Heavy Organic Deposition during Oil Production from a Hot Deep Reservoir: A Field Experience


Abstract
One of the problems confronting the Mexican petroleum industry is the deposition of heavy organics (asphaltene, resin, paraffin/wax and/or diamondoids) in the south-east of Mexico. The fields under study cover approximately an area 85 km² and are two of the most productive ones in the southern region of Mexico. Although the crude oil produced from these fields is of high quality (35-37°API) and highly appreciated in the international market, heavy organic deposition has been observed inside the producing wells since the initial development of the field in 1980. Oil production in these fields has generally implied the use of remedial approaches (i.e., chemical cleanings) to mitigate the effects of such a deposition problem. As a result, answers to questions such as “WHEN” deposition will occur? “HOW MUCH” heavy organics will flocculate out of solution under certain operating conditions? And “WHAT ARE” the economic implications of deposition? Have always been of high interest. Therefore, a systematic study of the phenomena of heavy organic deposition in the fields under consideration was initiated. In this paper we present an analysis of statistical, field, and experimental data related to heavy organic deposition. This analysis enabled the identification of the causes of heavy organic deposition in wells of the fields under study. A discussion pertaining to the interaction between heavy organic material and miscible solvents in regard to enhancement or prevention of deposition is presented. An outline of preventive schemes is introduced.

Introduction
A common problem faced by oil industries is the deposition of heavy organics inside the production tubing, storage vessels, processing equipment, and transfer pipelines (1-3). A survey of field experiences indicated that heavy organic deposition is one of the major factors that increases the costs of production and transportation of petroleum fluids (4). Therefore, it is paramount to be able to understand any potential problems that may arise during production, transportation, and storage of petroleum fluids. In addition, it is crucial to understand the multi-phase behavior of the heavy fraction of a crude oil under certain operating conditions of pressure, temperature, composition, and flow regimes. This would then enable the prediction of any potential deposition problem. It is also important to be able to predict the conditions at the onset of flocculation since by avoiding these conditions heavy organic deposition may be prevented.

The parameters that govern the precipitation of heavy organics from petroleum fluids appear to be composition of crude, injection fluid (if any), pressure and temperature, flow characteristics and properties of the conduit (pipeline, production tubing, etc.) Through which the reservoir fluids flow. With alterations in these parameters, the nature of the heavy organic substances that precipitate will vary (5). Also, it is a proven fact that precipitation of some heavy organics such as asphaltene is generally followed by polymerization and flocculation of the resulting precipitate. This process produces an insoluble material in the original reservoir fluid (6-11). Because of the complex nature of heavy organic substances, the phenomena of organic deposition are not well understood, despite the extensive research performed on the subject. Flocculated species may also interact with other particulate solids contained in the petroleum fluid increasing in this way the complexity of the deposition process. Also, in view of the complexity of the petroleum reservoirs, study and understanding of the in situ precipitation of organic substances seem to be challenging and timely tasks. Nevertheless, there has been extensive progress made in the past several years in the formulation of molecular thermodynamics of multicomponent mixtures, statistical-
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SPE 38989, 9 Pages, Proceed. 5th LACPEC, Rio de Janeiro, Brazil, 1997

mechanical mixing rules and conformal solution equations of state, polydisperse polymer solution theory, electrokinetic and transport phenomena, colloidal solution theory, kinetics of fractal aggregation, etc. This advanced knowledge has been successfully applied to the understanding and prediction of the reversible and irreversible multi-phase and flow behavior of reservoir fluids and other related mixtures (2,4,5,13-16). Thus, the current state-of-the-art understanding of the heavy organic deposition phenomena has been used in the analysis of the statistical, field, and experimental data available for the fields under study. This analysis was aimed at unraveling the causes of the deposition problem in the south-east of Mexico.

Reservoir and crude oil Characteristics
Oil production in the fields of interest is primarily obtained from the cretaceous and Jurassic Dolomitic Limestone’s. These two formations are located at depths ranging from 5,000 to 6,200m with temperatures ranging from 142 to 160°C. The reservoir is characterized by natural fractures with pay zones that vary from 60 to 200m in thickness. The initial reservoir pressure was 702 kg/cm² and the bubble point of the crude oils produced vary from 249 to 275 kg/cm². The GOR varies from 102 to 225 m³/m³ depending on the geographic location of the well within the fields. The crude oil produced in these fields is undersaturated with average API gravities from 35 to 37; the nC₁₄-asphaltene content ranges from 0.2 to 1.2 wt%; and the sulfur content is generally lower than 1 wt%. Table 1 shows a typical composition of bottom-hole samples. Generally, these crude oils contain ~67 mol% of light compounds (i.e., CO₂, N₂, C₁-C₄) of which ~42 mol% is methane, the heptane plus fraction accounts for ~27 mol%. Figure 1 shows a typical curve for the variation of the saturation pressure with respect to temperature for the crude oils under study. Figure 2 shows a typical curve for the variation of the dynamic viscosity of the crude oil (at reservoir temperature) with respect of pressure. The typical variation of the viscosity of the residual oil with respect to temperature (at atmospheric pressure) is depicted in Figure 3. Note that the data reported in Table 1 and Figures 1-3 are very useful in the analysis of statistical field data regarding the phenomenon of deposition during crude oil production.

Available Data for Deposition during Production
Extensive statistical data regarding deposition during oil production in the south-east of Mexico have been collected over a period of more than 16 years. This vast set of data implicitly contains the history and evolution of the phenomenon of deposition in the fields under study. This is true, however, only if the observed deposits are properly documented. The production history of the well(s) in which deposits are observed should be available (including oil and brine production rates, gas-to-oil ratios, etc.), the pressure and temperature at the site of deposition should also be available (or estimated). The extent (length), or at least the profile, of the deposit should also be known. Other information that can be of great help would be the bottom-hole flowing and static pressures. If available, the wellhead pressure can also be very useful. Also, any treatments (e.g., cleanings, stimulations, etc.) performed on wells and reservoir should also be available and properly documented.

It is worth to mention that when the instances of deposition are well documented, as explained above, the statistical field data can be used to extract the heavy organic deposition envelopes (HODE’S) for each well and for the whole reservoir. These HODE’s can then be used to validate any theoretical models formulated to predict heavy organic deposition. In addition, HODE’s obtained in this way may be more appropriate for the validation of these models than HODE’s measured in the laboratory under static conditions. Note that the formulated models must then account for the dynamic character of the system.

Data collected included the pressure and calibration records, as well as the production history for each well in the

<table>
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<tr>
<th>Component</th>
<th>Mol%</th>
<th>Density g/cm³</th>
<th>Mol. Weight g/g-mol</th>
</tr>
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<tr>
<td>Carbon Dioxide</td>
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<td>0.8961</td>
<td>41.992</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.086</td>
<td>10.599</td>
<td>1.086</td>
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<td>13.646</td>
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<td>Propane</td>
<td>6.399</td>
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<td>1.075</td>
<td>1.768</td>
</tr>
<tr>
<td>iso-Pentane</td>
<td>1.386</td>
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<td>2.636</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>1.768</td>
<td>2.395</td>
<td>2.636</td>
</tr>
<tr>
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<td>0.7031</td>
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</tr>
<tr>
<td>Total</td>
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</tr>
</tbody>
</table>

Asphaltene content (stock-Tank)= 0.57 wt%
Saturation pressure = 257 kg/cm²
Gas-to-oil ratio = 202.476 m³/m³
southeastern Mexican fields under study.

The pressure records contain the static bottom-hole pressure; the flowing bottom-hole pressures are also included (choke size is reported). The wellhead pressure is also available in these records. These data, collected over a period of 16 years, also point out the instances in which deposits were observed indicating the depth and the pressure at the site of deposition. The reported depths correspond to the top of the deposits and the pressure corresponds to the flowing pressure at the top of the deposit.

The calibration records contain information regarding the instances in which the well was calibrated. The diameter of the amerada used is reported as well as general observations made during this mechanical operation.

The production history of each well included the oil and gas production rates, gas-to-oil ratios, and water production. A sample of these data is given in Figure 4.

Statistical data regarding the chemical cleanings performed on each well are also available as well as statistical data for stimulation treatments.

Finally, the physicochemical characterization for most of the crude oils produced in the fields under study are also available.

It is worth noting that all the collected data allowed for a thorough evaluation of the deposition phenomena in the south-eastern fields of Mexico.

In order to analyze the collected one must understand the various phenomena taking place during production, cleaning, and stimulation operations.

Effect of Pressure on Heavy Organic Deposition

The most important effects on the multi-phase behavior of heavy organics introduced by changes in pressure are related to the overall solubility of this species in the original reservoir fluid (2,4,5). The compounds that constitute complex petroleum crudes, coal liquids, and the like are mutually soluble as long as a certain ratio of each type of molecule is maintained in the oil mixture (17,18). For instance, the ratio of sulfur- and nitrogen-containing molecules may occur due to hydrogen bonding and/or interactions among the sulfur- and nitrogen-containing segments. This irreversible aggregation produces a material that is insoluble in the original fluid. Note that asphaltene molecules possess a wide distribution of molecular weights and polarities. Therefore, asphaltenes may be assumed to exist in oil both dissolved and in the colloidal state. Consequently, segregation of heavy organics during crude oil production will be the result of multiple effects. One of which is the variation of the solubility of this species in the original fluid. Figure 5 shows a typical curve for the variation of the solubility of asphaltenes in a light crude oil with respect to pressure. The minimum observed in this figure is very close to the saturation pressure of the oil. According to this figure a light crude oil exhibits the highest tendency to precipitate at pressures around the bubble point.

The section of the curve to the right of the minimum represents the effect of pressure on the solubility of asphaltenes in the oil. Note that when a light crude oil is depressurized from pressures above the bubble point the solubility of asphaltenes decreases. This decrease in solubility can be attributed to the different compressibilities of the lighter ends and heavier components in the live crude oil. As the live crude oil is depressurized, the relative volume fractions of the lighter ends within the oil increase more rapidly than those of the heavier compounds. This effect is similar to adding a light hydrocarbon to a crude that could result in depeptization of the asphaltene fraction. Whether or not this destabilization will lead to deposition depends, to a great extent, on the amount of resins present in the oil. It also depends on the dynamics (i.e., turbulence) of the system.

Note from Figure 5 that when the oil is depressurized to pressures below its bubble point the solubility of asphaltenes increases very rapidly. This increase is attributable to compositional changes taking place as the light components of the oil are released into the gas phase. This release results in an increased resins-to-asphaltene ratio (i.e., more stable asphaltene particles).

Effect of Temperature on Heavy Organic Deposition

Changes in temperature during production operations primarily affect the stability of another well-identified heavy fraction (i.e., paraffin/wax). Paraffin/wax deposition generally results from cooling and subsequent crystallization of high-molecular-weight hydrocarbons. This type of deposition is particularly problematic during production of crude oils with a high content of paraffin/wax, especially if the production rates are low. Low production rates affect paraffin/wax deposition primarily because of the increased residence time of the oil in the wellbore. Larger residence times allow more heat loss and thus lower oil temperatures which in turn can lead to crystallization and deposition of paraffin/wax.

In deep hot reservoirs, fluids exist in equilibrium at conditions that exceed the critical pressure and temperature of several of the light ends and associated non-hydrocarbon gases. Therefore, these supercritical fluids act as effective solvents for many heavy organics. When production of oil and associated gases from a well begins, a pressure gradient is established resulting in movement of the reservoir fluids through the porous media. Therefore, the dissolving capacity of the supercritical fluids decreases in the direction of the wellbore and this may lead to paraffin/wax deposition. The sudden pressure and temperature drop experienced by the oil as it enters the wellbore also results in a decrease in the
dissolving power of the supercritical fluids. In the case of undersaturated oils, liberation of dissolved gases makes precipitation of paraffin/waxes more likely because solution gas acts, to some extent, as a solvent for these species.

Paraffin/wax deposition is a classical solid-liquid phase transition phenomenon of polydisperse compounds that are primarily affected by variations in the temperature of the system. Therefore, it can be explained on the basis of well-established principles of equilibrium thermodynamics. Because of this, the phase behavior of paraffin/wax species is better understood.

On the other hand, deposition of other heavy organic compounds such as asphaltenes is far from being a classical solid-liquid phase transition. It is the result of a multi-phenomenon effect that includes solid-liquid phase transition, colloidal-aggregate formation, growth of colloidal aggregates, and eventual collapse of the resulting colloids due to limitations in the size of Brownian particles suspended in a medium. Furthermore, when both paraffin/wax and asphaltene/resin are both present in a crude oil the process of deposition becomes increasingly more complex.

**Effect of Hydrodynamics of the System**

It is generally accepted that colloidal asphaltenes are stabilized by resin molecules (2,5,19). It has also been shown that these particles are electrically charged (20-22). Therefore, any action of a chemical, electrical, and/or mechanical nature that causes depertization of these particles could lead to flocculation and deposition.

It has been proven that when charged asphaltenes flow through porous media and large-bore tubings a streaming potential is generated which counterbalances the weak asphaltene charge; hence causing precipitation (21-22). This streaming potential increases with increasing average fluid velocity, decreases with increasing particle diameter, and decreases with increasing conductivity of the wall of the conduit. Note that asphaltene deposition near the perforated section of a well could also be the result of electrokinetic effects. This section of the well is generally prone to deposition because of the drastic changes the crude oil undergoes as it enters the wellbore (e.g., expansion, cooling, decrease in fluid velocity, increased turbulence, liquid stagnation, nucleation, etc.)

The hydrodynamics of the system could have a substantial effect on the deposition of suspended particles from a fluid in motion (14). Figure 6 shows the effect of particle diameter on the rates of deposition for a 30.21°API crude oil with a kinematic viscosity of 11 cSt at various production rates. The range of particle diameters investigated in this calculation was from 50 angstroms to 200 microns. The oil production rates were varied from 200 to 2500 m³/day (1258 to 15724 barrels/day). The results presented in Figure 6 show a decrease in transport coefficient (deposition rates) with increasing particle diameter. A minimum is reached at a given particle size for each production rate followed by a sharp increase in deposition rates. This can be explained considering that on the left-hand side of the minima (small particles) the process of deposition is diffusion controlled; whereas on right-hand side of the minima (large particles) the deposition process is momentum controlled. Figure 6 also shows that the rate of particle deposition increases with increasing production rates.

It has also been shown (14) that deposition rates increase with decreasing oil viscosity and decrease with increasing pipe diameter.

**Effects of Stimulation Treatments**

Serious problems have been experienced in many oil-producing areas around the world due to formation of asphaltic sludges during acid stimulation treatments (23-25). This seems to be a potential problem for every producing well at any time stimulation treatments are performed. Asphaltic sludge is a precipitate of colloidal materials present in the crude oil (i.e., asphaltene/resin) promoted by introduction of acids into the reservoir. Once formed, sludge is very difficult to remove since a great deal of asphalt-like material is returned with the treating chemicals. This often causes further deposition problems as it flows up the well.

Formation of asphaltic sludge during stimulation treatments could potentially render in irreversible formation damage. Therefore, the solution to sludge formation problems should preventive rather than remedial (i.e., cleaning). Thus, if a crude oil has been found to form asphaltic sludges upon contact with acids, then a stimulation treatment must be developed to prevent the formation of undesirable precipitates (e.g., sludge). It has been found that acid-in-aromatic-solvent emulsions and the use of additives in the treating acids seem to prevent the formation of sludge (26).

A decline in well productivity following a stimulation treatment indicates a distinct sensitivity of the reservoir fluids to the acids employed (25). Whenever this is observed, a different stimulation treatment must be developed to prevent the subsequent declines in well productivity.

**Other Effects of Poorly Designed Stimulation Treatments**

A number of other problems can arise during poorly designed/performed stimulation treatments:

a. Material from the tubing may enter the formation and cause irreversible formation damage.

b. Oil-wetting the reservoir by surfactants (e.g., corrosion inhibitors) which can create emulsion blocks.

c. Deconsolidation of formation rock due to excessive dissolution of cementing materials by acid.

d. Precipitation of byproducts from the reaction of acids with formation rock minerals. For instance, precipitation of gelatinous ferric hydroxide can completely plug pores.
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and can be difficult to remove. Fluosilicates can precipitate as individual crystals and block pore throats; iron sulfide can precipitate during acid stimulation of sour wells.

e. Sequestering agents added to acids to prevent secondary deposition of iron compounds can also form precipitates when the acid is spent and no iron is present.

Whenever it has been established that a given well is a candidate for stimulation, the true causes for low well productivity must be identified. In addition, the type of damage must also be identified in order to devise the most appropriate stimulation treatment. This way, secondary deposition problems resulting from poorly designed and/or performed treatments could be prevented.

Effects of Deposit-Cleaning Operations

It has been shown that precipitated and/or flocculated asphaltenes can be dissolved and re-stabilized by heavy aromatic compounds such as resins (neutral). This fact has enabled the development of remedial techniques in which the uses of chemicals (i.e., aromatic solvents with steric-stabilizing additives) allow the removal and stabilization of heavy organic deposits. However, cleaning operations must be properly designed and tailored to the specific needs of removal. Thus, experimental evidence must support the selection of the most appropriate solvent/additive system to be used for deposit removal. The selected system should exhibit high deposit dissolution rates and must be capable of maintaining the removed material in suspension (i.e., stabilize). Note that these properties must prevail even if the concentration of the removed material becomes very high. Also, the selected system must not form high-viscosity interfaces with the deposit otherwise it will be difficult for fresh solvent to reach the solid material to be removed.

Once the optimum solvent/system has been selected, the most appropriate cleaning procedure must be devised. It must be kept in mind that there may be insoluble material in the solid deposits that can complicate the cleaning process. This insoluble material may prevent the solvent from reaching the organic material resulting in removal of rather large chunks of deposit that may be difficult to stabilize. Should this be the case, further deposition problems will certainly be observed. Furthermore, these large particles could easily settle to the bottom of the well and could be introduced into the reservoir. This will be particularly problematic whenever cleanings are performed in the tubing followed by reservoir treatments to remove any damage.

Improperly designed/performed cleaning treatments can render in secondary deposition problems and/or irreversible formation damage.

Results Obtained from the Analyses Performed

All the available data regarding heavy organic deposition in the fields under study have been analyzed taking into consideration the various effects discussed above. The sole purpose of this analysis was to unravel the causes of the observed deposits.

Figure 7 shows a heavy organic deposition envelope (HODE) obtained from statistical deposition data. The distance reported in this figure corresponds to the top of the deposit measured from the midpoint of the perforated section of the well (MOPI). Depending on the profile of the deposit, the top of the deposit may not be very far from the point where initial deposition took place (deposits form over a period of time). Note that data specific to the conditions of flow prevailing at the time of deposition are also available for each point on Figure 7. Therefore, this HODE can easily be transformed into the more familiar Pressure-versus-Temperature diagram.

It may be observed from Figure 7 that a large number of deposits took place near the midpoint of the perforated section of the well. This suggests that careful attention must be paid to the various phenomena taking place in this section of the well during production operations as well as during cleaning and stimulation treatments. This will allow to make a distinction between deposits caused by changes in pressure, temperature, flow conditions, etc. and those caused by poorly designed treatments.

Figure 7 suggests that deposition in the fields under study is directly related to the overall solubility of heavy organics in the reservoir fluid. Note that very few deposits take place at conditions below the bubble point pressure of the crude (see Figure 1). This is not surprising considering that the crude oils produced in the fields under consideration contain as much as 67 mol% of light hydrocarbons and associated gases (see Table 1). Thus, it may be expected that the solubility of heavy organics will rapidly increase as the dissolved gas is released. Therefore, little or no precipitation might take place at pressures below the bubble point of the crude. It must be understood, however, that release of gas from the liquid phase results in a momentary imbalance in the nature of the media surrounding asphaltene/resin stable particles. This imbalance may lead to destabilization of these particles by stripping the resins from asphaltenes thereby facilitating aggregation.

Finally, asphaltene, as many other substances, requires a certain degree of supersaturation before any phase segregation takes place. Thus, eventual precipitation of heavy organics depends largely on the degree of supersaturation by pressure drop during production. Note that the degree of supersaturation needed for precipitation and subsequent deposition depends on a variety of factors. For instance, time, temperature, turbulence and nature of the surface on which heavy organics deposit. Turbulence plays an important role as to whether or not deposits will form. If the population of flocculated species is not high, then any amounts that eventually deposit may be eroded from the surface by high degrees of turbulence (i.e., shear stresses). However, if the
Deposition of inorganic material:

Poorly designed cleaning treatments:

Hydrodynamic effects:

Simultaneous deposition of organic and inorganic material: Deposits comprised primarily by inorganic material were observed in several instances.

Simultaneous deposition of organic and inorganic material: Many deposits comprised of a mixture of organic and inorganic material were reported. Inorganic material found in these deposits may have resulted from deconsolidation of reservoir rock and/or from byproducts from the reaction between acid and formation rock and/or brine during stimulation treatments.

Hydrodynamic effects: Many instances in which high production rates seem to have resulted in increased deposition of heavy organics were reported. Also, majority of the deposits were found in sections of the well where there was an increase in turbulence (e.g., perforated section, tubing/packer assembly, etc.)

Temperature and Pressure: Figure 7 suggests that heavy organic deposition in the fields under study took place in a well-defined region of the PT diagram. Therefore, thermodynamic changes of pressure and temperature are directly related to the phase segregation of heavy organics from the original reservoir fluid. It was also found that heavy organic deposition decreases as the pressure has fallen below the saturation point of the crude oil being produced. This suggests that deposition in these fields may be prevented by manipulation of pressure and temperature during crude oil production. However, secondary deposition problems resulting from poorly designed cleaning and/or stimulation treatments must be resolved as a preliminary step.

It needs to be proved whether heavy organic deposition can be prevented through manipulations of pressure and temperature. This can be done using comprehensive models for the prediction of the multi-phase and flow behavior of heavy organics. The formulated comprehensive models when validated with HODE's similar to the one presented in Figure 7 may prove useful in predicting the conditions under which deposition will take place. These predictions can then be tested in the field to prevent heavy organic deposition.

Conclusions

A field experience regarding heavy organic deposition in the South east of Mexico has been presented. It was found that the crude oils produced in the area are sensitive to the acids used for stimulation. It is suspected that asphaltic sludge is formed during stimulation treatments. It is also suspected that inorganic byproducts resulting from reaction between the acid(s) and formation rock and/or brine could have enhanced the problem of deposition. It was also found that poorly designed cleaning procedures could have lead to severe mechanical problems resulting from deposition of removed material. This might have been due to inability of solvent/additive system used for cleaning to maintain the removed material in suspension.

It was also found that heavy organic deposition in the fields of interest may be prevented and/or alleviated through manipulations of pressure and temperature during production operations. However, it suggested that theoretical studies must be performed to validate these field observations.

Acknowledgments

This research is supported by Institute Mexicano del petroleo (IMP) grant FIDE-PEMEX CDA-0401. We thank Petroleos Mexicanos (PEMEX) for their permission to publish this work.

References


Figure 2. Typical variation of the viscosity with respect to pressure (at reservoir temperature) for the crude oils produced in the fields under study.

Figure 3. Typical variation of the viscosity of the residual oil with respect to temperature (at atmospheric pressure) for the crude oils produced in the fields under study.

Figure 4. Typical production history data for oil producing well in the fields under consideration. Qo is the oil production rate in thousands of barrels of oil per day (Mbbpd); Cum. Qo is the cumulative oil production in millions of barrels (MMbbls); Qg is the gas production rate in millions of cubic feet per day (MMcfd); Cum Qg is the cumulative gas production (billions of cubic feet (MMMcfd); GOR is the gas-to-oil ratio in m³/m³; Water Prod. is the brine production in terms of percentages.
Figure 5. Variation of the solubility of asphaltenes in original reservoir light oil with respect to pressure. The observed minimum corresponds to the saturation pressure of the oil.

Figure 7. Heavy organic deposition envelope (HOD) for the crude oils produced in the fields under study. The reported distance corresponds to the top of the deposit measured from the midpoint of the producing interval (MOPI).

Figure 6. Effect of particle size on the transport coefficient (rate of deposition) for a 30.210API crude oil with a kinematic viscosity of 11 cSt at various production rates (reproduced from reference 14).