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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

**SIMULATION OF ASPHALTENE DEPOSITION IN
PETROLEUM RESERVOIRS DURING PRIMARY OIL
RECOVERY**

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

by

SHAOJUN WANG

Norman, Oklahoma

2000

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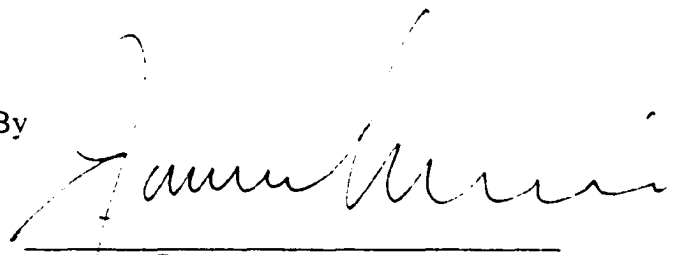
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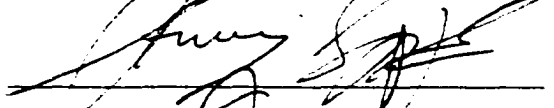
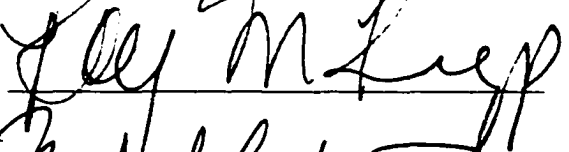
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A DISSERTATION

APPROVED FOR THE MEWBOURNE SCHOOL
OF PETROLEUM AND GEOLOGICAL ENGINEERING

By




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DEDICATION

To my parents, Wencei and Jinlan, for bringing me into this beautiful world and growing me up. To my dear wife, Zhe, for her love, support and understanding throughout this study and to my coming baby.

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Abstract

Asphaltene is known to precipitate and deposit in petroleum reservoirs during primary oil recovery. Previous research focuses on the asphaltene precipitation and deposition during hydrocarbon and carbon dioxide miscible flooding. The process of asphaltene precipitation and deposition during primary oil recovery is different. Although several attempts were made to model and simulate the asphaltene precipitation and deposition in petroleum reservoirs during primary oil recovery, they have not been fully successful because of the lack of sufficient understanding of the problem.

In this study, a polymer solution model for asphaltene precipitation was used to simulate the experimental data of asphaltene precipitation due to pressure depletion. The results predicted by the polymer solution model matched the experimental data accurately after several improvements. A model for asphaltene precipitation and deposition in core tests was developed and numerically solved and then applied to six sets of experimental data. The model satisfactorily matched the data and model parameters were determined to match the data.

By incorporating asphaltene precipitation, deposition and mass balance models into a three-dimensional and three-phase black oil simulator, a simulator for asphaltene deposition in petroleum reservoirs with vertical or horizontal wells was developed with respect to primary oil recovery. Two typical scenarios were evaluated. Case I involved the asphaltene precipitation and deposition in a reservoir developed by a vertical well during primary oil recovery. Case II involves the asphaltene precipitation and

deposition in a reservoir developed with a horizontal well. In both cases, the simulator predicted the reasonable distributions for pressure, dissolved asphaltene, asphaltene precipitate, asphaltene deposit, as well as porosity and permeability throughout the reservoir. The pattern of asphaltene deposition in reservoirs with a vertical well was shown to be significantly different from that in reservoirs with a horizontal well.

Finally, a model for the simultaneous deposition of paraffin and asphaltene in porous media was developed. The corresponding numerical model is developed using a fully implicit scheme. Because the numerical model is strongly coupled, a double iteration method was used to solve the equations. The model was verified using two sets of experimental data.

The model and simulator developed in this study can be used to analyze experimental data of asphaltene deposition in core tests. It can also be applied to simulate asphaltene deposition in petroleum reservoirs with vertical or horizontal wells during primary oil recovery and to assist in the development of strategies to alleviate asphaltene deposition problems.

CHAPTER I

INTRODUCTION

Asphaltene is the heaviest component of crude oil. Pure asphaltene is a solid and commonly in the form of black powder. They are initially dissolved in the crude oil and specific changes in reservoir pressure, temperature, and composition may cause asphaltene to precipitate from the crude oil. In fact, asphaltene can precipitate during primary oil recovery, stimulation, CO_2 flooding, and hydrocarbon miscible flooding. Asphaltene precipitates may deposit to the surface of pores or plug the pore throat, causing a decrease in pore space of the formation and reduction of the ability of fluid flow in the formation.

1.1 The Objective of This Study

Asphaltene deposition in the reservoir is a complex problem and it is virtually impossible to do field experiments. Laboratory tests are tedious and time consuming. In order to study effects of asphaltene deposition, it is becomes necessary to rely on modeling and simulation in place of field or some laboratory work.

Although the investigation of asphaltene in crude oil has been ongoing for many years, only a few facts have been established about the behavior of asphaltene in crude oil. The lack of information makes modeling and simulation of asphaltene deposition become difficult. Previous research focuses on asphaltene precipitation during

hydrocarbon and CO_2 miscible flooding, which is different from that during primary oil recovery. To date, little research has involved asphaltene deposition during primary oil recovery and has only achieved partial success mainly due to lack of information. No satisfactory model and simulator are available for asphaltene deposition in reservoirs during primary oil recovery. Therefore, it is necessary to obtain the better understanding of the problem and to establish a better model to simulate the asphaltene precipitation and deposition in petroleum reservoirs during primary oil recovery. The following are the specific objectives of this study:

1. To obtain a better understanding of asphaltene precipitation and deposition during primary oil recovery by critically and systematically reviewing the literature.
2. To choose a proper model of asphaltene precipitation to simulate the asphaltene precipitation process during pressure depletion and test the model with experimental data.
3. To establish a model for asphaltene deposition in core tests and verify the model with core test data.
4. To develop a model and simulator to simulate asphaltene precipitation and deposition in petroleum reservoirs during primary oil recovery by incorporating the verified asphaltene precipitation and deposition models into a black oil simulator.
5. To set up a model for the simultaneous deposition of paraffin and asphaltene in porous media and verify the model with experimental data.

1.2 The Scope of This Study

This study focuses on asphaltene precipitation and deposition during primary oil recovery. In primary oil recovery, pressure, temperature, and composition are the main factors that affect asphaltene precipitation.

In Chapter II, the relevant previous works about asphaltene precipitation and deposition are reviewed. These works involved describing the state of existence of asphaltene in crude oil, its molecular weight, factors which affect precipitation, precipitation experiment and models used to simulate asphaltene precipitation, and the experiments and models of asphaltene deposition in porous media.

In Chapter III, a polymer solution model for asphaltene precipitation is applied to simulate the experimental data of asphaltene precipitation that occurs as a result of pressure depletion. Some improvements are made in the calculations.

In Chapter IV, a model for asphaltene precipitation and deposition in core tests is developed. The model includes four parts: transportation, asphaltene precipitation, asphaltene deposition, and the permeability and porosity reduction. The mathematical model is numerically solved and verified using six sets of experimental data. Model parameters are determined using history matching techniques.

In Chapter V, the asphaltene precipitation and deposition models and the permeability and porosity reduction models are incorporated into a three-dimensional, three-phase black oil simulator. The simulator is then applied to two typical case studies: a reservoir with a vertical production well and a reservoir with a horizontal production well. In both cases, the simulator performed satisfactorily and generated reasonable

distributions of asphaltene precipitates and deposits, as well as corresponding permeability and porosity.

In Chapter VI, a model for the simultaneous deposition of paraffin and asphaltene caused by temperature decrease and pressure depletion in core tests is established. The model incorporates the mass, momentum, and energy balance equations and is numerically solved using a double iteration scheme and then verified using two sets of experimental results.

In Chapter VII, the conclusions of this study are made. Following the discussion of conclusions, several recommendations are made for future study of asphaltene deposition during primary oil recovery.

CHAPTER II

LITERATURE REVIEW

Although investigations of asphaltene precipitation in petroleum reservoirs have been ongoing for some time, the state and characterization of asphaltene in crude oil are still not clear. Increasingly, more researchers agree that asphaltene tends to dissolve in crude oil, so that the crude oil containing asphaltene is a real solution. This chapter contains a literature review of asphaltenes, with respect to the thermodynamic state, precipitation, and deposition.

2.1 Asphaltene

2.1.1 Definition

Asphaltene is defined by its solubility rather than its molecular structure. It is defined as a material contained in petroleum, which is insoluble in pentane or heptane but soluble in benzene or toluene (Speight and Long, 1996; Speight, 1996).

2.1.2 Elemental Compositions

Asphaltene mainly consists of carbon and hydrogen elements. It also contains some oxygen, nitrogen and sulfur elements. By weight, asphaltene contains 80.42~88.65% carbon, 7.44%~11.10% hydrogen, 0.3~4.9% oxygen, 0.3~10.3% sulfur, and 0.6~3.3% nitrogen elements (Koots and Speight, 1975; Speight, 1996).

2.1.3 Molecular Structure

The actual molecular structure of asphaltene is not well understood. Spectroscopic studies of asphaltene support the hypothesis that asphaltene contains condensed polynuclear aromatic ring systems. These systems carry alkyl and alicyclic side chains with heteroelements, such as nitrogen, oxygen and sulfur, scattered throughout its various locations (Speight, 1996).

2.1.4 Molecular Weight

The molecular weight of asphaltene is difficult to measure because it depends on the nature and amount of solvent, temperature, and the contact time (Mitchell and Speight, 1973; Speight et al., 1984; Speight, 1991; Anderson and Stenby, 1996). The molecular weight tends to be overestimated because asphaltene forms molecular aggregations even in dilute solution (Winniford, 1963; Speight and Moschopedis, 1977). A more accurate method of determining the molecular weight of asphaltene would require using solvents that prevent aggregation, and will result in molecular weights in the range of 1,500~2,500 (Speight, 1996; Speight, 1999).

2.2 Existence State of Asphaltene in Crude Oil

Describing the existence state of asphaltene in crude oil is difficult because it is extremely difficult to determine directly the existence state of asphaltene in crude oil, especially in live oil. However, it is important to know the existence state of asphaltene in crude oil because it is the basis of understanding asphaltene precipitation and deposition in petroleum reservoirs.

2.2.1 Experiments on Existence State of Asphaltene in Crude Oil

2.2.1.1 Electron Microscope Experiments

Preckshot et al. (1943) investigated oil films with and without solvent dilution under electron microscope. When crude oil was not treated with solvent, the oil film was very clear and uniform under the electron microscope, meaning there were no particles in the oil film. When crude oil was treated with solvent, many dark spots or particles appeared in the oil film under electron microscope. It was concluded that asphaltic particles in the colloidal range were formed when crude oil was treated with solvent and that the original state of asphaltene in the untreated crude oil was either molecular or an association of a relatively small number of molecules. Katz and Beu (1945) conducted similar experiments and observed the same results. This confirmation demonstrates that the state of asphaltene in natural crude oil is different from that in crude oil treated by solvent and that solvents cause asphaltene in crude oil to associate and form asphaltene particles.

2.2.1.2. Electrical Effect Experiments

An early electrical experiment was carried out by suspending two platinum electrodes in crude oil, spaced 0.5 to 1 mm and applying a 220-volt electrical potential (Katz and Beu, 1945). The crude oil was filtered using filter paper prior to the experiment. The electrical potential was applied to the electrodes for several days, and then the electrodes were removed. It was observed that there were some black materials on the positive electrode, but the negative electrode was clean.

Streaming potential can be caused by flowing crude oil containing asphaltene through silica (Dykstra et al., 1944). Before the experiment, the film of crude oil was

examined under the electron microscope to confirm it was clear, uniform and devoid of observable dark spots. After the crude oil flowed through the silica, some small dark spots appeared in the film of the crude oil. During the crude oil flowing through the silica, the streaming potential across the silica caused by the flow was measured at 39 millivolts (Dykstra et al., 1944). It was concluded that crude oil containing asphaltene has an electrical effect and flowing oil through silica may cause asphaltene in crude oil to precipitate resulting in visible dark spots or aggregates.

2.2.1.3 Ultracentrifuge Experiments

Ultracentrifuge experiments were performed by Ray et al. (1957) and Witherspoon and Munir (1958). At room temperature and under ultracentrifugal force, the black pellets were separated from crude oils and identified as asphaltene particles. Based on these experimental results, it was concluded that asphaltene existed in crude oil as particles with a diameter of 30 to 65 Å and a molecular weight of 30,000. Therefore, it was argued that crude oil containing asphaltene forms a colloidal system.

2.2.1.4 Reversibility Experiments

Reversibility experiments were performed in a high-temperature, high-pressure cell with observation windows by Hrischberg et al. (1982). As the pressure decreased below 300 bar, asphaltene crystals started to form on the windows. Below 280 bar, the asphaltene crystals then grew and liquefied. The asphaltene droplets begin to drop out around 200 bar and the windows became clean when the pressure decreased to 150 bar. Similar phenomenon was observed by Thawer et al. (1990).

A reversibility study of asphaltene precipitation and dissolution was also performed using a mixture of crude oil and solvent (Ramos et al., 1997). The asphaltene deposits in a mixture of crude oil and n-heptane were redissolved into crude oil by evaporation of n-heptane or by the addition of fresh oil into mixture. In the experiments, stirring and ultrasound were applied to the mixture to redissolve the asphaltene deposits into the mixture completely.

The reversibility of asphaltene precipitation and dissolution was also observed in the flowing experiments by Danesh et al. (1989) that involved visual micromodels. In their experiments, the asphaltene deposited in pores and the pressure drop across the model was increased when the mixture of propane and stock tank oil was injected the micromodel. Then, fresh oil was injected into the model, and asphaltene deposits in the model pores disappeared gradually and the pressure drop across the model decreased. Similar observations were also made in propane flooding of live oil in a visual micromodel by Danesh et al. (1987).

The reversibility of asphaltene precipitation process was observed in core test studies by Pedroza et al. (1995). When the n-pentane was injected into cores saturated with crude oil containing asphaltene, the permeability was reduced and pressure drop was increased. After the fresh oil was injected into the cores, the permeability of the cores was restored.

The above observations and experiments indicate that asphaltene precipitation is a reversible process. This is important fact to consider when dealing with asphaltene deposition in reservoir recovery.

2.2.1.5 Molecular Weight Measurement

Different methods yield different results, especially, since most methods measure the asphaltene molecular weight in a solvent. Asphaltene can form aggregates in solvent and the degree of aggregation depends on the nature of solvent, quantity of solvent, the concentration of asphaltene, and experimental conditions such as the temperature and contact time. Therefore, asphaltene molecular weights measured in solvent vary over a large range. For example, the molecular weight is 300,000 by ultracentrifuge (Ray et al., 1957, Witherspoon and Munir, 1958), 80,000 by the osmotic pressure method (Labout, 1950), 20,000 to 138,400 by the Small-Angle Neutron and X-Ray Scattering methods (Espinat and Ravey, 1993), 80,000 to 140,000 by the monomolecular method (Pfeiffer and Saal, 1940), 600 to 6,000 by the cryoscopic method (Labout, 1950), and 900 to 2000 by viscosity determinations (Reerink, 1973). The majority of these methods overestimate the molecular weight of asphaltene.

Recently, the asphaltene molecular weight was measured by using a solvent that can prevent asphaltene aggregation (Speight, 1996; Speight, 1999). With this method, asphaltene molecular weight ranged between 1,500 to 2,500 and may represent the closest measurement of asphaltene molecular weight.

2.2.2 Physical Model of Asphaltene in Crude Oil

There are two types of physical solution models for asphaltene in crude oil. They are the real solution model and the colloidal solution model.

2.2.2.1 Real Solution Model

A real solution model assumes that asphaltene dissolves in crude oil completely and form a uniform solution (Hirschberg et al., 1982; Burke et al., 1988; Novosad and Costain, 1990; Zhou et al., 1996; Nghiem et al., 1998). The essential feature of this model is that the process of asphaltene precipitation and dissolution is reversible. The models of this type can be grouped into two subgroups, which are the regular solution model and the polymer solution model. The regular solution model assumes that asphaltene dissolves in crude oil exactly like other small hydrocarbon molecules. However, this model may not accurately represent asphaltene in crude oil because asphaltene molecules are largely different in size from those of most components in crude oil. The polymer solution model assumes that asphaltene dissolves in crude oil as large molecules, similar to polymer molecules dissolved in water. The polymer solution model more accurately represents the dissolved asphaltene in crude oil. Because the reversibility of asphaltene precipitation and dissolution was proven by many researchers, the real solution theory may represent the real state of asphaltene in crude oil better.

2.2.2.2 Colloidal Model

Pfeiffer and Saal (1940) investigated the existent state of asphaltene in bitumen and first established a model for asphaltene existence in bitumen. In their model, the asphaltene was in the center of micelles. Compounds with the greatest molecular weight and with the most pronounced aromatic nature were arranged most closely to the nucleus and surrounded by lighter constituents of less aromatic nature. From the center of micelles to the intermicelle phase, a gradual and continuous transition formed without a

distinct interface. The micelles were formed by adsorption, and perhaps partly by absorption. This model was based on the research on bitumen (Pfeiffer and Saal, 1940).

Yen et al. (1961) first studied asphaltene micelles in crude oils with X-ray diffraction and concluded that the basic unit forming asphaltene micelles was a polynuclear aromatic ring layer with alkyl chains and functional groups (asphaltene molecule). The unit had a diameter of 8.5 ~ 15 Å. Three to five of these units (molecules) formed asphaltene micelles with a diameter of 16 ~ 20 Å. The distance between two layers (units or molecules) was 3.5 ~ 3.7 Å. The layers (molecules) were bonded by hydrogen bonding. Subsequent researches showed that a single asphaltene molecule might form the center of an asphaltene micelle or particle. Kotsu and Sleight (1975) investigated the relationship between asphaltene and resin and found that single asphaltene associated with resins was the dominant state, which allowed the asphaltene to exist in the colloidal state in a crude oil. Moschopedis and Speight (1976) investigated the hydrogen bonding between resins and asphaltene. It was found that when resins and asphaltene were present together, resin-asphaltene interactions were preferred over asphaltene-asphaltene interactions. Speight (1996, 1999) concluded that it was quite likely that the micelle in petroleum consisted of a single asphaltene molecular rather than as a stack of asphaltene molecules peptized or dispersed by resins.

The colloidal model of asphaltene was paid a lot of attentions in past ten years because many researchers investigated asphaltene using solvents. As pointed out in the previous section, solvents cause asphaltene aggregation. Therefore, the existence state of asphaltene in solvents is different from that in crude oil. Besides this, the basic

assumption of the colloidal model is that the process of asphaltene precipitation is not reversible. This assumption is proven to be incorrect as more and more experimental results prove that the process of asphaltene precipitation is reversible. Another major assumption of colloidal model is that the crude oil containing asphaltene is stable if the ratio of the resin content to the asphaltene content is greater than a certain value, such as 1.25 (Koots and Speight, 1975). However, the ratio of resin to asphaltene content in Hassi-Messaoud oil is as high as 22, and the crude oil still has asphaltene precipitation and deposition problems (Minssieux, 1997). Therefore, this model may only represent some behaviors of asphaltene in solvent, but it does not represent the behaviors of asphaltene in crude oil.

2.3 Asphaltene Precipitation during Primary Oil Recovery

2.3.1 Factors Affecting the Asphaltene Precipitation during Primary Oil Recovery

During primary oil recovery, the reservoir pressure, temperature, and composition are the three main factors that affect asphaltene precipitation in the reservoir. Each factor is discussed below.

2.3.1.1 Pressure

The pressure is the major factor that causes the asphaltene precipitation in reservoirs during the primary oil recovery. The Hassi Messaoud Field in Algeria experienced a significant problem with asphaltene deposits on tubing because the wellhead pressure was close to the bubble point pressure (Haskett and Polumbus, 1965). The wells had to be washed every 42 days. After the chokes on those wells were removed and the wellhead

pressure decreased well below the bubble point, the problem is much alleviated and the wells only had to be washed every 162 days. The Ventura Avenue Field in California also experienced serious problem with asphaltene deposition on tubing (Tuttle, 1983). When the bottomhole pressure fell below the bubble-point pressure, the problem diminished. Those actual field experiences indicate less asphaltene precipitation problems when the pressure is below the bubble point than when the pressure is at bubble point.

Thawer et al. (1990) studied the effects of pressure on asphaltene precipitation in live oil and found that asphaltene began to precipitate when the pressure decreased below a pressure higher than the bubble point of the crude oil. As the pressure decreased, more and more asphaltene precipitated and the amount of asphaltene precipitate reached the maximum at the bubble-point. Below the bubble point of the oil, some reduction of precipitated asphaltene was observed. Burke et al. (1988) investigated the solubility of asphaltene in live oils with an API gravity from 18 to 40. It was found that the solubility of asphaltene decreased with decrease in pressure when the pressure was above the bubble point, reached a minimum at the bubble point of the oil, and the solubility increased with decrease in pressure when the pressure is below the bubble point. Leerlooyer et al. (1995) also conducted pressure reduction experiments and obtained similar results.

In summary, when the pressure is above the bubble point pressure of crude oil, the solubility of asphaltene in the crude oil decreases with the decrease in pressure. The solubility reaches a minimum value at the bubble point pressure. When the pressure is

below the bubble point of the crude oil, the solubility of asphaltene in the crude oil increases with decrease in pressure.

2.3.1.2 Temperature

During primary oil recovery, the reservoir temperature remains almost constant. Therefore, the temperature is not as carefully studied as pressure. Only a few researchers have investigated the effect of temperature on asphaltene precipitation.

Thomas et al. (1992) showed that the solubility of asphaltene in crude oil increased with an increase in temperature. Burke et al. (1988) demonstrated that the solubility of asphaltene decreased with temperature increase. More specifically, both Leontaritis (1996) and Paramanu et al. (1999) suggest that the asphaltene solubility increases with the increase of temperature when the temperature is below the reservoir temperature, but decreases with the increase of temperature when the temperature is higher than the reservoir temperature.

Since above experimental results may be contrary to each other, no general conclusion can be drawn. More experiments are needed to investigate and clarify the effect of temperature on asphaltene solubility.

2.3.1.3 Composition

Burke et al. (1988) also investigated the effect of dissolved gas on the solubility of asphaltene in live oil. It was found that an increase in dissolved gas in live oil was associated with lower solubility of asphaltene in live oil. This result is also supported by the fact that the solubility of asphaltene increases with pressure decrease when the

pressure is below the bubble point because the dissolved gas in the crude oil becomes less.

2.3.2 Models for Asphaltene Precipitation during Primary Oil Recovery

Based on the physical model of the existence state of asphaltene in crude oil, there are two theories. Some researchers consider that asphaltene is dissolved in crude oil completely and therefore, real-solution theory can be applied to determine the solubility of asphaltene in crude oil (Hirschberg et al., 1982; Burke et al., 1988; Novosad and Costain, 1990; Kawanaka et al., 1991; Thomas et al., 1992; Chung, 1992; Non-Azian and Adewumi, 1993; Nghiem et al., 1993; Cimino et al., 1995; MacMillan et al., 1995; Boer et al., 1995; Yarranton and Masliyah, 1996; Nghiem and Coombe, 1996; Zhou et al., 1996; Nghiem et al., 1998). Others consider that asphaltene is suspended colloiddally in crude oil, and the crude oil containing asphaltene is a colloidal system, therefore, the colloidal theory can be applied to describe the peptization/flocculation of asphaltene in crude oil (Roger et al., 1957; Leontaritis and Mansoori, 1987; Mansoori, 1994 and 1996). Typical models for each theory are discussed in the following sections.

2.3.2.1 Real-solution Theory

The real solution model assumes that the asphaltene is dissolved in oil in a real solution state. The dissolution/precipitation of asphaltene in crude oil is then dependent on thermodynamic conditions, such as temperature, pressure and composition. The precipitation/dissolution of asphaltene is considered to be a thermodynamically reversible process. Experiments have already proven that the asphaltene precipitation/dissolution is a reversible process (Hirschberg et al., 1982; Danesh et al., 1989; Ramos et al., 1997).

This theory does not adequately explain the need for a certain amount of resin for asphaltene to completely dissolve in crude oil (Koots and Speight, 1975). After investigating stable solutions of asphaltene in several hydrocarbon solvents, Cimino et al. (1995) concluded that the presence of resin in crude oil is not a necessary condition of asphaltene dissolution in crude oil.

In the real solution theory, two models are applied to describe the precipitation/dissolution of asphaltene in crude oil: the regular solution theory and polymer solution theory.

2.3.2.1.1 Regular Solution Theory

Numerous models for asphaltene precipitation/dissolution have been developed using the regular solution theory (Chung, 1992; Thomas et al., 1992; MacMillan et al., 1995; Yarranton and Masliyah, 1996; Zhou et al., 1996;). Since these models are similar, only the Chung model for asphaltene precipitation/dissolution is presented in this report.

Under the assumptions that asphaltene is a pure component and there is no significant change in pressure, the equilibrium for asphaltene component can be expressed using following equation:

$$X_{AL} = X_{AS} \exp \left[-\frac{\Delta H_A}{R} \left(\frac{1}{T} - \frac{1}{T_{Am}} \right) - \frac{V_A}{RT} (\delta_{avg} - \delta_A)^2 - \ln \frac{V_A}{V_{avg}} - 1 + \frac{V_A}{V_{avg}} \right] \quad (2.1)$$

X_{AL} denotes the mole fractions of the asphaltene dissolved in the oil as a function of temperature, liquid-phase composition, and properties such as the heat of melting, melting temperature, molar volume, and solubility parameters for each component. X_{AS} is the mole fraction of the asphaltene precipitates in the total system. ΔH_A is the latent heat

of fusion of asphaltene. R is the ideal gas constant. T_{AM} is the melting point temperature of fusion of asphaltene. V_i and δ_i are the molar volume and solubility parameter of asphaltene. δ_{avg} is the volume-fraction-weighted average solubility parameter of the liquid phase, and V_{avg} is the mole-fraction-weighted average molar volume of the liquid phase.

Since the regular solution theory is applicable for a mixture of two or more components that are similar in size, it may not accurately simulate the asphaltene dissolution/precipitation in crude oil. Moreover, the assumptions that the pressure is low and does not change significantly make this kind of models improper to simulate the process of asphaltene precipitation in reservoirs during primary oil recovery.

2.3.2.1.2 Polymer Solution Theory

By simplifying the Flory-Huggins polymer solution theory and assuming that asphaltene is a monodisperse polymeric molecule, some researchers (Hirschberg et al., 1982; Burke et al., 1988; Boer et al., 1995) developed the following equation to represent the solubility of asphaltene in the crude oil:

$$\phi_i = \exp \left[\frac{V_i}{V_l} - 1 - \frac{V_i}{RT} (\delta_i - \delta_l)^2 \right] \quad (2.2)$$

where, ϕ_i is the volume fraction of asphaltene soluble in the crude oil. V_i and V_l are the molar volume of asphaltene and liquid phase, respectively. δ_i and δ_l are the solubility parameters of asphaltene and liquid phase, respectively.

The above model assumes that all asphaltene molecules have the same size and molecular weight. There may be different number of aromatic rings in various asphaltene

molecules in crude oil. Therefore, the size and weight of asphaltene molecules may have a range or distribution rather than a single value. Kawanaka et al. (1991) applied a polydisperse polymer solution theory to simulate asphaltene precipitation. It was assumed that asphaltene behaves as a heterogeneous polymer and applied the Scott and Magat theory to calculate the chemical potential of each fraction of asphaltene. The model was used to simulate the asphaltene precipitation during hydrocarbon miscible flooding. However, it was arbitrarily assumed that asphaltene in crude oil has a gamma distribution and calculated the precipitated and remaining asphaltene distributions based on that assumption.

Since the asphaltene molecules are much different in size from other component molecules, the polymer solution theory represents the asphaltene precipitation and dissolution satisfactorily.

2.3.2.2 Thermodynamic Colloidal Model

In this model, asphaltene is assumed to exist in crude oil as colloidal particles peptized by resins. A certain amount of resins is necessary to disperse asphaltene particles completely and the process of asphaltene precipitation is considered irreversible. Based on these assumptions, Leontaritis and Mansoori (1987) established a thermodynamic colloidal model to represent the asphaltene precipitation process using the following equation:

$$\frac{\Delta\mu_r}{RT} = \ln(\phi_r) + 1 - \frac{V_r}{V_L} + \frac{V_r}{RT} (\delta_L - \delta_r)^2 \quad (2.3)$$

where, $\Delta\mu_r$ is the chemical potential of the resins in the oil phase, ϕ_r is volume fraction of resin in the liquid, V_r and V_L are molar volume of resin and liquid, respectively and δ_r and δ_L are solubility parameters of resin and liquid, respectively. At the onset of flocculation,

$$\Delta\mu_r = \Delta\mu_r^c \quad (2.4)$$

where $\Delta\mu_r^c$ is the resin critical chemical potential and corresponds to the minimum amount of resins which is necessary to adsorb onto the asphaltene surface to peptize the asphaltene. When

$$\Delta\mu_r < \Delta\mu_r^c \quad (2.5)$$

the system is no longer stable and asphaltene will flocculate.

This model assumes that the asphaltene precipitation process is irreversible and a certain amount of resin is a necessary condition for complete peptizing of asphaltene in crude oil. The irreversible assumption directly conflicts with the results of reversible experiments of asphaltene precipitation/dissolution (Hirschberg et al., 1982; Danesh et al., 1989; Thawer et al., 1990; Pedroza et al., 1995; Ramos et al., 1997). Also, the assumption that a certain amount of resin is required to completely peptize asphaltene in crude oil is challenged by the result and conclusion of Cimino et al. (1995). According to colloidal theory, crude oil will be stable if the ratio of resin to asphaltene contents in the crude oil is larger than a certain value (1.25, Koots and Speight, 1975). However, some crude oil with a ratio of 22 of resin to asphaltene contents continued to exhibit asphaltene deposition problems (Minssieux, 1997).

2.4 Asphaltene Deposition during Primary Oil Recovery

2.4.1 Field Experience

In the VF-TR field in Italy, the critical formation damage caused by asphaltene deposition in the near-wellbore area was identified from the beginning of the field's production life (Galoppini and Tambini, 1994). The formation is a dolomite and located at 5568 m in depth. The porosity of the formation is 5% and permeability is 600 md. The initial reservoir pressure was 1014 atm, with a reservoir temperature of 168 °C. The gravity of crude oil is 45 °API and the bubble point pressure is 175 atm. The crude oil contains 0.4 % (weight) asphaltene. Since the beginning of production, an abnormal decline in production rate has been observed. This abnormal decline is attributed to asphaltene deposition in the near-wellbore formation.

In the Comalcalco area of Mexico, a well experienced a rapid production decline, from initial 2,291 BOPD to 1,483 BOPD over a six month period, during the primary depletion (Newberry and Barker, 2000). The production formation of the well is limestone, and 5800 meters deep. The bottom hole temperature is 127 °C. The well produces crude oil with a gravity of 32 °API. The content of asphaltene is 1-2% (weight). Asphaltene stability tests indicate that the crude oil is unstable and asphaltene could deposit during the production of the crude oil.

2.4.2 Experimental Study

Experimental studies in both time and cost intensive and therefore, most researchers prefer modeling over experimental study with respect to asphaltene deposition in porous media. Therefore, published experimental data about asphaltene deposition in porous media is very limited.

2.4.2.1 Minssieux's Experiments

Minssieux (1997) is the first person who extensively investigated asphaltene deposition in porous media. Minssieux used various natural core samples with different permeabilities and dead oils with different asphaltene contents. The permeabilities of core samples varied from 0.67 md to 107 md and porosities varied from 7.1% to 24.7%. Asphaltene contents of oil samples varied from 0.15% to 5.3% (weight). The experiments were performed under high temperature (either 50 °C or 80 °C) and high pressure (with backpressure of 10 bar). The experimental flow rates of experiments varied from 5 $cm^3 / hour$ to 80 $cm^3 / hour$. The experimental conditions are representative of the insitu conditions, except for the dead oils used rather than live oil. Asphaltene precipitation in dead oil may be different from that in live oil.

2.4.2.2 Ali and Islam's Experiments

Ali and Islam (1997) investigated the effect of asphaltene deposition on carbonate rock permeability. They prepared artificial core samples by packing limestone powder into the coreholder. The coreholder was vacuum saturated with a deasphalted crude oil and the deasphalted crude oil was injected into the coreholder until a stabilized pressure drop was established. The mixture of crude oil contained 3% asphaltene (weight) and

asphaltene with 60:40 volume ratio was used as “crude oil”. This mixture was injected into the artificial core sample at different flow rates to observe the effect of asphaltene deposition on carbonate permeability. Their experiments are not of high quality because of the use of the artificial core and oil samples.

2.4.3 Models and Simulations of Asphaltene Deposition in Core Test

Asphaltene deposition problems have occurred for a long time, but modeling of asphaltene deposition began only a few years ago. Civan (1995) first modeled the simultaneous deposition of paraffin and asphaltene in porous media using an improved form of the Gruesbeck and Collins (1982) parallel-pathway model. Following this study, Ali and Islam (1998) combined the surface access theory and Gruesbeck and Collins’ original parallel-pathway model to simulate the asphaltene deposition and adsorption in porous media. By modifying the model of Civan (1995), Wang et al. (1999) presented a model to simulate the simultaneous deposition of paraffin and asphaltene and applied their model to six typical cases.

2.4.3.1 Civan’s Model (1995)

Gruesbeck and Collins (1982) established a parallel-pathway model to simulate the deposition of fine particles in porous media. The key concept of Gruesbeck and Collins model is a parallel-pathway model of porous media. At any cross section in a column, the fluid flow pathways are grouped into two continuing and parallel branches: plugging pathway and non-plugging pathway. The plugging pathways consist of small size pores and plug-type deposition may occur. The non-plugging pathways consist of large size pores and only surface deposition can occur. In the non-plugging pathways, the deposits

can be re-entrained by moving fluid. When plug deposits grow, flow is diverted to nonplugging pathways. The fraction of plugging pathway to total pathways is defined by comparing particle size with pore size. Civan (1995) modified the Gruesbeck and Collins model and applied the parallel-pathway model into simulating the simultaneous deposition of paraffin and asphaltene. In the all mass balance equations, a source term was included for precipitation, plus the variation of porosity and permeability by precipitation was considered. In the mass balance equations for paraffin and asphaltene components, the dispersion effect was considered. An energy balance was also included in Civan's model.

2.4.3.2 Ali and Islam Model (1997)

Ali and Islam (1997) considered two mechanisms of formation damage caused by asphaltene precipitation: asphaltene adsorption and mechanical entrapment. Under the assumptions of oil-wet porous media and monolayer adsorption, the surface access theory was applied to describe the asphaltene adsorption. The Gruesbeck and Collins' model was applied to simulate mechanical entrapment. In Ali and Islam's model, it was assumed that asphaltene existed in crude oil as particles and was ready deposited or adsorbed. However, the asphaltene must first precipitate from crude oil prior to deposition or adsorption. Adsorption is not the major mechanism of formation damage caused by asphaltene deposition (Leontaritis, 1998).

2.4.3.3 Wang et al. Model (1999)

By modifying the Civan's model, Wang et al. (1999) established a model for the simultaneous deposition of paraffin and asphaltene in a core test, which included a modified Gruesbeck and Collins deposition model. This model was used to simulate two typical sets of experimental data for the simultaneous deposition of paraffin and asphaltene and four sets of experimental data for asphaltene deposition. Although excellent matches were obtained when simulating two sets of simultaneous deposition of paraffin and asphaltene, the matches for asphaltene deposition were not satisfactory possibly because the ideal solution theory was applied to simulate asphaltene precipitation.

2.4.4 Field Simulation of Asphaltene Deposition

2.4.4.1 Leontaritis' Model (1998)

Leontaritis (1998) reported the first model to simulate asphaltene deposition in the near wellbore region around a well with constant production rate. Transient flow period was neglected and the flow was assumed pseudo-steady state. It was assumed that asphaltene deposition occur only in near wellbore region and the area of formation damage caused by asphaltene deposition was constant. The pressure distribution outside of damage area did not change with time. The pressure inside the damage area change due to formation damage. The thermodynamic-Colloidal model was used to simulate the asphaltene phase behavior and distribution of asphaltene particles. The filtration rule of thump (that the particles with a diameter larger than $1/3$ of channel diameter will be retained in porous media) was used to calculate the number of particles retained in pores.

The permeability ratio was considered to be simply proportional to the ratio of the available flow area to the initial flow area. A simulation of asphaltene deposition in the near wellbore region within a radius of 5 feet and a production time of 5 hours was performed. The computational results of this model become unstable after three hours. Moreover, the asphaltene is dissolved in crude oil during primary oil recovery rather than suspended in crude oil as particles.

2.4.4.2 Nghiem et al.'s Model (1998)

Nghiem et al. (1998) evaluated the asphaltene precipitate process with a liquid-solid equilibrium. It was assumed that the process of asphaltene deposition was purely adsorption. The resistance factor for the polymer was used to model permeability reduction. Then, the liquid-solid equilibrium for asphaltene precipitation and adsorption for asphaltene deposition were incorporated into a compositional simulator to simulate the asphaltene deposition during primary oil recovery and CO_2 flooding.

The major disadvantage of Nghiem et al. model is the adsorption-only assumption used. Physical deposition in pore space is a dominant mechanism of asphaltene deposition (Leontritis, 1998). The surface deposition, pore throat plugging and deposit entrainment were observed in asphaltene deposition rather than adsorption (Danesh et al. 1989).

2.4.4.3 Wang and Civan's Model (2000)

In their model, a three-order, bi-variate truncated power series was used to represent the asphaltene deposition envelope. A deposition model including surface deposition, pore throat plugging and deposit entrainment was presented. Then, these models and

porosity and permeability reduction models were incorporated into a three-dimensional, three-phase black oil simulator. The simulator was used to simulate asphaltene deposition in reservoirs developed by vertical or horizontal wells during primary oil recovery. It was found that asphaltene can deposit everywhere rather than just near wellbore region and the pattern of asphaltene deposition in the reservoir with vertical well and horizontal well is quite different because of the large flowrate of horizontal wells. This is the first simulator that can simulate the formation damage caused by asphaltene deposition in the reservoir with a horizontal well during primary oil recovery. Although the bi-variate truncated power series model can reproduce the experimental asphaltene deposition envelope satisfactorily in the reservoir pressure and temperature range, this model does not have a theoretical basis. It is only a curve fitting to data.

2.5 Summary

Although a few models for asphaltene deposition in core test and petroleum reservoirs were reported, no satisfactory model and simulator is available for asphaltene deposition problems experienced during primary oil recovery. A satisfactory model for asphaltene deposition during primary oil recovery should theoretically describe the physical process of asphaltene precipitation and deposition, incorporate a reasonable asphaltene precipitation model, and include correct asphaltene deposition, and porosity and permeability reduction models. A satisfactory simulator should run reliably and provide reasonable asphaltene precipitate and permeability distributions.

Table 1.1 Basic information about asphaltene

Feature	Information	References	Comments
Definition	Materials in crude oil which is insoluble in n-heptane but soluble in benzene or toluene	Speight and Long, 1996 Speight, 1996	Defined by solubility rather than molecular structure
Elemental Compositions	Carbon: 80.42~88.65% Hydrogen: 7.44%~11.10% Oxygen: 0.3~4.9% Sulfur: 0.3~10.3% Nitrogen: 0.6~3.3%	Koots and Speight, 1975 Speight, 1996	The asphaltene from different sources has different elemental composition
Molecular Structure	Polynuclear aromatic ring systems with alkyl side chains	Speight, 1996	Different molecule may have different number of rings
Molecular Weight	1500~2500	Speight, 1996 Speight, 1999	Measured by the method that prevents asphaltene molecule aggregation

Table 2.2 Related experiments about asphaltene

Experiment	Equipment and Method	Fluid	Results	References	Comments
Electron Microscope	Electron Microscope, Observation	Crude oil	No dark spots or asphaltene particles	Preckshot et al., 1943 Katz and Beu, 1945	The oil film is clear and uniform
Electron Microscope	Electron Microscope, Observation	A mixture of crude oil with hydrocarbon solvent	There are many dark spots	Preckshot et al., 1943 Katz and Beu, 1945	Solvent makes asphaltene precipitation and aggregation
Electrical Effect	Electrodes, Apply electrical potential	Crude oil	Asphaltene adsorbs onto positive electrodes	Katz and Beu, 1945	
Electrical Effect	Silica, Electron Microscope, Flowing and observation	Crude oil	Clear and uniform before flowing. Some dark spots after flowing	Dykstra et al., 1944	Flowing through silica may cause the asphaltene to precipitate
Ultra-centrifuge	Ultra-centrifuge, Sediment	Crude oil	Asphaltene particles. Particle weight: 30,000	Ray et al., 1957 Witherspoon and Munir 1958	Strong centrifugal force may cause asphaltene precipitation and aggregation
Reversibility	Visual cell, Pressure depletion and observation	Crude oil	Precipitation/ Dissolution are completely reversible	Hrischberg et al., 1982	Reversible in pressure depletion

Table 2.2 Related experiments about asphaltene (continued)

Reversibility	Optical Microscope, Adding fresh oil into mixture , stirring and applying ultrasound	Mixture of crude oil and hydro-carbon solvent	Precipitation/ Dissolution are completely reversible	Ramos et al., 1997	Breaking aggregation needs extra energy.
Reversibility	Visual Micromodel, Flowing and observation	Inject mixture of oil and solvent first, and then inject fresh oil	Asphaltene precipitates and deposits in model and disappear gradually after injecting fresh oil	Danesh et al. (1987). Danesh et al. (1989).	Reversible during flowing in artificial porous media
Reversibility	Core, Flowing and observing pressure drop	Inject mixture of oil and solvent first, and then inject fresh oil	Pressure builds up first and goes down gradually after injecting fresh oil .	de Pedroza et al.,1995	Reversible during flow in natural porous media
Molecular Weight	Ultra-centrifuge	Crude oil	30,000	Ray et al., 1957 Witherspoon and Munir 1958	Strong centrifugal force may cause asphaltene precipitation and aggregation
Molecular Weight	Osmotic pressure	Solution of asphaltene in solvent	80,000	Labout, 1950	Solvent causes asphaltene aggregation
Molecular Weight	Small-Angle Neutron and X-Ray Scattering	Solution of asphaltene in solvent	20,000 ~ 138,400	Espinat and Ravey, 1993	Solvent causes asphaltene aggregation

Table 2.2 Related experiments about asphaltene (continued)

Molecular Weight	Cryoscopic method		600 ~ 6,000	Labout, 1950	
Molecular Weight	Viscosity determinations		900 ~ 2000	Reerink, 1973	
Molecular Weight	Mono-molecular method	Solution of asphaltene in solvent	80,000~140,000	Pfeiffer and Saal, 1940	Solvent causes asphaltene aggregation
Molecular Weight	Preventing aggregation method	Solution of asphaltene in solvent that prevents aggregation	1500 ~ 2500	Speight, 1996; Speight, 1999	This may represent real molecular weight of asphaltene

Table 2.3 Physical models of asphaltene in crude oil

Model	Assumptions	References	Comments
Real Solution	Asphaltene is dissolved in crude oil and crude oil is real solution	Hirschberg et al., 1982 Burke et al., 1988 Novosad and Costain, 1990 Kawanaka et al., 1991 Thomas et al., 1992 Chung, 1992 Non-Azian and Adewumi, 1993 Nghiem et al., 1993 Cimino et al., 1995 MacMillan et al., 1995 Boer et al., 1995 Yarranton and Masliyah, 1996 Nghiem and Coombe, 1996 Zhou et al., 1996 Nghiem et al., 1998	Reversibility experiments strongly support this model.
Colloidal Model	Asphaltene is suspended in crude oil and peptized by resins. The process of asphaltene precipitation is irreversible. If the ratio of resins to asphaltene contents is larger than 1.25, the crude oil is stable and create no precipitation and deposition problems.	Pfeiffer and Saal, 1940 Roger et al., 1957; Yen et al., 1961; Koots and Speight, 1975; Leontaritis and Mansoori, 1987; Mansoori, 1994 Mansoori, 1996; Speight, 1996; Speight, 1999;	Reversibility experiments are strongly against this model. Even the ratio of resin to asphaltene contents is as high as 22 in some crude oil, the crude oil still has asphaltene precipitation and deposition problem

Table 2.4 Factors affect asphaltene precipitation during primary oil recovery

Factors	Change of Factors	Asphaltene Solubility	References	Comments
Pressure	Pressure is above the bubble point and decrease	decrease	Haskett and Polumbus, 1965 Tuttle, 1983 Hirschberg et al., 1982 Burke et al. 1988 Thawer et al., 1990 Leerlooyer et al., 1995	
Pressure	Pressure is below the bubble point and decrease	increase	Haskett and Polumbus, 1965 Tuttle, 1983 Hirschberg et al., 1982 Burke et al. 1988 Thawer et al., 1990 Leerlooyer et al., 1995	
Temperature	Increase	increase	Thomas et al., 1992	
Temperature	Increase	decrease	Burke et al., 1988	
Temperature	Increase and below reservoir temperature	increase	Leontaritis, 1996; Paramanu et al.1999	
Temperature	Increase and above reservoir temperature	decrease	Leontaritis, 1996; Paramanu et al.1999	More experiments are needed to investigate the effect of temperature
Composition	Dissolved gas increase	decrease	Burke et al., 1988	

Table 2.5 Asphaltene precipitation models

Model	Assumptions	References	Comments
Regular Solution Model	Low pressure, Pressure change is small	Chung, 1992 Yarranton and Masliyah, 1996	Its assumptions make this model not applicable to primary oil recovery
Polymer Solution Model	Vapor-liquid equilibrium (VLE) and liquid-liquid equilibrium (LLE) LLE does not affect VLE	Hirschberg et al., 1982 Burke et al., 1988 Nor-Azian and Adewumi, 1993 Boer et al., 1995	
Colloidal Model	Asphaltene peptized by resins as particles. The precipitation process is irreversible. If the ratio of resin to asphaltene content is larger than certain critical value, the crude oil is stable.	Leontaritis and Mansoori, 1987 Mansoori, 1996	More and more evidences are against this model.

Table 2.6 Models for asphaltene deposition in core test

Model	Assumption	Transportation Model	Precipitation Model	Deposition Model	Comments
Civan's Model (1995)	The flow channels in porous media can be grouped into plugging and nonplugging pathways.	Mass balance equations for gas, oil, paraffin and asphaltene components.	Regular solution model	Surface deposition, pore throat plugging and entrainment of deposits.	Match experimental data very well.
Ali and Islam's Model (1998)	Asphaltene is suspended in crude oil and ready to deposit	Mass balance equation for asphaltene		Adsorption, surface deposition, entrainment of deposits	Asphaltene must precipitate first and then deposit.
Wang et al. Model (1999)	Asphaltene precipitation can be simulated by ideal-solution theory.	Mass balance equations for gas, oil, paraffin and asphaltene components.	Ideal solution model	Surface deposition, pore throat plugging and entrainment of deposits.	Precipitation model is too simple.

Table 2.7 Models for asphaltene deposition in reservoirs

Model	Assump- tions	Transportation Model	Precipitation Model	Deposition Model	Comments
Leontaritis' Model (1998)	Pseudo-steady state flow. Damage area does not change. Pressure does not change in the outside of damage area.	Darcy equation	Colloidal model	Surface deposition, entrainment of deposits	The model can only be used near wellbore region in short production time. Results are unstable.
Nghiem et al. Model (1998)	Asphaltene can be grouped into two parts: precipitating and non-precipitating components.	Composition simulator	Regular solution model	Adsorption	Adsorption is not major deposition mechanism. It does not represent the major feature of asphaltene deposition.
Kocabas et al. Model (1998)	Asphaltene is suspended as particles in crude oil and ready to precipitate.	One-dimensional mass balance equation for asphaltene		Adsorption, surface deposition, entrainment of deposits	Asphaltene must precipitate first and then deposit.
Wang and Civan's Model (2000)	Asphaltene deposition envelope can be simulated by a bi-variant truncated power series	Three-dimensional, three-phase black oil simulator.	Three-order bi-variate truncated power series	Surface deposition, pore throat plugging, and entrainment of deposits	The precipitation model is empirical curve fitting of data

Chapter III

Asphaltene Precipitation Model

As discussed in Chapter II, asphaltene dissolves in crude oil to form a real solution. However, the solution formed by asphaltene dissolving in crude oil is different from the regular solution because the size of asphaltene molecules is much larger than that of regular compositions in crude oil. The crude oil containing asphaltene is similar to a polymer solution in the molecular size difference between solute and solvent although the size of polymer molecules may be much larger than that of asphaltene molecules. Therefore, the polymer solution theory may best represent the asphaltene dissolving in crude oil.

The solubility of asphaltene in a crude oil is a function of pressure, temperature, and composition. During primary oil recovery, the asphaltene dissolved in crude oil can precipitate due to changes in pressure and composition. In this chapter, the asphaltene precipitate model derived from the polymer solution theory by Hirschberg et al. (1982) is first introduced and then applied to simulate the results of experiment of asphaltene precipitation during primary oil recovery. Finally, the effects of pressure, temperature and composition on asphaltene solubility are investigated.

3.1 Hirschberg et al. Model (1982) for Asphaltene Precipitation

Hirschberg et al. (1982) were first to use the polymer solution theory to simulate the asphaltene precipitation process. By combining the Flory-Huggins theory for polymer

solution and Hildebrand solubility concept, Hirschberg et al. (1982) obtained the following equation:

$$\phi_i = \exp \left[\frac{V_i}{V_l} - 1 - \frac{V_i}{RT} (\delta_i - \delta_l)^2 \right] \quad (3.1)$$

Where, ϕ_i is the volume fraction of asphaltene soluble in the crude oil. V_i and V_l are the molar volumes of asphaltene and liquid phase, respectively. δ_i and δ_l are the solubility parameters of asphaltene and liquid phase, respectively.

Essentially, the asphaltene precipitation process was simulated by two equilibria: vapor-liquid equilibrium and liquid-liquid equilibrium. The composition of liquid is first calculated in the vapor-liquid equilibrium and asphaltene solubility is calculated in the liquid-liquid equilibrium using Eq.(3.1). It is assumed that the second equilibrium does not affect the first equilibrium. In the liquid-liquid equilibrium, crude oil is treated as a solvent-rich phase and precipitated asphaltene is treated as a solute-rich phase because precipitated asphaltene contains some resins and oil. Soave-Redlich-Kwong (SRK) equation is applied in the vapor-liquid equilibrium calculation and used to calculate the internal energy change of solvent during vaporization in liquid-liquid equilibrium. The modified B. R. W. equation was used to calculate the molar value of solvent in liquid-liquid equilibrium. The molar volume of asphaltene was assumed a constant. By matching experimental data, Hirschberg et al. (1982) found that the asphaltene solubility parameter was related to temperature by the following equation:

$$\delta_A = 20.04 * (1 - hT) \quad (3.2)$$

where h is a constant specific to each oil and T is temperature. Then Eq. (3.1) was used to calculate the volume fraction of asphaltene dissolved in the crude oil. Hirschberg et al. applied their model to simulate asphaltene precipitation that occurs during the process of mixing dead oil with hydrocarbon solvent.

Following Hirschberg et al., Burke et al. (1988) applied the above model to simulate asphaltene precipitation while mixing live oil with hydrocarbon solvents. Boer et al. (1995) applied the model to screen oils for possible asphaltene precipitation. In the following section, the above model will be applied to match the experimental data of Burke et al. (1988).

3.2 Simulation of Burke et al.'s Data

In this section, the Burke et al.'s experimental data is first described, and then the Hirschberg et al.'s model is tested using the Burke et al.'s experimental data. A comparison of the results is made and a discussion of some improvements in phase equilibrium calculation is provided.

3.2.1 Burke et al.'s Experimental Data (1988)

Burke et al. (1988) investigated the effect of the amount of hydrocarbon solvent added to live oil on the asphaltene precipitation at different pressures, as well as the effect of pressure on the asphaltene precipitation. Table 3.1 lists the composition of oil used in the Burke et al.'s experiments. Table 3.2 lists the experimental results. The oil had an asphaltene content of 16.08% (weight) at stock tank conditions and a bubble point of 2,950 psia. Table 3.2 shows that asphaltene began to precipitate when the

reservoir pressure decreased to a pressure higher than the bubble point. The asphaltene precipitates continued to increase with the further decrease of pressure. When the pressure reached to 2,014.7 psia, the precipitation rate reached a maximum value and then decreased with further decrease in pressure. These experimental results were inconsistent with the reported bubble point. According to the other observations and field experience, the maximum quantity of asphaltene precipitates occurs at or around the bubble point pressure (Haskett and Polumbus, 1965, Hirschberg et al., 1982). However, the maximum quantity of asphaltene precipitate in the Burke et al. experiment occurred at the pressure of 2,014.7 psia, which is far below the bubble point pressure, 2,950 psia. Therefore, either the asphaltene precipitate data or bubble point is incorrect. The authors themselves (Burke et al., 1988) also noticed this inconsistency but did not provide an explanation.

3.2.2 Vapor-liquid Equilibrium Calculation

Before applying Hirschberg et al.'s model, the accuracy of Soave-Redlich-Kwong was evaluated with respect to the calculation of the vapor-liquid equilibrium. The vapor-liquid equilibrium of a three-component mixture was calculated with SRK equation to test the accuracy of the SRK equation. The initial compositions of the three components are provided in Table 3.3 (Sage and Lacey 1950). The calculated compositions of vapor and liquid with SRK equation as provided in Table 3.4 were compared to the experimental results reported by Sage and Lacey (1950). The calculated compositions of vapor and liquid using the SRK equation were not accurate. Therefore, the Peng-Robinson (PR) equation was used to calculate the vapor-liquid equilibrium.

The calculated results by Peng-Robinson equation were also shown in Table 3.4. It is obvious that the Peng-Robinson equation is more accurate than the SRK equation with respect to vapor-liquid equilibrium calculation, so the Peng-Robinson equation was used in vapor-liquid equilibrium. The Peng-Robinson equation is expressed as (McCain, 1990):

$$P = \frac{RT}{V_M - b} - \frac{a_T}{V_M(V_M + b) + b(V_M - b)} \quad (3.3)$$

where, P is pressure, R is universal gas constant, T is temperature, V_M is molar volume, b and a_T are coefficients. The following mixing rules were used in the vapor-liquid equilibrium calculation (McCain, 1990):

$$b = \sum_i y_i b_i \quad (3.4)$$

$$a_T = \sum_i \sum_j y_i y_j (a_{Ti} a_{Tj})^{1/2} (1 - \delta_{ij}) \quad (3.5)$$

where y_i is molar composition of i th component, b_i and a_{Ti} are the coefficients of Peng-Robinson equation for i th component, δ_{ij} is the interaction coefficient between component i and j .

The acentric and critical properties of all components except C_{7-} in the Table 3.1 are well defined and can be obtained from McCain (1990). Then the acentric and critical properties of C_{7-} are given some initial values according to their molecular weight and adjusted to match the bubble point. Table 3.5 lists the acentric and critical properties of all components after matching the bubble point.

3.2.3. Calculate the Amount of Asphaltene Precipitate

Before using Eg. (3.1) to calculate asphaltene solubility, it is necessary to define the solubility parameter, δ_L , for liquid. The solubility parameter is defined by the following equation (Hildebrand, 1929):

$$\delta_L = \left(\frac{\Delta U_{\text{vaporization}}}{V_M^L} \right)^{1/2} \quad (3.6)$$

where, $\Delta U_{\text{vaporization}}$ is the internal energy change during the vaporization of a unit mole liquid, which is calculated with the equation presented by Hirschberg et al. (1982). V_M^L is the molar volume of liquid. As pointed out by Jhaverl and Youngren (1988), Peng-Robinson underestimates the molar volume of vapor and overestimates the molar volume of liquid. Therefore, the modified Peng-Robinson equation (Jhaverl and Youngren 1988) should be used to calculate the liquid molar volume. The original Peng-Robinson equation is expressed as (Jhaverl and Youngren 1988):

$$E(T, P, V_M, y_i, a, b) = 0 \quad (3.7)$$

The modified three-parameter Peng-Robinson equation has the following format (Jhaverl and Youngren 1988):

$$E(T, P, \tilde{V}_M, y_i, a, b, c) = 0 \quad (3.8)$$

where $\tilde{V}_M$ is modified molar volume and given by the following equation:

$$\tilde{V}_M = V_M - c \quad (3.9)$$

and c is the third parameter for the modified Peng-Robinson equation, which is calculated using:

$$c = \sum_i y_i c_i \quad (3.10)$$

Since c_i and b_i have the same unit, a dimensionless shift parameter, s , is defined (Jhaverl and Youngren 1988):

$$s_i = \frac{c_i}{b_i} \quad (3.11)$$

By using the shift parameter concept, Jhaverl and Youngren (1988) matched experimental data of molar volume of liquid satisfactorily with the modified Peng-Robinson equation.

The modified Peng-Robinson was used to calculate the molar volume of liquid. The shift parameter values for most components reported by Jhaverl and Youngren (1988) were used in this calculation. The shift parameters for component nitrogen and carbon dioxide were not available, so were given a value of zero. The shift parameter for C_{7+} is not well defined and therefore treated as an adjustable parameter. The shift parameters for all components are reported in Table 3.6.

All parameters in Eq. (3.1) are defined except for the solubility parameter and molar volume of asphaltene. The solubility parameter of asphaltene was calculated using Eq. (3.2). Following previous researchers, the molar volume of asphaltene was treated as a constant and adjusted to match experimental asphaltene precipitation data. Hirschberg et al. (1982) used an asphaltene molar volume of $4 \text{ m}^3 / \text{kmol}$ to match asphaltene precipitation data obtained by mixing dead oil with solvent. As stated previously, even dilute solvents cause aggregation, which suggests that the Hirschberg

et al.'s value is unrealistically large. Cimino et al. (1995) claimed $1.5 \text{ m}^3 / \text{kmol}$ as the molar volume of asphaltene and Nghiem and Coombe (1997) claimed $1.04 \text{ m}^3 / \text{kmol}$ as the molar volume of asphaltene. This study used $1.5 \text{ m}^3 / \text{kmol}$ as asphaltene molar volume as an initial value, which was then adjusted to match asphaltene precipitation data. Three adjustable parameters are C_{7+} shift parameter, h in Eq. (3.2), and the molar volume of asphaltene. Experimental data of asphaltene precipitation can be matched by adjusting the values of these three parameters. Regardless of how these three parameters were adjusted, the prediction of maximum amount asphaltene precipitate always occurred at the pressure of 2950 psia rather than around 2014.7 psia. At this point, it is believed that either the experimental data of asphaltene precipitation or the bubble point is the source of error.

Closely observing the experimental data for asphaltene precipitation, the quantity of asphaltene precipitate increases slowly with pressure decrease when the pressure is greater than 2,014.7 psia. When the pressure drops below 2,014.7 psia, the quantity of asphaltene precipitate quickly decreases with a decrease in pressure. This tendency is consistent with other research observations and field experience (Haskett and Polumbus, 1965; Tuttle, 1983; Hirschberg et al., 1982; Burke et al. 1988; Thawer et al., 1990; Leerlooyer et al., 1995). Therefore, the precipitation data is probably correct and the reported bubble point value is the source of an error. After the bubble point was adjusted to 2,050 psia, the acentric factor and critical properties of C_{7+} were redefined by matching to the new bubble point value. The redefined values of acentric and critical

properties of C_{7+} are listed in Table 3.5. The previous calculations were repeated and then the data were matched by adjusting the C_{7+} shift parameter, h , and molar volume of asphaltene. The results are reported in Table 3.2 and Figure 3.1. It can be seen that the simulated results match the experimental data very well. This demonstrates that Eq.(3.1) can be used to simulate the asphaltene precipitation caused by pressure and composition changes.

By matching the experimental data, the values of C_{7+} shift parameter, molar volume of asphaltene and h are defined. The value of the C_{7+} shift parameter is given in Table 3.6. The molar volume of asphaltene was determined to be $1.02 \text{ m}^3/\text{kmol}$, which is very close to the value used by Nghlem and Coombe (1997). The defined h in this study is $0.0012815 \text{ 1/}^\circ\text{C}$, which is slightly different from the value of $0.00107 \text{ 1/}^\circ\text{C}$ reported by Hirschberg et al. (1982).

According to the model-calculated results, asphaltene begins to precipitate from the crude oil at 5,056 psia. When the pressure is greater than 5,056 psia, no asphaltene precipitation problems occur.

3.3 The Effect of Pressure on Asphaltene Solubility in Live Oil

When the data was successfully matched, then, it is necessary to investigate the effects of pressure on asphaltene solubility. Using the same data as before, the solubility of asphaltene was calculated at reservoir temperature and different reservoir pressures. The results are provided in Figure 3.2. The curve of the effect of pressure on asphaltene

solubility has the same tendency as those observed by previous researchers, which means the solubility of asphaltene in live oil decreases with pressure at pressures higher than the bubble point, reaches the lowest value at bubble point pressure, and then increases with the further decrease of pressure.

3.4. The Effect of Temperature on Asphaltene Solubility

The effect of temperature on asphaltene solubility is investigated and the results are reported in Figure 3.3. It was found that the solubility of asphaltene in crude oil increases with temperature.

Table 3.1 The composition and properties of oil using Burke et al.'s experiment (1988)

Oil Composition (mol %)	
Nitrogen	0.57
Carbon Dioxide	2.46
Methane	36.37
Ethane	3.47
Propane	4.05
i-Butane	0.59
n-Butane	1.34
i-Pentane	0.74
n-Pentane	0.83
Hexanes	1.62
Heptanes plus	47.96
Total	100.0
Oil Properties	
Heptanes plus molecular weight	329
Heptanes plus specific gravity	0.9594
Live-oil molecular weight	171.4
API gravity of stock tank oil	19.0
Asphaltene content in stock tank oil, wt%	16.08
Reservoir temperature, °F	212
Saturation pressure, psia (reported)	2950
Saturation pressure, psia (estimated)	2050

Table 3.2 Asphaltene precipitate at different pressure (temperature: 212 °F)

Pressure, psia	1014.7	2014.7	3034.7	4014.7
Experimental asphaltene precipitate (wt%)	0.403	1.037	0.742	0.402
Simulated asphaltene precipitate (wt%)	0.3577	0.9831	0.8249	0.3567

Table 3.3 Composition of three-component mixture (Sage and Lacey, 1950)

Component	Composition, mole fraction
Methane	0.5301
n-Butane	0.1055
n-Decane	0.3644

Table 3.4 Comparison of calculated and experimental compositions

	Equilibrium Compositions at 1000 psia and 160 °F					
	Experimental (Sage and Lacey, 1950)		Calculated with SRK		Calculated with PR	
Component	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid
Methane	0.9619	0.2420	0.9626	0.2624	0.9612	0.2418
n-Butane	0.0360	0.1520	0.0356	0.1488	0.0367	0.1517
n-Decane	0.0021	0.6060	0.0018	0.5888	0.0021	0.6075
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

Table 3.5 The acentric factor and critical properties of each component (McCain, 1990)

Composition	Acentric Factor	Critical Pressure (psia)	Critical Temperature (°F)
Nitrogen	0.0372	493.1	-232.51
Carbon Dioxide	0.0484	507.5	-220.43
Methane	0.0104	666.4	-116.67
Ethane	0.0979	706.5	89.92
Propane	0.1522	616.0	206.06
i-Butane	0.1852	527.9	274.46
n-Butane	0.1995	550.6	305.62
i-Pentane	0.2280	490.4	369.10
n-Pentane	0.2514	488.6	385.80
Hexanes	0.2994	436.9	458.00
Heptanes plus *	0.4714	428.9	628.0

* The acentric factor and critical properties of C_{7+} are obtained by matching the bubble point.

Table 3.6 The shift parameters for each component (Jhaverl and Youngren, 1988)

Component	Shift Parameter
Nitrogen ¹	0.0
Carbon Dioxide ¹	0.0
Methane	-0.1540
Ethane	-0.1002
Propane	-0.08501
i-Butane	-0.07935
n-Butane	-0.06413
i-Pentane	-0.04350
n-Pentane	-0.04183
Hexanes	-0.01478
Heptanes plus ²	0.04145

Notes: 1. The values are not available and set as 0.

2. The values are obtained by matching experimental asphaltene precipitation data.

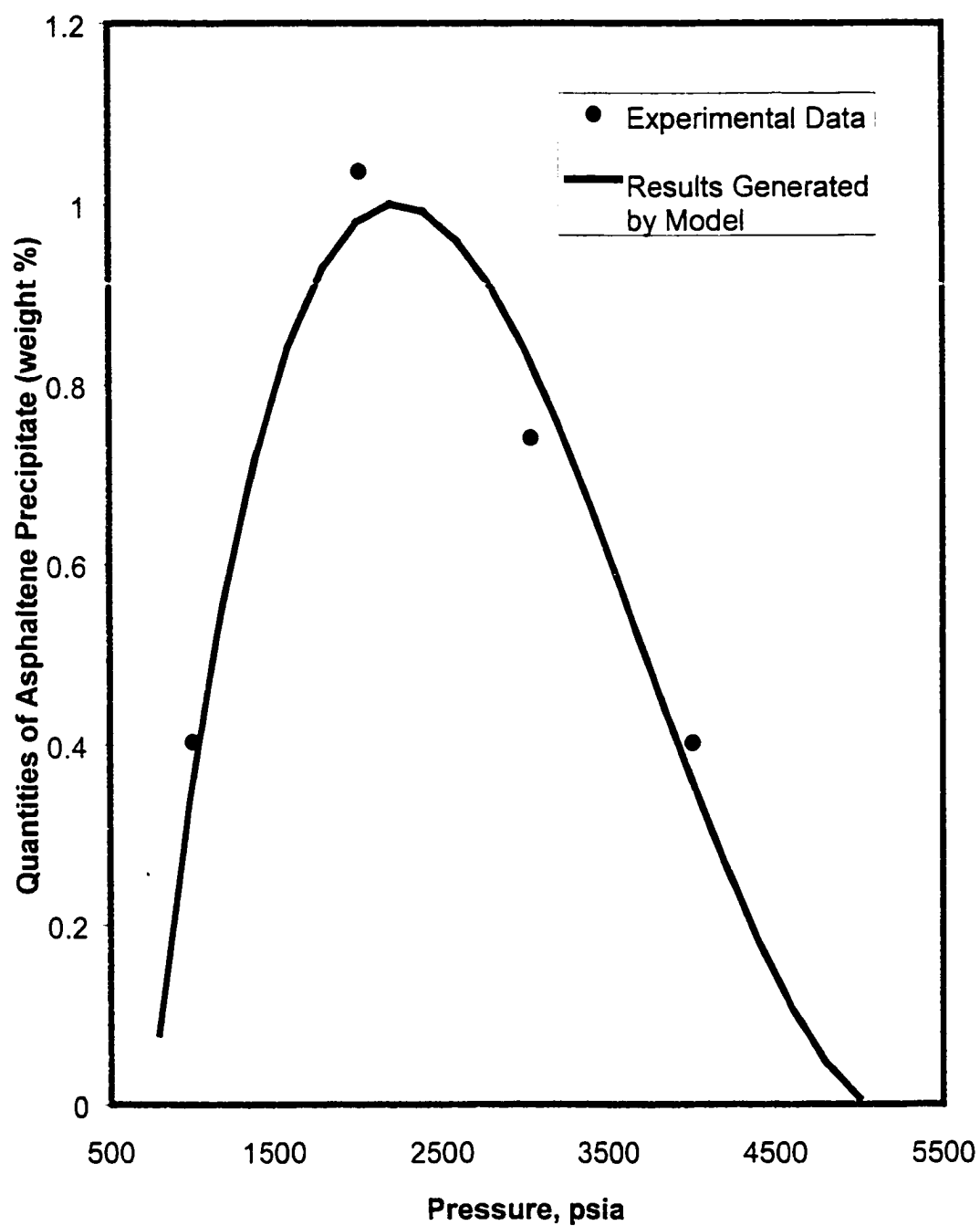


Figure 3.1 Comparison of Burke et al. experimental data with results generated by the model

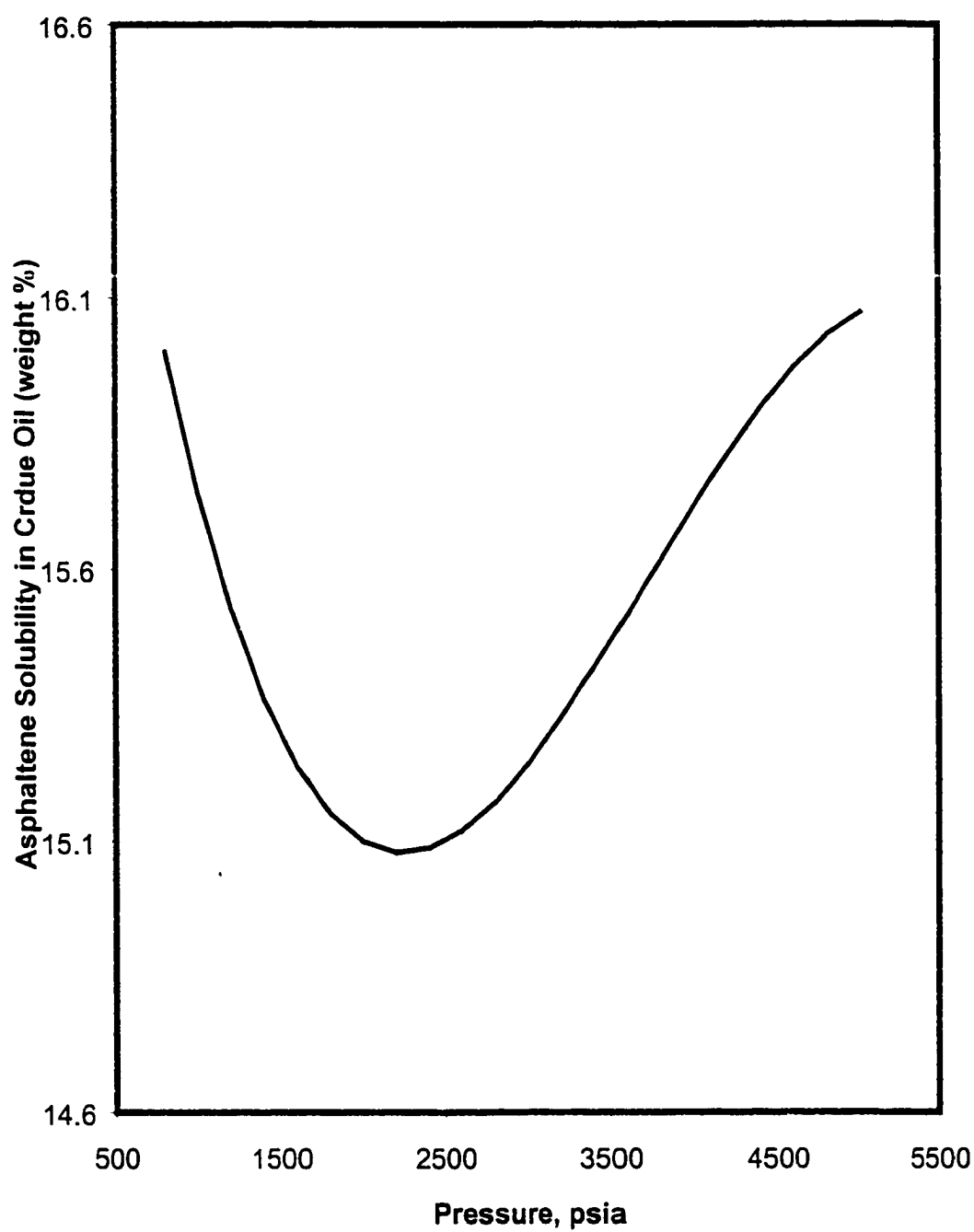


Figure 3.2 Effect of pressure on asphaltene solubility in crude oil at reservoir temperature

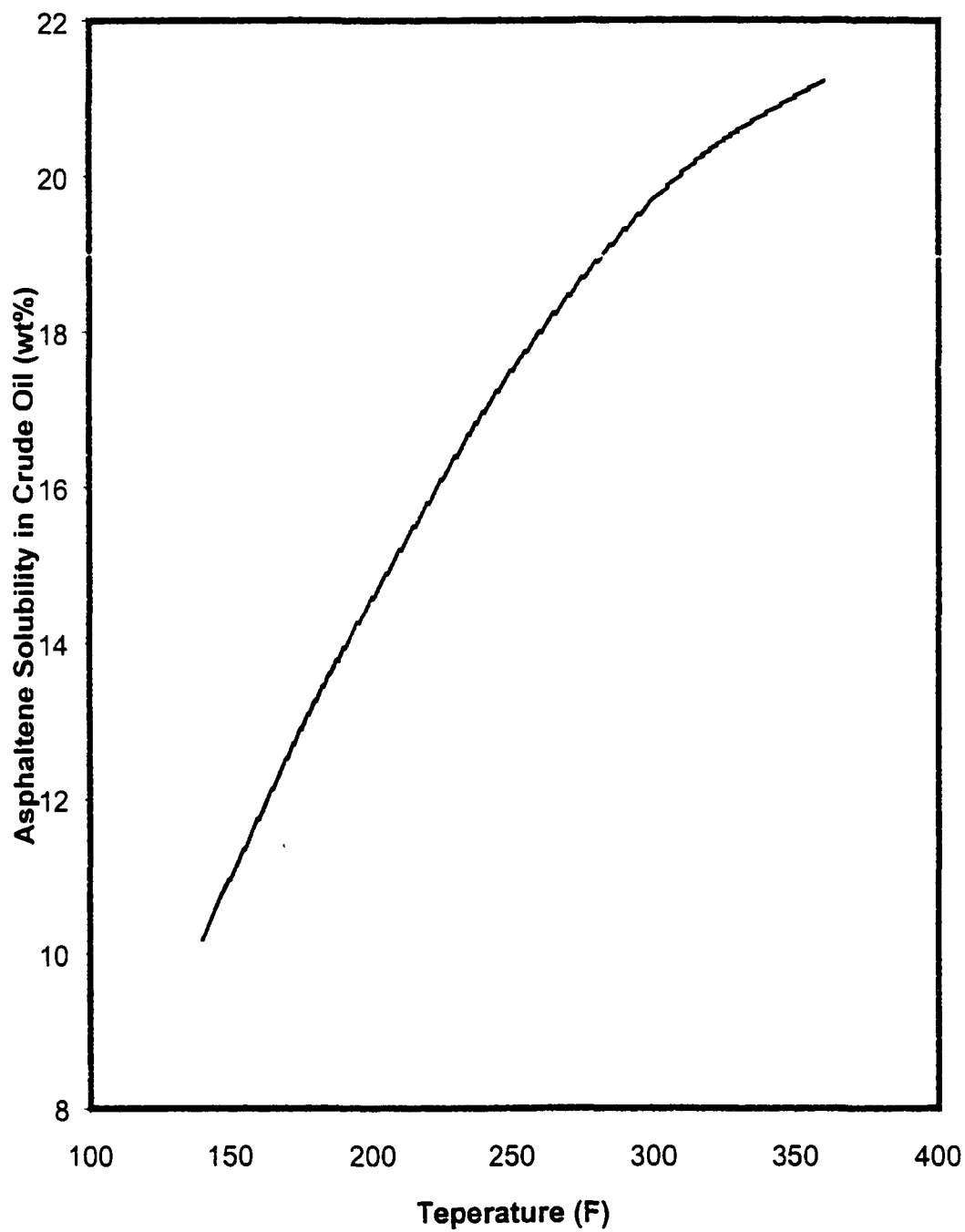


Figure 3.3 Effect of temperature on asphaltene solubility at the pressure of 3034.7 psia

Chapter IV

Modeling and Simulation of Asphaltene Deposition in Core Test

Since our target, the reservoir, is deeply located under ground, it is hard to do asphaltene precipitation and deposition experiments on it directly. By matching the reservoir conditions, core tests provide an important tool to investigate the phenomena that occurs in reservoirs. Modeling and simulation of core test results will provide new insight about asphaltene precipitation and deposition problems. In this chapter, an improved model for asphaltene precipitation and deposition in core tests is described. The model is then applied to a typical case and tested by matching to experimental results.

4.1 Formulation

The effects of gravity are not included in the derivation of models for simulating asphaltene precipitation and deposition in core tests, based on the assumption that the flow in core tests is usually one-dimensional and horizontal. Capillary pressure is also considered negligible because asphaltene precipitation and deposition involve only liquid phase. Finally, it is assumed that no connate water occurs in cores in asphaltene deposition tests.

Under the above assumptions, the process of asphaltene deposition in core tests can be modeled by mass balance, momentum balance, asphaltene precipitation model, asphaltene deposition model, and porosity and permeability reduction models.

4.1.1 Mass Balance Equations

Three components of concern in the core tests are gas, oil and asphaltene. The mass balance for each is considered separately as follows.

Gas can occur in vapor and liquid phases, so the gas mass balance is expressed (Wang et al., 1999):

$$\frac{\partial}{\partial t}(\phi S_v \rho_v + \phi S_L \rho_L w_{GL}) + \frac{\partial}{\partial x}(\rho_v u_v + \rho_L u_L w_{GL}) = 0 \quad (4.1)$$

where ϕ represents the porosity of the porous media, subscript V and L represent vapor and liquid phase, respectively; and subscript G denotes the gas component. Therefore, S_v and S_L are the saturations of vapor and liquid phase, respectively; ρ_v and ρ_L are the densities of vapor and liquid phase, respectively; u_v and u_L are fluxes of the vapor and liquid phase, respectively; and w_{GL} represents the mass fraction of the dissolved gas in the liquid phase.

The oil component can only be present in the liquid phase, so the mass balance for the oil component is expressed as (Wang et al., 1999):

$$\frac{\partial}{\partial t}(\phi S_L \rho_L w_{OL}) + \frac{\partial}{\partial x}(\rho_L u_L w_{OL}) = 0 \quad (4.2)$$

where the subscript O represents oil component. w_{OL} represents the mass fraction of the oil component in the liquid phase.

The asphaltene may be partly dissolved in the liquid phase, suspended in the liquid phase as precipitates, and deposited in the pore space. The mass balance for asphaltene is given as (Wang et al., 1999):

$$\frac{\partial}{\partial t} (\phi S_L C_A \rho_A + \phi S_L \rho_L w_{AL}) + \frac{\partial}{\partial x} (\rho_L u_L w_{SAL} + \rho_L u_L w_{AL}) = -\rho_A \frac{\partial E_A}{\partial t} \quad (4.3)$$

where subscript A represents asphaltene. C_A is the volume fraction of the suspended asphaltene precipitates in liquid phase; ρ_A is the density of asphaltene; w_{SAL} and w_{AL} represent the mass fraction of the suspended asphaltene precipitates and the dissolved asphaltene in the liquid phase, respectively; and E_A is the volume fraction of the deposited asphaltene in the bulk volume of the porous media.

4.1.2 Momentum Balance Equations

Darcy equations for multiphase flow were used to describe the momentum balances for vapor and liquid phases:

$$u_v = -\frac{kk_{RV}}{\mu_v} \frac{\partial P}{\partial x} \quad (4.4)$$

$$u_L = -\frac{kk_{RL}}{\mu_L} \frac{\partial P}{\partial x} \quad (4.5)$$

where k is the absolute permeability of the porous media, k_{RV} and k_{RL} are the relative permeabilities of the vapor and liquid phases, respectively; and μ_v and μ_L are the viscosities of the vapor and liquid phase, respectively. Since the capillary pressure between the vapor and liquid phases is considered negligible, P represents the pressure of the fluids in the pore volume.

4.1.3 Auxiliary Equation

An auxiliary equation was needed to describe the relationship between vapor and liquid phase saturations as the following:

$$S_v + S_L = 1 \quad (4.6)$$

4.1.4 Deposition Model

Although a few researchers (Ali and Islam, 1997; Nghiem et al., 1998) included the adsorption into their deposition model, physical blockage is the dominant mechanism of asphaltene deposition (Leontaritis, 1998). In the visual experiment of asphaltene deposition by Danesh et al. (1989), the surface deposition, the pore blockage and the entrainment of asphaltene deposits were observed. Therefore, it is important to include the surface deposition, pore throat plugging and entrainment of deposits in the deposition model.

Based on the experiments involving fine particles deposition in single-phase flow, Gruesbeck and Collins (1982) concluded that the surface deposition rate based on pore volume is only directly proportional to the concentration of fine particles present in the flowing suspension. For multiphase flow, the surface deposition rate based on the bulk volume of the formation should be directly proportional to the concentration of suspended asphaltene precipitates, C_A , the porosity, ϕ , and liquid saturation, S_L . The deposition rate is expressed by:

$$\frac{\partial E_A}{\partial t} = \alpha S_L C_A \phi - \beta E_A (v_L - v_{cr,L}) + \mu_L S_L C_A \quad (4.7)$$

where the first term represents the surface deposition. The second term represents the entrainment of asphaltene deposits by the flowing phase when the interstitial velocity is larger than a critical interstitial velocity. This term shows that the entrainment rate of the asphaltene deposits is directly proportional to the amount of asphaltene deposits and the difference between the actual interstitial velocity and the critical interstitial velocity necessary for asphaltene deposit mobilization. The last term represents the pore throat plugging rate, which is directly proportional to the superficial velocity, u_L , the liquid saturation, S_L , and the concentration of the asphaltene, C_A .

The second and last terms were modified after the model of Gruesbeck and Collins (1982). The equation includes rate coefficients, where α is the surface deposition rate coefficient, β is the entrainment rate coefficient, and γ is plugging deposition rate coefficient. The value of β is described as:

$$\beta = \beta_i, \text{ when } v_L > v_{cr.L} \quad (4.8)$$

$$\beta = 0, \text{ otherwise} \quad (4.9)$$

where β_i is the instantaneous entrainment rate coefficient. v_L is the interstitial velocity of liquid phase equal to u_L / ϕ ; and $v_{cr.L}$ is the critical interstitial velocity of liquid phase, which is considered to be constant. The value of γ is described as:

$$\gamma = \gamma_i (1 + \sigma E_A), \text{ when } D_{pt} \leq D_{ptcr} \quad (4.10)$$

$$\gamma = 0, \text{ otherwise} \quad (4.11)$$

where γ_i is the instantaneous plugging deposition rate coefficient, and σ is the snowball-effect deposition constant, which used to express that the pore throat plugging

deposition rate increases proportionally with the total deposits. D_{pt} is the average pore throat diameter; and D_{ptcr} is the critical pore throat diameter, assumed constant. When D_{pt} is less than D_{ptcr} , pore throat plugging deposition will occur.

4.1.5 Porosity and Permeability Reduction Models

The instantaneous, local porosity, ϕ , during asphaltene deposition is equal to the difference between the initial porosity and the fractional pore volume occupied by the asphaltene deposits (Civan, 1995):

$$\phi = \phi_0 - E_d \quad (4.12)$$

Civan et al. (1989) used the following cubic equation to express the reduced permeability as a function of porosity:

$$k = k_0 \left(\frac{\phi}{\phi_0} \right)^3 \quad (4.13)$$

where k_0 and ϕ_0 are the initial permeability and porosity. Liu and Civan (1996) and Chang and Civan (1997) modified the above relation to include pore throat plugging effects. Eq. (4.13) can be modified to account for pore throat plugging effect and the difference of real porous media from the pipe model using the following equation:

$$k = f_p k_0 \left(\frac{\phi}{\phi_0} \right)^3 \quad (4.14)$$

where f_p is a permeability modification coefficient.

This model used in this study contains seven model parameters, namely the surface deposition rate coefficient, entrainment rate coefficient, pore throat plugging rate coefficient, snow-ball deposition effect coefficient, critical interstitial velocity, critical

mean diameter of pores, and permeability modification coefficient. These parameters are determined by history matching.

4.2 Applications

There are only two sets of reported results of asphaltene deposition in core tests in the literature. Ali and Islam (1997) used artificial unconsolidated core samples and a mixture of crude oil and asphaltene with a 60:40 volume ratio. The crude oil contained 3%(weight) asphaltene, resulting in an unrealistically high asphaltene content (totally over 50% by weight). Therefore, that experimental data will not be used in this application. Minssieux (1997) reported another set of experimental data of asphaltene deposition in core tests, involving the dead oil and natural core samples. The experiments were carried out at reservoir temperature and high pressure. The Minssieux experiments are reasonable and used in this application.

4.2.1 Description

In Minssieux's (1997) experiments, two types of dead oils were used: the Weyburn and Hassi-Messaoud crude oils. The Weyburn oil contains 5.3% (by weight) asphaltene and the Hassi-Messaoud oil contains 0.15% asphaltene. Four different natural sandstones were used: the Fontainebleau, Vosges, and Palatinat sandstones, as well as a HMD reservoir rock. The permeabilities of the sandstones varied from 0.67 md (HMD reservoir rock) to 107 md (Fontainebleau sandstone). The porosities of the sandstones range from 7.1% (HMD reservoir rock) to 24.7% (Vosges sandstone). The core samples were 5 to 7 cm in length and 2.3 cm in diameter. The experimental test temperatures were 50 °C and 80 °C with a backpressure of 145 psia.

Since the compositions of both Weyburn and Hassi-Messaoud oils were not available, the compositions of two dead oils reported by Hirschberg et al. (1982) were used to simulate the compositions of Weyburn and Hassi-Messaoud oils. The reported first dead oil has an API gravity of 30, which is very close to the API gravity of Weyburn oil, so it was used to simulate the composition of Weyburn oil. The second reported dead oil has an API gravity of 35, which is smaller than that of Hassi-Messaoud oil. Since a better composition is not available, it was used to simulate the Hassi-Messaoud oil. Both compositions are provided in Table 4.1. The critical properties and shift parameter of C_{7+} were adjusted to match the asphaltene contents in the Weyburn and Hassi-Messaoud oils.

4.2.2 Simplification of Models

Since the dead oil is used in this application, a single-phase flow was assumed and the models described in last section were simplified. The gas mass balance disappears. The mass balance of oil is given by:

$$\frac{\partial}{\partial t}(\phi \rho_L w_{OL}) + \frac{\partial}{\partial x}(\rho_L u_L w_{OL}) = 0 \quad (4.15)$$

The mass balance for asphaltene was reduced to:

$$\frac{\partial}{\partial t}(\phi C_A \rho_A + \phi \rho_L w_{AL}) + \frac{\partial}{\partial x}(\rho_L u_L w_{SAL} + \rho_L u_L w_{AL}) = -\rho_A \frac{\partial E_A}{\partial t} \quad (4.16)$$

and Eq. (4.5) becomes

$$u_L = -\frac{k}{\mu_L} \frac{\partial P}{\partial x} \quad (4.17)$$

The deposition rate equation becomes

$$\frac{\partial E_A}{\partial t} = \alpha C_A \phi - \beta E_A (v_L - v_{cr,L}) + \mu_L C_A \quad (4.18)$$

The porosity and permeability reduction equations do not change.

Eqs. (4.12), and (4.14)-(4.18) form the mathematical model for this special application. In total there were six equations and six unknown, P , u_L , k , ϕ , C_A and E_A . Since these experiments were performed as constant flow-rate experiments, the boundary condition can be described as:

$$u_L = \frac{Q}{A}, \quad x = 0, \quad t > 0 \quad (4.19)$$

Since the backpressure of these experiments was 145 psia, so, another boundary condition is defined as:

$$P = 145 \text{ psia}, \quad x = L, \quad t > 0 \quad (4.20)$$

where, L is the length of core. It was assumed that no asphaltene precipitation or deposition occurs before the fluid begins to flow, so, the following initial condition apply:

$$C_A = 0, \quad 0 \leq x \leq L, \quad t = 0 \quad (4.21)$$

$$E_A = 0, \quad 0 \leq x \leq L, \quad t = 0 \quad (4.22)$$

$$\phi = \phi_0, \quad 0 \leq x \leq L, \quad t = 0 \quad (4.23)$$

$$k = k_0, \quad 0 \leq x \leq L, \quad t = 0 \quad (4.24)$$

The asphaltene precipitate model described in Chapter III was used to calculate the amount of asphaltene precipitate.

4.2.3 Numerical Solution

Eqs. (4.12) and (4.14)-(4.18) are highly coupled. The numerical model is established by discretizing the above equations backward both in space and time. Since the numerical equations are highly coupling and implicit, the iteration method was used to solve the numerical equations. When the equations were solved, the sensitivity analyses were performed and the results were provided in Figure 4.1 and 4.2. The program was not sensitive to time step and block number, so, values of 400 second and 20 blocks were used as time step and block number, respectively, in all applications.

4.2.4 Validation

The program was applied to six experiments of Minssieux (1997). The data for experiments are given in Table 4.2. Trial and error was used to match all six experimental data. The simulated results are reported in Figures 4.3 - 4.8. Clearly, the simulated results match experimental data very well. The model parameters obtained by matching experimental data are reported in Table 4.2. According to these parameters, surface deposition occurred in all six experiments. Pore throat plugging occurred in experiment GF1 and HMD26. The deposit entrainment occurred in experiment GF3, GV5, GV10, and GP9.

4.3 Summary

In this chapter, a model for asphaltene deposition in core test was described. This model and the asphaltene precipitation model described in Chapter III were applied to six sets of experimental data of asphaltene deposition in core tests. In all six cases, experimental data were matched satisfactorily, which demonstrates that the model has

the ability to simulate asphaltene deposition in core tests. Based on the deposition parameters obtained in matching experiment data, surface deposition always occurs and was the dominant deposition mechanism, with deposit entrainment and pore throat plugging occurring only in some cases.

Table 4.1 The compositions and properties of Weyburn and Hassi-Messaoud oils

Oil Composition (mol. %) (Hirschberg et al., 1982)		
	Weyburn Oil	Hassi-Messaoud Oil
Methane	0.10	0.07
Ethane	0.48	0.07
Propane	2.05	0.87
i-Butane	0.88	0.53
n-Butane	3.16	2.44
i-Pentane	1.93	1.71
n-Pentane	2.58	2.36
Hexane	4.32	4.32
Heptane plus	84.50	87.63
Total	100.00	100.00
Oil Properties (Minssieux, 1997)		
	Weyburn Oil	Hassi-Messaoud Oil
API gravity of stock tank oil	29	43
Asphaltene content in stock tank oil, wt%	5.3	0.15
Reservoir temperature, °C	50	119
Viscosity, cp	13 (20 °C)	1.5 (80 °C)

Table 4.2 Data used in the simulation and the model parameters determined by trial and error

	GF1	GF3	GV10	GV5	GP9	HMD26
Core Properties						
Initial Permeability, <i>md</i>	107	77.4	18.0	29.0	1.1	0.67
Initial Porosity, %	13.1	13.7	24.3	24.7	22.6	7.1
Length of Core Sample, <i>cm</i>	6.0	6.0	6.0	6.0	6.0	6.0
Diameter of Core Sample, <i>cm</i>	2.3	2.3	2.3	2.3	2.3	2.3
Oil Properties						
API of Crude Oil	29.0	29.0	29.0	29.0	43.0	43.0
Asphaltene Content wt. %	5.3	5.3	5.3	5.3	0.15	0.15
Experimental Data						
Flow Rate, <i>cm³ / hour</i>	50	10	10	10	10	8
Temperature, °C	50	50	50	50	80	80
Data for Simulation						
Block Number	20	20	20	20	20	20
Time Step, sec	400	400	400	400	400	400
Deposition Parameters by History Match Using Trial and Error						
D_{per} , <i>cm</i>	0.00048					0.00016
$v_{cr,L}$, <i>cm / sec</i>	0.0	0.0145	0.01	0.01	0.000643	0.0
α , 1 / sec	0.0017	0.0018	0.0051	0.0128	0.0275	0.0065
β_i , 1 / <i>cm</i>	0.0	0.69	0.003	0.012	0.0006	0.0
γ_i , 1 / <i>cm</i>	0.07	0.0	0.0	0.0	0.0	0.035
σ , constant	35	0.0	0.0	0.0	0.0	0.0
f_p , constant	1.0	1.0	1.0	1.0	1.0	1.0

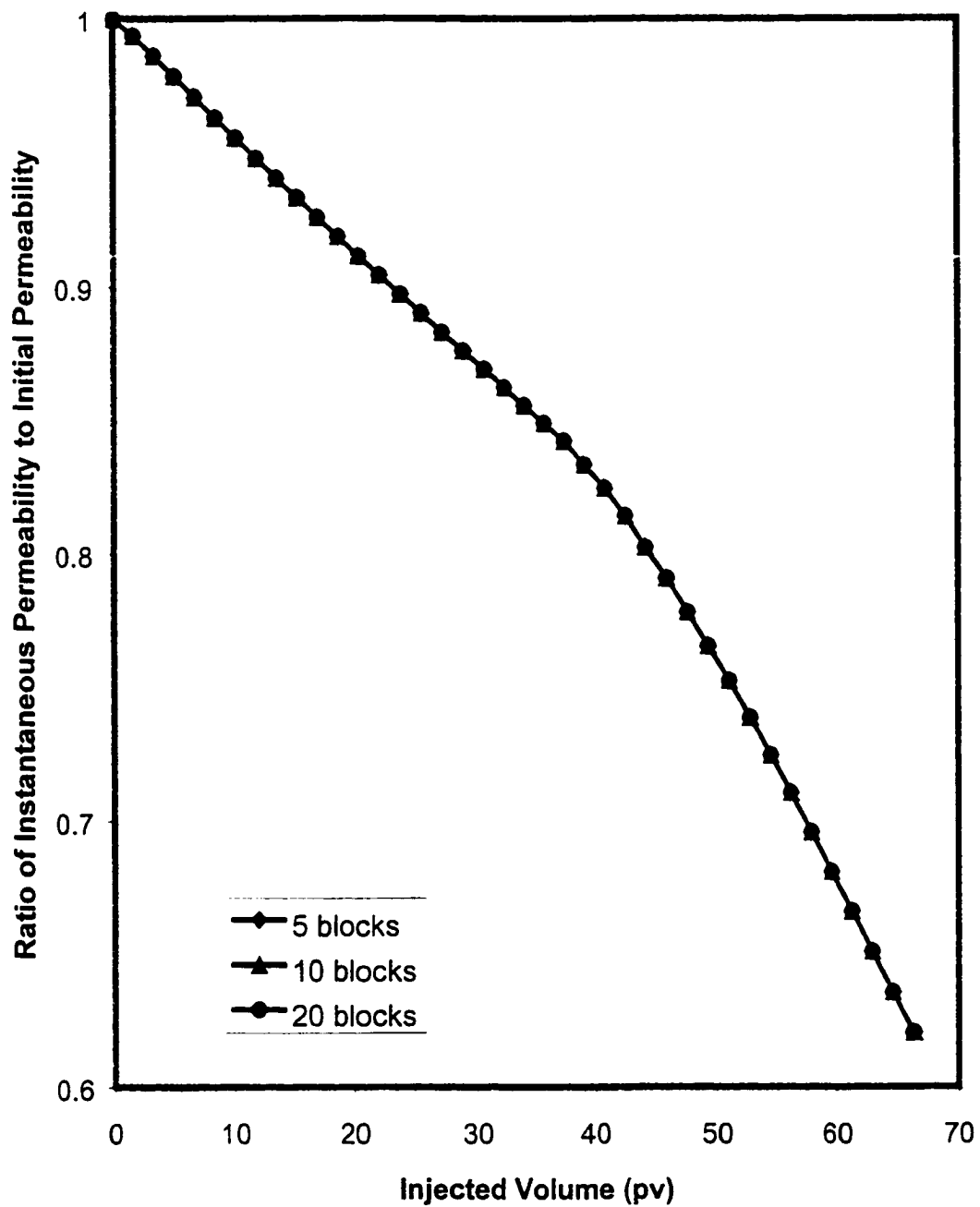


Figure 4.1 Effect of the block number on the simulated permeability reduction (time step = 400 sec)

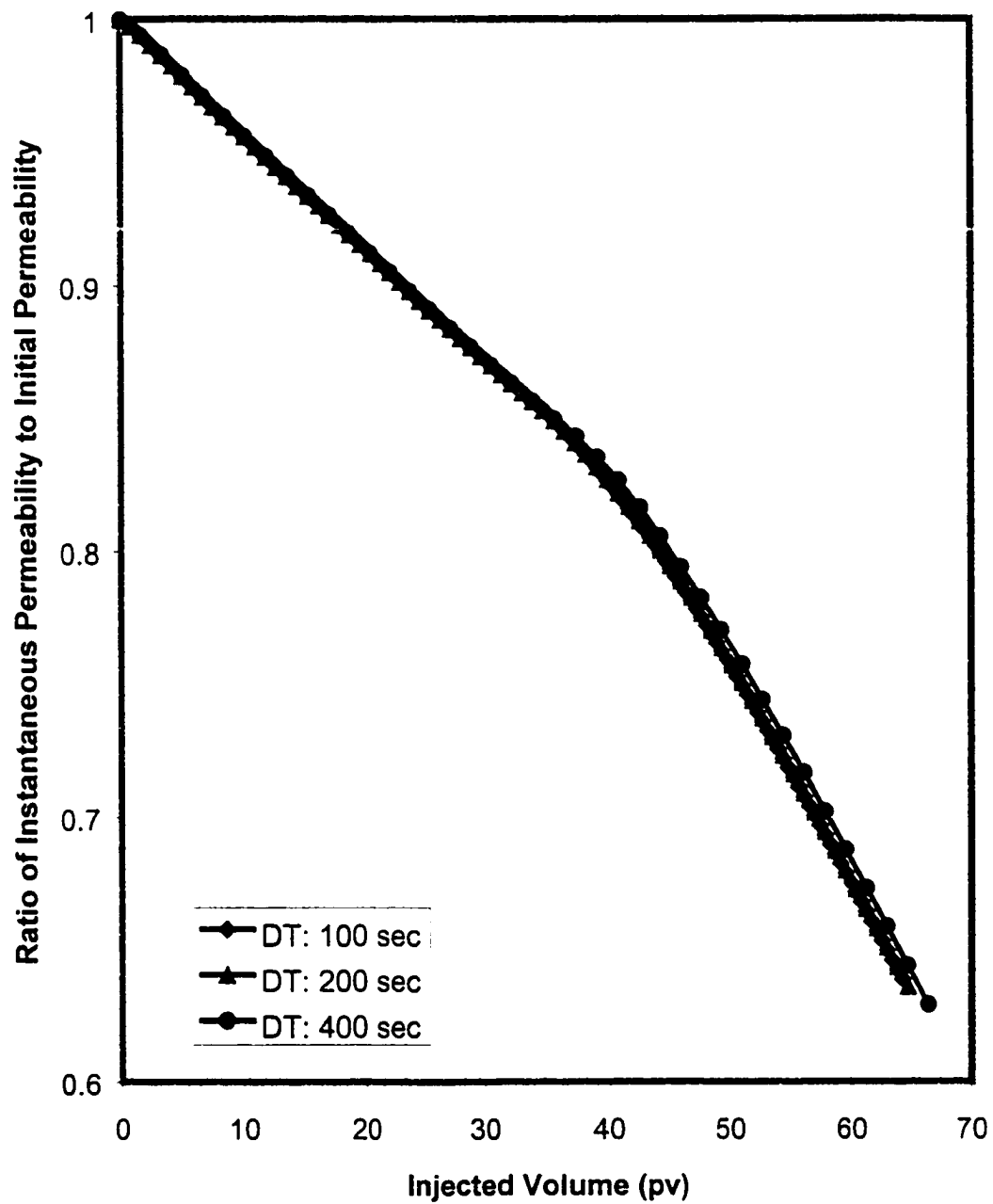


Figure 4.2 Effect of the time step on the simulated permeability reduction (number of blocks: 10)

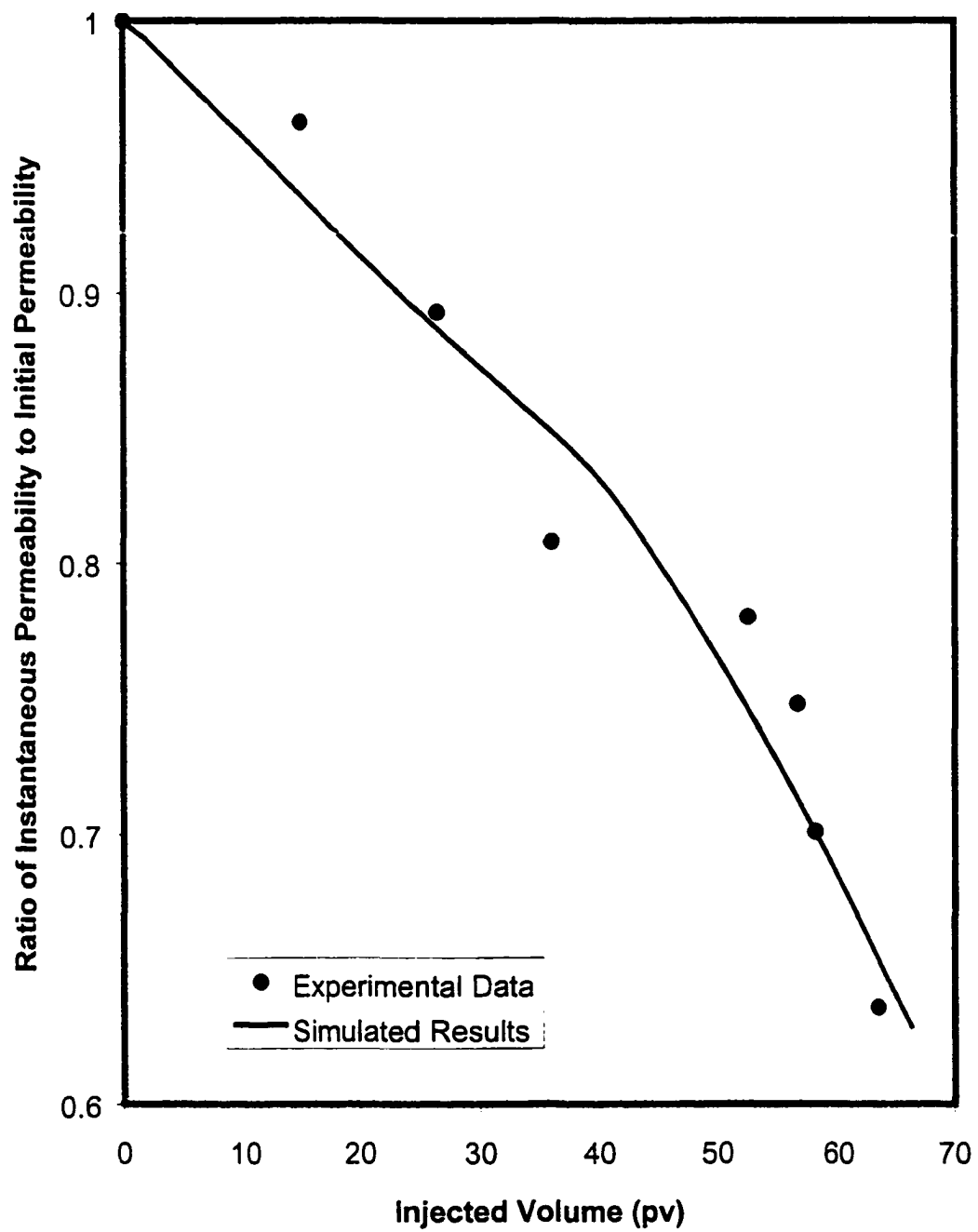


Figure 4.3 Comparison of experimental and simulated results for the GF1 Minssiux test

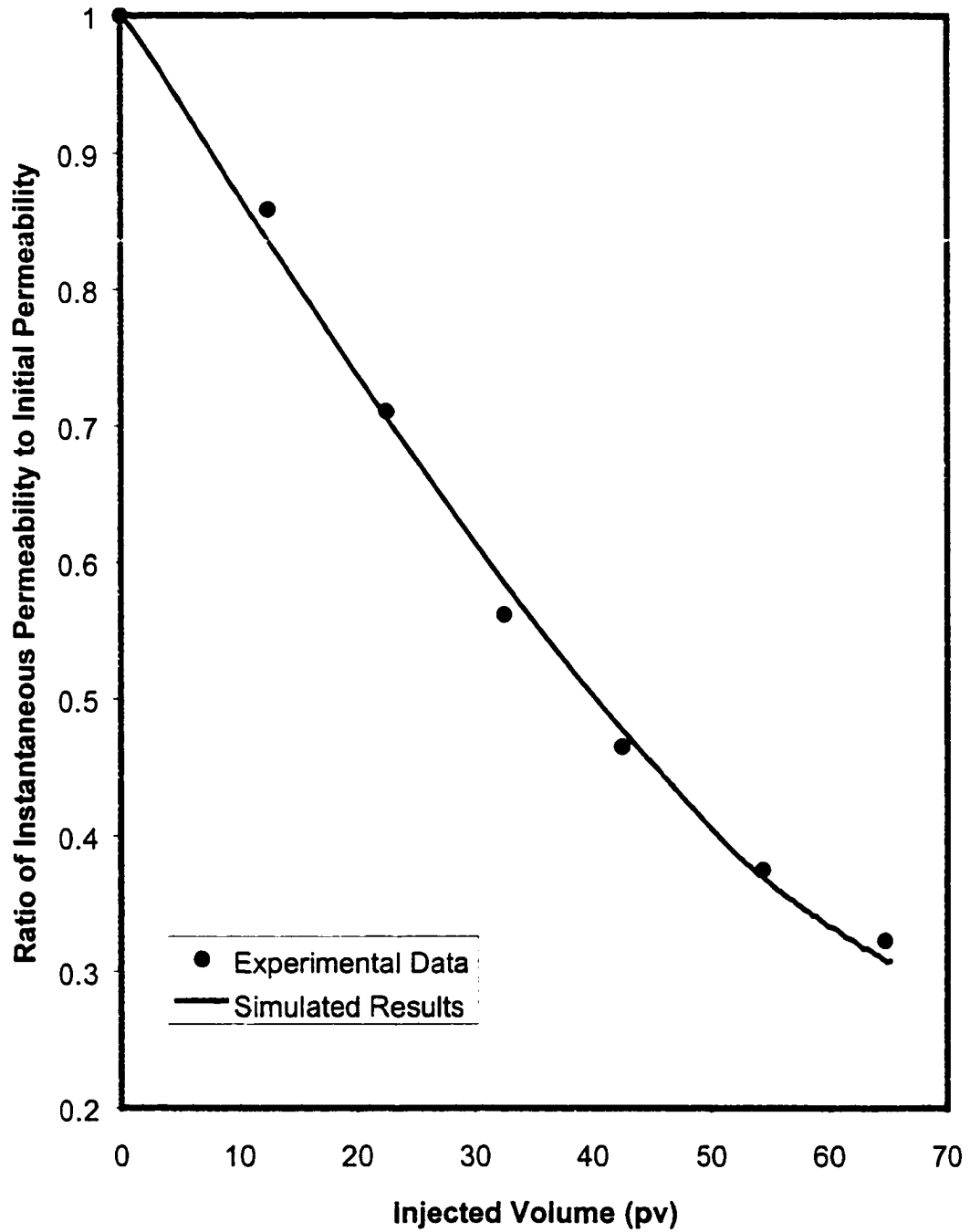


Figure 4.4 Comparison of experimental and simulated results for the GF3 Mnssiuex test

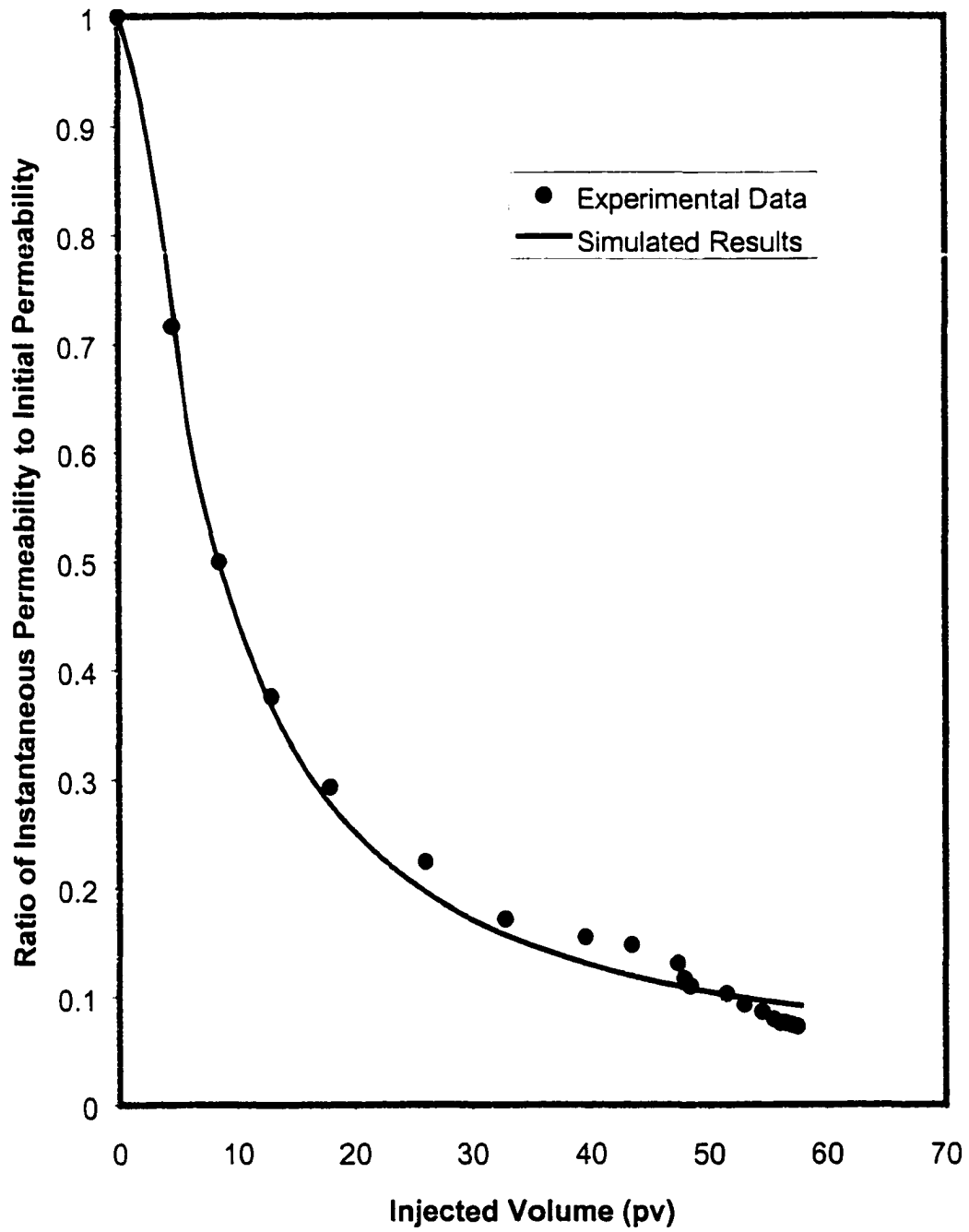


Figure 4.5 Comparison of experimental and simulated results for the GV5 Minssiux test

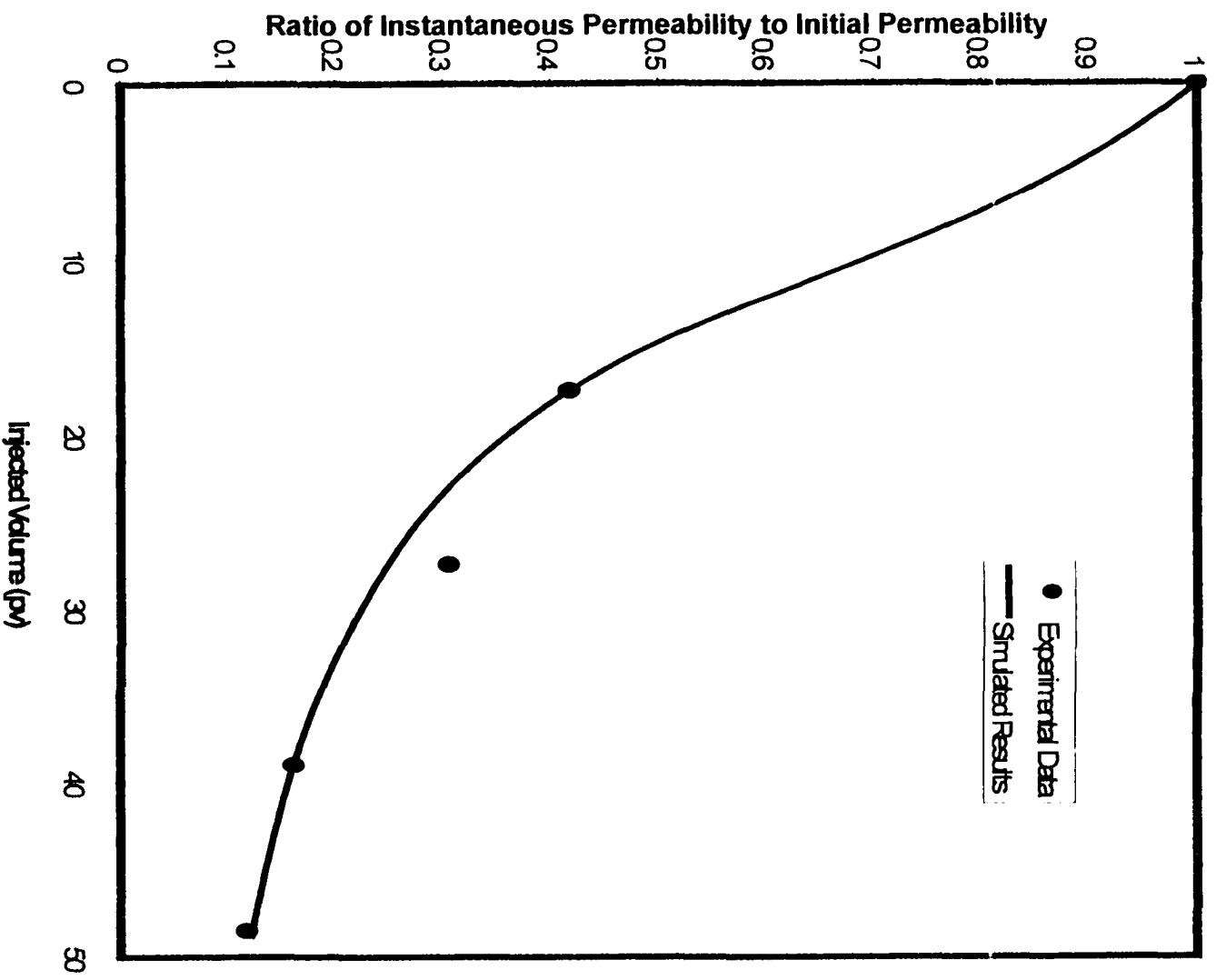


Figure 4.6 Comparison of experimental and simulated results for the GV10 Minisieve test

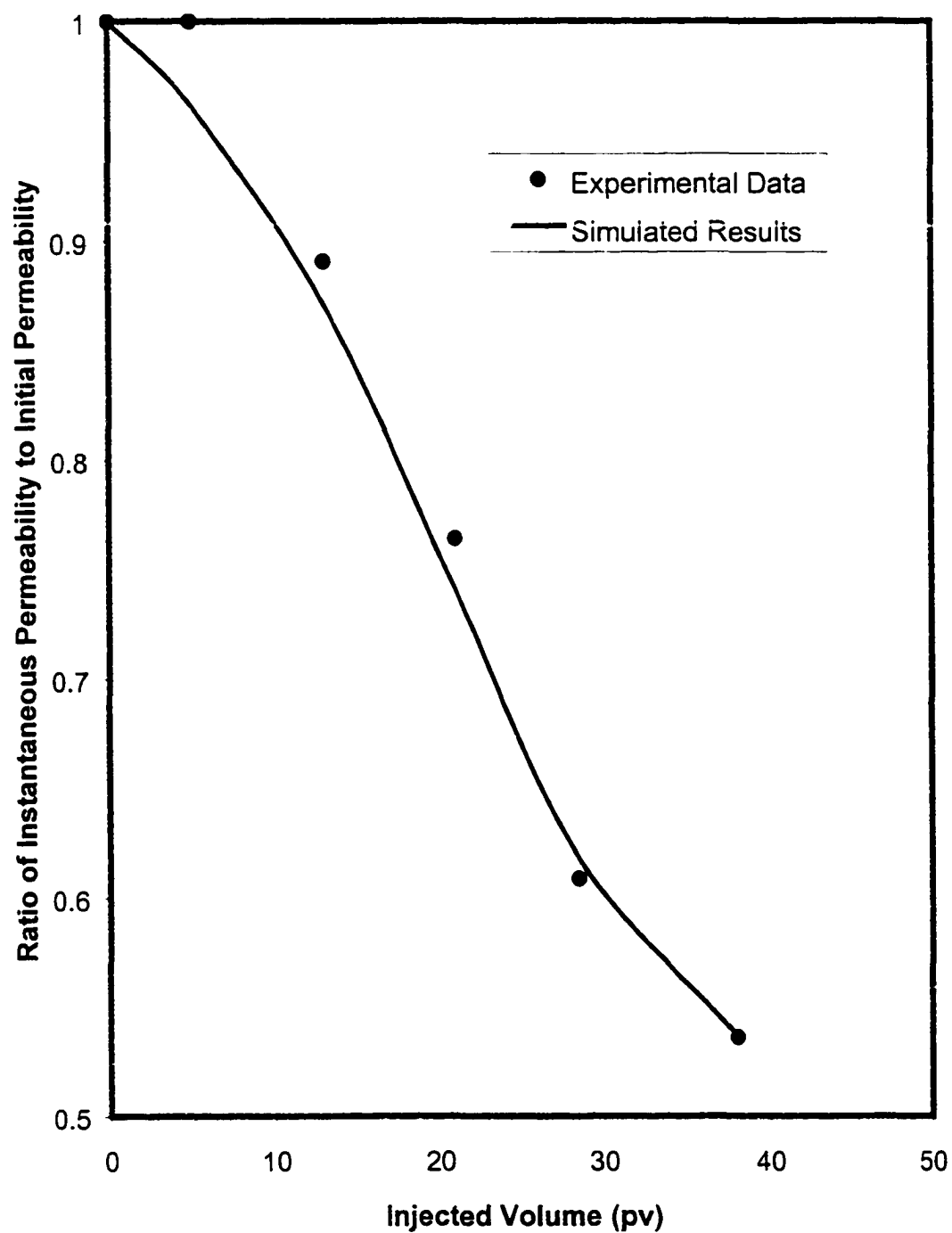


Figure 4.7 Comparison of experimental and simulated results for the GP9 Minssiuex test

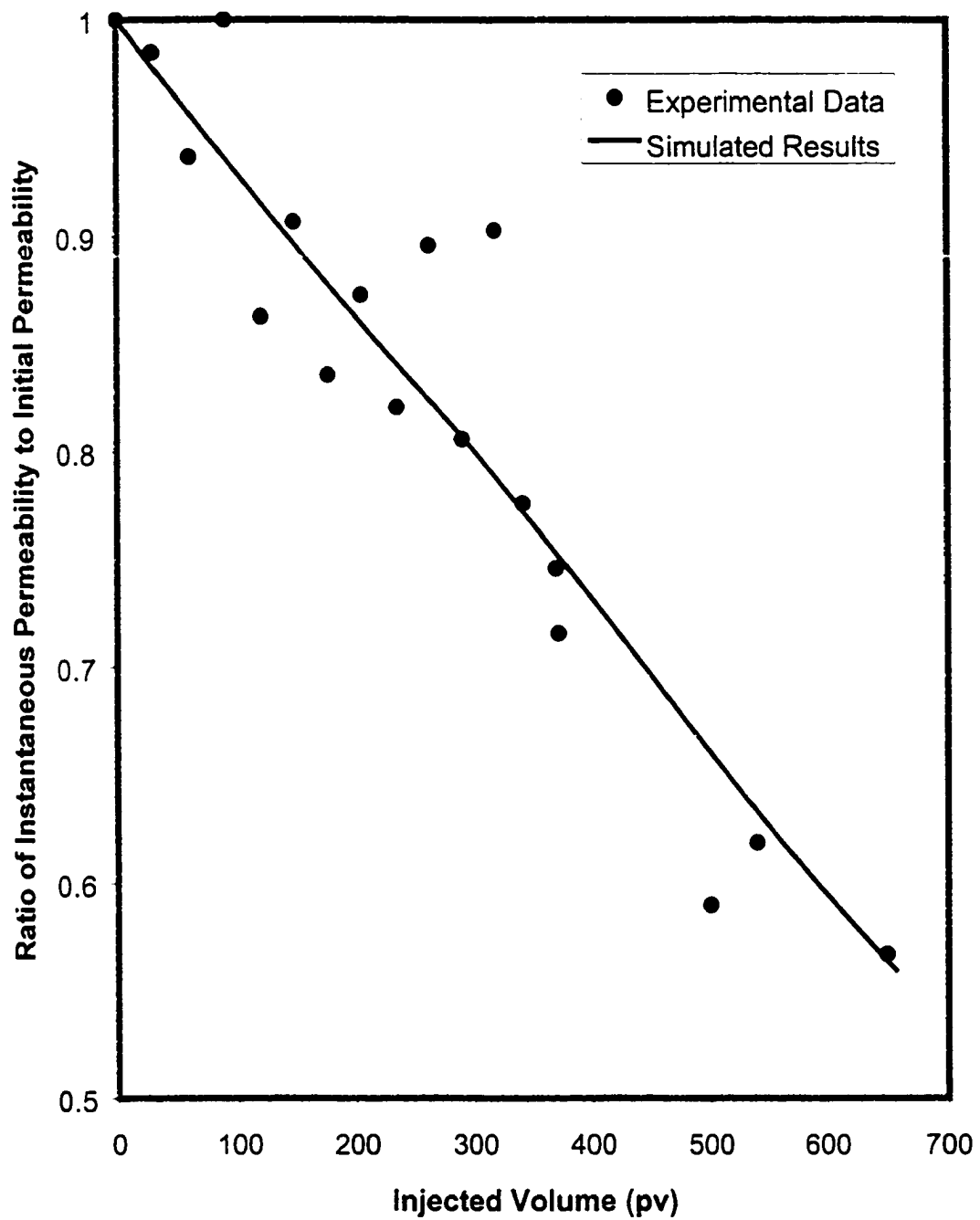


Figure 4.8 Comparison of experimental and simulated results for the HMD26 Minssiux test

CHAPTER V

FIELD APPLICATIONS

Asphaltene can precipitate and deposit in petroleum reservoirs during primary oil recovery. Although this problem was identified in oil industry a long time ago, no satisfactory model and simulator is available to model and simulate the process and investigate the mechanism of asphaltene precipitation and deposition in petroleum reservoirs.

In this chapter, the asphaltene precipitation model, asphaltene deposition model and permeability reduction model described in previous chapters are incorporated into a three-dimensional, three-phase black oil simulator. The simulator was used to simulate the asphaltene deposition in reservoirs with vertical or horizontal wells. The simulation results are presented in this chapter.

5.1 Asphaltene Mass Balance

In addition to the asphaltene precipitation model described in Chapter III and the asphaltene deposition, porosity and permeability reduction models described in Chapter IV, an asphaltene mass balance model is required for the simulator. The three dimensional asphaltene mass balance equation is expressed as:

$$\begin{aligned} & \frac{\partial}{\partial t}(\phi S_L C_A \rho_A + \phi S_L \rho_L w_{AL}) + \frac{\partial}{\partial x}(\rho_L u_L w_{SAL} + \rho_L u_L w_{AL}) + \\ & \frac{\partial}{\partial y}(\rho_L u_L w_{SAL} + \rho_L u_L w_{AL}) + \frac{\partial}{\partial z}(\rho_L u_L w_{SAL} + \rho_L u_L w_{AL}) = -\rho_A \frac{\partial E_A}{\partial t} \end{aligned} \quad (5.1)$$

where, all variables except y and z are the same as those defined in the previous Chapters; y is the independent space variable in y direction; and z is the independent space variable in z direction.

5.2 Incorporation

A three-dimensional, three-phase black oil simulator, BOASTVHS, was modified by incorporating the asphaltene precipitation model, the asphaltene mass balance model, the asphaltene deposition model, and the porosity and permeability reduction models. The original simulator employs implicit pressure, explicit saturation finite-difference equations, which means the pressure distribution for a given time step is implicitly solved and then the saturation distribution for the same time step is explicitly established. Then the asphaltene-related models and formation damage models are incorporated there after the new saturation distribution is established. The asphaltene precipitation model is incorporated as a subroutine, which is called by the main program. The asphaltene mass balance differential equation is replaced by the difference equation with backward quotients in both time and distance. Since the asphaltene mass balance model, asphaltene deposition model, and porosity and permeability reduction models are highly coupled together, iteration is used to solve these equations simultaneously. After the dissolved, precipitated, and deposited asphaltene

distributions, as well as porosity distribution and permeability distribution for the current time step are established, all variable such as pore volume, transmission between blocks, and production index, which are related with permeability and porosity, are updated and then the simulator goes to the next step.

5.3 Applications

5.3.1 Description

The simulator was used to applied a reservoir that was 2100 ft long, 2100 ft wide, and 50 ft thick, at a depth of 4000 ft. The reservoir was horizontal, homogeneous, and isotropic. The permeability was 25 md and the porosity was 0.25. The reservoir was undersaturated with an initial pressure of 5261 psia, temperature of 212 °F and bubble point of 2050 psia. The crude oil of the reservoir had a gravity of 19 API at stock tank condition. The oil contained 16.08% (weight) asphaltene [Burke et al., 1988]. All reservoir parameters are listed in Table 5.1. The asphaltene precipitation curve (Figure 3.1) illustrates that no asphaltene precipitation occurs at pressure above 5056 psia. At 5056 psia, asphaltene begins to precipitate, and the precipitated asphaltene concentration increases with decrease in pressure for a specific temperature. The precipitated asphaltene concentration reaches the highest value at the bubble point pressure of 2050 psia and then decreases with further decrease of pressure for specific temperature.

5.3.2 Case 1

In the center of the reservoir, there is a vertical well producing oil with bottom flow pressure of 1000 psia and initial flow performance index of 0.048115 bbl/day-psi-ft. The radius of the wellbore is 0.5 ft. The reservoir is divided into 21 blocks in both x and y directions with a block length of 100 ft. There is one block in vertical direction with block length of 50 ft. The vertical well is located in block 11 and 11 in x and y direction. The grid system and well location is shown in Figure 5.2. The data for grid and well are reported in Table 5.2. The coefficients for the asphaltene deposition model are reported in Table 5.3.

Nearly three-years of production was predicted and the results are provided in Figures 5.4 ~ 5.10. The production rate of the well declined quickly from more than 4000 bbl/day to less than 100 bbl/day due to formation damage caused by asphaltene deposition even though the average reservoir pressure remained high (Figure 5.4). The reservoir pressure decreased quickly at first, then declined slowly at the end of three-year production period (Figure 5.5) because the oil production rate was very high at the beginning and decreased to a very low value at the end of the period. The pressure at the near-wellbore region was the first to fall below the pressure at which asphaltene begins to precipitate. As a result, the solubility of asphaltene decreased (Figure 5.6) and the asphaltene began to precipitate and deposit in the near wellbore region (Figure 5.7, 5.8). After 25-days of production, the pressure in whole reservoir fell below the pressure at which asphaltene starts to precipitate and asphaltene was found to precipitate and deposit everywhere (Figure 5.5, 5.6, 5.7, 5.8). As a result, the porosity and permeability

declined only in the near wellbore region at the beginning, and then, the decline propagated throughout the reservoir (Figure 5.9, 5.10). The asphaltene exhibited the lowest solubility (during most production period) and largest precipitate concentration in the near wellbore region. Therefore, more asphaltene deposition occurred in the near well bore region than in the region close to the reservoir boundary per unit bulk volume, resulting in the more damage occurring in the near wellbore region.

Previously, the asphaltene deposition was thought to occur only in the near wellbore region. This study shows that it can occur throughout the reservoir, but the near wellbore region will be damaged more severely than the rest of the reservoir.

5.3.3 Case 2

Case 2 involved a horizontal well in a reservoir with bottomhole flowing pressure of 1,000 psia and initial flow index of 0.11891 bbl/day-psia-ft. The horizontal wellbore was 800 ft long, located in the middle of the reservoir, and extended in western-eastern or x` direction (Figure 5.3). The radius of horizontal wellbore was 0.5 ft. The reservoir was divided into 20 blocks with a block length of 105 ft in x direction, 21 blocks with the block length of 100 ft in y direction, and one block with block length of 50 ft in z direction. In the x direction, the horizontal wellbore located in the block 7, 8, 9, 10, 11, 12, 13, and 14. In the y direction, it located in block 11 (Figure 5.3). All grid data and well information are provided in Table 5.4. The coefficients of asphaltene deposition models were the same as those in Case 1.

At the beginning of production, the horizontal well produced at more than 70,000 bbl/day. Due to the high production rate, the average reservoir pressure decreased

quickly, and therefore, the production rate decreased rapidly (Figure 5.11). The high production rate also resulted in the pressure of the blocks around the wellbore to decrease quickly and fall below the pressure at which asphaltene starts to precipitate. (Figure 5.12). Asphaltene began to precipitate and deposit in the near wellbore region during the first 5 days of production, and the asphaltene had the lowest solubility, the highest precipitate concentration, and the highest quantity of deposits in the blocks where the horizontal wellbore was located. After five days, the pressure in the blocks where the wellbore was located dropped to below the bubble point pressure. At that point, the dissolved asphaltene concentration in the blocks where horizontal wellbore was located increased with the decrease in pressure. The minimum asphaltene solubility and maximum concentration of asphaltene precipitates move from the near-wellbore region towards the outside boundary (Figure 5.13, 5.14,) because the asphaltene solubility decreased with the pressure decrease at the beginning and increased with the pressure decrease after the pressure dropped below 2050 psia. The maximum asphaltene precipitate concentration occurred in the blocks next to the wellbore-located blocks for more than 400 days (Figure 5.14) and the highest quantity of asphaltene deposits was calculated in these blocks (Figure 5.15). As a result, the porosity and permeability in those blocks decreased severely. The most severe damage occurred in the “outer” near wellbore region rather than the blocks where the wellbore was located (Figure 5.16, 5.17).

5.4 Summary

In this chapter, the asphaltene precipitation model, deposition model, mass balance model, and porosity and permeability models were successfully incorporated into a three-dimensional and three-phase black oil simulator. The simulator was used to study two cases involving asphaltene precipitation and deposition in petroleum reservoirs, one developed by a vertical well and another developed by a horizontal well. It was demonstrated that the pattern of asphaltene precipitation and deposition in petroleum reservoirs with the vertical well and horizontal well are different because of the larger production rate of the horizontal well. Based on these successful applications, it can be concluded that the model and simulator reported in this chapter can simulate the asphaltene precipitation and deposition in petroleum reservoirs with vertical or horizontal wells during primary oil recovery.

Table 5.1 Reservoir description

RESERVOIR CONDITIONS	
Depth, <i>ft</i>	4000.0
Width, <i>ft</i>	2100.0
Length, <i>ft</i>	2100.0
Thickness, <i>ft</i>	50.0
Initial Permeability, <i>md</i>	25.0
Initial Porosity, fraction	0.25
Initial Pressure, <i>psi</i>	5261.0
Bubble Point Pressure, <i>psi</i>	2050.0
Temperature, $^{\circ}F$	212.0
CRUDE OIL (Burke et al., 1988)	
Gravity, API	19.0
Asphaltene Content, % (weight)	16.08

Table 5.2 Parameters used in simulator for vertical well

GRID PARAMETERS	
Number of Blocks in x direction	21
Number of Blocks in y direction	21
Number of Blocks in z direction	1
Length of Blocks in x direction, <i>ft</i>	100.0
Length of Blocks in y direction, <i>ft</i>	100.0
Length of Blocks in z direction, <i>ft</i>	50.0
WELL PARAMETERS	
Radius of Wellbore, <i>ft</i>	0.5
Location (x, y, z)	11, 11, 1
Bottomhole Flow Pressure, <i>psia</i>	1000.0
Initial Flow Performance Index, <i>bbl / day - psia - ft</i>	0.048115

Table 5.3 Deposition parameters used in simulator
for both of Case1 and Case2

DEPOSITION PARAMETERS	
D_{pcr} , cm	0.0
$v_{cr,L}$, cm/sec	0.0
α , 1/sec	0.028
β_i , 1/cm	0.0
γ_i , 1/cm	0.0
σ , constant	0.0
f_p , constant	1.0

Table 5.4 Parameters used in simulator for horizontal well

GRID PARAMETERS	
Number of Blocks in x direction	20
Number of Blocks in y direction	21
Number of Blocks in z direction	1
Length of Blocks in x direction, <i>ft</i>	105.0
Length of Blocks in y direction, <i>ft</i>	100.0
Length of Blocks in z direction, <i>ft</i>	50.0
WELL PARAMETERS	
Radius of Wellbore, <i>ft</i>	0.5
Location (x, y, z)	7, 11, 1
	8, 11, 1
	9, 11, 1
	10, 11, 1
	11, 11, 1
	12, 11, 1
	13, 11, 1
	14, 11, 1
Bottomhole Flow Pressure, <i>psia</i>	1000.0
Initial Flow Performance Index, <i>bbl / day – psia – ft</i>	0.11891

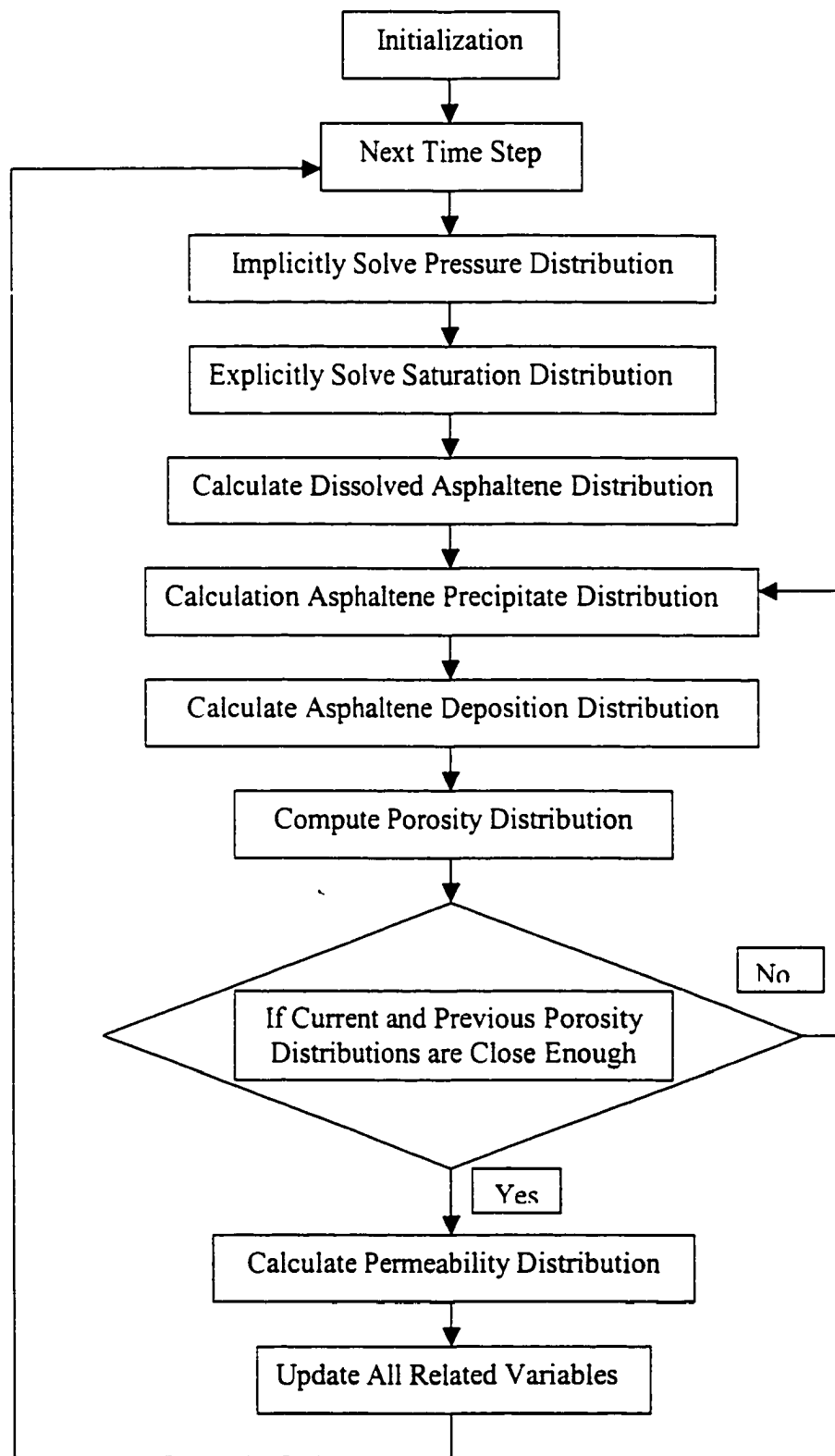


Figure 5.1 Flowchart for asphaltene deposition in reservoirs

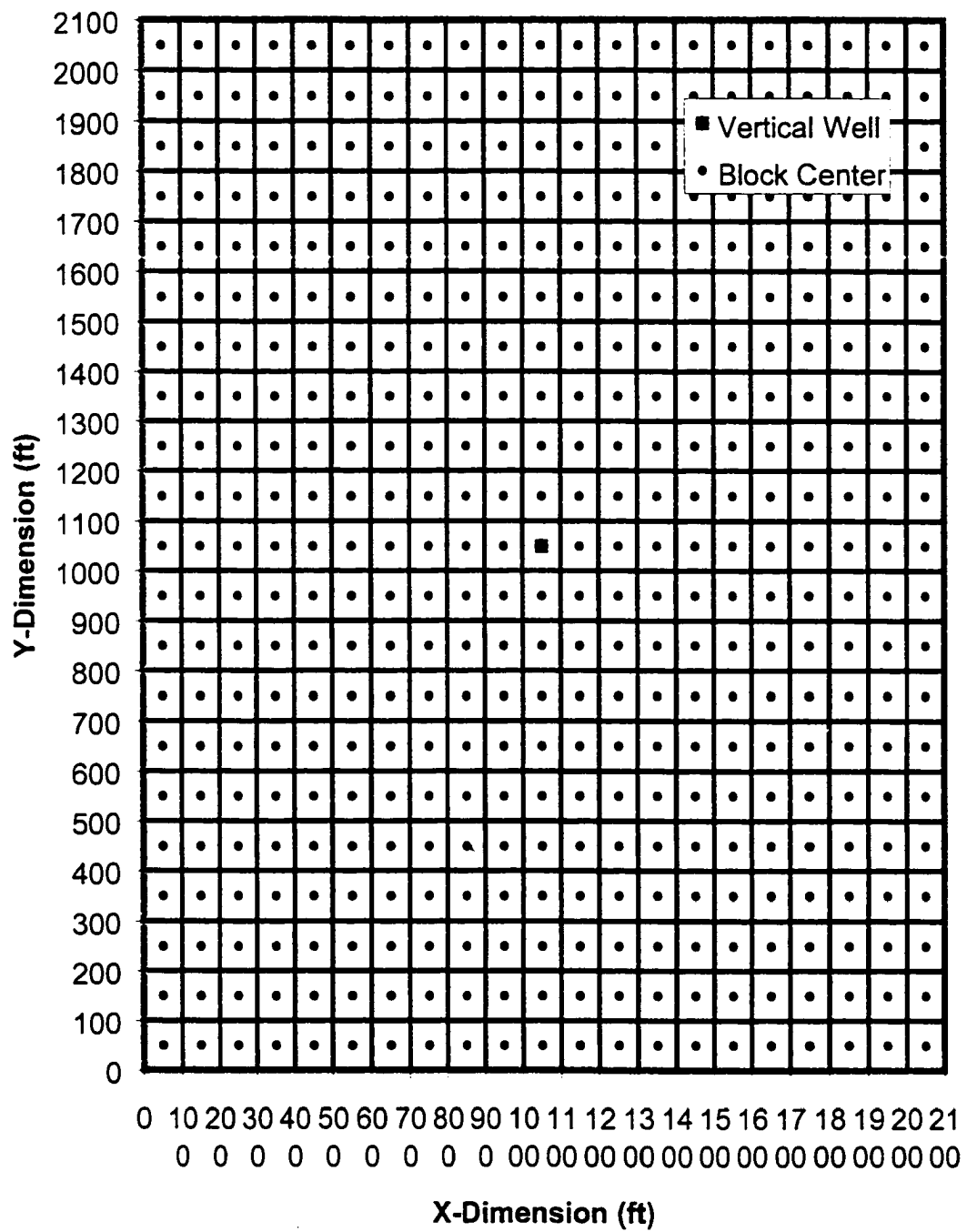


Figure 5.2 Grid system and well location for vertical well

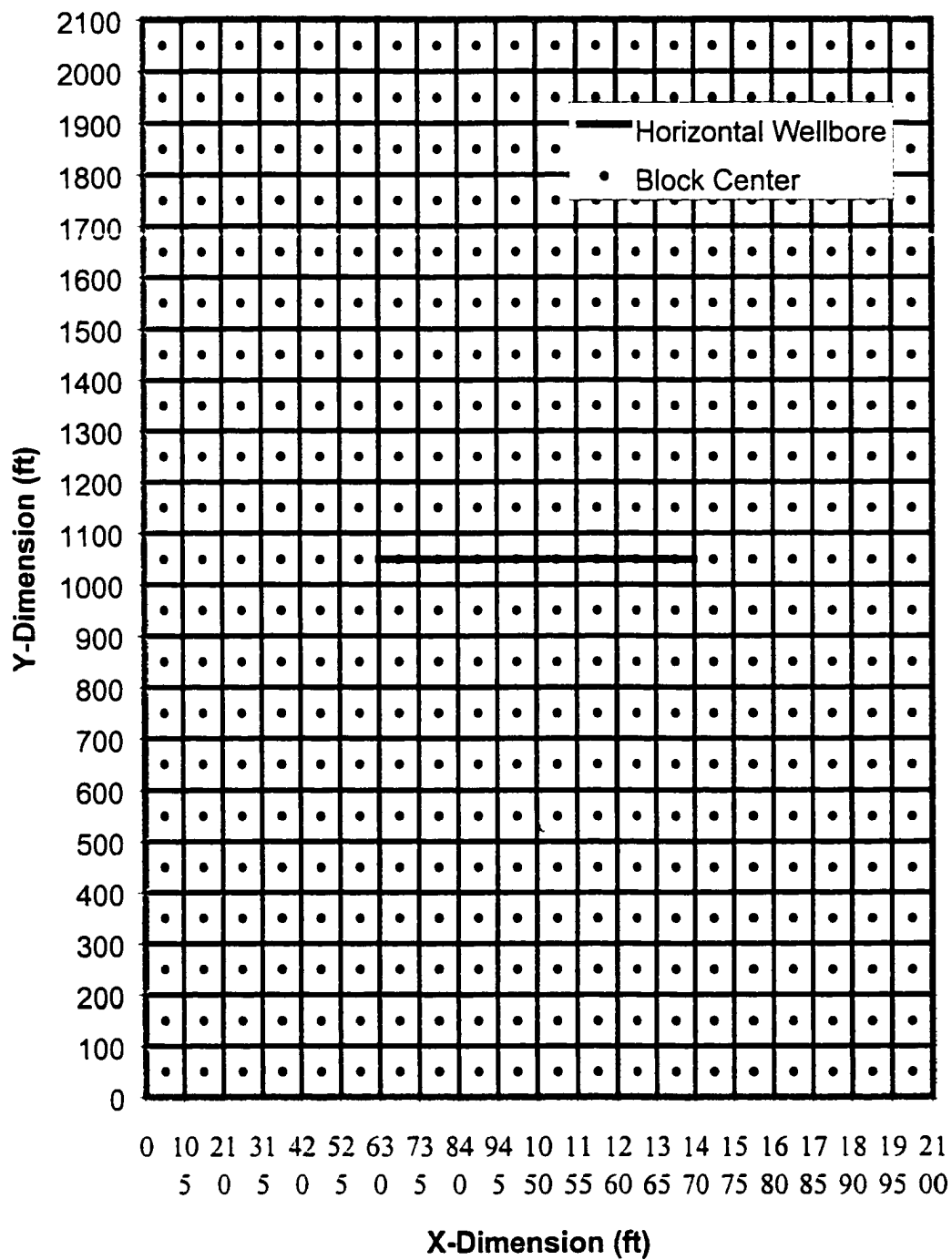


Figure 5.3 Reservoir and horizontal wellbore location

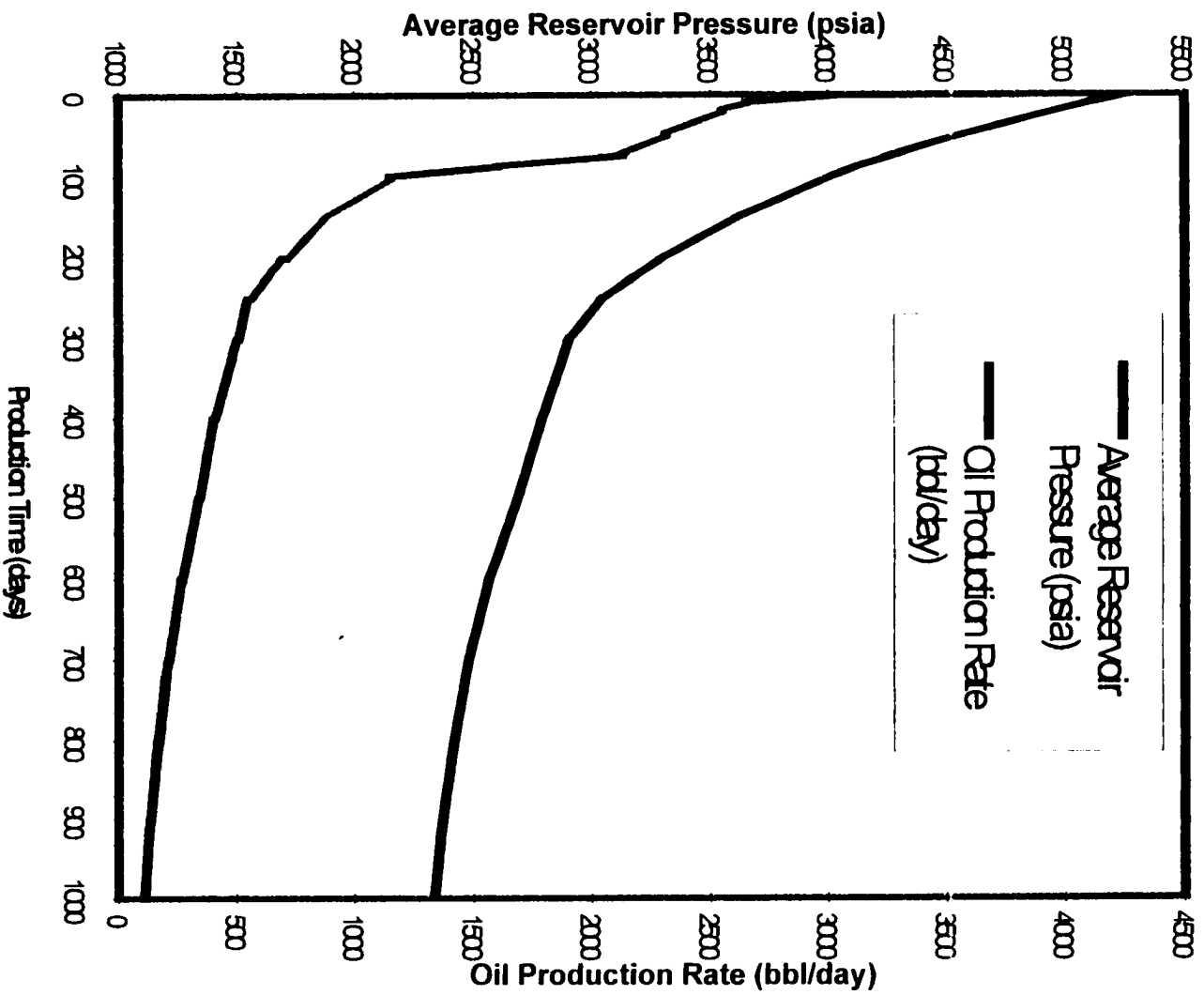


Figure 5.4 The change of average reservoir pressure and oil production rate with production time for vertical well

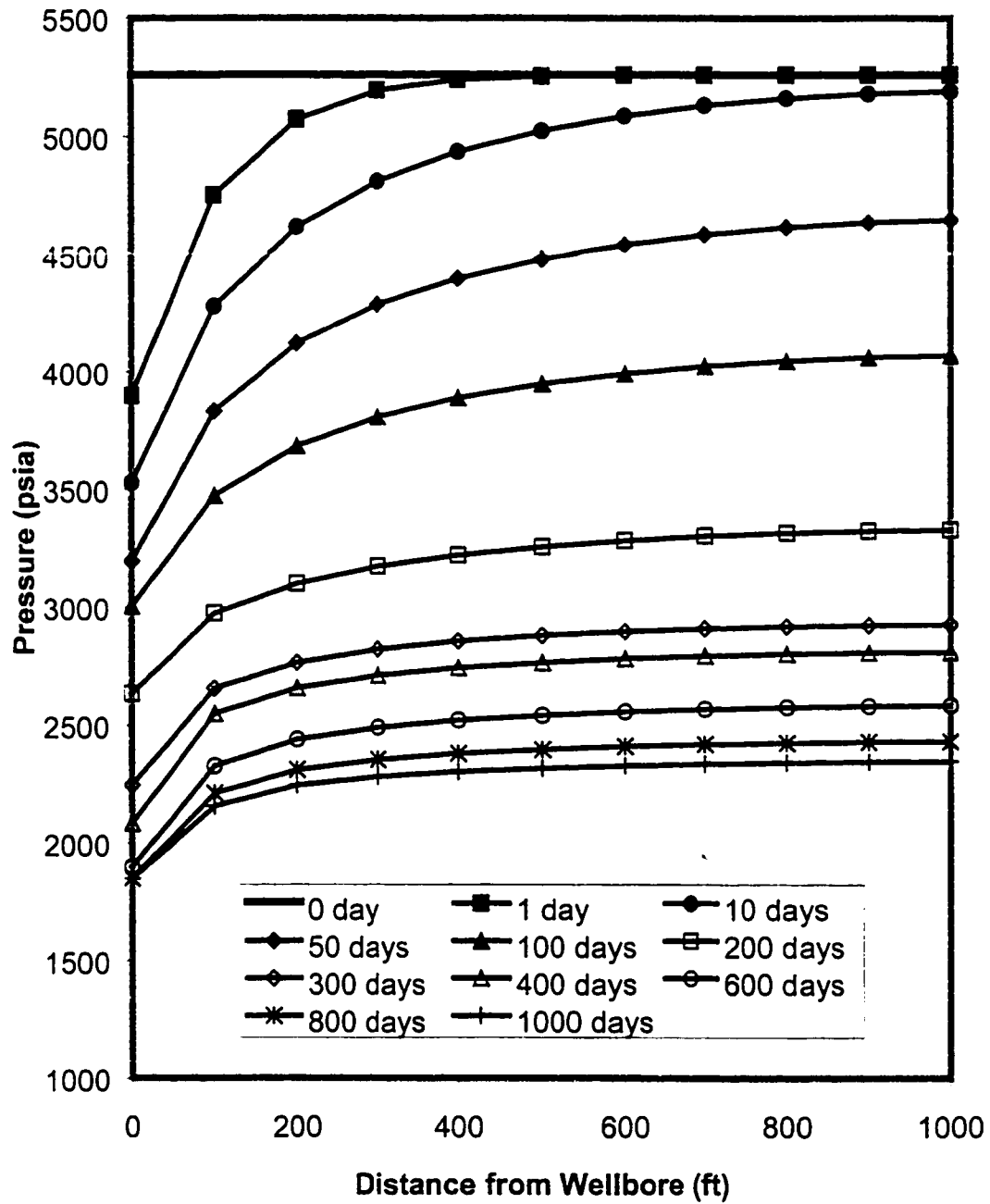


Figure 5.5 Pressure distribution along x-direction at different production time for vertical well

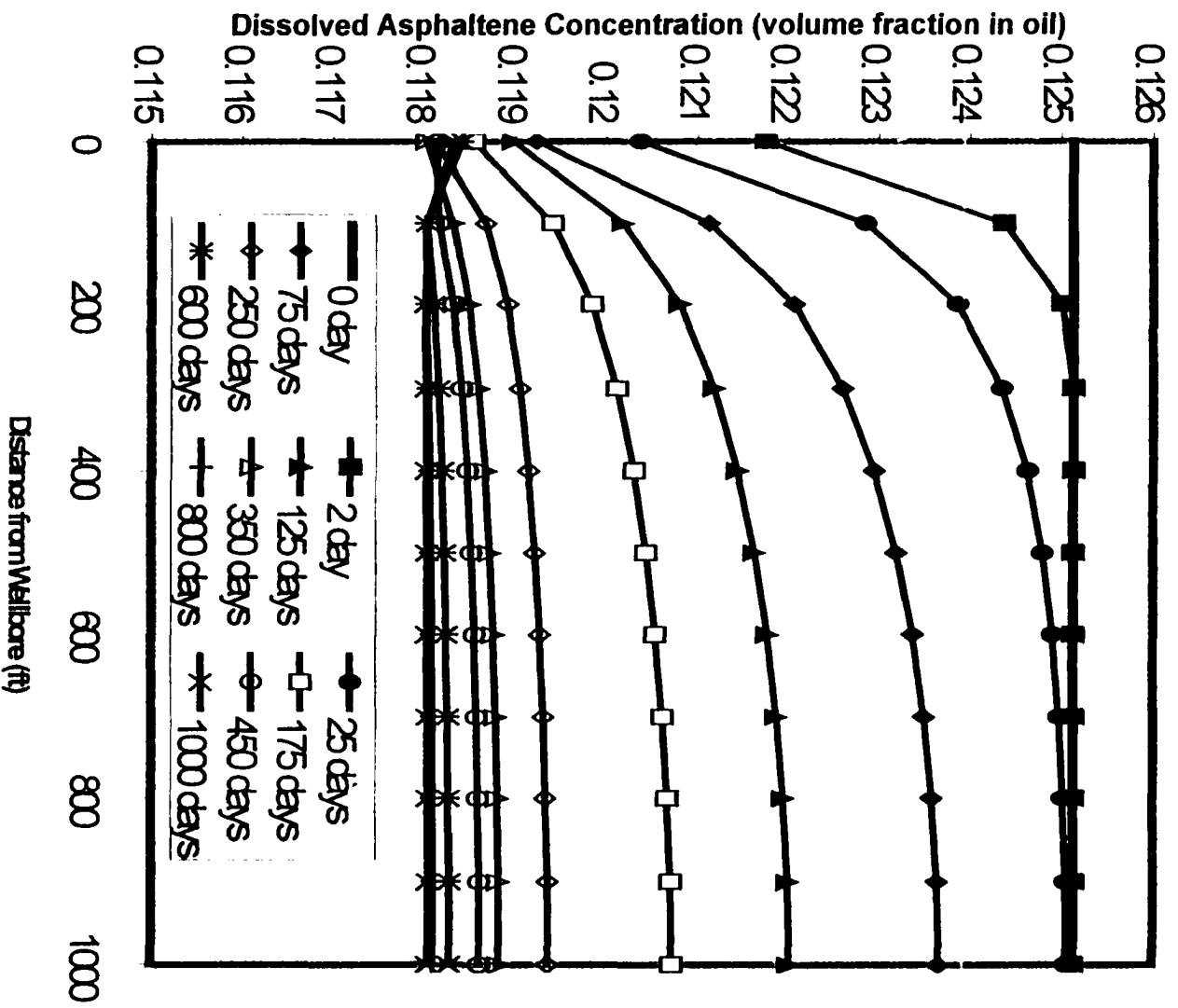


Figure 5.6 Dissolved asphaltene distribution along x-direction at different production time for vertical well

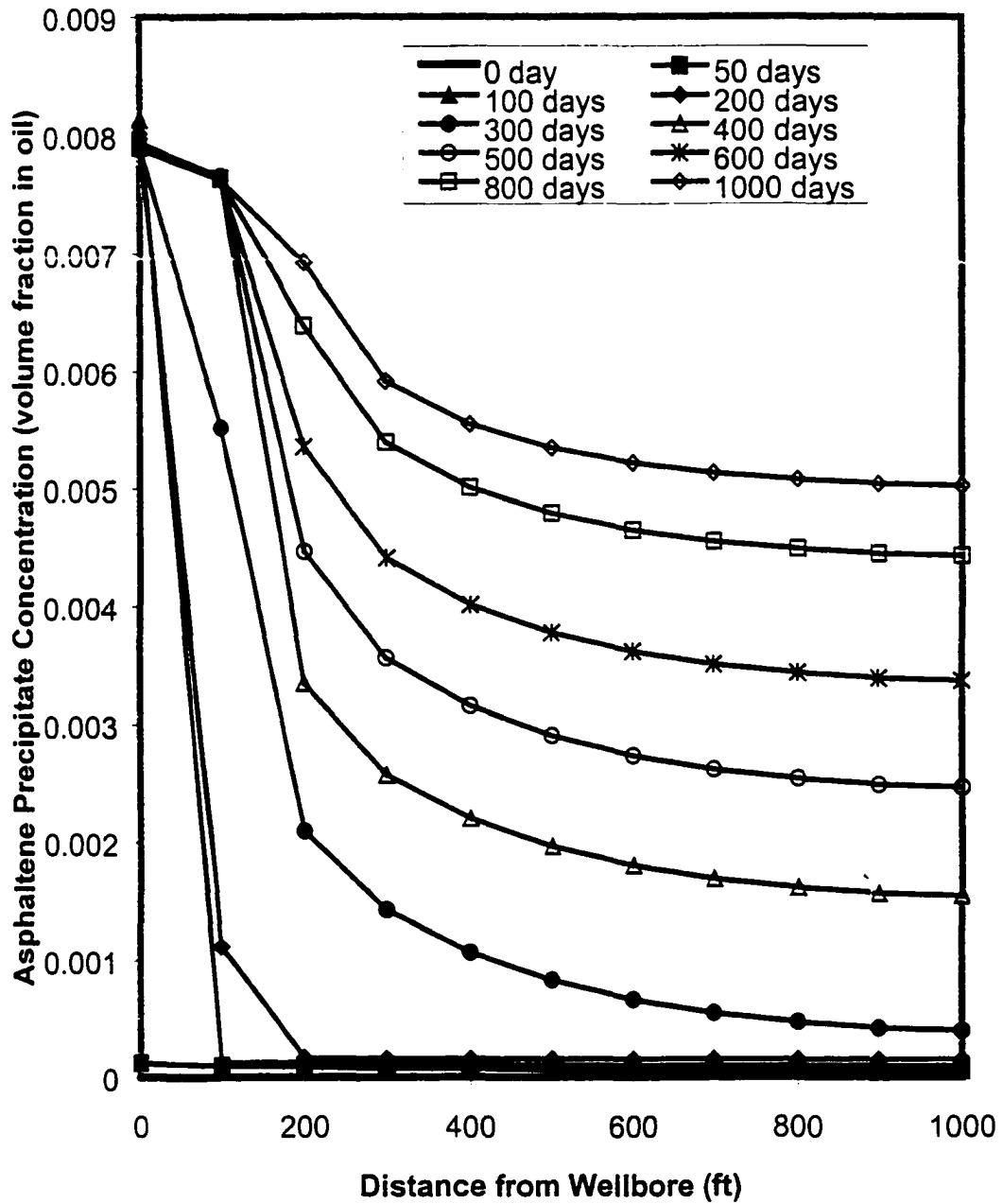


Figure 5.7 Asphaltene precipitate distribution along x-direction at different production time for vertical well

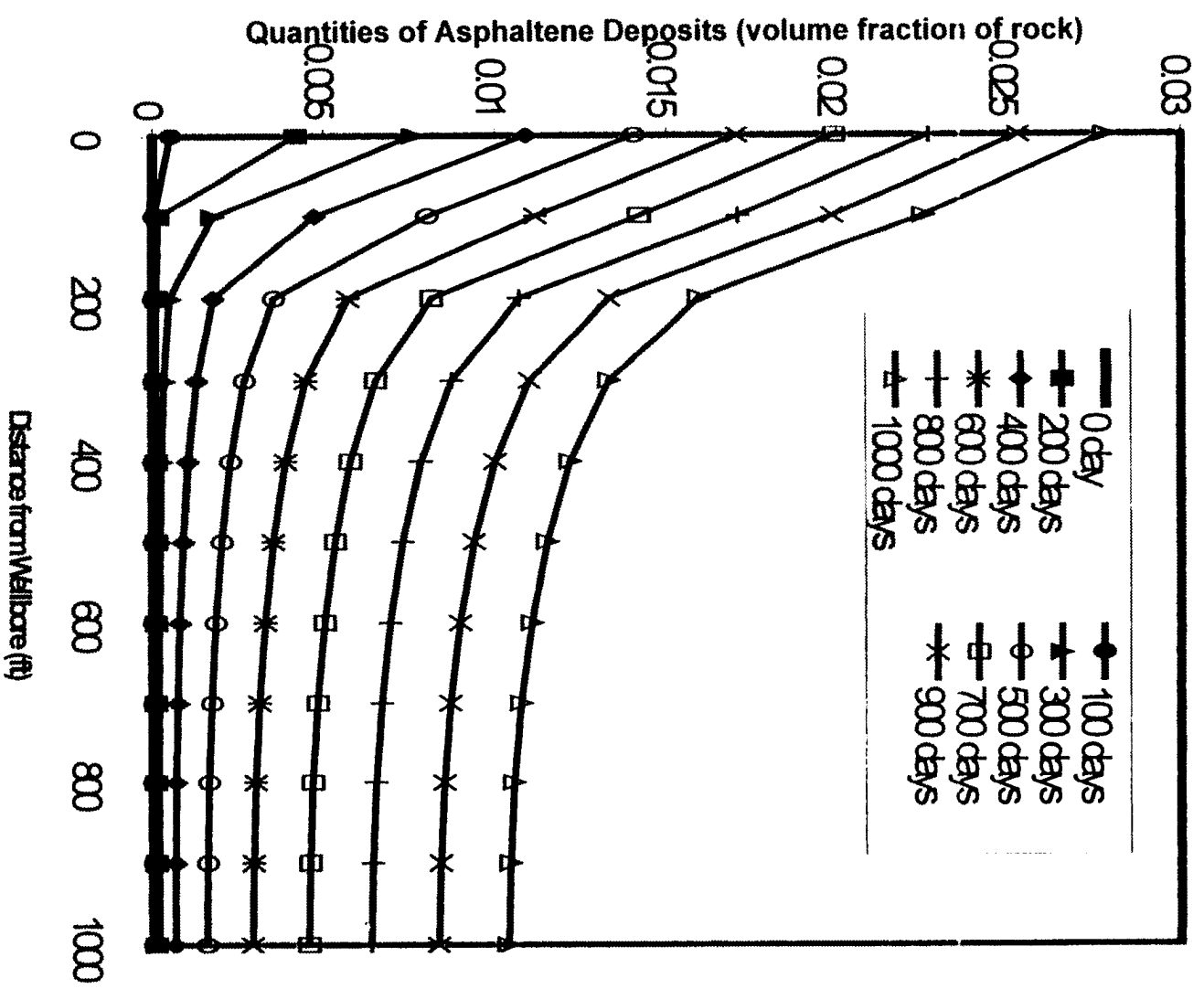


Figure 5.8 Asphaltene deposit distribution along x-direction at different production time for vertical well

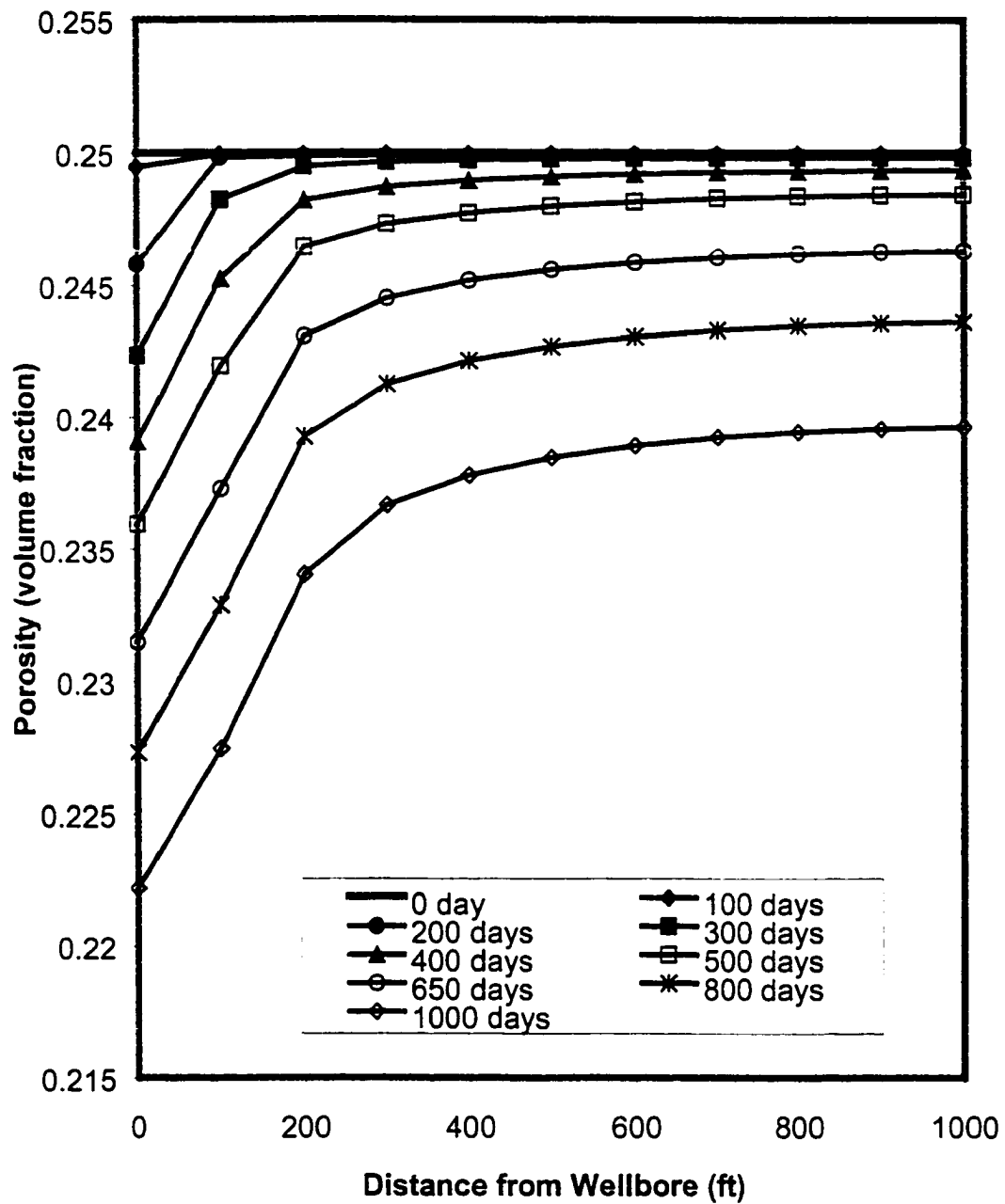


Figure 5.9 Porosity distribution along x-direction at different production time for vertical well

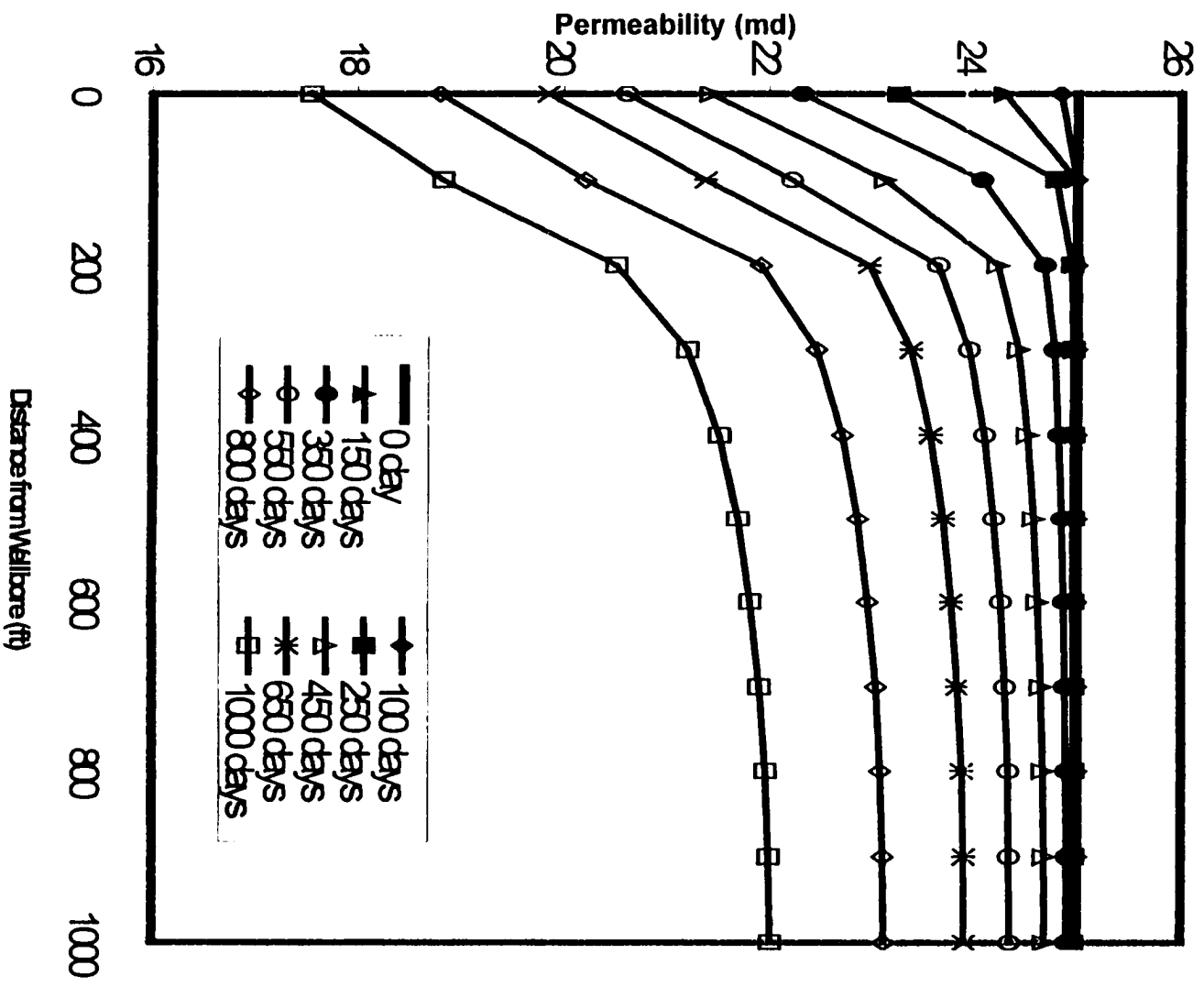


Fig. 5-10 Permeability Distribution Along X-Direction at Different Production Time for Vertical Well

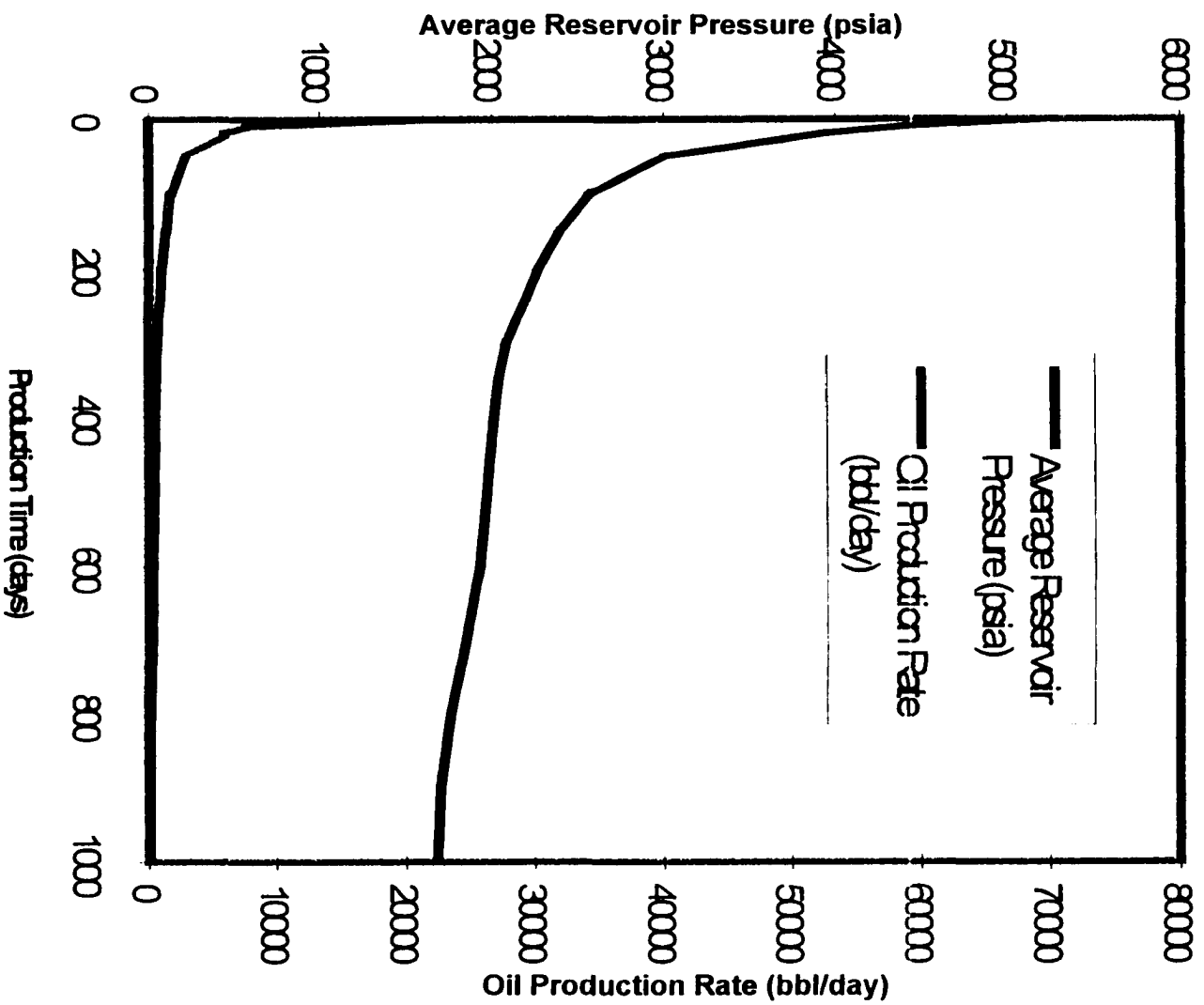


Figure 5.11 The change of average reservoir pressure and oil production rate with production time for horizontal well

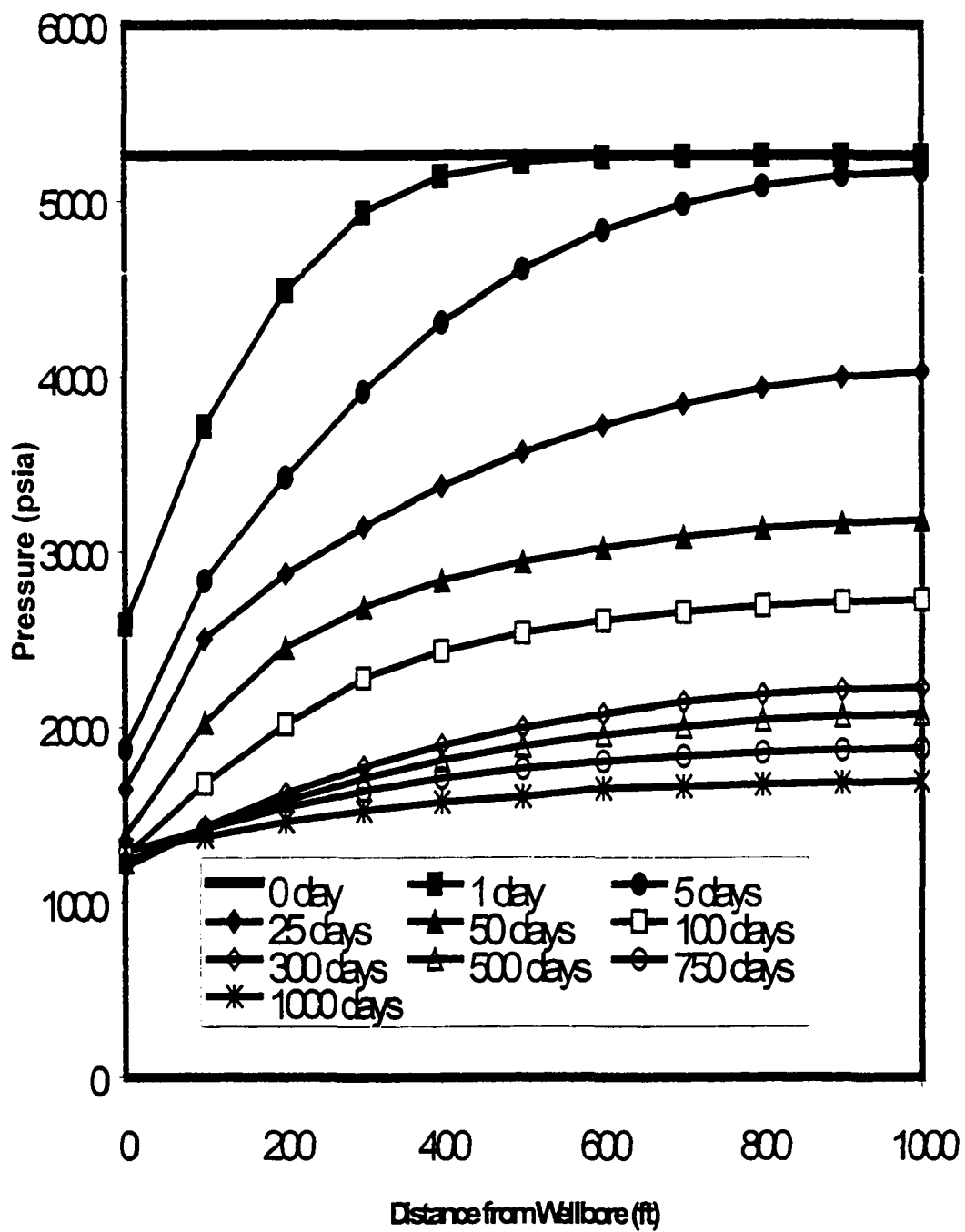


Figure 5.12 Pressure distribution in direction perpendicular to horizontal wellbore at different production time

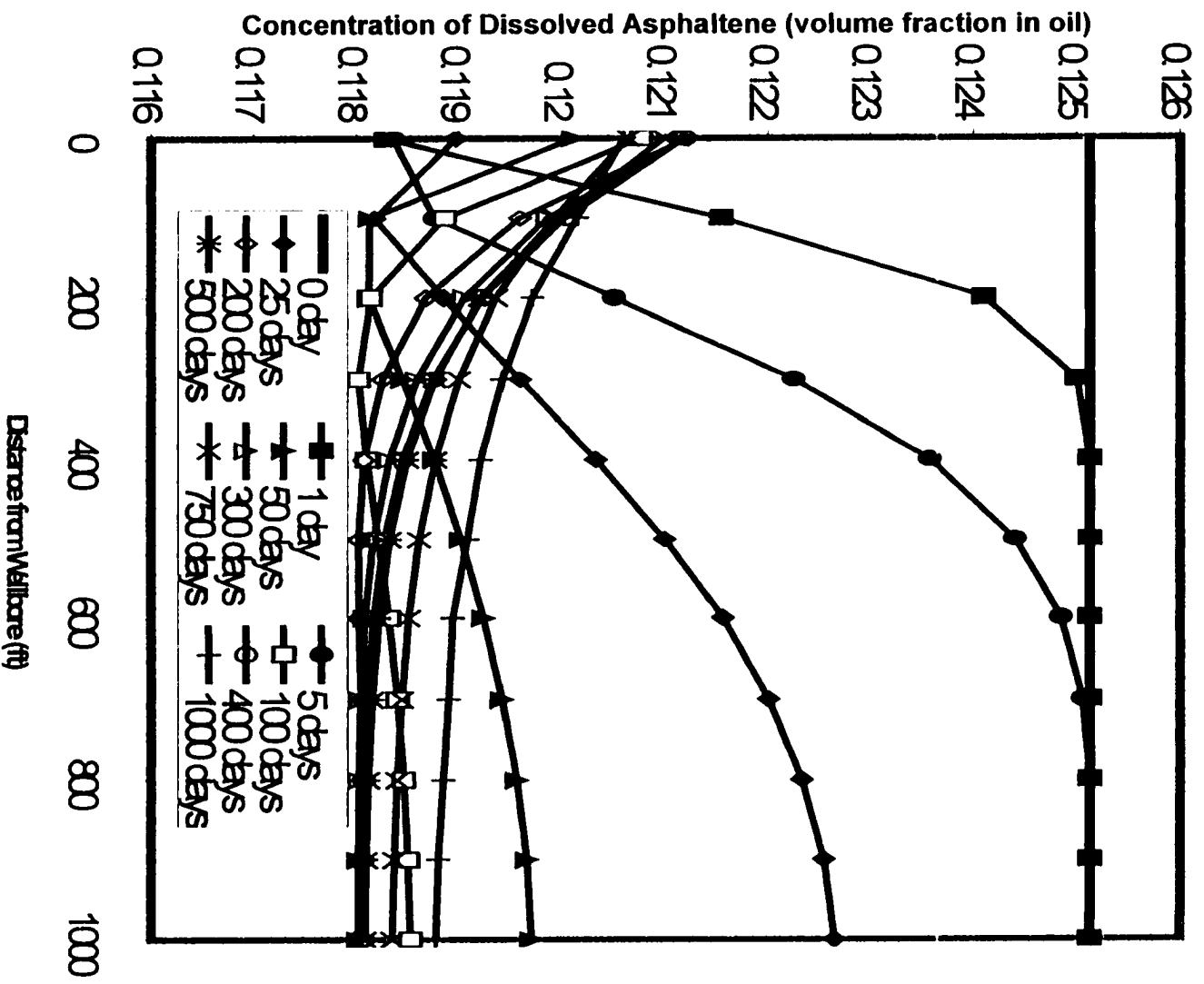


Figure 5.13 Dissolved asphaltene distribution in direction perpendicular to horizontal wellbore at different production time

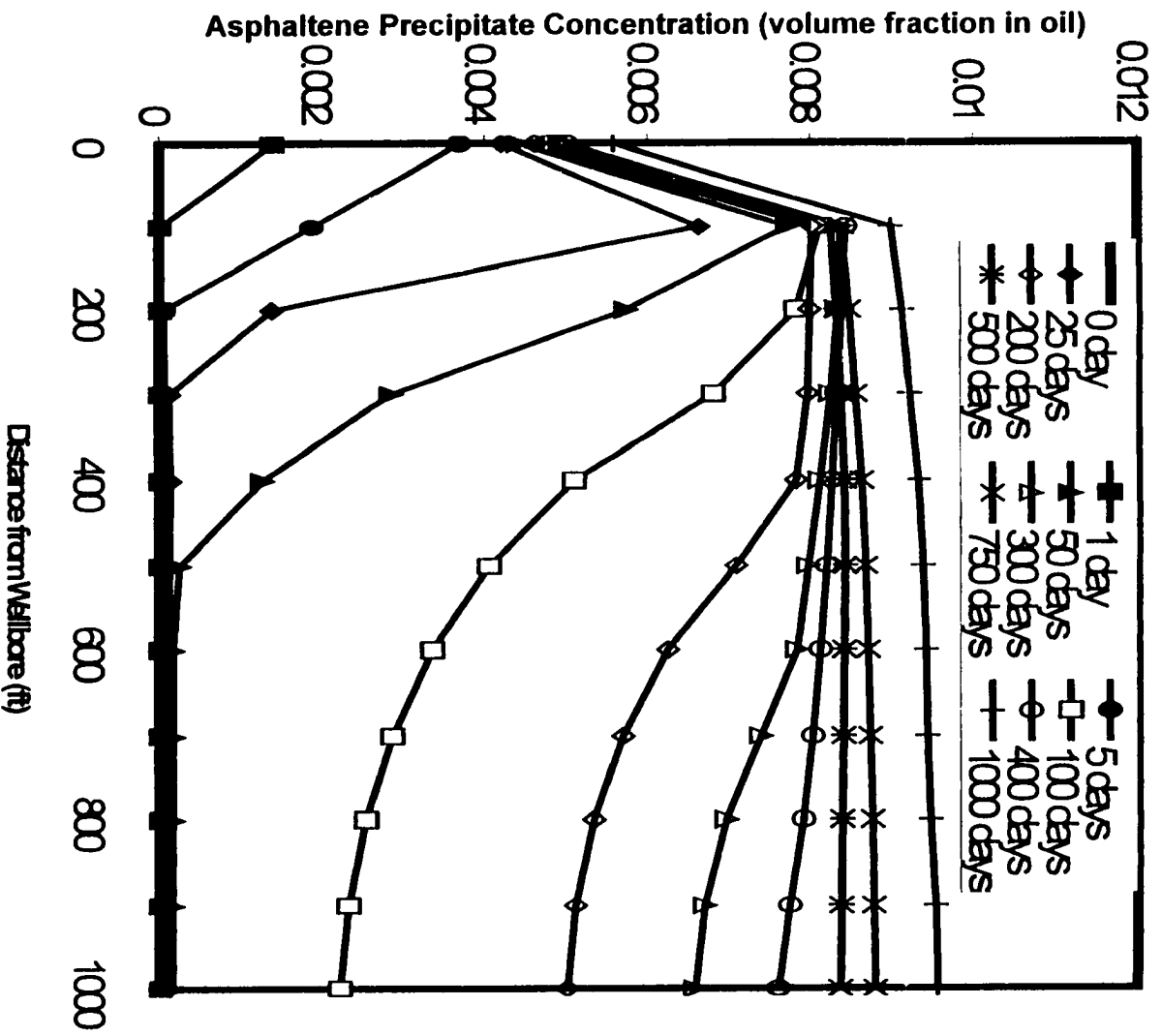


Figure 5.14 Asphaltene precipitate distribution in direction perpendicular to horizontal wellbore at different production time

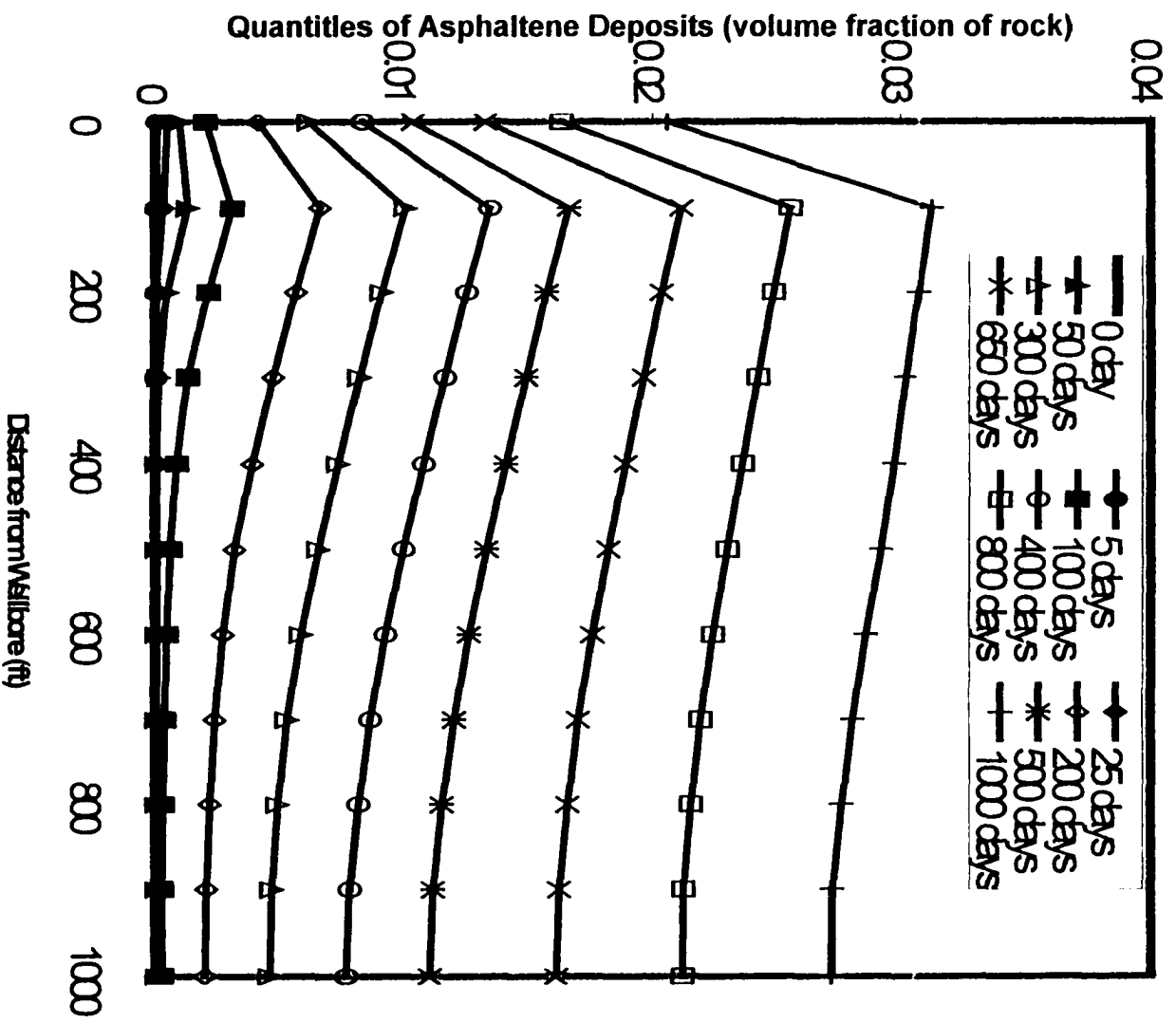


Figure 5.15 Asphaltene deposit distribution in direction perpendicular to horizontal wellbore at different production time

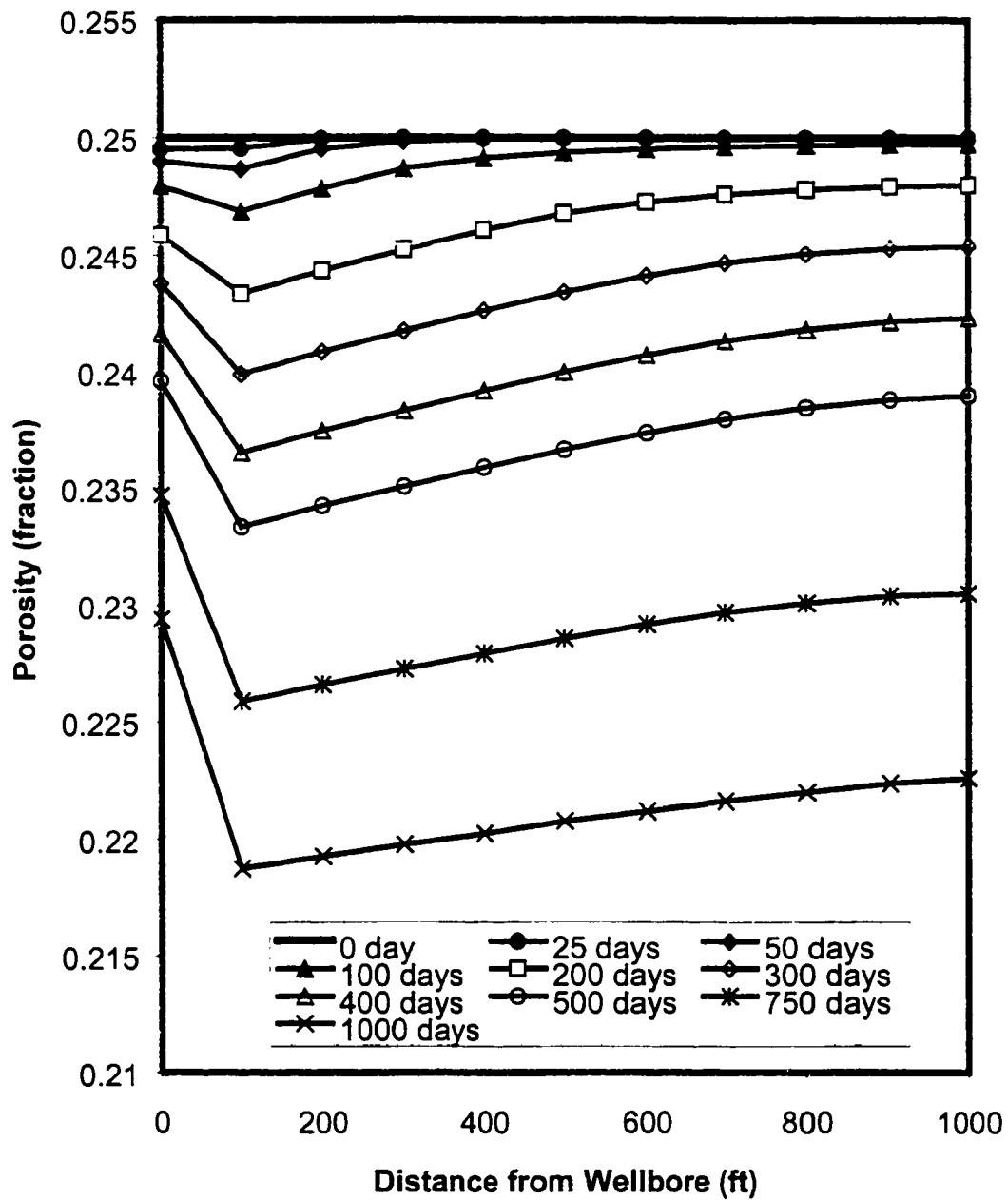


Figure 5.16 Porosity distribution in direction perpendicular to horizontal wellbore at different production time

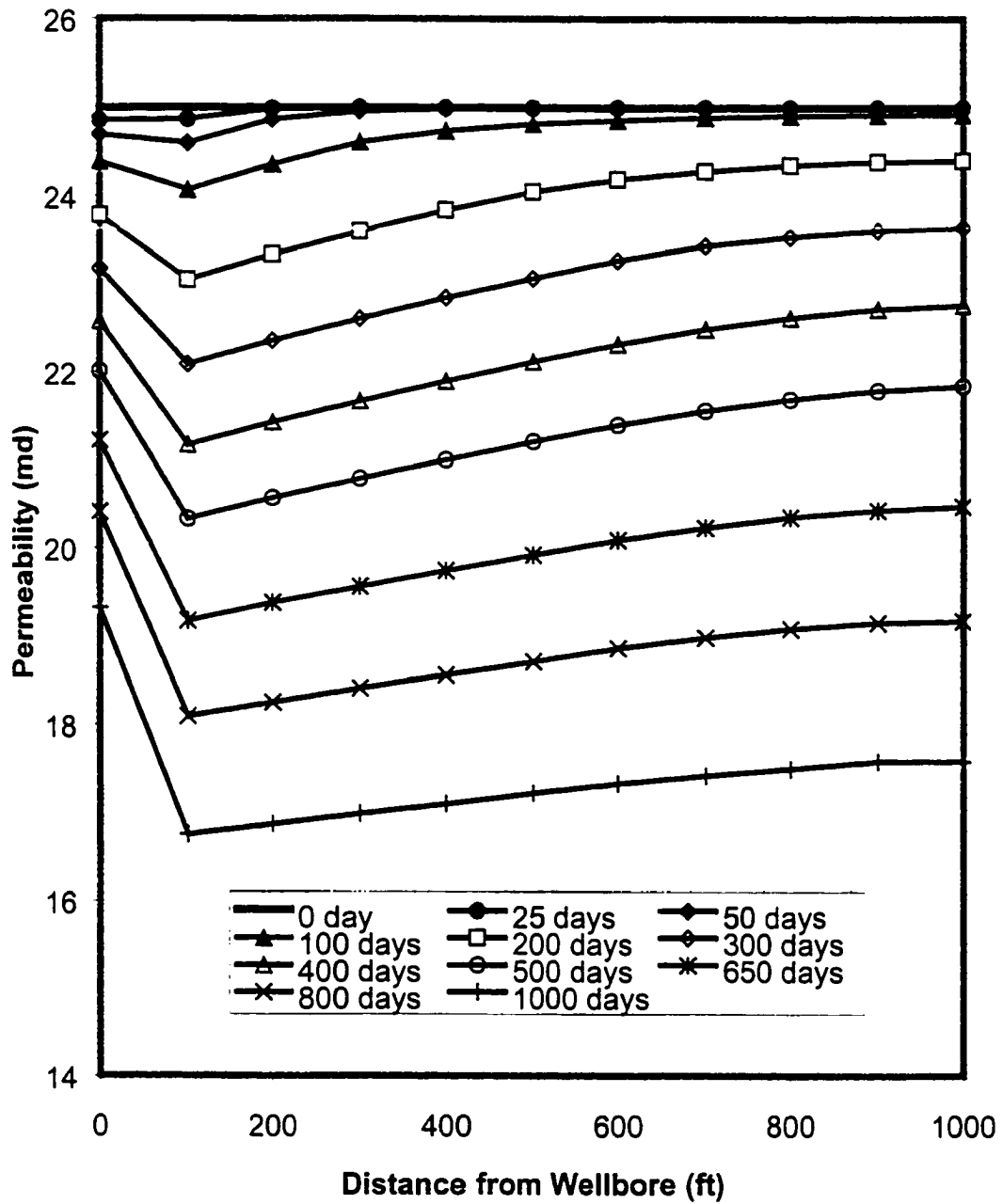


Fig. 5-17 Permeability Distribution in Direction Perpendicular to Horizontal Wellbore at Different Production Time

Chapter VI

Simulation of Simultaneous Deposition of Paraffin and Asphaltene in Core Test

In some situations, paraffin and asphaltene may precipitate and deposit together. For example, during the fracturing or acidizing process, the temperature in the region around the wellbore may decrease below the cloud point because of contact with these fluids. After the fracturing, the well begins to produce oil and the pressure in the near wellbore region declines. The temperature decrease and pressure depletion will cause the paraffin and asphaltene to simultaneously deposit in the near wellbore region. Therefore, it is necessary to investigate the simultaneous deposition of paraffin and asphaltene in porous media.

In this chapter, a model for simultaneous deposition of paraffin and asphaltene in core test is described and numerically solved by a double iteration method. It is then validated by two sets of experimental data.

6.1 Formulation

Horizontal flow is assumed and the effects of gravity are considered negligible. It is also assumed that capillary pressure does not affect the paraffin and asphaltene precipitation and deposition, and thus not considered. With these assumptions, the simultaneous deposition problem can be described using mass balance equations, momentum balance equations, energy balance equation, precipitation and deposition

models for paraffin and asphaltene, porosity and permeability models, and other auxiliary equations.

6.1.1 Mass balance equations

There are two phases and four components in the simultaneous deposition problem. The two phases are vapor and liquid phases, and the four components are gas, oil, paraffin and asphaltene. It is necessary to write mass balance equations for each component.

The gas can exist in the vapor phase as a free gas or dissolved in liquid as a dissolved gas. The gas balance equation can be expressed as follows (Wang et al., 1999):

$$\frac{\partial}{\partial t}(\phi S_v \rho_v + \phi S_L \rho_L w_{GL}) + \frac{\partial}{\partial x}(\rho_v u_v + \rho_L u_L w_{GL}) = 0 \quad (6.1)$$

where, the subscript v and L represent vapor and liquid phases, respectively; ϕ is the porosity; S_v and S_L are the saturation of vapor and liquid phases, respectively; ρ_v and ρ_L are the densities of vapor and liquid phases, respectively; w_{GL} is the mass fraction of the dissolved gas in the liquid. u_v and u_L are the velocities of vapor and liquid phases, respectively; and t and x represent time and space independent variables, respectively.

Since the oil component can exist only in liquid phase, the mass balance for the oil component can be simply expressed as follows (Wang et al., 1999):

$$\frac{\partial}{\partial t}(\phi S_L \rho_L w_{OL}) + \frac{\partial}{\partial x}(\rho_L u_L w_{OL}) = 0 \quad (6.2)$$

where w_{OL} is the mass fraction of the oil in the liquid.

The paraffin component can be dissolved in liquid, suspended in liquid as paraffin precipitate, or deposited in the pore as deposits. Therefore, the mass balance equation of paraffin has the following format (Wang et al., 1999)

$$\frac{\partial}{\partial t}(\phi S_L C_p \rho_p + \phi S_L \rho_L w_{pL}) + \frac{\partial}{\partial x}(\rho_L u_L w_{sPL} + \rho_L u_L w_{pL}) = -\rho_p \frac{\partial E_p}{\partial t} \quad (6.3)$$

In this equation, C_p is the concentration of paraffin precipitate in liquid phase (volume fraction); w_{pL} and w_{sPL} are the mass fractions of the dissolved paraffin and suspended paraffin precipitate in the liquid; ρ_p is the density of paraffin; and E_p is the volume fraction of paraffin deposits in bulk volume of porous media.

Similarly, asphaltene can be dissolved in liquid, suspended in liquid as asphaltene precipitate, or deposited in the pore. Its mass balance equation is expressed as follows (Wang et al., 1999):

$$\frac{\partial}{\partial t}(\phi S_L C_A \rho_A + \phi S_L \rho_L w_{AL}) + \frac{\partial}{\partial x}(\rho_L u_L w_{sAL} + \rho_L u_L w_{AL}) = -\rho_A \frac{\partial E_A}{\partial t} \quad (6.4)$$

where, C_A is the concentration of asphaltene precipitate in liquid phase (volume fraction); w_{AL} and w_{sAL} are the mass fractions of the dissolved asphaltene and suspended asphaltene precipitate in the liquid phase; E_A is the volume fraction of asphaltene deposits in the bulk volume of porous media.

6.1.2 Momentum Balance Equation

Darcy equations for multiphase flow are used for the momentum balance equations, and are expressed as follows:

$$u_v = -\frac{k k_{rv}}{\mu_v} \frac{\partial P}{\partial x} \quad (6.5)$$

$$u_L = -\frac{kk_{RL}}{\mu_L} \frac{\partial P}{\partial x} \quad (6.6)$$

where, k is the absolute permeability of porous media; and k_{RV} and k_{RL} are the relative permeabilities for vapor and liquid phases, respectively. Since the capillary pressure between the vapor and liquid phase is neglected, P represents the pressure for both vapor and liquid phase. μ_V and μ_L are the viscosities of vapor and liquid phases, respectively.

6.1.3 Energy Balance Equation

Assuming that the oil, gas, paraffin, asphaltene, and formation have the same temperature at a certain space point, the total energy balance equation of the oil, gas, and solid system can be expressed as (Wang et al, 1999):

$$\begin{aligned} & \frac{\partial}{\partial t} [\phi S_V \rho_V H_V + \phi S_L \rho_L H_L + (\phi S_L C_P + E_P) \rho_P H_P + \\ & (\phi S_L C_A + E_A) \rho_A H_A + (1 - \phi - E_P - E_A) \rho_F H_F] \\ & + \frac{\partial}{\partial x} (\rho_V u_V H_V + \rho_L u_L H_L + \rho_L u_L w_{SPL} H_P + \rho_L u_L w_{SAL} H_A) = \\ & \frac{\partial}{\partial x} \left\{ \phi S_V K_V + \phi S_L K_L + (\phi S_L C_P + E_P) K_P + \right. \\ & \left. (\phi S_L C_A + E_A) K_A + (1 - \phi - E_P - E_A) K_F \right\} \frac{\partial T}{\partial x} \end{aligned} \quad (6.7)$$

In this equation, H_V, H_L, H_P, H_A and H_F are the enthalpies of the vapor, liquid, paraffin, asphaltene, and porous media, respectively. K_V, K_L, K_P, K_A and K_F are the thermal conductivities of the vapor, liquid, paraffin, asphaltene, and porous media, respectively. T is the temperature of the system.

6.1.4 Paraffin and Asphaltene Precipitation Model

The major factor that affects the solubility of paraffin in crude oil is temperature. The solubility of paraffin in crude oil is given by the following equation (Ring et al, 1994, Wang et al, 1999)

$$X_{PL} = X_{PS} \exp \left[-\frac{\Delta H_f}{R} \left(\frac{1}{T} - \frac{1}{T_{PM}} \right) \right] \quad (6.8)$$

where, X_{PL} represents the mole fraction of the paraffin dissolved in the oil as a function of temperature, T ; X_{PS} is the mole fraction of the paraffin precipitate in the total precipitates of paraffin and asphaltene; ΔH_f is the latent heat of fusion of the paraffin; R is the ideal gas constant; and T_{PM} is the melting point temperature of fusion of the paraffin.

The model described in Chapter III was used to calculate the asphaltene solubility in the crude oil.

6.1.5 Deposition Models for Paraffin and Asphaltene

The deposition model must include surface deposition, pore throat plugging, and entrainment of deposits, as shown in the following relationship:

$$\frac{\partial E_p}{\partial t} = \alpha_p S_L C_p \phi - \beta_p E_p (v_L - v_{cr,L}) + \gamma_p u_L S_L C_p \quad (6.9)$$

$$\frac{\partial E_A}{\partial t} = \alpha_A S_L C_A \phi - \beta_A E_A (v_L - v_{cr,L}) + \gamma_A u_L S_L C_A \quad (6.10)$$

In Eqs. (6.9) and (6.10), it is assumed that the critical interstitial velocities of liquid to move paraffin and asphaltene deposits are the same. The first term represents the surface deposition, and α_p and α_A are the surface deposition coefficients for paraffin

and asphaltene. The second term represents the entrainment of deposits, and β_p and β_A are the entrainment coefficients for paraffin and asphaltene. The last term represents the pore throat plugging deposition, and γ_p and γ_A are the pore throat plugging deposition coefficients for paraffin and asphaltene.

Whether or not the plugging deposition will occur is determined by the following criteria:

$$\gamma_j = \gamma_{ji}[1 + \sigma_j(E_p + E_A)], D_{pt} \leq D_{p_{cr}}, j = P, A \quad (6.11)$$

$$\gamma_j \equiv 0 \text{ otherwise, } j = P, A \quad (6.12)$$

γ_{ji} is the instantaneous plugging deposition rate constant. σ_j represents σ_p or σ_A , both of which are constants. Other variables are the same as those described in Chapter IV.

6.1.6 Porosity and Permeability Reduction Models

The instantaneous, local porosity, ϕ , can be calculated using the following equation (Wang et al., 1999):

$$\phi = \phi_0 - E_p - E_A \quad (6.13)$$

The instantaneous, local permeability, k , is given by the following:

$$k = f_p k_0 \left(\frac{\phi}{\phi_0} \right)^3 \quad (6.14)$$

6.1.7 Auxiliary Equation

The sum of the saturation of vapor and liquid phases should be equal to 1, as expressed by:

$$S_v + S_L = 1 \quad (6.15)$$

The above equations form the mathematical model for the simultaneous deposition of paraffin and asphaltene in core test. In addition to these model equations, other correlations are required to calculate the properties of fluids, such as viscosities of vapor and liquid. The related correlations reported by McCain (1990) were used in these calculations.

6.3 Numerical Solution

The numerical model of the equations described in the previous section was developed using an implicit finite-difference method. The time derivative was discretized with first order backward approximation and space derivative was discretized using two-order central finite difference approximation. It was assumed that time step and grid size were constants. A point-centered grid system was used. Because the equations are strongly coupled and nonlinear, they were solved by a double iteration method as shown in Figure 6.1. The two inside iterations solve for the pressure and the temperature distributions with parameters and coefficients from the last outside iteration. Then, the outside iteration solves for all the variables (pressure, temperature, saturations, porosity, and permeability) together with renewal of the values of the parameters and coefficients.

6.3 Applications

For validation of the model developed in this Chapter, two sets of the reported core test data, involving a simultaneous deposition of the paraffin and asphaltene by cooling of the oil, was used. In each case, the simulated results were compared to the experimental data in order to determine the model parameters. The fluid and core data, the time increments and grid point spacing used in the numerical solution and the best estimates of the parameters are presented in Tables 6.1 and 6.2. In this application, it is assumed that paraffin and asphaltene have the same values of deposition model parameters.

Since the compositions and bubble point pressures of crude oils were not reported in Sutton and Roberts' paper (1974), the typical composition of the crude oil given in Table 3.1 was used as compositions of crude oils in both Case 1 and Case 2. The bubble point pressures of crude oils in both cases was assumed to be 2050 psia. The value of C_{7+} shift parameter was adjusted to match asphaltene content in crude oils used in each case. The flowrates were not reported in the paper and assumed $0.38 \text{ ft}^3 / \text{day}$ in Case 1 and $0.30 \text{ ft}^3 / \text{day}$ in Case 2 following Ring et al. (1994). The backpressure is assumed 1900 psia in both cases.

Case 1 involved one set of experimental results of Sutton and Roberts (1974). A description of the experimental procedure follows. First, a Berea sandstone core saturated with a Shannon Sand crude oil was heated to 54.4°C without flow. Then, the outlet of the core was cooled to 21.1°C (the cloud point of the oil is 37.8°C) for 2 hours

without flow. Finally, the flow experiment was carried out by injecting the Shannon Sand crude oil at the temperature of 54.4°C. The temperature of the outlet of the core was kept at 21.1°C, which is 16.7°C below the cloud point temperature of the oil sample. The Shannon Sand crude oil contains 4.1% (weight) paraffin and 0.7% (weight) asphaltene. Following Ring et al. (1994), 12 grid blocks were also used in this study. Other data are given in Table 6.1 and 6.2. The simulated results were satisfactory as illustrated in Figure 6.2. The 2-hour cooling process at the outlet of the core before the initiation of the fluid flow was simulated first. Some surface deposition was found to occur during this cooling process. After the fluid began to flow, only surface deposition occurred. Pore throat plugging and entrainment of deposits did not occur in this experiment based on the estimated values of deposition parameters reported in Table 6.2.

Case 2 involved the flow of a Muddy formation crude oil through a Berea sandstone core. Similarly, the temperature at the outlet of the core was kept at 21.1°C, which is 13.9°C below the cloud point temperature (35°C) of the oil sample. This oil sample contained 6.1% (weight) paraffin and 0.1% (weight) asphaltene. Other data are given in Table 6.1. The simulated results were also satisfactory as shown in Figure 6.3. In this experiment, only surface deposition occurred. Pore throat plugging and entrainment of deposits did not occur based on the values of deposition parameters obtained in history match (Table 6.2).

6.4 Summary

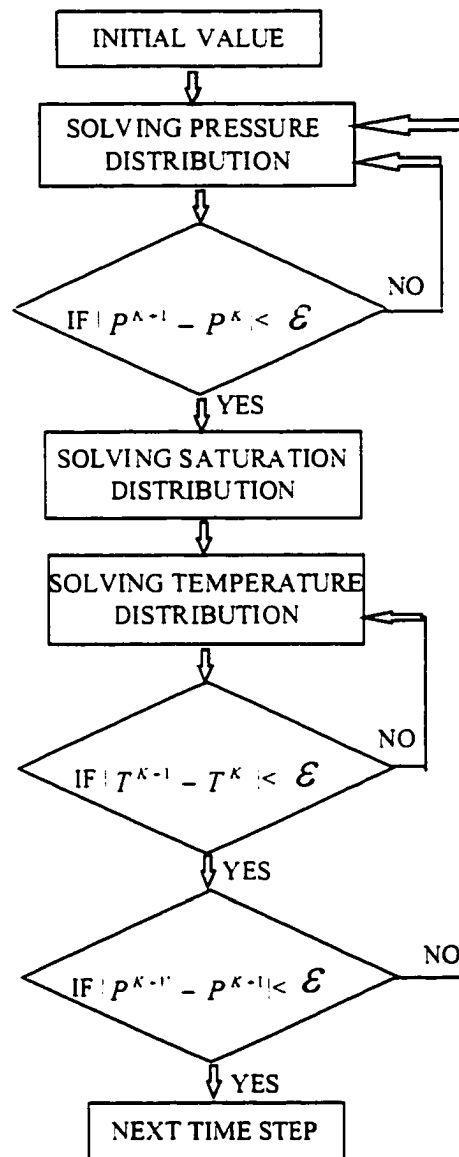
In this chapter, a model involving the simultaneous deposition of paraffin and asphaltene in porous media caused by temperature decrease and pressure depletion was presented. The model was numerically solved by a double iteration method, and then applied to two sets of experimental data. Good matches between experimental data and simulated results were achieved, indicating that the method described in this chapter can adequately simulate the simultaneous deposition of paraffin and asphaltene in porous media. The surface deposition may occur before and after fluid flowing when the conditions of temperature and pressure become suitable. Based on the parameter values, the surface deposition is the dominant mechanism of organic deposition.

Table 6.1 Data used for Cases 1 and 2

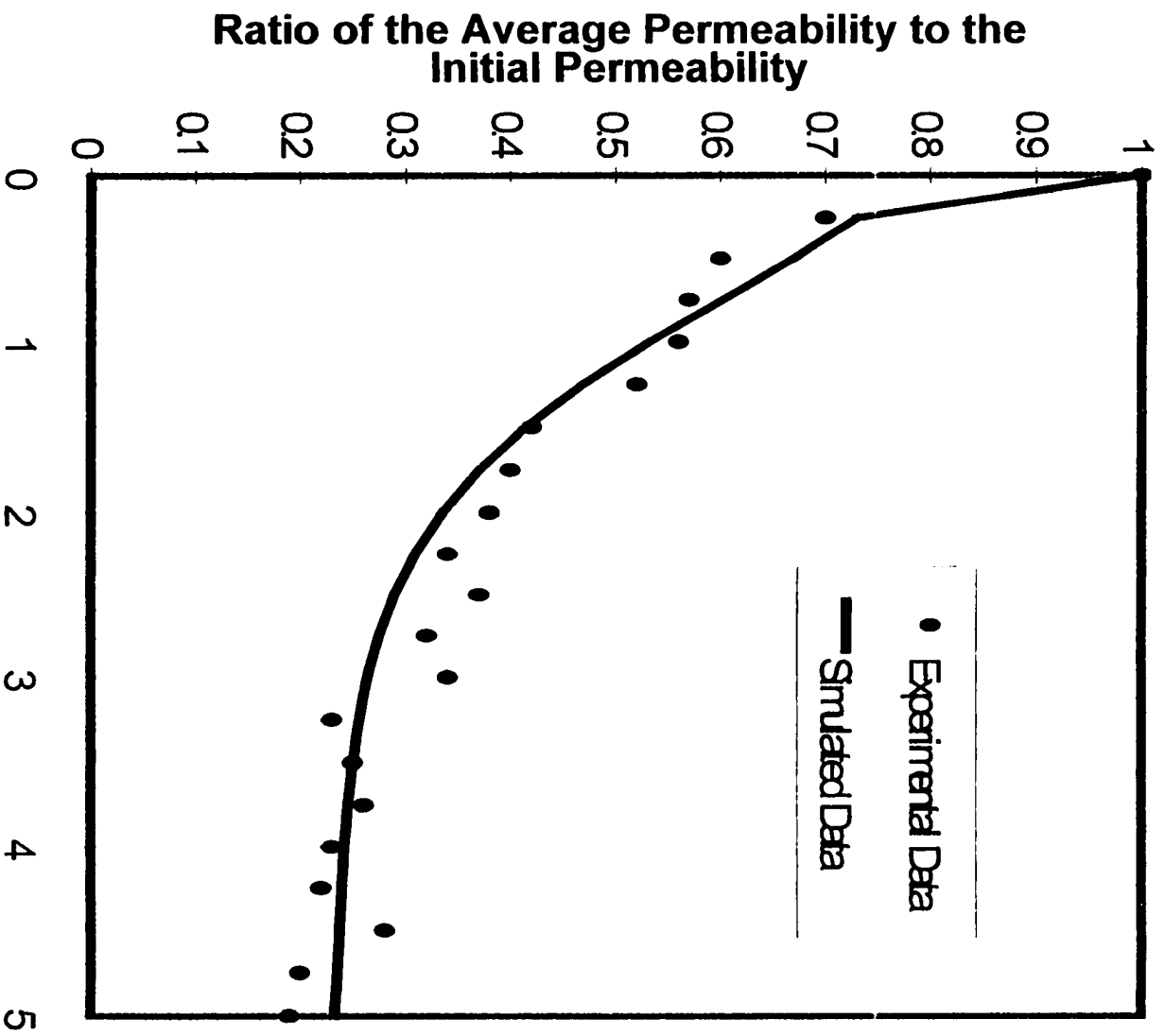
CASE	1	2
Temperature		
T_{in} , °C	54.4	54.4
T_{out} , °C	21.1	21.1
Gas pseudo-component		
M_g , g/gmole	16.0	16.0
ρ_{gc} , g/cm ³	0.00083	0.00083
Oil pseudo-component		
M_o , g/gmole	104.11	122.51
ρ_{oc} , g/cm ³	0.72	0.75
Paraffin pseudo-component		
M_p , g/gmol	522.4	478.7
w_{ps} (%)	4.1	6.1
ρ_{pic} , g/cm ³	0.83	0.98
T_{pm} , °C	75.7	71.7
ΔH_p , cal/g-mole	26,000	23,600
Asphaltene pseudo-component		
M_A , g/gmol	2,500.0	2,500.0
w_A (%)	0.7	0.1
ρ_{ac} , g/cm ³	1.1	1.1
V_A , cm ³ /mole	1020	1020
δ_A , (MPa) ^{1/2} (at 0 °C)	20.04	20.04
Core Properties		
L, cm	30.5	30.5
D, cm	2.5	2.5
ϕ_0 , fraction	0.25	0.25
k_0 , darcy	0.405	0.314
Experimental Data		
Bubble point pressure, <i>psia</i>	2050	2050
Flowrate, <i>ft</i> ³ / <i>day</i>	0.38	0.30
Back pressure, <i>psia</i>	1900	1900

Table 6.2 Data used to simulate the experimental data and parameter values obtained in history match

Data for Simulation		
Δx , cm	2.54	2.54
Δt , sec	40.0	40.0
Number of blocks	12	12
Deposition Parameters		
D_{ocr} , cm		
$v_{cr,L}$, cm/sec		
$\alpha_p = \alpha_A$, 1/sec (before flow)	0.000105	0.000121
$\alpha_p = \alpha_A$, 1/sec (after flow)	0.0243	0.0186
$\beta_{p_i} = \beta_{A_i}$, 1/cm	0.0	0.0
$\gamma_{p_i} = \gamma_{A_i}$, 1/cm	0.0	0.0
$\sigma_p = \sigma_A$, constant	0.0	0.0
f_p , constant	1.0	1.0



**Figure 6.1 Flowchart for the computing scheme
(Wang et al., 1999)**



**Figure 6.2 Comparison of the simulation and
Sutton and Roberts(1974) experimental results
for Case 1**

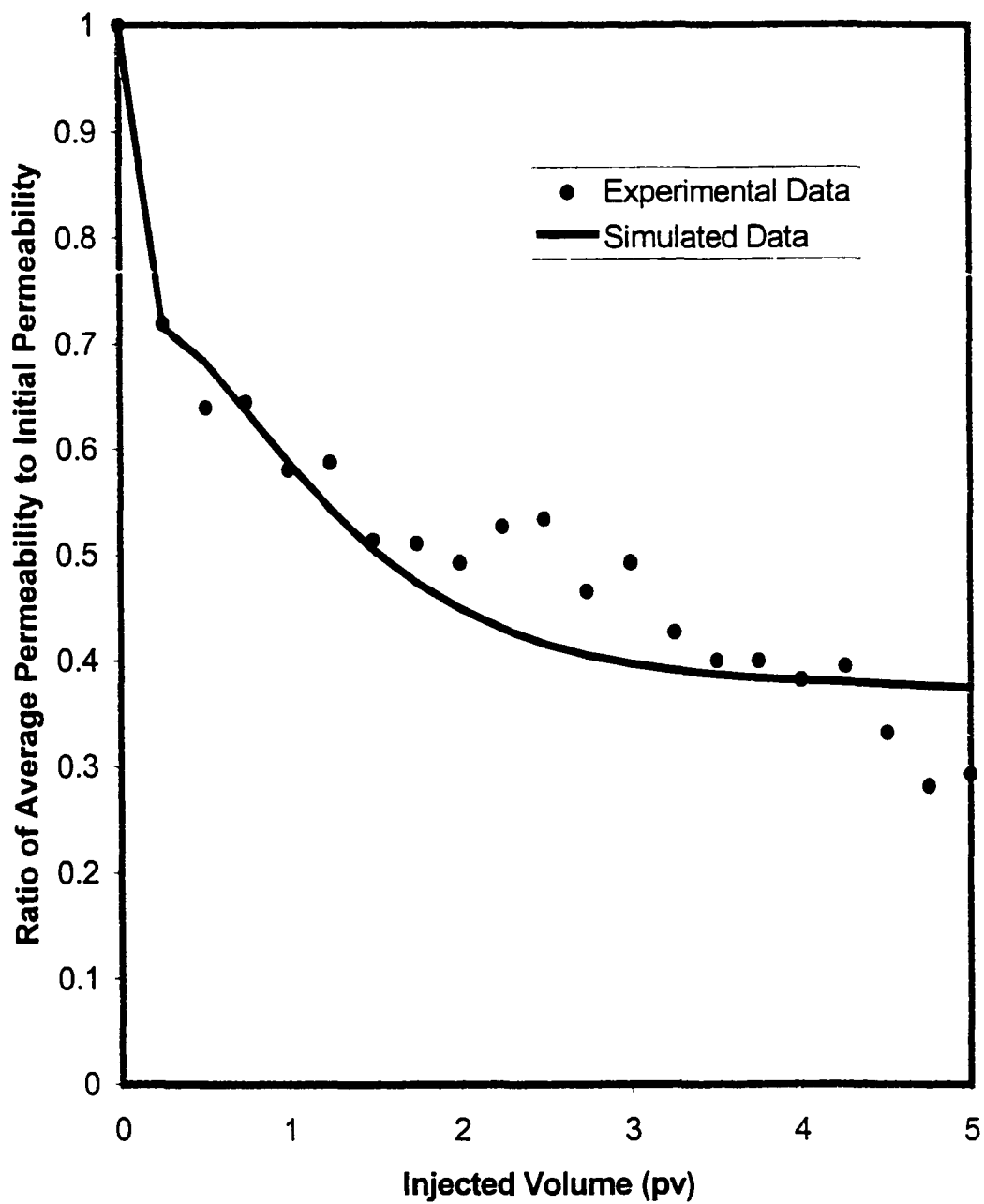


Fig.6.3 Comparison of the Simulation with Sotton and Roberts (1974) Experimental Results for Case 2

Chapter VII

Conclusions and Recommendations

7.1 Conclusions

In this study, a polymer solution model for asphaltene precipitation was applied to simulate asphaltene precipitation during pressure depletion. With some improvements in calculations, the model matched the experimental data of asphaltene precipitation very well. An asphaltene deposition model was established and tested against six sets of experimental data. In all cases, good matches were achieved. This is the first model that was extensively tested. The asphaltene precipitation and deposition models were then incorporated into three-dimensional and three-phase black oil simulator. Two typical cases involving asphaltene deposition in reservoirs developed by a vertical or a horizontal well were run with the simulator. In both cases, the simulator produced reasonable results, demonstrating the ability of the simulator for field application. This is the first simulator that has the ability to simulate asphaltene deposition in reservoirs with horizontal well during the primary oil recovery. Finally, the model for the simultaneous deposition of paraffin and asphaltene in porous media was established and numerically solved by a double iteration method. The model was successfully applied to simulate two experimental data. Based on the above studies, the following conclusion can be drawn:

1. The polymer solution model can successfully simulate asphaltene precipitation during primary oil recovery.

2. The deposition model described in this study can sufficiently simulate asphaltene deposition in porous media.
3. Whenever the asphaltene deposition occurs in porous media, surface deposition always occurs. Therefore, the surface deposition is a predominant mechanism of asphaltene deposition.
4. The model and simulator presented in this study can adequately model and simulate the asphaltene precipitation and deposition in petroleum reservoirs with either vertical or horizontal wells during primary oil recovery.
5. The pattern of asphaltene deposition in the reservoir with vertical wells and the reservoir with horizontal well were different because of the large production rate of horizontal well.
6. The asphaltene may deposit throughout the petroleum reservoir, and not just in the near wellbore region.
7. The model for the simultaneous deposition of paraffin and asphaltene presented in this study can be successfully applied to simulate the simultaneous deposition of paraffin and asphaltene in porous media.

7.2 Recommendations

Based on this study, the following recommendations are made,

1. The present model and simulator are recommended to simulate real asphaltene deposition problems in petroleum reservoirs during primary oil recovery.

2. Although the asphaltene molecular weight distribution occurs within a relatively small range, the asphaltene molecular weight distribution effect should be considered in further research.
3. More experimental results are needed to test the present model for the simultaneous deposition of paraffin and asphaltene in porous media.
4. The model for the simultaneous deposition of paraffin and asphaltene can be extended to three-dimensional case and applied to simulate the simultaneous deposition of paraffin and asphaltene in petroleum reservoirs.

NOMENCLATURE

a_T	coefficient in Peng-Robinson equation
A	cross-sectional area of core samples, cm^2
API	oil gravity, API
b	coefficient in Peng-Robinson equation
c	coefficient in modified Peng-Robinson equation
C_p	paraffin concentration in liquid phase, volume fraction
C_A	asphaltene concentration in liquid phase, volume fraction
D_{pt}	mean diameter of pore throats, cm
$D_{p_{ter}}$	critical diameter of pore throats, cm
E	volume fraction of deposited asphaltene in bulk volume
E_A	volume fraction of deposited asphaltene, dimensionless
E_p	volume fraction of deposited paraffin, dimensionless
f_p	permeability modification coefficient
H_v	enthalpy of vapor phase, cal/cm^3
H_L	enthalpy of liquid phase, cal/cm^3
H_p	enthalpy of paraffin, cal/cm^3
H_A	enthalpy of asphaltene, cal/cm^3
H_F	enthalpy of formation, cal/cm^3

ΔH_A	latent heat of fusion of asphaltene, cal/g-mole
ΔH_p	latent heat of fusion of paraffin, cal/g-mole
K_v	thermal conductivity of vapor, cal/sec-cm- $^{\circ}K$
K_L	thermal conductivity of liquid, cal/sec-cm- $^{\circ}K$
K_p	thermal conductivity of paraffin, cal/sec-cm- $^{\circ}K$
K_A	thermal conductivity of asphaltene, cal/sec-cm- $^{\circ}K$
K_F	thermal conductivity of formation, cal/sec-cm- $^{\circ}K$
k	instantaneous permeability, md
k_0	initial permeability, md
k_{RV}	relative permeability of vapor phase, dimensionless
k_{RL}	relative permeability of liquid phase, dimensionless
L	length of the core sample, cm
M_g	molecular weight of gas, g/g - mole
M_o	molecular weight of oil, g/g - mole
M_p	molecular weight of paraffin, g/g - mole
M_A	molecular weight of asphaltene, g/g - mole
P	pressure, psia or atm
R	ideal gas constant, 1.987 cal/(mole- $^{\circ}K$)
Q	flow rate, cm^3 / sec
s_i	shift parameter of i th component, dimensionless

S_V	saturation of vapor phase, dimensionless
S_L	saturation of liquid phase, dimensionless
t	time independent variable, sec
T	temperature, $^{\circ}F$ or $^{\circ}R$
T_{AM}	melting point temperature of asphaltene, $^{\circ}C$
T_{PM}	melting point temperature of paraffin, $^{\circ}C$
u	superficial velocity, cm/sec
u_V	velocity of vapor, cm/s
u_L	velocity of liquid phase, cm/s
U	total energy of a system, erg
$\Delta U_{\text{vaporization}}$	internal energy change during the vaporization of a unit mole of liquid, $kJ / mole$
v	interstitial velocity, cm/sec
v_{cr}	critical interstitial velocity for entrainment, cm/sec
V_A	molar volume of asphaltene, $m^3 / kmole$
V_{avg}	molar-fraction-weighted average molar volume of asphaltene, $m^3 / kmole$
V_L	molar volume of liquid phase, $m^3 / kmole$
V_r	molar volume of resin, $m^3 / kmole$
V_M	molar volume, $m^3 / kmole$
V_M^L	molar volume of liquid phase, $m^3 / kmole$

$\tilde{V}_M$	modified molar volume, $m^3 / kmole$
w_{GL}	mass fraction of dissolved gas in the liquid phase, dimensionless
w_{OL}	mass fraction of oil in the liquid phase, dimensionless
w_{PL}	mass fraction of dissolved paraffin in the liquid phase, dimensionless
w_{AL}	mass fraction of dissolved asphaltene in the liquid phase, dimensionless
w_{SPL}	the mass ratio of the paraffin precipitates suspended in liquid to the liquid phase, dimensionless
w_{SAL}	the mass ratio of the asphaltene precipitates suspended in liquid to the liquid phase, dimensionless
x	space independent variable, cm
X_{AL}	mole fraction of asphaltene dissolved in liquid, dimensionless
X_{AS}	mole fraction of the precipitated asphaltene of the total volume of the precipitated paraffin and asphaltene, dimensionless
X_{PL}	mole fraction of paraffin dissolved in liquid, dimensionless
X_{PS}	mole fraction of the precipitated paraffin of the total volume of the precipitated paraffin and asphaltene, dimensionless
y	space independent variable, cm
y_i	molar fraction of i th component
z	space independent variable, cm
z_i	molar fraction of i th component

Greek

ϕ	instantaneous porosity, fraction
ϕ_0	initial porosity, fraction
ϕ_A	volume fraction of asphaltene soluble in the crude oil, fraction
ϕ_r	volume fraction of resin soluble in the crude oil, fraction
ρ_v	density of vapor, g/cm ³
ρ_L	density of liquid phase, g/cm ³
ρ_P	density of paraffin, g/cm ³
ρ_A	density of asphaltene, g/cm ³
ρ_F	density of formation, g/cm ³
ρ_{gsc}	gas density at standard condition, g/cm ³
ρ_{osc}	oil density at standard condition, g/cm ³
μ_v	viscosity of vapor phase, cp
μ_L	viscosity of liquid phase, cp
$\Delta\mu_r$	chemical potential of the resins in the oil phase
$\Delta\mu_r^{cr}$	critical chemical potential of the resins in the oil phase
α_P	surface deposition rate coefficient for paraffin, 1/sec
β_P	entrainment rate coefficient, 1/cm
β_{P0}	instantaneous entrainment rate coefficient, 1/cm

γ_P	plugging deposition rate coefficient for paraffin, 1/sec
γ_{Pi}	instantaneous plugging deposition rate coefficient for paraffin, 1/sec
σ_P	snow-ball effect rate coefficient for paraffin, constant
α_A	surface deposition rate coefficient for asphaltene, 1/sec
β_A	entrainment rate coefficient, 1/cm
β_{A0}	instantaneous entrainment rate coefficient, 1/cm
γ_A	plugging deposition rate coefficient for asphaltene, 1/sec
γ_{Ai}	instantaneous plugging deposition rate coefficient for asphaltene, 1/sec
δ_A	solubility parameter of asphaltene, $(MPa)^{1/2}$
δ_{avg}	volume-fraction-weighted average solubility parameter of liquid phase, $(MPa)^{1/2}$
δ_L	solubility parameter of liquid phase, $(MPa)^{1/2}$
σ_A	snow-ball effect rate coefficient for asphaltene, constant

Subscripts

0	instantaneous
A	asphaltene
cr	critical
e	entrainment
F	formation
G	gas

<i>i</i>	instantaneous
<i>L</i>	liquid
<i>M</i>	melting point
<i>O</i>	oil
<i>p</i>	plugging deposition
<i>P</i>	Paraffin
<i>pt</i>	pore throat
<i>V</i>	vapor

Superscripts

<i>cr</i>	critical
<i>L</i>	liquid phase

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