtures. Figures 15 and 16 show the effective volume fraction as a function of n-heptane in the mixture for the Maya and Isthmus crude oils, respectively. From these figures we observe a point after which the theoretical effective volume fraction increases more rapidly with solvent concentration. This point obviously coincides with the onset of asphaltene flocculation as seen in Figures 11 and 12. This can be explained considering that the onset marks the beginning of phase separation. Therefore, as concentration of n-heptane increases the amount of asphaltenes flocculated out of solution increases as well. We also notice that there is a maximum asphaltene effective volume fraction followed by a decrease. The maximum in Figure 15 and 16 can be explained by experimental measurements of the amounts of asphaltenes precipitated out of solution for a given amount of precipitating solvent. This kind of experimental data has been successfully predicted by
Kawanaka, et al. using a continuous thermodynamic model (3). Figure 1 in reference 3 shows the effect of solvent concentration on the amount of asphaltene precipitation. As we can see from that figure, the amount of asphaltene precipitation increases rapidly after the onset of deposition to approach a somewhat constant value. This explains the maximum observed in the effective volume fraction. The decrease in the effective volume fraction can be explained considering the fact that at large dilution ratios the diameter of the precipitated asphaltene clusters could be as high as 250+ µ (depending on the crude oil) (7). These particle diameters are well beyond the Brownian range and therefore hydrodynamic effects dominate the picture. Also, experimental observations demonstrated that these large clusters are not rigid and can easily be fragmented by shear stresses during flow or agitation. Thus, it is expected that during viscosity measurements these large clusters will break up and the resulting fragments recombine due to shear stresses resulting in a decrease in the effective volume fraction.

This section demonstrates, beyond any doubt, that the onset of asphaltene flocculation can be accurately determined from viscosity measurements.

**Heavy Organic Deposition in Wells of the Fields Tecominoacan and Jujo in Mexico [56]**

There is another class of heavy organic deposition which is not induced by the addition of miscible solvents. It is not caused either by blending a crude oil with other petroleum fluids (as in the previous two cases). This type of heavy organic deposition takes place during primary recovery production operations. Here, there is no miscible injection and the crude oils are produced by natural drive forces which prevail inside the reservoir. In this case the phenomenon of deposition is induced solely by hydrodynamic effects as well as compositional changes that take place during the production process. We present next the case history of heavy organic deposition in Mexican oil fields.

The Tecominoacan and Jujo fields are formed by two lithological zones, the first is the lower cretaceous sandstone (calcareous) and the second is the lower cretaceous and upper jurassic sandstones. Their reservoir is comprised of structural traps, primarily anticlines represented by deformation layers and faults in the structure located at a depth of 6500 m with a pay zone varying from 60 to 200 m. The initial reservoir pressure was 702 kg/cm² and the bubble point of crude varies from 265 to 380 kg/cm². The initial gas-oil ratio (GOR) varied from 102 to 225 m³/m³ depending on the geographic location of the well within the fields. The crude produced in these fields is considered to be undersaturated with an average API gravity of 37.8. Its average sulfur content is usually less than 1 wt%, and its n-pentane-asphaltene content varies from 1 to 5 wt%. The production completion tubing size is generally 3.5 inches OD. There is another tubing of 1.25 inches OD utilized for circulating chemicals inside the well (i.e. inhibitors for asphaltene deposition and/or chemicals for cleaning purposes) (57, 58).

Recently [58] a severe reduction in light-oil production from the Tecominoacan and Jujo fields in the Chiapas-Tabasco area was experienced. This was found to be due to heavy organic deposition on the walls of the production tubing. This led to a reduction in the flow area of the well and in some cases it resulted in complete plugging of the production tubing. Well workovers had to be performed to re-initiate production operations, the economic implication of which were severe. It was suggested that chemical and/or mechanical removal of the organic deposits was the fastest way to remedy the problem [58]. A blended solvent, named "IMP-System", capable of dissolving the major fraction of organic deposits of the Tecominoacan and Jujo fields, was developed by trial and error using a laboratory-scale extraction unit simulating the well conditions [58].

Table 3 contains characterization data of crudes and deposits from Tecominoacan Field. From this table we notice that organic deposition has occurred during the production of a light crude with a relatively small asphaltene content. The difference in the metal contents of crude and deposits reported in Table 3 indicates that while asphaltic compounds precipitate they carry with them the metal content of the crude. we also notice that the resin content in the crudes is relatively high (8-9 wt%) compared to asphaltenes concentration (1-1.5 wt%). It has been found (59) that asphaltene content of crude may be less important than the resin concentration in the flocculation process. In other words, we may find a crude with a high content of asphaltene and no deposition problem if the amount of resins (peptizing agents) is large enough to keep the asphaltene particles suspended in the solution. For instance, production of the Maya crude in Mexico with an asphaltene content of 16-18 wt%, and a large content of neutral resins (more than 23 wt%) does not present any asphaltene deposition problem (60).

The data in Table 3 suggest that the resin content in these crude oils may be enough to stabilize the small amount of asphaltenes present. Therefore, heavy organic deposition is hardly expected to occur. Nevertheless, according to Table 3, asphaltene deposition is observed causing severe problems. This peculiarity can be explained by comparing the resin/asphaltene ratio in the T-127 crude (5.87) with that of the deposit sample collected from the same crude (0.24). This suggests that in the deposition process the asphaltene particles are probably depetized to a certain extent but not completely. A possible explanation for this could be that the streaming potential generated by the flow of charged asphaltenes is large enough to break the stability of the micelles. This would then result in desorption of resins from the asphaltene particle surface leaving empty sites. If two asphaltene particles collide with one another on their empty sites aggregation takes place, a process which is irreversible (21).

The streaming potential generated during production of the crude oil under study was estimated using the model proposed by Leontaritis and Mansoori [18] and the well data of Silva et al., (61). This results are shown in Table 4. According to this table streaming potential generated is rather high. This represents a strong possibility for asphaltene deposition (4).
TABLE 3. Characterization of Crudes and Deposits from Tecominoacan field [Garcia, 1989].

<table>
<thead>
<tr>
<th>CRUDE AT-127</th>
<th>CRUDE AT-145</th>
<th>ORGANIC DEPOSITS DT-127</th>
<th>ORGANIC DEPOSITS DT-448</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon wt%</td>
<td>86.1</td>
<td>86.0</td>
<td>84.5</td>
</tr>
<tr>
<td>Hydrogen wt%</td>
<td>12.5</td>
<td>12.5</td>
<td>8.6</td>
</tr>
<tr>
<td>Nitrogen wt%</td>
<td>0.4</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Iron ppm</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>267.0</td>
</tr>
<tr>
<td>Copper ppm</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>3.0</td>
</tr>
<tr>
<td>Nickel ppm</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>20.0</td>
</tr>
<tr>
<td>Vanadium ppm</td>
<td>1</td>
<td>1</td>
<td>171.0</td>
</tr>
<tr>
<td>Zinc ppm</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>6.0</td>
</tr>
<tr>
<td>Spec. gravity @20/4°C</td>
<td>0.837</td>
<td>0.839</td>
<td>46.6</td>
</tr>
<tr>
<td>API Gravity</td>
<td>36.7</td>
<td>37.2</td>
<td>42.2</td>
</tr>
<tr>
<td>Viscosity sus., @70°F</td>
<td>45.2</td>
<td>45.2</td>
<td>41.0</td>
</tr>
<tr>
<td>@77°F</td>
<td>45.2</td>
<td>41.2</td>
<td></td>
</tr>
<tr>
<td>Pour Point °C</td>
<td>-30</td>
<td>-24</td>
<td></td>
</tr>
<tr>
<td>Sulfur wt%</td>
<td>0.9</td>
<td>0.9</td>
<td>2.9</td>
</tr>
<tr>
<td>n-C5 Asphaltenes</td>
<td>1.5</td>
<td>1.0</td>
<td>42.0</td>
</tr>
<tr>
<td>Solubles wt%</td>
<td>89.7</td>
<td>90.9</td>
<td>48.0</td>
</tr>
<tr>
<td>Saturated wt%</td>
<td>52.3</td>
<td>58.5</td>
<td>42.1</td>
</tr>
<tr>
<td>Aromatics wt%</td>
<td>37.4</td>
<td>32.4</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Table 4. Calculated streaming potential.

<table>
<thead>
<tr>
<th>Production rate (m³/day)</th>
<th>U_avg (m/s)</th>
<th>Potential E (Volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0.51</td>
<td>13.12</td>
</tr>
<tr>
<td>443 (field data)</td>
<td>1.132</td>
<td>52.79</td>
</tr>
<tr>
<td>600</td>
<td>1.532</td>
<td>88.69</td>
</tr>
<tr>
<td>800</td>
<td>2.044</td>
<td>146.88</td>
</tr>
<tr>
<td>1000</td>
<td>2.555</td>
<td>216.85</td>
</tr>
</tbody>
</table>

The bubble-point-depth (depth at which the bubble point pressure of the oil is encountered) and organic-deposition-depth data for thirteen different wells in the Tecominoacan and Jujo fields have been reported by Garcia et al., (57). Figure 18 shows a plot of these data. According to these data, for the majority of the deposits occurs after the bubble point pressure has been reached reached (i.e. in the two phase region).

It is well known that as crude oil flows through the well tubing pressure drops gradually. When the bubble point pressure of the crude oil is reached, the light fractions of the crude oil are released. This is thought to prevent the asphaltene deposition, since the concentration of the light hydrocarbons dissolved in the crude decreases gradually as it moves through the two-phase envelope region (62). There exists no fundamental theory by which one would be able to explain the results reported by Garcia et al., (57) as to why the Mexican crude oils present heavy organic deposition in the two phase region. For this reason we believe that more theoretical studies should be performed to elucidate the behavior of heavy organics during flow conditions.

Due to the charge nature of the asphaltene particles, it has been observed that the interactions with the conduit walls can disturb the stabilizing electrical forces around the asphaltene micelle causing aggregation of the asphaltene particles. When crude oil is being produced or transported a streaming potential is generated due to the charged character of this colloidal
particles. Furthermore, this streaming potential has been found to assist their flocculation by neutralizing the weak asphaltene charge (4). It has also been found that the generated streaming potential is a function of the flow regime, pipe-wall conductivity, physical properties of the suspending media, and of size, shape and electrical properties of the asphaltene particles (18). Lichaa (4) found that the amount of asphaltene deposition due to electrical effects is a function of temperature as well. The streaming potential has a direct effect on the diffusivity of asphaltene particles to the walls, which combined with Brownian and eddy (if turbulent flow) diffusivity effects can render in a disastrous heavy organic deposition. Roughness of pipe-wall surface plays, also, an important role in the heavy organic deposition. A very rough surface may be sufficient to initiate the deposition process and trigger simultaneously the effect of other phenomena. Another important phenomenon is the asphaltene charge (4). It has also been found that the generated streaming potential is a function of the flow regime, pipe-wall surface roughness as well. The streaming potential has a direct effect on the diffusivity of asphaltene particles to the walls, which combined with Brownian and eddy (if turbulent flow) diffusivity effects can render in a disastrous heavy organic deposition. Roughness of pipe-wall surface plays, also, an important role in the heavy organic deposition. A very rough surface may be sufficient to initiate the deposition process and trigger simultaneously the effect of other phenomena. Another important phenomenon is the appearance of paraffin/wax crystals at the cloud point of a petroleum fluid. Large and soft paraffin/wax crystals appear to serve as nuclei about which asphaltene particles deposit.

As we can see the heavy organic deposition phenomenon inside a well is very complex. In order to develop a model capable of describing the behavior of heavy organics during the production process one has to account for the streaming potential generated and for the effects of this potential on the asphaltene aggregation. One has to account also for the effect of eddy and Brownian diffusivities on the rate of particle deposition. We must also take into consideration the appearance of the gas bubbles once the bubble point pressure of the crude oil is reached. This gas bubbles will certainly have an adverse effect on heavy organic deposition. When sour crude oils are produced, as is the case in Mexico, the walls of the production channel may present an increased roughness due to corrosion. This will also affect the deposition process.

Figure 18 shows a schematic representation of a producing well. We notice that as the bubble point pressure of the crude oil is reached gas bubbles. As the crude oil proceeds through the well different flow regimes are observed according to the gas-bubble size. This phenomenon only enhances the complexity of the deposition mechanism.

In what follows we perform a theoretical analysis of the effect of eddy and Brownian diffusivities on the rate of particle deposition during turbulent flow conditions. The work presented here is only the first building block towards the development of a comprehensive model for the behavior of heavy organics during flow conditions.

### Solid Particle Deposition During Turbulent Flow Conditions (63)

Substantial work has been done on the area of particle deposition on the walls of channels or pipes in turbulent flow by many researchers (64-71).

A key assumption in the development of the present model is that a fully developed turbulent flow of crude oil has a structure as proposed by Lin et al. (64) From experimental observations, they proposed a generalized velocity distribution for turbulent flow of fluids in pipes, as depicted in Figure 1 of their paper. This velocity distribution is comprised of three main regions (Details of this generalization are given elsewhere, (64)): a) A sublaminar layer adjacent to the wall, b) The transition or buffer region, and c) the turbulent core. In the sublaminar layer, in which there is no turbulence or eddy diffusion, particle flux is due to Brownian diffusion. Velocity distribution and mass transfer in the turbulent core are governed primarily by eddy diffusivities both of momentum and mass. Whereas in the buffer layer the mass transfer is governed by a combined action of Brownian and eddy diffusivities.

It has been observed experimentally that even in the sublaminar layer near the wall a slight amount of eddies is present (64). However, it cannot be measured or correlated based on experimental observations. Nevertheless, empirical correlations have been proposed for the eddy diffusivity in the turbulent boundary layer as we will see later. These correlations are based on analogies with the laminar diffusion boundary layer (64,71).

The theoretical analysis that follows has been done for a system of constant density, and viscosity. Therefore it is applicable to the region above the bubble pressure where only the liquid phase is present. However, it could be extended to the region below the bubble point (gas-liquid) if reliable correlations for viscosity and density versus pressure and composition are available. Due to the scarcity of such correlations, and because multi-phenomena occur in the two phase region of the well tubing (i.e. release of the light ends of the crude, chemical composition variation, etc) which affect the diffusivity of the suspended particles, no attempt is made to extend this model to that region. The assumption of constant viscosity, and constant density is partly justified since density changes are not appreciable until the bubble point pressure is reached inside the well. It is also assumed that suspended particles are all of the same diameter, and that interactions between them are only due to their Brownian and eddy motion (i.e. we have neglected particle-particle interactions).

If we assume that the thickness of the boundary layer is very small compared to the radius of the pipe, then we can neglect any curvature effects. Thus, the equation used to describe the particle flux, N, in terms of the diffusivities and the concentration gradient is:

\[ N = (D_B + \epsilon) \frac{dC}{dr} \]

(29)

\( D_B \) is the Brownian diffusivity (\( D_B = k_B T/3\pi \mu d^4 \)); \( k_B \) is the Boltzmann constant (1.38X10^-23 g-cm²/mole.°K-s); T is the absolute temperature; d is the particle diameter; \( \mu \) is the viscosity of the suspending medium; \( \epsilon \) is the eddy diffusivity; \( C \) is the particles concentration; and \( r \) is the radial distance. Eq. 29 is subject to the boundary condition, at \( r = S \), \( C = C_s \). \( C_s \) is the particle concentration at \( r = S \), where S is the particle stopping distance measured from the wall. The concept of a stopping distance was first postulated by Friedlander and Johnstone in 1957 (66). They argued that a particle needs to diffuse

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only within one stopping distance from the wall. And from this point on, due to the particle momentum, it would coast to the wall. For small particles the stopping distance is small compared to the boundary layer and consequently diffusion dominates. The proposed expression for the particle stopping distance is (66, 67):

\[ S = \frac{0.05 \rho_p d^2 V_{avg} \sqrt{f/2}}{\mu} + \frac{d}{2} \]  

(30)

\( \rho_p \) is the density of particles; \( V_{avg} \) is the Crude oil average velocity; \( f \) is the friction factor.

Eq. 29 may be integrated following the procedure for the calculation of temperature drop across a composite wall. We will find the concentration profiles from point to point across the boundary layer. That is, we will calculate the concentration differences through the sublaminar layer, the buffer region and the turbulent core. By adding these concentration differences we can find the overall particle flux in terms of the average and wall concentrations.

Before we integrate equation 1, we need expressions for \( N \) and \( \varepsilon \) as functions of the radial distance (r). Johansen, S.T. (71) proposed the following correlation to express the eddy diffusivity as a function of radial distance (r) for the sublaminar layer:

\[ \varepsilon = \nu \frac{r^{+}}{11.15} \quad r^+ \leq 5 \]  

(31)

\( \nu \) is the Kinematic viscosity of the fluid (crude oil); \( r^+ \) is the Dimensionless radial distance \( r^+ = (r V_{avg} \sqrt{f/2})/\nu \).

Note that Eq. 31 is only valid for dimensionless radial distances smaller than 5, which is the limit of the sublaminar layer.

The molar Flux, \( N \), is taken to vary linearly from the wall to the center line of the channel, as proposed by Beal (69):

\[ N = \frac{N_0 (1 - \frac{2r^+}{D_0^+})}{D_0^+} \]  

(32)

\( N_0 \) is the particle flux at the wall; \( D_0^+ \) is the dimensionless well diameter, \( D_0^+ = (D_0 V_{avg} \sqrt{f/2})/\nu \), \( D_0 \) is the diameter of the well tubing.

In order to utilize the above two expressions in the integration of Eq. 29 we must define another dimensionless variable, \( s^+ = (s V_{avg} \sqrt{f/2})/\nu \), called the dimensionless stopping distance.

Introducing all the new dimensionless variables and the expressions for \( N \) and \( \varepsilon \) into Eq. 29, we get:

\[ N = \frac{N_0 (1 - \frac{2r^+}{D_0^+})}{D_0^+} \left[ \frac{D_0}{v} + \left( \frac{r^+}{11.15} \right)^3 \right] \frac{V_{avg} \sqrt{f/2}}{D_0^+} \frac{dC}{dr^+} \]  

(33)

subject to the boundary conditions:

at \( r^+ = s^+ \) \hspace{1cm} \( C = C_{s^+} \) \hspace{1cm} and \hspace{1cm} \( r^+ = 5 \) \hspace{1cm} \( C = C_5 \).

Rearranging Eq. 33, integrating and applying the above boundary conditions we find:

\[ C_s - C_{s^+} = \left( \frac{N_0}{V_{avg} \sqrt{f/2}} \right) \left[ \frac{1}{3} \left( 11.15 S_{c}^{1/3} \right)^{3/2} + \left( \frac{11.15}{S_{c}^{1/3}} \right)^{1/2} \right] F_1(s^+, S_c) + 2 \left( \frac{11.15}{S_{c}^{1/3}} \right)^{1/2} F_2(s^+, S_c) \]  

(34)

\[ S_c = \frac{\nu}{D_0} \]  

is the Schmidt number.

\[ F_1(s^+, S_c) = \ln \left[ \left( \frac{1 + \frac{5}{11.15} S_{c}^{1/3}}{1 + s^+ + \frac{5}{11.15} S_{c}^{1/3}} \right)^{1/2} \right] + \sqrt{3} \tan^{-1} \left( \frac{-\frac{10}{11.15 S_{c}^{1/3}}}{\sqrt{3}} \right) \sqrt{3} \tan^{-1} \left( \frac{2 s^+ - S_{c}^{1/3}}{\frac{11.15}{\sqrt{3}}} \right) \]  

(35)

\[ F_2(s^+, S_c) = \ln \left[ \left( \frac{1 + \frac{5}{11.15} S_{c}^{1/3}}{1 + s^+ + \frac{5}{11.15} S_{c}^{1/3}} \right)^{1/2} \right] - \sqrt{3} \tan^{-1} \left( \frac{-\frac{10}{11.15 S_{c}^{1/3}}}{\sqrt{3}} \right) + \sqrt{3} \tan^{-1} \left( \frac{2 s^+ - S_{c}^{1/3}}{\frac{11.15}{\sqrt{3}}} \right) \]  

(36)

Eqs. 34-36 describe the transport of suspended particles to the wall in terms of the concentration difference between the limits \( r^+ = s^+ \) (dimensionless stopping distance) and \( r^+ = 5 \) (limit of the sublaminar layer). The next step is the calculation...
of the particle flux between the concentration at \( r^+ = 5 \) and \( r^+ = 30 \) (limit of the buffer layer). The eddy diffusivity expression for the buffer layer was assumed to be:

\[
\varepsilon = \left[ \frac{r^+}{11.4} \right]^2 - 0.1923 \quad \frac{r^+}{11.4} \geq 30
\]  

(37)

Integration of Eq. 29, using Eq. 37 for \( \varepsilon \) gives:

\[
C_{30} - C_{30} = \frac{N_0}{V_{w_0} \sqrt{2}} \left( 1.25 \frac{r_c r^+}{DSc} \ln \left( \frac{1 + 2.5 r_c r^+ S_c}{1 + 75 S_c} \right) \right) \left( \frac{5 r_c r^+}{DSc} + 150 \right)
\]

(41)

\( r_c \) is the dimensionless radial distance (measured from the wall) where \( V = V_{avg} \). Eq. 41 describes the particle transport in terms of the concentration difference between the bulk (average) and the upper limit of the buffer layer.

Until now, only dimensionless stopping distances \( s^+ \) less than 5 have been considered. However, for particles large enough, \( r^+ \) could be greater than 5. If so, then the preceding analysis is not valid under these conditions. This difficulty may be overcome if Eq. 29 is integrated between the limits \( C = C_{8} \) at \( r^+ = s^+ \) and \( C = C_{30} \) at \( r^+ = 30 \) using the eddy diffusivity correlation for the buffer layer (equation 37).

Introducing Eq. 37 into Eq. 29 and integrating using the assumptions noted previously, we get:

\[
C_{30} - C_{30} = \frac{N_0}{V_{w_0} \sqrt{2}} \left( 1.25 \frac{r_c r^+}{DSc} \ln \left( \frac{1 + 2.5 r_c r^+ S_c}{1 + 75 S_c} \right) \right) \left( \frac{5 r_c r^+}{DSc} + 150 \right)
\]

(42)

\( F_3(s^+, S_c) = \tan^{-1} \left( \frac{30}{11.4} \frac{S_c}{1 - 0.1923 S_c} \right) \left( \frac{1}{1.4} \frac{S_c}{1 - 0.1923 S_c} \right) \tan^{-1} \left( \frac{30}{11.4} \frac{S_c}{1 - 0.1923 S_c} \right) \left( \frac{1}{1.4} \frac{S_c}{1 - 0.1923 S_c} \right) \]

(43)

If \( s^+ = 5 \) then Eqs. 42 and 43 reduce to equation 38 and 39. Eq. 41 still applies to the turbulent core.

**For particles with a dimensionless stopping distance:**

\( 0 \leq s^+ < 5 \)

We add equations 34, 38, and 41, to obtain an expression for the mass transfer coefficient defined as \( \frac{N_0}{(C_{avg} - C_{s^+})} = K \). \( K \) is the transfer (transport) coefficient and has dimensions of velocity (cm/sec). The expression for the transport coefficient obtained is:

\[
K = V_{avg} \sqrt{2} \left[ \frac{11.15 S_c^{u_3} F_3(s^+, S_c) + 2 (11.15)^2 S_c^{u_3} F_3(s^+, S_c) + 11.4 \frac{S_c}{1 - 0.1923 S_c}^{1/2} \left[ F_3(s^+, S_c) \right]}{3 Dc^3 \ln \left( \frac{1 + 6.7329 S_c}{1 + 0.000067 S_c} \right) + 2.5 + 12.5 \left( \frac{1 + 2.5 r_c r^+ S_c}{1 + 75 S_c} \right) Dc^3 + 150} \right]^{-1}
\]

(44)
For particles with a dimensionless stopping distance: \( 5 \leq S^* < 30 \)

We add Eqs. 42 and 43, solving for \( K \) we get:

\[
K = \frac{V_{sw} \sqrt[4]{2}}{F_3 (s^*, s_c)} \left[ \frac{11.4}{1 - 0.1923 S_c} \frac{\sqrt{2}}{D_0^*} \left( \frac{1.4}{1 - 0.1923 S_c} + \left( \frac{1.4}{1 - 0.1923 S_c} \right)^2 \frac{S_c}{11.4} \right) \ln \left( 1 - 0.1923 S_c + \left( \frac{30}{11.4} \right)^2 S_c \right) \right] + \frac{2.5 + 12.5}{D_0^* S_c} \left[ \ln \left( 1 + 2.5 \frac{r_{stw} S_c}{D_0^*} \right) \frac{5 r_{stw}}{D_0^*} + \frac{150}{D_0^*} \right]
\]

\( F_3 \) is the same as previously defined.

With the previous analysis we have found analytical expressions for the mass transfer coefficient for different particle sizes in terms of the dimensionless stopping distance. Inertial effects are also taken into consideration. For details see reference (63)

The analysis for particle deposition onto the walls of a flowing channel from turbulent fluid streams is concluded by taking into account the inertial effects as in Eq. 46. At this point all the parameters influencing the deposition rate (Brownian diffusivity, eddy diffusivity, and inertial effects) have been taken into account.

Comparison of the Proposed Model with Experimental Data and other Models

In order to apply the preceding analysis to particle deposition during turbulent flow production operations we must compare the theoretical predictions against some experimental data. Unfortunately experimental data for particle deposition from turbulent flows is very scarce. There is however more data for deposition from aerosols than from liquid suspensions. We do comparisons here for particle deposition from turbulent gas streams. The results of this analysis for particle deposition from turbulent fluid streams are in good agreement with the experimental deposition rates for iron particles in air (66, 67). The predictions of the present model show a better agreement with the mentioned experimental data than the models proposed by Friedlander and Johnstone (66), and Beal (69).

Figure 19 shows a comparison of the proposed model predictions with the experimental data and model proposed by Friedlander and Johnstone (66) for 0.8\( \mu \) iron particles suspended in a turbulent air stream at 298\( ^\circ \)K (pipe diameter is 0.54 cm). It can be seen the fairly good agreement of the predicted deposition rates with experimental data. It is also noticeable the better prediction capabilities of the present model compared to those of Friedlander and Johnstone (66). In the Friedlander and Johnstone's model, Brownian diffusion is not taken into account; it takes into consideration particle momentum and eddy diffusion as the governing mechanisms for particle mobility. The reasons for the good predictions of the present model are attributed to the fact that it takes into account Brownian diffusion as well as the other two parameters (particle momentum and eddy diffusivity). The particles studied by Friedlander and Johnstone (0.8\( \mu \)) are small enough to be affected by Brownian diffusion, therefore, it cannot be neglected.

Figure 20 shows a comparison of the present model predictions with the experimental data of Friedlander and Johnstone for iron particles in air (66, 67), and with the model proposed by Beal (69). Although, Beal's model also takes into account Brownian diffusion, however, it utilizes a different expressions for the eddy diffusivities in the subliminal layer and in the buffer region. It also uses a different expression for the turbulent core. It can be seen from this figure that the proposed model posses better prediction capabilities.

Figure 21 shows the experimental deposition coefficient data (66, 67) for 0.8\( \mu \) and 1.57\( \mu \) iron particles suspended in a turbulent air stream at 298\( ^\circ \)K (pipe diameter is 1.3 cm). It also shows the experimental data for 1.81\( \mu \) aluminum particles suspended in a turbulent air stream at 298\( ^\circ \)K (pipe diameter is 1.38 cm). From Figure 21 one can notice the fairly good prediction capabilities of the proposed model for all the three sets of data.

In Figure 22 we examine the effect of pipe diameter on the transport coefficient. The results presented in this figure correspond to 0.8\( \mu \) iron particles suspended in flowing air at 298\( ^\circ \)K. As we can see from Figure 22 there is a dramatic decrease in the transport coefficient as the diameter of the pipe increases. This is not surprising, since the larger the diameter the longer the distance particles have to travel prior to deposition.

We have also studied the effect of particle diameter on the transport coefficient for various Reynolds numbers as reported in Figure 23. These results were obtained for iron particles in air at 298\( ^\circ \)K flowing through a pipe of 0.54 cm inner diameter. From this figure we can notice that the curves have the same shape as those predicted by Beal (69) for Aitken nuclei, drops of tricresyl phosphate, and polystyrene spheres. There is no numerical data for these particles reported in Beal's
paper and no experimental data for iron particles. As a result we may conclude that this analysis for the effect of particle diameter is qualitatively correct. From Figure 23 we can notice a decrease in transport coefficient with increasing particle diameter and at a certain particle diameter a minimum is reached after which a sharp increase in the transport coefficient is observed. An explanation for this is that in the left-hand-side of the minima (small particles) the process is diffusion controlled whereas in the right-hand-side of the minima (large particles) the process is momentum controlled.

Model Predictions for Solid Particle Deposition Inside Tubings and Wells

Despite the good agreement of the present model predictions with experimental data of Friedlander and Johnstone (66, 67), it does not indicate that it could be applicable to predict the behavior of solid particles in turbulent flow production operations (liquid phase). In order to justify the validity of the proposed model for this purpose one has to determine experimentally the solid particle deposition coefficients in a turbulent crude oil flow, and compare them with the model predictions. However, no experimental data is reported in the literature regarding this subject. Therefore, we believe the model is good enough to make, at least, qualitative predictions of the solid-particle deposition coefficient from turbulent crude oil flow, and is used as such.

Figure 24 shows the predicted transport coefficients for solid particles as a function of particle diameter for various crude oil production rates. The particle sizes analysed ranged from 50Å to 200µ. The results presented in this figure were obtained for a crude oil with a gravity of 30.21°API and with a kinematic viscosity of 11 centiStokes (cSt). We can notice from Figure 24 that the transport coefficients are in general small except at high production rates and for very large particles. As in Figure 23 we notice a minimum after which the transport coefficient increases more rapidly with increasing particle diameter this is due to the fact that at this point the deposition process is momentum controlled. Judging from Figure 24, the amounts of particle deposition expected from turbulent crude oil production may be very small when the diameter of the suspended particles is less than 1µ. However, higher amounts of deposition may be expected when the suspended particles have diameter larger than 1µ specially at high production rates when the turbulence is high.

We performed model predictions varying the kinematic viscosity of the crude oil to study the effect of this parameter on the deposition coefficient. Figure 25 shows the predicted values for a crude oil containing suspended particles of 1µ in diameter. We can see a decrease in the deposition coefficients with increasing kinematic viscosity. This means that the lighter the crude oil the higher the probability of having particle deposition. We also notice an increase in the transport coefficient with increasing production rate. However, these predicted values are still very small.

It should be emphasized here that the calculations performed for crude oils (Figs. 24 and 25) must be taken as qualitative. In order to obtain more quantitative conclusions, the proposed models for solid particle deposition must be compared with actual experimental deposition data from crude oils. However, these data are not available at the present time. Further work is underway in our laboratory for the two-phase section of the of a producing well in which multiphase flow exists and multiphenomena affect the process of heavy organic deposition.

CONCLUSIONS

In this paper we have presented an overview of the cumbersome heavy organic deposition problem. The causes, effects and preventive techniques for this deposition phenomenon have been outlined. Predictive schemes have been introduced to be used for preventive measures in various cases of deposition in the production, transportation, and handling of petroleum fluids.

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Figure 1. Volume percentage of sedimentation from Abkatun-93 crude versus temperature for centrifugal angular velocities of 1200 & 2400 rpm's and for durations of 10 (upper graph) and 30 (lower graph) minutes [Data of Chavez et al., 1991].

Figure 2. The same as in Figure 2 but for Pol-73 crude.

Figure 3. The same as in Figure 2 but for a 50/50 mixture (by volume) of Abkatun-93 and Pol-73 crudes.

Figure 4. The same as in Figure 2 but for a 63/20/17 mixture (by volume) of Pol-73/Chuc/Abkatun-93, crudes at 1200 rpm.

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Figure 5. Relations between molar concentration distributions of asphaltene in different phases in equilibrium resulting from the addition of a given amount of miscible solvent (20.00 cu. cm n-heptane) to one gram of the tank oil.

Figure 6. Asphaltene particle peptization.

Figure 7. Phase diagram for mixtures of Brookhaven stock-tank oil and carbon dioxide at 317°K. Region 1F is the homogeneous liquid phase area; 2F is the vapor-liquid phase area; and 3F is the liquid-vapor-solid phase area. The region to the right of line A and to the top of line B is the predicted 3F region by the FA model. The shaded area is the experimental 3F region. The experimental data are taken from reference 34.

Figure 8. Kinematic Viscosity (v) vs. wt. fraction of solvent in solutions of Maya Crude with various solvents. The Onset of asphaltene flocculation was located at 32.9 wt% (39.87 vol%) for n-heptane and at 35.8 wt% (41.8 vol%) for n-nonane. The THF-S is a 64.333 vol% solution of THF in toluene. This solution has approximately the same kinematic viscosity as that of n-Heptane.

NOTES
1. O represents resin molecules
2. ● represents aromatic molecules
3. ○ represents oil molecules of different size and paraffinic nature
4. □ represents asphaltene particles of different sizes and shapes

Figure 6. Asphaltene particle peptization.
Figure 9. Kinematic Viscosity (v) vs. wt. fraction of solvent in solutions of Maya Crude with various solvents. The Onset of asphaltene flocculation was located at 27.5 wt% (35.95 vol%) n-pentane in the mixture. As in Figure 8 the Location of the onset is enhanced by comparison with the toluene and THF-S curves.

Figure 10. Relative Viscosity (v_r) (with respect to pure solvent) vs. vol% of solvent in solutions of Isthmus Crude with various solvents. The Onset of asphaltene flocculation was located at 41.17 vol% n-Heptane in the mixture.

Figure 11. Prediction of the kinematic viscosity of THF-S - Maya crude oil with Eq. 21. This predicted data is compared with experimental data (40).

Figure 12. Prediction of the kinematic (v) viscosity of THF-S - Isthmus crude oil with Eq. 21. This predicted data is compared with experimental data (40).
Figure 13. Specific viscosity ($\eta_{\text{sp}}$) of Maya crude oil - n-heptane suspensions as a function of precipitating solvent concentration in the mixture.

Figure 14. Specific viscosity ($\eta_{\text{sp}}$) of Isthmus crude oil - n-heptane suspensions as a volume fraction of flocculant in the mixture.

Figure 15. Theoretical effective volume fraction (calculated from equation 27) vs. n-heptane volume fraction in the mixture. This results are for the Maya crude oil.

Figure 16. Theoretical effective volume fraction (calculated from Eq. 27) vs. n-heptane volume fraction in the mixture. These results are for the Isthmus crude oil.
MODELING AND CONTROL OF ORGANIC DEPOSITS IN PETROLEUM PRODUCTION SYSTEMS

Figure 17. Comparison between Depth at which the bubble point pressure (BPD) occurs and depth at which the organic deposits (ODD) are found. Field data are taken from reference 61.

Figure 18. Schematic representation of an oil producing well [mansoori.people.uic.edu/Pressure.Effect.on.HOD.html].

Figure 19. Comparison of the proposed model with the experimental data and model proposed by Friedlander and Johnstone (66) for 0.8µ iron particles suspended in a turbulent air stream at 298°C.

Figure 20. Comparison of the proposed model with the experimental data and model proposed by Beal (69) for 0.8µ iron particles suspended in a turbulent air stream at 298°C (66).

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Figure 21. Comparison of the proposed model prediction with Friedlander and Johnstone's data (66) for various particles in air.

Figure 22. Effect of particle diameter on the transport coefficient for iron particles suspended in turbulent air streams flowing through a pipe with an internal diameter of 0.54 cm.

Figure 23. Effect of pipe diameter on the transport coefficient for 0.8µm iron particle suspended in a turbulent air stream.

Figure 24. Effect of particle size on the transport coefficient for a 30.21 °API crude oil with a kinematic viscosity of 11 cSt at various productions rates.
Figure 25. Effect of crude oil kinematic viscosity on the transport coefficient for 1µ suspended particles.