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DEVELOPMENT OF NMRI SPECTROSCOPY FOR
IMPROVED PETROLEUM RECOVERY--ANNEX VI

Annual Report for 1991

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ABSTRACT

The overall objectives are to develop and apply Nuclear Magnetic Resonance Imaging (NMRI) and CT X-Ray Scanning methods for determining rock, fluid, and petrophysical properties and for fundamental studies of multiphase flow behavior in porous media. Specific objectives are to: 1) develop NMRI procedures for measuring porosity, permeability, pore size distribution, capillary pressure, and wetting characteristics, 2) apply imaging methods for improved methods of determining two- and three-phase relative permeability functions, 3) apply NMRI for development of a better understanding of dispersed phase displacement processes, and 4) apply imaging methods to develop a better understanding of saturation distribution and fingering during miscible displacements. The objectives have been organized into four subtasks. Annual progress reports for each subtask are provided.

New methods have been developed for quantitative determination for fluid saturation distribution during displacement experiments in rocks with different characteristics. A computer code which incorporates saturation information obtained from imaging experiments has been developed for estimating relative permeability and capillary pressure functions from dynamic displacement experiments. The method has been tested with experimental data obtained using x-ray computed tomography. Experiments are being conducted in which saturation is monitored with NMRI for further testing of the method. Pulsed field gradient NMR diffusion measurement have been conducted in porous media to characterize microscopic structure of porous media, and the analysis of the experimental data has been initialized. The results indicate that restricted diffusion is observed and that theory developed for the bulk fluid case does not adequately represent the experiments in porous media. More detailed analysis of these experiments will be conducted in the future.

Significant progresses have been made in characterizing wettability of porous media using NMR relaxation time measurement. Various model systems have been tested, and those factors which are critical for such measurements have been identified. NMR restricted diffusion was used to determine droplet size distribution in bulk emulsion samples. The distribution agreed with the measurement by optical method. Studies of thin film stability have also been very fruitful. Preparation for the surfactant based imbibition and solution gas drive experiment is underway. Construction of the apparatus is near completion.

EXECUTIVE SUMMARY

The overall objectives of this project are to develop and apply Nuclear Magnetic Resonance Imaging (NMRI) and CT X-Ray Scanning methods for determining rock, fluid, and petrophysical properties and for fundamental studies of multiphase flow behavior in porous media. The project has been organized into four subtasks that deal with the development and application of NMRI and CT Scanning for determination of rock-fluid and petrophysical properties, characterization of conventional multiphase displacement processes, characterization of dispersed phase processes, and studies of miscible displacements.

New methods have been developed for quantitative determination for fluid saturation distribution during displacement experiments. The methods allow for the accurate determination of saturations for a number of different characteristic rock types. A computer code which incorporates saturation information obtained from imaging experiments has been developed for estimating relative permeability and capillary pressure functions from dynamic displacement experiments. The method has been tested with experimental data obtained using x-ray computed tomography. Experiments are being conducted in which saturation is monitored with NMRI for further testing of the method. Analysis of pulsed field gradient NMR experiments to characterize the microscopic structure of porous media has been initiated. The results indicate that restricted diffusion is observed and that theory developed for the bulk fluid case does not adequately represent the experiments in porous media. More detailed analysis of these experiments will be conducted in the future.

The study of using NMR relaxation times to characterizing wettability of porous media is near completion. Summarized report of this study is expected to be ready early next year. Several experiments are being performed to study the dispersed phase properties in porous media. CT scanning method is used to study dynamic displacement of dispersed phase in porous media. Various tests are being performed and specific results will be reported soon. The studies of thin film stability has provided useful data for understanding dispersed phase stability in porous media. An experiment designed to improve oil recovery will be performed. The output of this last experiment is believed to be able to provide direct economic benefits for the oil industry. The overall studies of Subtask 3 is being executed smoothly toward our designed objectives.

Work to develop the CT scanner as a viable instrument to study viscous fingering is continuing and is nearly complete. Developmental work completed to date includes: (1) designing a core containment device, (2) designing a flow system, (3) developing viable CT scanner operating procedures, (4) developing data transfer procedures from the CT scanner to post-processors, and (5) developing post-processing software for image reconstruction. Several unit mobility ratio core tests have been carried out to test the viability of our experimental procedures. Adverse mobility ratio core tests are now underway to study viscous fingering using the CT scanner.

SUBTASK 1: THE DEVELOPMENT OF MRI AND CT SCANNING FOR THE DETERMINATION OF ROCK-FLUID AND PETROPHYSICAL PROPERTIES

**Principal Investigators: J. W. Jennings / Maria A. Barrufet
Department of Petroleum Engineering**

Introduction

In the fourth quarterly report for this grant I introduced myself as the proposed replacement principal investigator for this project due to the retirement of professor Jennings. This annual report is based upon the information I collected up to this point, based upon the previous reports submitted to DOE as well as the documentation left by three graduate students who graduated this summer with an M.S. degree in Petroleum Engineering.

The global objective of this research is the development of NMRI and CT scanning techniques to estimate rock-fluid and petrophysical properties. To accomplish this objective several subordinate tasks were proposed:

- (1) Measure porosity and porosity distribution of typical reservoir rocks.
- (2) Measure saturation and saturation distributions of typical reservoir rocks.
- (3) Statistical analysis of the data and correlation of (1) and (2).
- (4) Permeability determinations using standard NMR spectroscopy.
- (5) Pore connectivity information and fluid velocity determinations.
- (6) Wettability studies.

During the course of this research several technical difficulties were found and several operational procedures had to be customized to properly analyze data from a porous media.

Technical Progress:

The paragraphs to follow indicate the accomplishments claimed and a brief explanation of whether a particular objective has been fully or partially achieved, and/or should be continued /improved or modified.

In the past year measurements of rock porosity and two-phase saturation were made on Austin chalk, German sandstone, and Bentheim sandstone rocks. The properties were measured on a global as well as on a local basis (i.e. profiles). The local values allowed the determination of the distribution of these properties within the core. From the distribution of porosity a correlation length was calculated.

The correlation length is a statistical method for describing the heterogeneity of the core. A goal of this project was to determine the relationship between porosity distribution and saturation distribution. According to the work accomplished only a qualitative relationship could be established. More data and different process conditions in the flow displacement experiments are required to establish a quantitative relation.

a) Statistical Analysis and Software Development:

The students Matt Marek and Blake Shivers developed algorithms for reading 3-D local porosity data, convert it to profile data, and have it ready for further statistical manipulation. The transformation of the raw NMR signal to useful data appears not to be applicable to other forms of NMR sequences. Therefore this software is not of general use.

The graduate student Blake Shivers, applied spatial statistics to summarize the spatial variability of porosity in reservoir rocks. These statistical indicators provide a means for quantifying the similarity between sample values as a function of the distance between their locations. The statistical indicators were: the h-scatterplot, correlation coefficient, autocorrelation, semivariance and porosity correlation length. This work has been completed.

Software to determine saturation distributions within the core has also been written and it limited to the experimental conditions used.

b) NMR Flow-Experiments

Detailed preparations for a two-phase immiscible flow experiment were made. These included the design of the flow cell, flow system and the establishment of adequate experimental procedures. The experimental procedure allowed a determination of two-phase saturation distributions during an immiscible displacement process.

Saturation and porosity profiles in the directions perpendicular to flow (x and y) as well as parallel to the flow direction (z) were reported for a variety of core samples. The saturation profiles, under the process conditions used, in the x- and y- directions do not show a significant channeling or fingering. More realistic reservoir pressures, and additional displacement conditions should be further analyzed. Figures 1 and 3 show these distributions at breakthrough and floodout for an Austin Chalk core sample. These figures were included in the third quarterly report.

Three-dimensional saturation data sets were collected on cores with various porosity distributions as well as composite cores with two distributions. This preliminary analysis includes correlating the two-phase saturation distributions with the results from the porosity distribution experiments. Saturation profiles for various cores were compared with porosity distributions. Saturation values are essentially uniform at breakthrough regardless of the core average porosity, suggesting that porosity does not affect the saturation distribution during the initial stages of the displacement process. Non uniformity of water saturations at gas floodout suggest that the porosity distributions affect the saturation distribution towards the end of the displacement process. Again, additional data is required at a variety of confining pressures and displacement fluid flow rates. This constraint points the need of building an appropriate core holder for more realistic reservoir pressures.

c) Technical Problems:

From a practical view point, imaging of most sandstone reservoir rocks was not very successful with the MRI. This is because of the line broadening effect of some paramagnetic materials composing the rocks.

The intensity of the recorded NMR signal consists of two components. The first component is the portion of the signal generated by the sample. The second component is

the portion of the signal generated by the MRI instrument itself and it is random. One of the major problems of this work was to minimize this random noise or to improve the signal to noise ratio.

As an effort to solve this problem the following techniques were tried:

- 1) Increase the number of data acquisitions from 1 to 4. The variance was reduced by half at the expense of increasing the imaging time by four.
- 2) Use of block averaging. The variance is reduced but the cost is a coarser resolution from 0.106 mm^3 to 1.696 mm^3 .

Currently, there are available more efficient pulsing techniques and a new coil design has been bought which will maximize the signal to noise ratio.

Publications:

During the course of this grant three students graduated with an M.S. degree in Petroleum Engineering. Information concerning thesis title, author and date are as follows:

"The Development of Magnetic Resonance Imaging for the Determination of Porosity in Reservoir Core Samples"

Byron Blake Sherman, May 1991.

"The Development of MRI for the Determination of Porosity Distribution in Reservoir Core Samples"

Jon Blake Shivers, August 1991.

"The Development of MRI for the Determination of Fluid Saturation Distributions in Reservoir Core Samples"

Matt Marek, August 1991.

Future Plans:

Among the original objectives stated in this proposal were: (1) use of standard NMR spectroscopy for indirect determination of permeability on a global as well a local, or spatial, basis, and (2) determine or estimate pore connectivity for the development and application of theoretical models for multiphase flow through porous media. Up to this point no attempts have been made yet to accomplish these goals. Dr. Carl Edwards and I discussed the available experimental techniques, the various forms of data processing, the research capabilities and limitations and we expect to have positive results for these two objectives by the end of this grant. The fourth quarterly report has more details about the future plans.

FIGURE 1 - AUSTIN CHALK SATURATION PROFILE IN THE X- AND Y-DIRECTIONS

FIGURE 2 - AUSTIN CHALK SATURATION PROFILE IN THE Z-DIRECTION

FIGURE 3 - COMPOSITE SATURATION PROFILE IN THE Z-DIRECTION

SUBTASK 2: DEVELOPMENT OF MRI AND CT SCANNING FOR CHARACTERIZING CONVENTIONAL MULTIPHASE DISPLACEMENT PROCESSES

**Principal Investigator: A. T. Watson
Department of Chemical Engineering**

INTRODUCTION

Many reservoir processes involve the flow of two immiscible fluid phases (e.g., oil and water) or three fluid phases (e.g., oil, water and gas). In spite of its fundamental importance for oil recovery, many aspects of multiphase flow are not well understood. Flow in macroscopically homogeneous porous media is normally described using relative permeability and capillary pressure functions. However, there are no reliable methods for predicting those quantities from microscopic observations, and no reliable relationships for predicting variations of that property with different conditions, such as wettability, flow velocity, surface chemistry and temperature. The lack of reliable methods for determining both two- and three-phase relative permeability functions from laboratory experiments has hindered the development of useful predictive methods.

Nuclear magnetic resonance spectroscopy and imaging (NMR and MRI) techniques can provide unprecedented information about fluid states in porous media. To date, such information has largely been used in a qualitative fashion. We are developing NMR spectroscopic and imaging techniques to provide useful quantitative information for obtaining a better understanding of the storage and transport of multiple fluid phases in porous media. In this report new methods for quantitative determination of fluid saturation distributions under both static and dynamic (flowing) situations are described. We have developed a method to obtain accurate, simultaneous estimates of three-phase relative permeability and capillary pressure functions from two-phase dynamic displacement experiments using saturation information obtained with MRI. This procedure is being extended to provide estimates of three-phase relative permeability functions from laboratory experiments. We have developed pulsed field gradient NMR techniques to determine information regarding the self-diffusion process of fluids in porous media. Since porous media restricts molecular diffusion, these experiments can be used to extract information concerning the microscopic structure of porous media. We have begun our analysis of these NMR experiments.

OBJECTIVES

The objectives of this subtask are to: (1) demonstrate NMR imaging methods to determine saturation distributions during unsteady (transient) displacement experiments, (2) further develop the methodology for simultaneously estimating relative permeability and capillary pressure curves from unsteady displacement experiments and analyze the accuracy with which they are estimated, and (3) develop NMR methods for characterizing local fluid

distributions. The research work pertaining to each of the objectives is reported in separate sections below.

PART I. DETERMINATION OF FLUID SATURATIONS DURING DISPLACEMENT EXPERIMENTS

(a) Introduction

The determination of fluid saturation in porous media is a fundamental measurement to characterize fluid storage and transport in porous media. Saturation is also an intermediate quantity that is required in describing most of the basic properties concerning the flow of multiple fluid phases in porous media. The description of such processes is essential for effective development and use of enhanced oil recovery methods. Flow in macroscopically homogeneous media is normally described using relative permeability and capillary pressure functions. For two-phase flow, these functions can be determined from experiments on laboratory core samples.

Most conventional methods for measuring saturation provide only a measure of a single average value for the saturation in an entire sample. Such measurements are not adequate for characterizing heterogeneous systems where the saturation may vary appreciably throughout the sample. In fact, most conventional methods are not useful for measurements in any dynamical system. The use of magnetic resonance imaging techniques opens new avenues to characterize fluid saturations corresponding to relatively small, local regions within a porous medium sample⁽¹⁻³⁾. For both steady state and dynamic displacement experiments, the inclusion of measured saturation profiles into the estimation process can substantially improve the accuracy with which relative permeability and capillary pressure functions are estimated.

As one of the pioneering groups of using MRI to determining local saturations, we have made many improvements since our first experiment on the saturation study of immiscible fluid displacement experiments. We have developed a method with which the effects due to spatial variation and the saturation-dependence of the spin-spin relaxation time T_2 can be largely taken into account in determining fluid saturations from profile images, thereby substantially improving the accuracy of saturation determination. We found that in different types of cores, different extrapolating functions may be warranted. In particular, we investigated the single and stretched exponential type relaxation decay functions and the validity of using these functions in determining the intrinsic proton spin intensities.

To implement these developments, we conducted two-phase displacement experiments in sandstone and limestone core samples. In those experiments, one fluid phase is immiscibly displaced from the core sample by a second fluid phase. MRI profile imaging data are collected before, during and after the displacement. Those data represent the porosity or saturation information.

Many sandstones exhibit heterogeneous structures, commonly as laminated structures where the bedding planes are only one to a few millimeters apart. Brown (Massialon) sandstone cores are among examples of heterogeneous cores. In particular, Brown sandstone usually exhibits nonparallel bedding planes, especially on larger dimensions (on the order of 10^0 to 10^1 cm), where the bedding planes may merge or disappear. Although some of the

bedding planes in those cores can be visually observed from surfaces, the pore structure and the fluid distribution at different layers during multiphase flow have not been studied in the sub-millimeter pixel scale. Furthermore, the nonparallel feature of laminations in these sandstones makes prediction and modeling even more difficult. Yet, such a study is of great importance for understanding fluid dynamics in heterogeneous porous media in general and for modeling flow in such systems in particular.

Heterogeneous structures usually can be visualized by taking cross sectional two-dimensional porosity images. However, we demonstrate that it can be more efficiently observed using multiple slices of slice-selective one dimensional cross sectional profiles if the core is properly oriented such that the observation gradient is perpendicular to the bedding planes. We conducted experiments in a Brown sandstone, and identified actual flow paths as a function of time during imbibition and drainage processes. We further investigated the wetting characteristics in the sample using the flow-rate dependence of saturation results obtained in both processes. The present study provides a convenient way of observing fluid dynamics in porous media, specifically for laminated structures, which are otherwise difficult to probe.

(b) Theory

(1) Determining Saturations Using Proton Spin-Density Imaging with A Reference Standard

The validity of using MRI technique to detect fluid saturation is based on the fact that the observed NMR signal intensity $I(\omega)$ is proportional to the proton density $P(z) = \rho(z)\Delta z$ in the region subjected to NMR excitation. When $P(z)$ is determined, the fluid phase saturation can be calculated by

$$S_0(z) = P(z)/P_i(z), \quad (1)$$

where $P_i(z)$ corresponds to the linear density determined while the core is fully saturated prior to displacement. The porosity $\phi(z)$ is determined by

$$\phi(z) = P_i(z)/nA, \quad (2)$$

where n is the proton density of the observed phase and A is the cross sectional area.

In displacements with two fluid phases for which the liquid phase can be separated by chemical shift, NMR can be used to observe single fluid phase. In our experiments, we frequently use deuterium oxide (D_2O) as the aqueous phase, and refined oils, such as n-hexadecane, as the oleic phase. We then observe the oil by tuning to the proton NMR frequency.

The proton spin-density images have been extensively used for medical images⁽⁴⁾. However, it is not straight-forward to obtain saturations from measured intensity profiles in a porous media. The difficulty arises from the fact that the spin-spin relaxation time T_2 of fluid protons in porous media is much shorter than that in the corresponding bulk fluid. Thus, the proton NMR signal intensity measured at a finite echo time TE , the time interval between the first rf pulse and the echo formation, does not represent the intrinsic intensity of all protons, since during the time TE part of the signal is lost due to T_2 decay. For one dimensional

profiles, each pixel has a one-to-one correspondence with the spatial location on the core determined by $\omega = \gamma Gz$, the data acquisition starts $t = TE$, and the measured signal intensity, in the frequency domain, can be expressed as

$$I(t) \propto \int \rho(z) \exp(-i\gamma Gz(\Delta t) - \Delta t/T_2^*) \exp(-TE/T_2) \quad (3)$$

where $\rho(z)$ is the one dimensional proton density along the flow direction z , γ is the gyromagnetic ratio, and G is the applied field gradient. It is obvious that the measured intensity depends on the TE time used for the experiment. The discrepancy between the intensity measured at finite TE and the intrinsic magnetization may become a significant source of error in accurate determination of saturations in porous media if not corrected.

Initially, we presented a method which involves the use of an agarose gel reference standard that is prepared such that the relaxation times of the reference standard matches that of the fully-saturated porous medium bulk sample⁽⁵⁾. An important assumption in using this method for estimation of saturation as originally reported was that the measured relaxation times for the core are a function of neither position nor saturation. A finite TE and an average value of T_2 were used to determine the saturations in the original method. Obviously, the structural-heterogeneity caused spatial variation of T_2 as well as the saturation dependence of T_2 cannot be addressed by this method. Subsequent examination of observed values of the transverse relaxation time T_2 with different saturations indicated that the above mentioned assumption may not always be met, and that the errors encountered in such cases can be significant in certain porous rock structures. Consequently, we developed a new method for performing imaging experiments whereby the effects due to spatial variation and saturation-dependence of T_2 can be largely taken into account. The method involves the determination of the intrinsic NMR proton spin-density by extrapolating echo amplitudes, measured at different TE's, to zero echo time ($TE=0$); local variation for T_2 are determined on a pixel-by-pixel basis.

It is known that for a given fluid in porous media, the T_2 value depends primarily on the pore sizes and surface chemistry⁽⁶⁾. In a bulk fluid or in a homogeneous medium, the transverse relaxation time T_2 corresponding to the i th pixel can be described by a single exponential type decay function

$$M_i(TE) = M_{0i} \exp(-TE/T_{2i}), \quad (4)$$

where M_i is the echo intensity at any given TE and M_{0i} is the echo intensity at $TE=0$. In porous media, the single-exponential extrapolation is expected to work well for systems with relatively uniform pore sizes over the spatial dimension of the pixel size (typically 0.4mm in our experiments), but will be less accurate for systems in which pore sizes vary within each pixel. In some experiments, examination of the residuals formed during the extrapolation procedure indicates that a single exponential model is not suitable for describing the magnetization decay. This situation becomes most obvious during stages of the displacement processes for which the signal intensity is relatively small, as well as in samples with microscopic heterogeneous pore structure. Generally speaking, in porous media with a wide

distribution of pore sizes, or significant variation in surface chemistry, T_2 may no longer decay in single exponential form. Therefore, a multiexponential or a stretched exponential extrapolations may be used. The stretched exponential relaxation model

$$M_i(TE) = M_{0i} \exp(-TE/T_{2i})^\alpha, \quad (5)$$

has been shown to be suitable for describing relaxation in highly-disordered or heterogeneous systems⁽⁷⁾. It has also been shown⁽⁸⁾ that the wide distribution of pore sizes in a porous medium may result in a distribution of relaxation rates, which has been known to be described by stretched exponential model. The stretched exponential description is a most practical approach for representing larger numbers of relaxation components, since strictly discriminating each individual component in such systems is practically impossible. It is also important to emphasize that our primary purpose is to obtain the true intensity M_{0i} ; determination of the actual number of T_2 components is not of interest for our current objectives.

Use of the T_2 extrapolation method for improving the accuracy in saturation determination has not been studied previously elsewhere. In addition, the stretched exponential model has been used only in analyzing the spin-lattice relaxation in spectroscopic NMR, while our development of using this approach for improving accuracy in saturation evaluation by MRI is a pioneering study in this field.

(2) Studying Core Heterogeneity in Laminated Structures Using Multiple Slices Cross Sectional Profiles

Structural heterogeneity usually can be visualized by taking cross sectional 2D porosity images. However, we found that it can be more efficiently observed using multiple slices of slice-selective 1D cross sectional profiles if the core is properly oriented such that the observation gradient is perpendicular to the bedding planes. We will describe in the following sections how we can use this technique to determine permeability variations among bedding planes as well as variations of other petrophysical properties in porous media associated with the structural heterogeneity.

If a displacement experiment is conducted in a macroscopically homogeneous system, the fluid displacement during the displacement can be well characterized by monitoring the saturation using one-dimensional profiles along the flow direction. If displacement experiments are conducted in a structural heterogeneous sample, such as cores with laminated bedding planes, such profiles along the flow direction only gives the saturation value averaged over individual cross sections perpendicular to the flow directions; the saturation variation over different bedding planes within a cross section, and the actual fluid flow paths during the experiment, are not revealed. In order to enhance our ability to elucidate the laminated structures, we developed a new imaging sequence to acquire multiple slices of thin sliced cross sectional 1D profiles, with the imaging observation gradient being perpendicular to both the flow and the laminations. This pulse sequence is illustrated in Fig. 1.

Core heterogeneity may result from pore structural variations in a bulk sample, as well as lithological and mineralogical variations. In many experiments, it is desirable to observe

fluid dynamics in cases for which fluid distribution is not simply uniform across the core. NMR images can detect core heterogeneity due to the pore structures since NMR signal intensity within a pixel is proportional to the spin density in that region. On the other hand, a large lithological and mineralogical variation among different beddings may affect surface chemistry, resulting in different NMR relaxation rates, and wetting characteristics, as well as variations in other properties associated with the surface chemistry. At different saturation levels, the observed NMR intensity corresponding to different pixels primarily reveals pore-structure information. During the displacement, however, the observed nonuniform oil distribution may result either from pore-structural heterogeneity or from unstable flows. MRI can be used to distinguish the two causes since the structural heterogeneity is more readily observed at full saturation and is smeared out at low saturations while the unstable flow appears only during the displacement. Thus, the slice-selective profiles is a very valuable technique for characterizing unstable displacement, or stable flow in heterogeneous media. In addition, slice-selective profiles have advantages over 2D images in studying flow through laminated cores due to the following reasons. (1) When the observation gradient is chosen to be perpendicular to the bedding plane, this technique concentrates on each bedding plane where the pore structures are relatively uniform, and distinguishes the difference between different planes where appreciable variation is expected. Such treatment improves the S/N compared to 2D images thus making quantitation more accessible. (2) It is a rapid technique, which allows data acquisition to be completed within a few seconds so that the fluid distribution does not vary noticeably during data acquisition.

(c) Experimental Work

Several different types of cores have been studied for the displacement experiments in conjunction with the theoretical developments. All these core samples were prepared in cylindrical shape with the dimension of 1" in diameter and 2.75" in length.

The displacement experiments includes both the imbibition and drainage processes. In our experiments, refined oil, either *n*-octadecene or *n*-hexadecane, has been used as the oleic phase, and deuterium oxide (D₂O) has been used as the aqueous phase. The vacuumed core samples were saturated with an oleic phase fluid using a flow-through method. An epoxy-cured core holder was used for the experiments. This core holder is designed such that the core embedding part can be easily replaced after each displacement experiments. Pressure drops between the inlet and outlet of the core sample were recorded during the experiments. The core samples were initially evacuated and then saturated with the refined oil. A reference sample, consisting of a gel of agarose powder and 0.005M CuSO₄ solution, was taped on to the core holder as a reference standard for signal intensity calibration.

An Indiana limestone core and a building block limestone were used in two displacement experiments, respectively. Visually, the Indiana limestone has a macroscopically homogeneous structure, yet microscopically consists of large variations in pore structures. A thin section photograph reveals that there exists large pores at the 0.1-1mm scale as well as micropores in sub- μ m scale. The building block appears to be relatively homogeneous.

In these studies, one-dimensional images along and perpendicular to the core axis and two dimensional images at various locations were taken. These experiments were used to

evaluate the necessity for using T_2 extrapolation to obtain accurate saturations, and to establish standard procedures for performing extrapolation with single or stretched exponential relaxation models.

A Brown (Massialon) sandstone core with visible laminated structures has been used in another set of experiments. The bedding planes in this sample are nearly parallel to each other but are *not* parallel to the core axial direction (the axial direction was chosen to be the flow direction). We believe that this sample represents a typical structural pattern in Brown sandstones.

In this Brown sandstone study 1D slice-selective cross section profiles with slice-thicknesses of 4mm were taken during displacements and at different saturation stages. This thickness ensures that there is enough signal to obtain a satisfactory S/N, yet it is still thin enough so that bedding planes within a given slice are still approximately parallel so that the resolution of the lamination is not sacrificed. Eight slices with 7.5mm spacing between the centers of two adjacent slices were taken during the displacement processes as well as at different saturation levels corresponding to different steady states which are achieved by using different flow rates. In addition, several non-selective 1D profiles along the flow direction and 2D images were taken at various stages of displacement and saturation levels.

(d) Results and Discussion

(1) T_2 Extrapolation for Obtaining Accurate Saturations: Limestones Study

Figure 2 shows the calculated saturation profiles of the limestone (building block) taken at three stages of the experiments: a. at initial saturation, b. after 1.25 pore volume of fluid was passed through, and c. at the final steady state after 21 pore volume was passed through. Two methods were used to calculate the saturation profiles - the original method that used a single averaged value of T_2 for all pixels at all saturation levels, and the second method that allows local variation of T_2 with single exponential relaxation behavior. The solid curves with bullet marks correspond to calculations using the original method and the curves without bullet marks correspond to that using the single-exponential T_2 extrapolation method. From this figure, we observe that the spin-spin relaxation time is indeed a function of saturation in this limestone, and the extrapolation is absolutely necessary for obtaining accurate values of saturation. Without this procedure, the errors in saturation determination at low saturation levels can be as much as 10%. By examining T_2 decay curves for several individual pixels at different saturation levels, we observed that, within the experimental uncertainty, the data departure from the single exponential curve is not significant. This observation is consistent with the fact that this building block limestone has a more or less homogeneous structure.

The situation may become quite different if a microscopically heterogeneous core is studied. Figure 3 shows calculated saturation profiles corresponding to different times during the primary imbibition process for the Indiana limestone. Similarly, the results calculated from the two methods were used. The saturation differences obtained from the two methods do not appear to be as large as that in Fig. 2; however, it was found that the computed T_2

values did not seem to vary in a regular pattern. On closer inspection it was determined that the single exponential frequently did not adequately describe the relaxation response. An example of this behavior is illustrated in Fig. 4. The datum points on the figure are the signal intensities obtained at different echo times, TE, for one particular pixel. The straight line in the figure represents the least squares fitting using single exponential decay. This figure illustrates that the observed data are not well represented by single-exponential relaxation, which is not surprising considering that there is a significant pore size variations in this core. Figure 5 shows the result obtained with least squares fitting using a stretched exponential model with the same data; a value of 0.62 is calculated for the exponent α . The experimental data appear to be well represented by this model. Note that the values of intrinsic magnetization calculated using the single and stretched exponential model are different, indicating the importance in selecting the correct model for extrapolation.

Using the same least squares fitting procedures as that for obtaining results shown in Fig. 5, we calculated the stretched exponent α on the pixel-by-pixel basis. The average value of α over the entire core length is approximately 0.65-0.70, a quantity very close to that which has been reported using bulk T_1 relaxation measurements in rocks⁽⁸⁾. Such an agreement supports the validity of our procedure of using stretched exponential T_2 to obtain the intrinsic intensity. It is also a first observation of T_2 stretched exponential behavior in rock. We are continuing our analysis of these measured data.

A petrographic analysis of the Indiana limestone indicated that the pore volume is largely comprised of primary intergranular pores that locally appear to have been mechanically enhanced. Secondary pores are present in relatively minor amounts and result from the partial dissolution of skeletal grains in which there is a significant amount of microporosity. This description indicates significant heterogeneity at the sub-pixel scale, which validates the observed relaxation response.

(2) Displacements in Heterogeneous Cores: Brown Sandstone Study

Several displacement experiments, including both the primary imbibition and drainage processes, were conducted on a Brown (Massialon) sandstone core. In this experiment, six flow rates, ranging from 2cc/hr to 100cc/hr, were chosen for both imbibition and drainage processes. The lowest flow rate, equivalent to a superficial velocity of 1.5ft/day, is typical of reservoir flow velocities. This flow rate was maintained for more than three hours from the beginning of each process, during which time approximately one pore volume of displacing fluid passed through the core. Each consecutive flow rate was maintained sufficiently long so that a new steady state was reached. Pressure drops between the ends of the core were recorded during displacements corresponding to the larger flow rates; our pressure transducer does not have sufficient sensitivity to detect the very low pressures corresponding to the low flow rates. The steady state pressure drops corresponding to the various flow rates are listed in Table I.

Table I

	<i>imbibition</i>			<i>drainage</i>				
θ (cc/hr)	15	40	100	4	7.5	15	40	100
ΔP (psi)	2.3	4.3	7.1	1.0	1.1	1.2	2.2	4.2

2a. Flow paths investigations

One of our interests in the laminated structured cores is to observe the actual time dependent flow paths through different bedding planes during displacements. Figure 6(a) shows 12 profiles at one slice location perpendicular to the flow direction during the first stage of imbibition ($\theta=2\text{cc/hr}$). A digital filtering process was applied to the raw data to eliminate certain noise. From this figure, it appears that unstable flow was not observed at this flow rate. However, the flow in different regions (beddings) does respond differently during the experiment. Oil in one bedding plane corresponding to the right-side peak in the figure was displaced prior to that from the other planes. In general, for this particular cross section, the oil in the bedding planes on the right side seems to be displaced faster than that in the left side. This phenomenon can be explained by different permeabilities among the different beddings. After reaching steady state, oil is relatively uniformly distributed throughout the entire sample, and the profile curve becomes closer to that which is expected for a circularly homogeneous core.

Figure 6(b) shows profiles taken from the same cross section during the drainage. Similarly to Fig. 6(a), this graph only includes profiles taken during the lowest flow rate ($\theta=2\text{cc/hr}$). From this figure, we can see that the right side beddings are more quickly filled with invading nonwetting phase than the left side beddings. The right side beddings in this cross section seem to be more permeable to both the wetting and nonwetting fluids. This observation supports the contention that this phenomenon is not due to the flow instabilities, but due to pore structure variations in different bedding planes.

Note that the profiles in Fig. 6 were taken from a circularly shaped cross section. A geometrical factor,

$$2\sin(\cos^{-1}(x/r)), \quad (6)$$

should be taken into account for a quantitative evaluation of saturation. In this equation, x represents pixel locations within the core cross sectional region, with $x=0$ corresponding to the center of the core, and $2r$ is the total number of pixels corresponding to the core sample region on the profile. For each pixel, original data is divided by the value of Eq. (6) associated with the x position of the pixel. Figure 7 is the modified result of Fig. 6(b) in which the circular geometrical factor, Eq.(6), has been taken into account. Therefore, the relative intensities in each bedding plane are readily observed in Fig.7, as if a rectangularly shaped cross section were used. Figure 8 shows data for the average proton density as a function of time within a unit pixel length of each bedding plane during the first 60 minutes after the start of imbibition.

The corresponding bedding planes are defined in Table II. From the data shown on Fig. 8, it is obvious which are the more permeable bedding planes.

Table II

pixel number	73-80	80-105	105-117	117-135	135-146	146-163
plane	1	2	3	4	5	6

2b. *Observation of wettability in each bedding plane*

We further demonstrate that our slice-selective 1D profiles allow us to visualize in certain detail of the variation of fluid wetting characteristics in different laminations. Fig. 9(a) shows slice-selective profiles of the same cross section as in Fig. 6 taken during the period of primary imbibition. Each curve on the figure represents the oil saturation at the initial state and different steady states. These steady states were achieved by applying the following flow rates: 2cc/hr, 4cc/hr, 7.5cc/hr, 15cc/hr, 40cc/hr and 100cc/hr, respectively, for a long enough period of time such that the corresponding saturation level is obtained. It is quite clear that essentially all the mobile oil was displaced during the first stage of flow ($\theta=2\text{cc/hr}$); increasing the flow rate does not result in further oil displacement. In contrast, the primary drainage profiles (Fig. 9(b)), taken from same cross section of the core at the steady states achieved using the same flow rates as for the imbibition case, show that the oil saturation is a function of flow rate. This difference may be explained by the core wettability.

The observed saturation profiles, showing flow rate dependence in drainage and independence in imbibition, is consistent to what is expected for a water-wetting core. Based on the fact that the same flow rate dependency observed in Fig. 9 is common to all 8 slice profiles, it does not appear that the structural heterogeneity of the Brown sandstone results in significant heterogeneity of fluid wetting characteristics in the core. It is noteworthy that the slice-selective 1D profile technique could possibly be used to visually observe wettability variation among different bedding planes, if any, in laminated cores, by studying the relative difference among individual beddings for flow-dependence on the quantities of fluid being displaced during imbibition and drainage processes.

(e) **Future Studies**

We will continue our stretched exponential extrapolation procedures in many core samples, carbonates and sandstones, in order to establish the validity of the treatment in different type of cores. It is also desirable to obtain independent measures of fluid production for further verification of saturation determinations. Due to the similarity in densities of light oil and water, it is difficult to determine the quantities of the two fluids by gravimetric methods. We realized that the dielectric constants of oil and water, which differ more than one order of magnitude, can be used to determine the amounts of oil and water produced simply by measuring the capacitance of the mixed fluid and converting the capacitance back to the fluid quantities. We are now building a production-collecting device as an electrical capacitor, and using a digibridge device to ensure the sensitivity in the capacitance measurements.

For the continuation of the studies that use slice-selective 1D cross sectional profiles to study heterogeneity, we will investigate quantitatively the time-dependent saturation in each bedding plane and use the saturation information to obtain permeability and capillary pressure function variations among individual bedding planes.

We intend to extend our current pressure measurement procedure, which determines the pressure drops between the core ends, to include the capability of measuring pressures at several locations along the core flow direction during displacements. We plan to install pressure taps at several locations along the core holder to avoid the problem of directly embedding pressure transducers inside the core holder, since the latter approach may disturb the NMR signals. A thin polymeric membrane will be sandwiched between the core surface and the pressure tap. This membrane will keep the fluid inside the core from mixing with the fluid in the capillary tube extending from pressure tap to pressure transducer.

We also intend to extend our flow experiments to include the capability of determining fluid saturations in three-phase cases (e.g., oil, water and gas). In such experiments, cores will be first saturated with one fluid, then a mixture of two liquids will be introduced. Finally the gas phase will be introduced. The separation of water and oil phases can be obtained using the phase identification technique⁽⁹⁻¹¹⁾, or the asymmetric echo technique⁽¹²⁾. After the gas phase is introduced, the gas saturation can be determined from the reduction of the total signals of the two liquids.

PART II. ESTIMATION OF FLOW FUNCTIONS FROM DISPLACEMENT EXPERIMENTS

(a) Introduction

Accurate estimates of two and three-phase relative permeability and capillary pressure curves (flow functions) are critical to simulate multiphase flow through porous media. These functions are used in numerical simulators of oil fields to predict reservoir behavior and help make decisions about recovery methods, well locations, flow rates, etc. Since most oil recovery processes occur with the simultaneous flow of two or three phases, reliable methods for accurate determination of multiphase flow functions are very desirable. As part of this project, we are developing a parameter estimation method for estimating multiphase relative permeability and capillary pressure functions from laboratory displacement experiments.

At this time, two-phase flow functions can be estimated from steady-state or unsteady-state experiments. Production and pressure drop data are obtained from these experiments. In the steady-state procedure, the two phases should be injected simultaneously until a steady-state is attained. Pressure drop and production data are measured and then the injection rate is changed until another steady-state is reached. The values of relative permeability obtained at different steady-states in the experiment are assumed to correspond to an average value of saturation in the sample. In fact a range of these values of saturation may exist in the core, so assignment of the relative permeabilities to an average saturation value may lead to significant errors in the estimates. Besides, the steady-state experiment is very long and tedious to carry out, and the very few values of relative permeability determined from such experiments do not allow for adequate resolution of the relative permeability curves.

The unsteady-state displacement experiment is fast and a great deal of data are collected. For this reason it is usually the preferred experiment. However, the process of estimating the flow functions is more complex. In this experiment, the core is flooded with one of the fluids and then this fluid is displaced by injecting the other phase. Data are collected during the dynamic displacement. Usually the JBN method⁽¹³⁾ is used to estimate two-phase relative permeability functions using production and pressure drop data. This method is based upon Buckley-Leverett⁽¹⁴⁾ displacement which, in particular, neglects capillary pressure effects. In an attempt to achieve this condition, experiments are performed at high flow rates that greatly exceed fluid velocities encountered in reservoir production. Great inaccuracies in the estimates of relative permeabilities may be obtained when the capillary pressure is neglected⁽¹⁵⁾. To simulate fluid displacement using the functions estimated with the JBN analysis, the capillary pressure curve must be obtained from an independent experiment.

Watson and coworkers⁽¹⁶⁾ developed a parameter estimation procedure to estimate simultaneously two-phase relative permeability and capillary pressure functions. In this method, production and pressure drop data from unsteady-state experiments are used in the history matching process. The displacement experiments can be carried out using fluid velocities that are typically encountered in the field, so it is likely that the functions obtained are more representative of reservoir behavior. The relative permeability and capillary pressure functions are represented as functions of saturation. In their work they found that representing the curves as simple functions with just a few parameters may lead to poor estimates of the flow functions. Hence, they propose to use B-splines as a convenient representation for these functions. The coefficients in the B-spline representation are the ones to be estimated according to a minimization criterion. In the parameter estimation procedure, the criterion is the sum of squares of residuals.

In recent years, CT scanning has been used to obtain in situ saturation data during displacement experiments. These data are an excellent source of information to help understand the mechanisms of multiphase flow through porous media and to estimate the basic properties of the media. Recently, we developed the capability of using in situ data in the parameter estimation procedure. We evaluated the improvement in the accuracy with which the relative permeability and capillary pressure functions can be estimated by analyzing hypothetical experiments. Results obtained show the great potential of the parameter estimation method for estimating two-phase flow functions. These results motivate the use of the parameter estimation process to estimate three-phase flow functions. Currently, as part of the objectives of this project, we have extended our parameter estimation procedure to estimate simultaneously three-phase relative permeability and capillary pressure functions. We are using a model that can provide a more accurate simulation of the experiment than the Buckley-Leverett model to simulate the experiment. The method also uses in situ data in the estimation procedure. We have also developed a computer code to analyze the accuracy of the estimated functions using constrained Monte Carlo simulation. We will use our method to analyze two and three-phase flow data obtained using NMR imaging in our Engineering Imaging Laboratory. Preliminary results obtained using simulated data for a simple three-phase flow case show great potential of this method to obtain good estimates of three-phase flow functions from laboratory experiments.

Oil recovery usually occurs with the simultaneous flow of three fluid phases. Accurate estimates of three-phase flow functions are critical to understand and simulate correctly three-phase flow through porous media. Although several models for estimating three-phase relative permeabilities have been proposed, a reliable method for estimating these functions does not exist. Different models based on probability have been proposed for the three-phase relative permeabilities. With these models, three-phase relative permeability functions are calculated using measured two-phase relative permeabilities. However, these methods are still controversial⁽¹⁷⁾ and sufficient measured data are not available to evaluate them. Another approach is to obtain estimates of relative permeability data from steady or unsteady-state experimental data.

The unsteady-state method currently used to estimate three-phase relative permeabilities was developed by Sarem⁽¹⁸⁾. This method is an extension of JBN method and, consequently, it is subject to the same assumptions. In particular, it neglects capillary pressure effects and assumes linear isoperms. Under these assumptions poor estimates of the flow functions may be obtained. Several works show that the isoperms may be concave or convex⁽¹⁹⁻²⁵⁾. Hence, a reliable method for estimating accurate three-phase relative permeability and capillary pressure functions has become critical to describe adequately three-phase flow through a porous material.

(b) Theory

In this section we present the mathematical model used to describe two and three-phase flow through porous media. The B-spline representation for the flow functions is described. Then we discuss the estimation procedure and the Monte Carlo method for computing confidence intervals for the estimated functions.

1) Mathematical Model of Displacement Process.

To estimate multiphase flow functions, we need a model capable of describing unsteady-state multiphase flow through a core sample. The experiments considered for the two-phase case are imbibition or drainage for which a single fluid phase is injected. These are the standard experiments used to analyze multiphase flow through porous media. The three-phase experiment is more complex than the two-phase experiment and we are in the process of designing the experiment. At this time we are considering injecting one or two phases. However, the computer code for solving the model will be flexible for further changes if necessary.

We are using the following equations which forms the standard model for simulating multiphase flow in porous media⁽²⁶⁾:

$$\nabla \cdot \left(\frac{K k_{rw} \rho_w}{B_w \mu_w} (\nabla P_w + g \nabla z) \right) = \frac{\partial (\phi \rho_w S_w / B_w)}{\partial t} + q_w \quad (7)$$

$$\nabla \cdot \left(\frac{K k_{ro} \rho_o}{B_o \mu_o} (\nabla P_o + g \nabla z) \right) = \frac{\partial(\phi \rho_o S_o / B_o)}{\partial t} + q_o \quad (8)$$

$$\nabla \cdot \left(\frac{K k_{rg} \rho_g}{B_g \mu_g} (\nabla P_g + g \nabla z) \right) = \frac{\partial(\phi \rho_g S_g / B_g)}{\partial t} + q_g \quad (9)$$

$$P_{cow} = P_o - P_w \quad (10)$$

$$P_{cgo} = P_g - P_o \quad (11)$$

$$S_o + S_w + S_g = 1 \quad (12)$$

where

- ϕ = porosity of the porous medium
- S_i = saturation of phase i
- ρ_i = density of phase i
- μ_i = viscosity of phase i
- K = absolute permeability of the porous medium
- k_{ri} = relative permeability of phase i
- P_i = pressure of phase i
- P_{cij} = capillary pressure between phases i and j
- q_i = sink of phase i
- B_i = formation volume factor of phase i
- g = gravitational constant

The subscripts o , w , and g refer to oil, water, and gas.

These equations can be simplified to represent the two-phase case. With this model we have greater flexibility than Buckley-Leverett model since we can specify in different sections of the core permeability, porosity, and initial water saturation. To solve this model, a representation of these curves as functions of saturation is proposed and the curves can be estimated simultaneously using production, pressure drop, and in situ saturation data. We propose the use of B-splines to represent these curves due to their ability to represent arbitrary smooth function^(27,28):

$$k_{ri}(S_w, S_o) = \sum_{j=1}^{n_i} a_j^i N_j^m(S_w, S_o) \quad (13)$$

$$P_c(S_w, S_o) = \sum_{j=1}^{n_i} a_j^i N_j^m(S_w, S_o) \quad (14)$$

where

- $N_j^m(S_w, S_o)$ = bivariate B-spline
- a_j^i = coefficients to be estimated
- n_i = dimension of the spline
- m = total order of the spline

Several finite difference methods have been proposed to solve these equations. We solved them using an implicit approach for one or two saturations and one pressure depending if it is a two or three-phase case. This is a variation of the simultaneous solution method reported by Aziz and Settari⁽²⁶⁾. To validate the computer program generated, results of this program were compared with results of previous study cases at Texas A&M University⁽²⁹⁾ and with results of simulators at Arco Oil and Gas Co. The computer program was designed to be run on the Cray supercomputer. Using this computer we can estimate the flow functions fast and efficiently.

2) Estimation Procedure.

The coefficients in the B-spline representation are the ones to be estimated with our parameter estimation procedure. In this procedure, the optimum parameters are those which minimize the sum of squared differences between the calculated with the model and the measured data:

$$Q(\vec{\beta}) = (\vec{y} - \vec{f}(\vec{\beta}))^T W (\vec{y} - \vec{f}(\vec{\beta})) \quad (15)$$

where

$$\begin{aligned} Q(\vec{\beta}) &= \text{objective function} \\ \vec{y} &= \text{vector of experimental data} \\ \vec{f}(\vec{\beta}) &= \text{vector of predicted values} \\ W &= \text{weighting matrix} \end{aligned}$$

In this expression, the vector of parameters to be estimated is:

$$\vec{\beta} = [a_1^w, \dots, a_{N_w}^w, a_1^o, \dots, a_{N_o}^o, a_1^g, \dots, a_{N_g}^g, a_1^{p_1}, \dots, a_{N_{p_1}}^{p_1}, a_1^{p_2}, \dots, a_{N_{p_2}}^{p_2}]^T \quad (16)$$

where w , o , and g represent water, oil and gas respectively; p_1 and p_2 represent the two capillary pressures. The number of parameters to be estimated may be increased to find an appropriate representation for the flow functions⁽²⁹⁾. The matrix W usually is chosen as the inverse of the variance of the data. The vectors of experimental and predicted data include the pressure drop, production, and in situ data. We included linear inequality constraints in the estimation process since we desire that the functions be monotonic:

$$G\vec{\beta} \geq \vec{g} \quad (17)$$

where

$$\begin{aligned} \vec{g} &= \text{right hand side of inequality constraints} \\ G &= \text{matrix of inequality constraints} \end{aligned}$$

The form of the inequality matrix and the right hand side vector is discussed in detail by Richmond⁽¹⁷⁾.

3) Accuracy of Estimates.

Approximate pointwise confidence intervals for the estimated functions can be obtained using constrained Monte Carlo simulation⁽²⁹⁾. The solution of the following minimization problem gives parameters errors that correspond to a specific error vector:

$$\min L(\delta\vec{\beta}) = [\vec{\epsilon} - A_t\delta\vec{\beta}]^T W^{-1} [\vec{\epsilon} - A_t\delta\vec{\beta}] \quad (18)$$

$$\text{subject to : } G\delta\vec{\beta} \geq \vec{g} - G\vec{\beta}$$

where

$$\begin{aligned} L(\delta\vec{\beta}) &= \text{objective function} \\ \delta\vec{\beta} &= \text{vector of variations in parameters} \\ \vec{\epsilon} &= \text{vector of residuals} \\ A_t &= \text{sensitivity matrix} \end{aligned}$$

Using a pseudo-random number generator, N_{mc} sets of random errors are generated. With these random errors and the variances of the pressure drop, production, and in situ data, we generate N_{mc} different vectors of residuals. Solving Eq. 18 for each vector of residuals we find N_{mc} vectors of variations in the parameters. With these vectors and the vector of the specified parameters we can compute N_{mc} different relative permeabilities and capillary pressure curves. For example, for the two-phase case, ordering values for these functions at any given saturation S_w , we can approximate 95% confidence intervals by discarding the outer 5% of these calculated values:

$$\begin{aligned} k_{rn}(S_w, \vec{\beta}_{i1}) &\leq k_{rn}(S_w, \vec{\beta}_{i2}) \leq \dots \leq k_{rn}(S_w, \vec{\beta}_{iN_{mc}}) \\ k_{rw}(S_w, \vec{\beta}_{j1}) &\leq k_{rw}(S_w, \vec{\beta}_{j2}) \leq \dots \leq k_{rw}(S_w, \vec{\beta}_{jN_{mc}}) \\ P_c(S_w, \vec{\beta}_{k1}) &\leq P_c(S_w, \vec{\beta}_{k2}) \leq \dots \leq P_c(S_w, \vec{\beta}_{kN_{mc}}) \end{aligned} \quad (19)$$

The same ordering can be done to approximate confidence intervals for three-phase flow functions at any given values of saturation. Analyzing the shape of the confidence intervals obtained, we can study the influence of the data in the accuracy of the estimated flow functions.

(c) Results and Discussion

At this time we have obtained results for simulated two-phase cases at low and high flow injection rates. In these cases, we assumed "true" flow functions of typical reservoir samples. With these functions we simulated experiments and collected predicted data. Then, we added

random errors to the data to obtain "simulated" data. As an example of the improvement in accuracy of the estimated relative permeability and capillary pressure functions when in situ data are included in the parameter estimation process, we discuss the estimated functions obtained using two-phase flow simulated data. This example was presented by Richmond⁽²⁹⁾. The core was initially flooded with water at residual oil saturation. Oil was injected at low flow rate to displace the water from the core and production and pressure drop data were collected. The initial water saturation was 0.80 and the lowest value of saturation reached was around 0.425. Starting with an initial guess of the parameters, Richmond estimated the flow functions using the parameter estimation procedure. He found that sometimes incorrect estimates of the flow functions could be obtained if few parameters were used in the B-spline representation of the flow functions. These incorrect estimates corresponded to local, nonglobal, minima encountered in minimizing the objective function defined by Eq. 15. We considered the same case but now we included in situ data in the estimation process. We estimated the flow functions by solving a sequence of estimation problems in which the number of parameters in the B-spline representation were increased until significant reductions in the residual value of the objective function were no longer achieved. The results obtained in all runs using in situ data did not show incorrect estimates of the flow functions corresponding to nonglobal minima and their accuracy was better. Using the constrained Monte Carlo procedure, we computed confidence intervals for the "true" flow functions since we knew them when we simulated the data. These confidence intervals were computed using three equally spaced interior knots in the region of water saturation between 0.25 and 0.80.

Figs. 10 and 11 show the estimated functions using production and pressure drop data (case 1) in the parameter estimation procedure. Figs. 12 and 13 show the results including in situ data (case 2). Clearly, we obtained better accuracy in the estimated flow functions when we included in situ data in the estimation procedure. This shows the great sensitivity that our estimation procedure has for the in situ data. Figs. 10 and 11 show good estimates of the relative permeability and capillary pressure functions but the accuracy is poor. Since the lowest value of water saturation reached was around 0.425, we could not obtain accurate estimates of the flow functions below this value. Hence, the estimated functions have big confidence intervals in the region of water saturation below this value in both cases. The bottleneck in the confidence intervals for the capillary pressure in Fig. 11 corresponds to the region of water saturation reached after the breakthrough time. This region of saturation corresponds to the steady-state where we collected half of the production and pressure drop data (400 values). Since a great amount of data were available for estimating the flow functions in this region of saturation, great accuracy in the estimated capillary pressure was obtained.

This summer we used our estimation procedure to analyze experimental production, pressure drop, and in situ data at ARCO Oil and Gas Co. in Plano, TX. The in situ saturation data were obtained using X-ray CT scanning. The data analyzed corresponded to two core samples. For one core, in situ saturation data were obtained at both low and high flow rates. These data, together with production and pressure drop data, were used in our parameter estimation method to estimate simultaneously relative permeability and capillary pressure functions. The predicted production and pressure drop data using our estimated functions showed a better match of the experimental data than the predicted data using the estimates obtained with the JBN analysis. The second core was composed of two different samples of

rock. We estimated the flow functions using production, pressure drop, and the available in situ saturation data. The results predicted with our estimated functions showed great improvement compared with the results predicted using the estimated flow functions obtained with the JBN analysis. The results and discussion of the work at ARCO will be presented or published in a few weeks or months.

At this time, using our parameter estimation procedure, we have estimated three-phase relative permeability and capillary pressure functions for a simple simulated case. The results obtained show great accuracy in the estimated flow functions. Details about these results and the proposed solution of the three-phase flow model will be available in a few weeks in Mr. Mejia's Ph.D. dissertation.

(D) Future Work

At this time we are designing and running experiments for characterizing the properties of the rock. We are working on experiments to obtain accurate in situ saturation data using NMR. We intend to use these data to validate and test our parameter estimation method. Several experiments with different core samples will be conducted and relative permeabilities and capillary pressure functions will be estimated using our parameter estimation procedure. To analyze the data in the supercomputer, we have obtained a grant from Cray Research Inc. We have estimated three-phase flow functions for a simple simulated experiment assuming "true" flow functions. The results seem to be rewarding and motivate future research in estimating three-phase flow functions using experimental data. Further work in the three-phase flow experiment will be conducted in the next year. We will estimate three-phase flow functions using experimental data obtained with MRI. The results of this work should lead to a better understanding of mechanisms of three-phase flow through porous media and better simulations of reservoir behavior.

PART III. CHARACTERIZATION OF LOCAL FLUID DISTRIBUTION BY NMR

(a) Introduction

An important focal point of the oil-recovery research is to understand fluid flow behavior in porous media at the microscopic level. Since microscopic events control displacement processes in porous rocks, studies of properties that characterize local pore structures are expected to yield important information for understanding macroscopic flow behavior. In addition, a comprehensive theory for predicting the properties on the basis of microscopic experimental results is desired in order to better understand and predict oil recovery processes.

NMR techniques are sensitive to local structural arrangements and interactions in the vicinity of the resonating nuclei. Consequently, these techniques provide unique noninvasive probes for elucidating pore structure and fluid transportation in reservoir rocks at a microscopic level.

The new method of using NMR for characterizing pore structure is based on the fact that the molecular self-diffusion in porous media is hindered by the presence of pore boundaries. Therefore, the apparent diffusivity will be time dependent, with apparent

diffusivity decreasing with the diffusion time. Such restricted diffusion phenomenon have been observed by using pulsed field gradient (PFG) NMR in systems of fluids in restricted geometries and emulsions^(30,31). The capability for measuring diffusivity values over a large interval of diffusion times by PFG NMR techniques makes it unique for studying restricted diffusion.

(b) Theory

There are several PFG NMR pulse sequences^(32,33) available for diffusion measurement. For specific application to our porous systems, our preliminary studies showed that the PFG stimulated echo sequence⁽³⁴⁾ is the most favorable choice. This sequence allows a relatively large dynamic range of diffusion time for measuring the apparent diffusivity for systems such as fluids in porous media that characteristically exhibit larger spin-lattice relaxation time (T_1) than spin-spin relaxation time (T_2).

The magnetization decay after the application of PFG stimulated echo sequence is represented by^(34, 35):

$$M = \frac{M_0}{2} \exp \left[-\frac{2\tau_1}{T_2} - \frac{\tau_2 - \tau_1}{T_1} \right] \times \exp \left\{ -\gamma^2 D \left[\delta^2 \left(\Delta - \frac{\delta}{3} \right) g^2 + \tau_1^2 \left(\tau_2 - \frac{\tau_1}{3} \right) g_0^2 - \delta \left(t_1^2 + t_2^2 + \delta(t_1 + t_2) + \frac{2}{3} \delta^2 - 2\tau_1 \cdot \tau_2 \right) g \cdot g_0 \right] \right\} \quad (20)$$

where Δ is the diffusion time and g and g_0 are the applied and internal gradients, respectively. The pulse sequence is illustrated in Fig. 14.

Using this sequence, two types of experiments can be conducted to yield information leading to pore structure characterization. First, the decay in the stimulated echo is measured as the applied pulse gradient strength g is varied but the diffusion time Δ is kept constant. Carrying out this type of experiment in the different pore size systems is expected to reveal the dependence of apparent diffusivity on the pore sizes. It is expected that media with smaller size pores will show greater effects of restricted diffusion, while those with larger size pores will more closely resemble the free, unrestricted diffusion case. In a porous medium with a narrow distribution of pore sizes, the apparent diffusivity D can be considered as a single value. On the other hand, if the pore size distribution is wide, a multiple component of D should be encountered. Thus, using a semilog plot with

$$\ln[M(\text{TE}=0)/M_0] = -\gamma^2 D [A g^2 + B g_0^2 + C g \cdot g_0], \quad (21)$$

where

$$M(\text{TE}=0) = M_0/2 \exp[-2\tau_1/T_2 - (\tau_1 - \tau_2)/T_1], \quad (22)$$

and

$$A = \delta^2 (\Delta - \delta/3), B = \tau_1^2 - (\tau_2 - \tau_1/3), C = -\delta(t_1^2 + t_2^2 + \delta(t_1 + t_2) + 2/3 \delta^2 - 2\tau_1 \tau_2),$$

we may distinguish a narrow from wide distribution of pore sizes in a porous medium by examining the linearity of such dependence.

Second, another type of echo decay can be obtained if the diffusion time Δ is varied but g is kept constant. Such measurements directly observe the diffusion-time dependence of the apparent diffusivity. In a bulk fluid, the diffusivity is time-independent. In a geometrically confined medium, the apparent diffusivity measured by NMR is a function of time. The moment a pulse sequence is applied, protons are labeled simultaneously by phases. As diffusion time increases, more protons experience restrictions before they exchange phase with other protons, resulting in a time-dependent apparent diffusivity. This time-dependent behavior can be an important parameter for characterizing pore structures.

(c) Experimental Work

The PFG NMR stimulated echo sequence has been used in studying model porous media made of 8 different size ranges of closely-packed glassbead packs. The bead size range of these 8 samples are, 1-38, 45-63, 63-90, 90-125, 125-180, 180-250, 250-355, 500-710 μm , respectively. These beads were obtained from a commercial source. We sieved the sizes, cleaned using 0.06M NaOH first, rinsed with distilled water to neutral acidity, cleaned again using 6M HCl solution, and rinsed thoroughly with distilled water. Fluid saturated beads packs were centrifuged to ensure the close-packing before NMR measurements. Excessive amounts of fluid were carefully removed from the tops of the bead packs.

(d) Results and Discussion

(1) Pore Size Dependence and Restricted Diffusion Observations

We performed measurements of echo attenuation as a function of magnetic field gradient strength g and as a function of diffusion time Δ . Figure 15 shows the echo attenuation of 8 different size glass bead packs as a function of g when measured at $\Delta=56$ ms while keeping all the relevant time parameters of the sequence, t_1 , t_2 , τ_1 , τ_2 , δ , the same in all the measurements. From the figure it is clear that the echo attenuations exhibit strong pore size dependence. Echo magnitude drops faster in larger size media and slower in smaller size media, consistent with the fact that proton encounters more barriers in smaller pore size media, and therefore the apparent diffusivities in these media are smaller. As a first order approximation we fitted the data assuming a linear dependence of $\text{Log}(M/M_0)$ vs. g^2 , which is equivalent to assuming the internal field gradient g_0 is negligible. We found that while in the largest beadpack the apparent D (see Table III for the values) is close to that for bulk water ($2.2 \times 10^{-5} \text{cm}^2/\text{sec}$), in the smallest pack the apparent D is approximately an order of magnitude smaller. This observation is a very encouraging result for the prospect of using the apparent diffusivity to characterize pore sizes. A detailed numerical analysis will be given in the following section with more experimental data to be discussed.

Measurements of echo amplitude as a function of diffusion time Δ were also performed in the same samples. Figure 16 shows the experimental results of one set of such

measurements. Restricted diffusion effects were directly observable from these experimental data. Should the proton self-diffusion encounter no barrier restrictions, the decay curve would then be a straight line in the semilog scale. Strong pore size dependence is also evident from this figure. This size-dependence is in agreement with the fact that more restrictions occur in smaller pores, therefore the restricted diffusion effect is observable for shorter diffusion times Δ in smaller size beadpack media, while it is only observed for longer times Δ in larger size beadpacks.

(2) Numerical Analyses of Experimental Results

The assumption of neglecting effects due to g_0 in using Eq. (20) for approximate estimation of apparent diffusivity, described in the last section, breaks down when measurements are performed for larger Δ 's. Examination of similar data of $\log(M/M_0)$ vs. g^2 taken at other larger Δ 's indicate that the slopes are no longer a straight line for larger Δ . Figure 17 shows a set of results taken at four different Δ 's for the 125-180 μ m beadpack. Apparently the slopes are curved more at larger Δ 's. This nonlinearity dependence may result from several possibilities. First, the terms in Eq. (20) corresponding to the internal gradient g_0 may not be negligible. Second, each bead pack sample, although sieved, still has a finite range of distribution in bead size. This distribution can result in pore size (note that pore size is considerably smaller than the corresponding bead size in beadpack porous media), and a nonuniformity in pore structure since a regular close pack is not possible if the bead size is not identical. This may result in multicomponents of apparent diffusivities, as each different sized pores may have a different D_{app} . Third, the general equation (Eq. 20) was derived from an infinitely large uniform media, for which the mean squared displacement of a molecule can be described as $\langle r^2 \rangle = 6D\Delta$. The validity of using this equation to a hindered diffusional case, such as in our beadpack, has not been fully established.

Our numerical work for analyzing these beadpack data is focused on finding the best computational solution of apparent diffusivities in each sample following the three possibilities described above as guidelines. Naturally, the first approach is to include the effects due to g_0 . Without adding any restrictions, parameter estimation methods were used to evaluate D with the presence of g_0 in Eq. (20). The parameter estimation of D and g_0 is based on the following equation

$$M_i/M_1 = \exp[-\gamma^2 D (Ag_i^2 + Cg_i g_0)], \quad (23)$$

where M_i/M_1 is the experimental result with

$$M_1 = M_0 \exp(-\gamma^2 D B g_0^2) \quad (24)$$

being the datum taken at $g=0$. The (nonlinear) least squares method is used in the parameter estimation problem with objective function being

$$Obj \ Fcn = \left\{ (M_i/M_1) - \exp[-\gamma^2 D (Ag_i^2 + Cg_i g_0)] \right\}. \quad (25)$$

The best fits are shown in Figure 18 (a-d). From this figure, we see that the inclusion of the background gradient effect only improves the estimation slightly; the departure from the theoretical curve is still significant for those sets of data taken at larger diffusion times (Figs. 18 (b-d)). It seems that the fitting is satisfactory only for smaller diffusion times. Table III shows the comparison of apparent diffusivity calculated using linear regression and parameter estimation, for this single case of $\Delta=56\text{ms}$. The results obtained from linear regression (D_1) and from parameter estimation (D_2) shows noticeable difference especially for smaller beads. The internal gradient is expected to be large in a beadpack consisting of small beads, therefore, the inclusion of g_0 effect in the calculation for those samples are necessary.

Table III

bead size (μm)	1-38	45-63	63-90	90-125	125-180	180-250	250-355	500-710
D_1 ($10^5 \text{ cm}^2/\text{sec}$)	.20	.24	.66	.90	1.2	1.5	1.7	2.1
D_2 ($10^5 \text{ cm}^2/\text{sec}$)	.15	.18	.35	.72	1.1	1.4	1.6	2.1

The results shown in figure 18 and in Table III indicate that the g_0 effect *alone* can not be the sole source responsible for the departure of data from the theoretical curves. However, the above estimation is a necessary step. Only after this analysis may one be convinced that further investigation of exhausting all the other possibilities are necessary.

It is worthwhile to point out that the values of the internal gradient calculated from parameter estimation do not show agreements for the same sample measured at different Δ , which is another indication that the curvature is not explained by g_0 alone.

The data curvatures appearing in Fig. 18 are in agreement with that which would be expected for a multicomponent D . Comparison of the data from the same beadpack but different Δ 's may also be explained in multicomponent D fashion. At small Δ , only the fastest diffusion component, corresponding to molecules in the largest pores in the sample, are the dominant source for the echo decay. The rest of the slower components do not contribute significantly at this diffusion time even at the highest gradient applied (18G/cm). At large Δ , the fastest component has already dropped significantly, but the contribution from the rest of the components become significant. Quantitative analyses of this work is underway.

(e) Future Studies

In addition to continuing the analysis work described in the last section, we intend to use various porous medium models to simulate molecular diffusional motion in these media and develop parameter estimation procedures for extracting pore-size information from the NMR diffusion study. In particular, we will select a few geometrical and stochastic models, solve the random walk problem to model the process of diffusion, and compare the NMR

measurements in similar systems. Theoretical development and experimental measurements will be conducted in parallel.

There are few previous studies on interpore diffusional motion in the literature, both theoretically and experimentally. However, we believe that this topic is of fundamental importance for quantitative determination of diffusivity in porous media since in most cases, the pores are connected and not completely isolated. Previous works are either for free diffusion system, or for the completely isolated system. We intend to focus our attention to the interpore diffusion and their impact on the NMR diffusion measurements. Various sizes of pore/throat ratio and throat lengths will be used in the modeling for understanding the relation between the interpore diffusion and throat dimensions. The diffusion-time dependence of the interpore diffusion will be investigated in detail so that the time-dependent apparent self-diffusivity can be understood quantitatively.

We also intend to work on analyzing the possibility of multicomponent apparent diffusivity--specifically, the relationship between the multiple components and the pore size distributions. The impact on the diffusion measurements due to pore-size distribution and due to interpore diffusion will also be investigated. We believe that these analytical work and NMR experimental comparison will be very useful in understanding the fluid transportation and distribution in porous media.

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Fig. 1. Pulse sequence for slice-selective 1D profiles

Figure 2. Comparison Of Saturation Profiles - Building Block Limestone

Figure 3. Comparison of Calculated Saturation Profiles - Indiana Limestone

Figure 4. Signal Intensity with Single-Exponential Fit

Figure 5. Signal Intensity with Stretched-Exponential Fit

Fig. 6. Saturation profiles of a circular cross section during the first stage of (a) imbibition process, (b) drainage process. The flow-rate is 2cc/hr. In (a), the curves corresponding to $t=0$, 5.5min, 13min, 21min, 30min, 42min, 51min, 63min, 100min, 118min, 133min, 161min, and 190min after starting of flow, respectively. In (b), the curves corresponding to $t=0$, 2.5min, 9min, 18min, 29min, 53min, 72min, 93min, 108min, 129min, 163min, and 200min, after starting of flow, respectively.

Fig. 7 Using same drainage data as that in Fig. 6(b). However, the rescaled profiles has removed effect due to geometrical factor circular cross section.

Fig. 8 Oil distribution among different planes during the initial 60 minutes of drainage.

Fig. 9. Saturation profiles of a circular cross section showing the steady state saturations after different flow-rate is applied in (a) imbibition process, (b) drainage process.

Fig. 10.- Relative permeability curves for Case 1.

Fig. 11.- Capillary pressure curves for Case 1.

Fig. 12.- Relative permeability curves for Case 2.

Fig. 13.- Capillary pressure curves for Case 2.

Fig. 14 PFG NMR stimulated echo sequence.

Fig. 15 NMR diffusion measurements in 8 different size beadpacks. The diffusion time is fixed at $\Delta=56\text{ms}$, and the gradient strength was varied.

Fig. 16 Echo amplitude decays as functions of diffusion time in glassbead packs.

Fig. 17 Comparison of echo attenuations among different Δ 's in the 125-180 μ m beadpack.

Fig. 18 Parameter estimation of diffusion measurements in different size beadpacks measured at four diffusion times: (A) $\Delta=56\text{ms}$, (B) $\Delta=106\text{ms}$, (C) $\Delta=206\text{ms}$, (D) $\Delta=406\text{ms}$.

(A)

(B)

(C)

(D)

SUBTASK 3. DEVELOPMENT OF NMR AND CT SCANNING FOR CHARACTERIZING DISPERSED PHASE PROCESSES

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I. Objectives

The objective of this work is to obtain a detailed understanding of the mechanisms and behavior of dispersed phase systems in porous media using advanced NMR and CT imaging methods. Specific projects include the studies of fractional wettability characterization, dispersed phase displacement, and enhanced imbibition processes.

II. Characterization of Fractional Wettability

Background

In a formal sense, wetting of a fluid on a surface can be represented in terms of an equilibrium contact angle. However, on rough surfaces and surfaces with heterogeneities, advancing and receding angles are measured. In mixed wettability systems, one often measures the fraction of the surface associated with "oil wet" behavior and the fraction with "water wet" behavior. In porous media, the characterization of wetting is generally complicated by all these effects, and a complete description is not possible. In most cases, one is limited to measuring relative wettability effects of different fluid systems in a given porous medium using capillary pressure measurements. The global nature of such measurements often obscures the mixed wettability conditions which can arise in reservoir samples. As a result, it is possible to have pore samples exhibiting similar relative wettability behavior, but producing different results with respect to relative permeabilities, displacement efficiencies, etc. Obviously, determination of the distribution of relative wettability associated with a porous medium would be more desirable.

The use of nuclear magnetic relaxation methods to measure fractional wettability is based on the observation that the surfaces of porous media contribute greatly to the relaxation rate of fluids in the pores. NMR measurements of T_1 and $T_{1\rho}$ for H_2O and D_2O in glass bead packs and selected rock samples were reported by several investigators [Brown and Fatt³, Kumar et. al⁴, Saraf et. al⁵, Fung and McGaughy⁶, Williams and Fung⁷], with apparent contradictory results. The results of Brown and Fatt showed a linear relation between the relaxation rate ($1/T_1$) and fractional wettability, with the highest relaxation rates observed with water-wet systems. Williams and Fung obtained opposite results and claimed that the T_1 of water in porous media is dominated by the magnetic properties of the surface and not the effect of wettability. They proposed the use of deuterium $T_{1\rho}$ to characterize fractional wettability. Deuterium has a much smaller magnetic moment than that of a proton, and the measurement of $T_{1\rho}$ enhances the contrast in the relaxation times between the bulk and surface deuterons.

It is generally believed that the fluid in the vicinity of a surface will undergo spin-lattice relaxation at a faster rate than the fluid far from the surface. If the diffusion to and from the surfaces is much faster than the relaxation rate, the "two fraction, fast exchange" model⁸ may be applicable for the characterization of relaxation rate for heterogeneous systems. Two distinct fluid regions are assumed to exist: (1) fluids far from the surface

(bulk phase), and (2) fluids near the surface (bound phase). The observed spin-lattice relaxation time (T_1) is a single exponential decay and first given by Brownstein and Tarr⁸ as:

$$\frac{1}{T_1} = \frac{f_b}{T_{1b}} + \frac{f_s}{T_{1s}} \quad (1)$$

where f_b and f_s are the fractions of bulk and surface fluids, T_{1b} and T_{1s} the relaxation times for the bulk and surface fluids and T_1 is the experimentally measured relaxation time. If the fluid is mostly contained in the bulk phase, i.e., $f_b \gg f_s$, Eq. (1) can be rewritten in terms of the pore volume V to pore surface area A ratio as⁹

$$\frac{T_{1b}}{T_1} = 1 + \frac{A \times \delta}{V} \frac{T_{1b}}{T_{1s}} \quad (2)$$

where δ is the thickness of the surface layer. The A/V ratio is determined by pore structure, and the T_{1s} is related to fluid-surface interactions and pore surface chemistry. Differences in wettability of porous media may result from differences in δ and T_{1s} . From NMR relaxation measurements of fluids in the porous media, the aim is to obtain the fraction of the total surface that is the preferentially oil-wet or preferentially water-wet.

Results and Discussion

Two types of relaxation times were used in our experiments: the longitudinal relaxation time in laboratory frame (T_1) and that in rotating frame ($T_{1\rho}$). Procedures for measuring T_1 and $T_{1\rho}$ of protons and deuterons in porous media have been developed during the past year. T_1 was measured by the inversion recovery method and $T_{1\rho}$ by the spin-locking technique. Both T_1 and $T_{1\rho}$ are affected by the interaction between water molecules and the solid surfaces, as discussed in the previous section. However, $T_{1\rho}$ can be more sensitive to the motions of molecules near the surfaces if the characteristic energy of these molecules are close to that of the driving RF field used in the spin-lock method. The values of a certain relaxation time, T_1 or $T_{1\rho}$, measured in our experiment for a given system during different runs agreed with each other within an error range of 5%.

Several groups of bead packs with different wetting and surface properties were used as model systems in our NMR measurements (Table 1). All beads were sieved such that their sizes were between 44 and 62 μm . Beads in each group listed in Table 1 can be either water-wet or oil-wet. Group 1 contained commercial coated (oil-wet) and uncoated (water-wet) glass beads. The oil-wet beads in Group 2 were obtained by treating cleaned uncoated glass beads with a silicone fluid, SF99 (GE Co.), at 400°F for several hours. The polymer beads in Group 3, made of polydivinylbenzene, were obtained from Bangs Laboratory Inc. These beads were water-wet when purchased, and could be treated to obtain oil-wet surfaces.²⁷ Two crude oils, Syncrude Coker bitumen and Kyparuk crude oil, were used to prepare oil-wet beads through the deposition of asphaltenes and other polar compounds from the crude oil onto uncoated glass bead surfaces (Group 4 and Group 5). The general procedures to deposit asphaltene on surfaces of the glass beads were similar to the methods described in elsewhere.²⁸⁻²⁹ After treatment, the glass beads were preferentially oil-wet.

Bead Pack	Water-Wet	Oil-Wet
Group 1	uncoated glass bead	coated glass bead
Group 2	uncoated glass bead	uncoated glass bead treated with SF99
Group 3	polymer bead with silica layer	polymer bead with silica layer removed
Group 4	uncoated glass bead	uncoated glass bead treated with Syncrude bitumen
Group 5	uncoated glass bead	uncoated glass bead treated with Kuparuk crude oil

Table 1. Model porous media of different wetting characteristics

	$T_1(\text{H}_2\text{O})$	$T_{1\rho}(\text{H}_2\text{O})$	$T_1(\text{D}_2\text{O})$	$T_{1\rho}(\text{D}_2\text{O})$
bulk water	2.92	2.75	0.39	0.40
uncoated glass beads, cleaned	1.15	0.33	0.38	0.17
coated glass beads, cleaned	0.62	0.17	0.38	0.18
uncoated beads treated with SF 99	2.70	0.84	0.40	0.36
polymer beads with silica layer	1.44	0.43	0.40	0.22
polymer beads with silica layer removed	2.00	0.56	0.40	0.32
uncoated beads treated with Syncrude	0.34	0.17	0.39	0.25
uncoated beads treated with Kuparuk	2.15	0.60	0.37	0.24

Table 2. Relaxation times of model porous media saturated with water (H_2O and D_2O)

To make the relaxation time measurements, the beads were saturated with either H_2O or D_2O . Measurements were taken separately on water-wet beads and oil-wet beads. The results are given in Table 2. On the basis of wetting considerations, the relaxation times of water in an oil-wet bead pack is expected to be higher than that for water-wet systems. However, for beads in Group 1, the proton relaxation times of H_2O in the uncoated bead packs (water-wet) were much higher than those in coated bead packs. This indicates that some mechanisms other than wettability dominate the proton relaxation. Therefore we were not able to observe any effects of wetting alternation from proton T_1 and $T_{1\rho}$ measurements in such systems. The T_1 of D_2O saturated oil-wet and water-wet beads are the same as bulk D_2O . The deuteron $T_{1\rho}$ in this group of beads showed no difference between oil-wet and water-wet systems although they were much smaller than that of bulk D_2O . Similar results were reported by Williams and Fung⁷ who used the same beads as our Group 1. Their explanation for this phenomenon was that the dipole-dipole interaction between the methyl groups in the coating surface and the water enhanced relaxation of protons; thus smaller relaxation times were observed for coated beads systems than uncoated ones.

In order to check this conclusion, we treated uncoated glass beads with SF99 (Group 2). SF99 is similar to the commercial coating material used in Group 1. However, this group of beads showed different behavior than Group 1 beads. All relaxation times measured in oil-wet beads were considerably higher than those measured in water-wet beads. These results were in agreement with expected behavior based upon wetting considerations. The measurements on the polymer beads, Group 3, also confirmed

that the proton and deuteron relaxation times for oil-wet systems were higher than those for water-wet systems. From these studies, we concluded that the behavior of relaxation times for our bead Group 1 and for the beads by Williams and Fung⁷ were not caused by the interaction between the methyl groups and the water molecules. The unexpected behavior was probably due to the magnetic impurities left in the commercial coated beads during the manufacturing.

We studied these effects further through tests on beads of Group 4 and Group 5. We found the results for Group 4 to be different than expected and similar with that of Group 1. The proton relaxation times of H₂O in the treated beads (oil-wet) were smaller than those of untreated beads (water-wet). However, the deuteron T_{1ρ} showed a opposite trend than the proton. The latter results agreed with wetting interpretations. On the other hand, both proton and deuteron relaxation times measured for the Kuparuk crude oil deposited beads (Group 5) agreed with the expectations from wettability consideration.

The different behavior of Group 4 and Group 5 could be attributed to the effect of ferro- and paramagnetic trace metals in the crude oils. The importance of ferromagnetic (Fe, Co, Ni) and paramagnetic (Mn, V, etc) impurities on proton T₁ and T_{1ρ} were significant. If the trace metals existed in the crude oil, the deposited layer of asphaltene on the glass surface could also contain these ions. The relaxation due to the dipolar interactions between the ferro- and paramagnetic ions and protons of water is the dominate relaxation mechanism for the system. Therefore, the wetting effect on proton relaxation were not observed for the Syncrude Coker bitumen deposited beads (Group 4). However, since the deuteron relaxation is less sensitive to the ferro- and paramagnetic impurities than proton, we were able to observe wetting effects from deuteron T_{1ρ} measurements. The trace metals contained in those crude oils were verified by the inductively coupled plasma (ICP) methods. The Syncrude Coker bitumen showed very high concentrations of those impurities, while the Kuparuk crude oil contained only small amounts of these ions.

In conclusion, we found that the proton relaxation time measurements (T₁ and T_{1ρ}) can be related to the wetting characteristics of the surfaces of porous media if the concentrations of ferro- and paramagnetic ions are sufficiently low. Measurement of the deuteron relaxation time (T_{1ρ}) can be used where proton relaxation time measurements fail, although with much less sensitivity.

Future Work

At the time of this report, NMR relaxation time methods are being used to determine wettability of rock samples. In rock samples, due to the much more complicated local geometry, the measured NMR intensities in relaxation time measurements do not show single exponential decay. Stretched exponential fit can be used to obtain the relaxation time data. These complicated local geometry will also affect the absolute values of measured relaxation times. Thus for a given type of rock, pure water-wet and pure oil-wet samples will have to be prepared and NMR relaxation times of both protons and deuterons will be measured on these pure systems to obtain calibration points. Rock with unknown wettability will be studied based on these calibration points.

III. Dispersed Phase Processes

Introduction

The use of relative permeabilities in terms of fluid saturations is appropriate for conventional oil and gas displacement processes. However, such representations are totally inadequate for describing chemically stabilized dispersed phase displacements, the latter arising when multiple phases move through a porous media in the presence of film stabilizing surface active agents.

The key elements in describing and simulating dispersed phase flows and displacements in porous media are:

- (1) The identification and description of the phase dispersion and re-connection processes and transient variations in the number and size distributions of the dispersed phase bodies¹⁰⁻¹³.
- (2) The determination of the mobilization and trapping conditions for the dispersed phase. This will require accurate determination of threshold and capillary pressure curves (functions)¹⁴⁻¹⁶ for dispersed phase systems which heretofore have not been obtained.
- (3) The specification of suitable mobility relations for the dispersed phase with closure achieved through appropriate displacement tests (analogous to relative permeability determinations in conventional non-dispersed multi-phase flows)¹⁷.
- (4) The integration of the above descriptions in a comprehensive dispersed phase flow/displacement simulator with the ability to predict the superficial phase velocities and the phase saturation (trapped and flowing) under prescribed conditions and over reservoir length scales.

It is believed that NMR and CT X-ray imaging techniques can provide information of temporal and spatial phase distributions¹⁸⁻¹⁹, in-situ phase texture (by restricted diffusion)²⁰, foam drainage and stability²¹, and mobility data heretofore unattainable in reservoir rock. When coupled with other indirect observations and data, as well as appropriate pore level analyses, such information can provide the basis for the development of new dispersed phase mobility representation.

Several experiments are being conducted under the current project to study dispersed phase systems: determination of dispersed phase texture by NMR restricted diffusion measurements, studies of thin film stability in a film drainage apparatus and dynamic displacement of dispersed phase system by CT scanning, and the investigation of enhanced imbibition process by NMRI.

Dispersed Phase Texture

Background

Dispersed phase systems, either foams or emulsions, play important roles in many petrophysical processes. The existence of the dispersed phase will greatly affect the mobility of the fluid systems in porous media. During oil recovery in porous media, different dispersed phase system can either enhance or slow down the process. Despite its

importance in multiphase flow processes, no effective methods have been employed to study the dispersed phase texture inside porous media. The NMR restricted diffusion measurement may provide a new nondestructive method to achieve this purpose.

It has been known for some time that the self diffusion of molecules having nuclear magnetic moments can be detected by NMR in the presence of various magnetic field gradients.²²⁻²³ Diffusion of such molecules in a magnetic field gradient causes the intensity of the NMR responses to be different from the responses in the absence of gradients.²⁴ NMR attenuation, normally used to describe the effect of molecular self-diffusion, is defined as the ratio of the pulsed NMR signal intensities with and without external field gradients. Particularly, when a spin echo pulse sequence is used together with two pulsed field gradients on a bulk liquid sample, a simple relation exists between the NMR attenuation R and the diffusion coefficient D :

$$\ln R = -\gamma^2 g^2 \delta^2 (\Delta - \frac{1}{3} \delta) D \quad (3)$$

where g is the external field gradient, δ the gradient pulse width, and Δ the interval between the two gradient pulses.²⁴ Diffusion occurred during Δ , the observation time, can be observed. The diffusion coefficient D can be easily determined from such measurements.

However, in the dispersed phase, simple relations such as Eq.(3) do not exist. The NMR attenuation of the dispersed elements will be not only functions of various experimental parameters, but also functions of the geometry of such elements. The term *restricted diffusion* is used to describe such behavior. Instead of being able to diffuse through effectively infinite space, some of the molecules will hit and bounce off the boundaries of dispersed elements, and their motions are said to be restricted by these boundaries. In the presence of external magnetic field gradients, such restriction can greatly affect the observed NMR attenuations. The more molecules that hit the boundaries during the observation time Δ , the stronger the restricted diffusion effects are. The number of molecules hitting the boundaries during Δ is determined by properties of the dispersed phase such as the amplitude of diffusion coefficients and the size of dispersed elements. By measuring the effects of restricted diffusion, the information about the size of dispersed phase systems can be obtained.

The technique of using NMR restricted diffusion measurements to determine dispersed phase size distributions can be applied to the case of bulk liquid emulsions, where the dispersed phase are spherical in shape. During the measurement, NMR attenuation can be recorded for various values of the observation time Δ and the gradient pulse duration δ . The measured NMR attenuation $\langle R(\Delta, \delta) \rangle$ are combined effects of restricted diffusion of molecules in all the droplets of the emulsion sample. Mathematically, the observed NMR attenuation $\langle R(\Delta, \delta) \rangle$ can be expressed in terms of a distribution function of droplet size $P(a)$, and the calculated NMR attenuation $R(\Delta, \delta, a)$ in a sphere of diameter $2a$:

$$\langle R(\Delta, \delta) \rangle = \frac{\int_0^{\infty} a^3 P(a) R(\Delta, \delta, a) da}{\int_0^{\infty} a^3 P(a) da} \quad (4)$$

where the factor a^3 reflects the fact that NMR intensity is proportional to the number of protons.²⁵ The function $R(\Delta, \delta, a)$ can be calculated theoretically.²⁵ The choice of the distribution function is not unique. A commonly used size distribution function for bulk emulsion system is the log-normal function:²⁵

$$P(a) = \frac{1}{2a\sigma(2\pi)^{1/2}} \exp\left[-\frac{(\ln 2a - \ln \xi)^2}{2\sigma^2}\right] \quad (5)$$

By fitting Eq.(4) and Eq.(5) with experimental data, the distribution parameters σ and ξ can be obtained.

Results and Discussion

In this experiment, the NMR restricted diffusion measurement was used to determine the droplet size distribution function of bulk oil-in-D₂O emulsions. An optical method was also used to verify the results of NMR measurements. D₂O has very similar chemical properties as H₂O. It was used because the NMR resonance frequency of deuterons in D₂O is very different from that of protons in oil. The experimental parameters were set such that only the NMR signals from oil molecules could be observed. The emulsion samples were generated by adding oils, either hexadecane or n-octane, to D₂O containing a surfactant alpha olefin sulfonate (AOS).

The diffusion coefficients D of both oils were measured from bulk oil samples using the spin echo method described previously (Eq.(3)). The NMR relaxation time T_1 of oil phase were measured for emulsion samples using the inversion recovery method. Both D and T_1 are listed in Table 3. The NMR attenuations were measured by means of spin echo method for short observation time Δ (<150 ms), and by means of stimulated echo method for long observation time.

	Hexadecane	n-Octane
D (cm ² /sec) (in bulk oil)	6.0×10^{-6}	2.1×10^{-5}
T_1 (sec) (in emulsion)	0.7	1.8

Table 3. Diffusion coefficients and spin-lattice relaxation times of the oils.

Although emulsion samples made from hexadecane and n-octane were believed to have similar droplet sizes, only n-octane samples showed strong restricted diffusion effects. Measured NMR attenuation for a n-octane emulsion sample were shown in Fig. 1 by discrete symbols as functions of observation time Δ and two different gradient pulse width δ . Effects of restricted diffusion were reflected by the nonlinear behavior of the data. On the other hand, the NMR attenuation of hexadecane samples as functions of Δ showed little curvature up to $\Delta \sim 2$ sec. This phenomenon is due to the fact that the diffusion coefficient of hexadecane is about an order of magnitude less than that of n-octane which causes fewer hexadecane molecules to bounce off the boundaries.¹

The experimental data in Figure 1 were used to fit with Eq.(4) and Eq.(5) to obtain distribution parameters σ and ξ . The corresponding distribution function $P(a)$ is plotted in Figure 2 as solid line, and the calculated NMR attenuation using Eq.(4) is plotted in Figure 1 as solid lines in comparison with experimental data.

The emulsion droplet size distribution of the same n-octane sample was also measured using an optical system, which consisted of a microscope, a video camera, a personal computer and an image analysis software. The two dimensional projection of the emulsion sample was captured by the camera and stored in the computer. These data were later analyzed to obtain a size distribution which is represented in Figure 2 by discrete symbols. It can be seen that the distribution obtained by NMR restricted diffusion and by optical method match very well.

The conclusion of this work is that the NMR restricted diffusion measurement is a effective method to determine the droplet size distribution of bulk emulsion samples. A paper has been submitted for publication¹.

Future Work

Although we were able to determine droplet size distribution of bulk emulsion samples, greater difficulties are expected in measuring textures of bulk foam system and textures of dispersed phase system in porous media. Studies are now underway to determine bubble size distribution of bulk foam systems. In such systems, one can only observe the restricted diffusion of liquid in the Plateau borders which have more complicated geometry than spheres. The bubble size distribution can be indirectly obtained if sizes of the Plateau borders are known. Instability of the foam systems can also cause experimental difficulties. Appropriate experimental procedures must be developed for good restricted diffusion measurements in foam systems. Theoretical modeling of the restricted diffusion in foam systems has also been initiated. Such studies may provide additional information for determining dispersed phase texture using NMR restricted diffusion measurements.

Stability and Dynamic Displacement of Dispersed Phase Systems

Results and Discussion

Comprehensive studies of the dynamic displacement of foam systems in porous media are conducted under this part of the project. A flow system has been constructed which can be used to measure the spatial distribution of dynamic capillary pressure. The in situ saturation of the foam systems generated in this apparatus can also be determined by CT X-ray scanning methods. Furthermore, at the end of the displacement process a pressurization method will be used to study foam texture. During this pressurization process, the system pressure will be increased to such an extent that the bubble volume will be much less than the typical pore volume, and the subsequent displacement of the foam through an viewing cell will allow the pressurized bubble size distribution to be recorded. A back calculation to the original pressure will give the size distribution of the bubbles inside the porous media.

In order to establish techniques for characterizing foam stability, a thin film drainage experiment has been used to study film stability under controlled capillary pressure conditions. The apparatus consists of an optical imaging system and a film drainage cell. Thin films are generated from a surfactant solution in the cell. A computer

Figure 1. NMR attenuation of an n-octane emulsion sample.

Figure 2. Size distribution functions of the n-octane emulsion sample.

operated microsyringe is used to control liquid drainage of the films and thus the film thickness. The corresponding film thickness is then calculated from the light intensity recorded by a photomultiplier using light interference method³³⁻³⁵. This setup also allows us to study film behavior under different drainage rates. This part of the research has been very fruitful during the past year. A paper was presented at the ACS annual meeting in June, 1991 on these studies.² The major results can be summarized as follows:

Thin films generated from surfactant solutions containing sodium dodecyl sulfate (SDS) were studied in the low disjoining pressure range. Disjoining pressures and thin film thicknesses were measured for various experimental parameters such as SDS concentration, solution age, and drainage rate. Film lifetime data were also collected, especially for low surfactant concentration systems where the films were relatively unstable. We have also tested the effect of oil on the thin film stability by adding octane into the SDS/water solution. The experimental results have been analyzed using DLVO theory^{31,32}.

The surfactant solutions used in this experiment had SDS concentration below, near, and above the critical micelle concentration (CMC). Thin films generated from surfactant solutions with different SDS concentrations displayed very different behavior. In Figure 3, measured disjoining pressure π for films with SDS concentrations below the CMC, $C_{SDS}=0.003M$, are plotted against measured film thickness h . The theoretical prediction, calculated according to DLVO theory, is also presented as solid curve. DLVO theory describes the behavior of thin film disjoining pressure arising from dispersive and electrical double layer interactions. However, such conditions of pure surface charge interaction could not be satisfied in our drainage cell when the film was relatively thick. This phenomenon is demonstrated in Figure 3 where the measured disjoining pressure is shown to be much higher than that predicted by DLVO for thick films. To effectively apply DLVO theory to the films generated in our drainage cell, the film thickness must be lower than certain value h_0 . For SDS concentration $C_{SDS}=0.003M$, the lifetime of films were relatively short. Most of the films would break before h_0 could be reached. However, for films with higher SDS concentrations, the film lifetimes could be long enough for these films to reach h_0 . In Figure 4, the measured disjoining pressure for films with $C_{SDS}=0.007M$, which was near the CMC, showed agreement with DLVO predictions when the film became sufficiently thin. For films with SDS concentrations above the CMC, i.e. $C_{SDS}=0.03M$, the situation was more complicated. The measured disjoining pressure did not agree with the DLVO prediction even when the films were very thin (Figure 5). We believe this was caused by the under estimation of the amount of surfactant ions adsorbed on the film surfaces in the DLVO calculation.

Another phenomenon which was observed at SDS concentrations above the CMC was the thickness of these films did not change continuously, but rather showed sudden changes at certain thicknesses. This could be explained as micelle layer jumps. In high concentration films, surfactant micelles form layers inside the films. When such layers are sequentially squeezed out during drainage, a jump will be observed in film thickness. We have compared our experimental data from films of $C_{SDS}=0.03M$ and $C_{SDS}=0.1M$ with the theory by Nikolov et. al.³⁰ The results are listed in Table 4, where h_{cr} is the film thickness at the jump point. The experimental data agreed very well with calculated values.

$C_{SDS} = 0.03M$			$C_{SDS} = 0.1M$		
Layer	$h_{cr,theory}$	$h_{cr,observed}$	Layer	$h_{cr,theory}$	$h_{cr,observed}$
1	49.4 nm	51.7 $\pm$ 4.3 nm	1	38.4 nm	37.0 nm
2	65.5 nm	63.4 $\pm$ 3.6 nm			
3	82.0 nm	82.3 $\pm$ 3.1 nm			

Table 4. Critical thicknesses for changes in layer number

It was observed that adding octane into the SDS surfactant solution had little effect on the π -h relation (Figure 6). This indicates that the surface concentrations of SDS, and hence the interactions between liquid surfaces, were not affected by the addition of octane. The age of the solution, however, did affect the π -h relation (Figure 7). This could be caused by the impurities contained in the surfactant. In order to verify this, we are purifying the commercial SDS samples using recrystallization and foaming methods to obtain ultra pure surfactant (>99.9% SDS).

We have also tested the effect of drainage rate on film behavior. Dimples were observed on the film surfaces when fast suction speeds were used (Figure 8). These phenomena were more obvious in low surfactant concentration films. The observed dimples were believed to be responsible for the short life of these low SDS concentration films.

Future Work

Effects of salt, such as NaCl, on film stability will be investigated. The apparatus will be modified to extend the film studies to higher disjoining pressure.

The dynamic displacement of dispersed phase systems in porous media is also underway. Measurement have been taken to study the spatial distribution of pressure along the direction of displacement. A new probe is being designed to improve the dynamic capillary pressure measurements. More results of this research will be given in the next report.

Enhanced Imbibition Processes

Background

Conventional oil recovery methods, such as water flooding, are of limited effectiveness in low permeability, fractured reservoirs. While these methods tend to recover oil in fractures and in the immediate neighborhood of the fractures, they leave the majority of oil in the low permeability rock almost untouched. A portion of this remaining oil can be recovered through water soak imbibition processes. The imbibition process makes use of the effect of capillary force to displace oil in the rock with water. However this process is very slow and marginally economical.

Recent studies of carbonated water imbibition processes showed promising results.²⁶ The inclusion of CO₂ in water has several important effects. It alters the interfacial properties between water and rock as well as between water and oil. It also causes significant swelling of the oil phase and decreases the oil viscosity. The acidic nature of the carbonated water can also clean up acid-soluble clay contaminants in the pore

figure 3. π -h curve for $c=0.003M$ films.

figure 4. π -h curve for $c=0.007M$ films.

figure 5. π -h curve for $c=0.03M$ films.

figure 6. Comparison of SDS system and SDS/octane system.

Figure 8.
Drainage rate effects for
 0.003M SDS surfactant solution.

Figure 7.
Solution age effect for
 0.03M SDS surfactant solution.

space and widen pore throats in carbonated rocks. All these changes are believed to be beneficial for an increased imbibition rate. Furthermore, a gas drive process can be applied at the end of imbibition to further increase the total amount of recovered oil.

Two of the major factors in the above carbonated water imbibition process, the surface tension between water and oil and the solution gas drive process, can be further improved by introducing surfactants into the carbonated water solution.

A gas drive process is a process where the system pressure drops rapidly from several thousand psi to certain much lower pressure, and the CO₂ component previously dissolved in the fluid under high pressure may come out the solution and form a gas phase. The evolution of the gas phase will result in the displacement of water and oil if the gas evolution rate in the pore space exceeds the rate at which gas escapes. However, because of the high mobility of CO₂ gas relative to the liquid, the escape rate of the gas phase can be very high if carbonated water is used alone. When a surfactant is used together with carbonated water, it is possible (1) to enhance the gas evolution rate through the promotion of gas nucleation, and (2) to reduce the gas phase mobility through the in-situ formation of a foam. As a result of this process, the evolved CO₂ gas will provide a low mobility, highly efficient, solution-gas drive mechanism.

Introducing surfactants into the imbibition process may also improve the efficiency of the process through the reduction of the interfacial tension between the water and oil phases. Also, because of spatial variation of surfactant concentration, a gradient of capillary pressure will build up near the imbibition surface, providing an additional drive mechanism to displace oil from the rock matrix. With proper surfactant selection, imbibition fluid wetting can be promoted and the oil phase mobility increased.

Experimental Work

Nuclear magnetic resonance imaging will be used to study the surfactant based imbibition and solution gas drive process. In our studies, it is important to obtain information about the temporal and spatial distribution of the oil phase as the imbibition proceeds. NMRI provides a good tool for such measurements. The local oil saturation at any cross section of the rock sample at a given moment can be recorded by NMRI almost instantly. Such information can not be provided by conventional saturation measurements.

A carefully designed apparatus has been constructed. This apparatus will be able to perform experiments under high pressures (~3000 psi) and high temperatures (~90°C). A flow diagram of the apparatus is shown in Figure 9. The Hassler sleeve type core holder (Figure 10) is made of non-metal materials in the center part. This will allow the NMR measurements. Water at elevated temperatures will flow through the outer sleeve of the core holder to maintain the rock at a given temperature. High pressure conditions are provided and regulated by high pressure nitrogen gas. These high pressure and high temperature conditions are necessary in this experiment in order to simulate reservoir environments.

To do the experiment, the 3" long and 1" in diameter cylindrical rock sample will be saturated first with D₂O, then with oil to form a partial oil saturated rock system. During the imbibition process, D₂O will be used as water phase to carry CO₂ and surfactant. Such solution are to be pushed to the rock surface under a system pressure of about 3000 psi. As oil in the rock are being displaced by incoming water, the proton profile of the oil inside the rock will be recorded (via NMRI) as functions of time. By analyzing these data, imbibition rate as well as total amount of recovered oil can be obtained. At the end of imbibition, a solution gas drive process will be induced by reducing the system pressure

Figure 9: Experimental flow diagram.

Figure 10: Core Holder

rapidly and causing the evolution of a gas phase; the oil profile will also be recorded during this process.

Future Plan

Various check out tests are being performed on the apparatus. The studies of the imbibition will start upon the completion of these tests.

We will test the effects of different surfactants, and different surfactant concentrations on the imbibition process. We will also investigate the optimum pressure and temperature conditions for the induced solution gas drive process. This information should provide the basis for analyzing the effectiveness for such processes.

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SUBTASK 4: MISCIBLE DISPLACEMENT STUDIES

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OBJECTIVES

The objectives of Subtask 4 are to: (1) develop the CT scanner for use in dynamic flow tests and (2) study the effects of viscous fingering in laboratory core displacements.

INTRODUCTION

Application of miscible flooding agents such as carbon dioxide, methane, nitrogen, or enriched hydrocarbon gas has been demonstrated as a viable means to recover additional oil from previously depleted reservoirs. Application of miscible flooding, however, is complicated by the formation of viscous fingers which complicate the process and lower volumetric sweep efficiency. Part of this work is a systematic experimental study investigating the factors affecting finger growth in laboratory cores.

The theory of finger propagation and growth is intimately related to viscous, gravity, and dispersive crossflow. Viscous crossflow is known to initiate and propagate viscous fingers; gravity crossflow is responsible for the formation of gravity tongues; dispersive (transverse) crossflow is known to dampen or mitigate fingers or tongues. All of these factors affect vertical sweep efficiency. Part of this work involves the development of mathematical models to study fingering.

METHODOLOGY

Our approach to study viscous fingering is to use a CT scanning apparatus. This unique approach allows us to obtain accurate flood front shapes as a function time and position. This in-situ data together with elution history and cumulative recovery data is much more meaningful in characterizing the displacement behavior than elution history and recovery data alone. By gathering this type of data for a wide range of conditions, i.e., core lengths and diameters, injection rates, density differences, and viscosity ratios, a unified theory for vertical sweep efficiency in miscible systems can be developed.

A second goal of this work is to simulate these crossflow mechanisms in order to characterize their effect on vertical sweep efficiency. One purpose of our model study is to formulate appropriate dimensionless groups which properly characterize the different flow regimes which are observed. The dimensionless groups will be helpful in screening target reservoirs. The data obtained from the CAT-scan and NMR experiments will also be useful in validating reservoir simulators.

DISCUSSION

Two graduate students are working on Subtask 4. Michael D'Souza is carrying out the experimental work and Kenji Seto is carrying out the mathematical modeling work.

Experimental Work

Three core tests have been carried out to date. The purpose of these tests have been to develop experimental methods using the CT scanning apparatus. The experimental work carried out thus far includes: (1) designing a core containment device, (2) designing a flow system, (3) developing viable CT scanner operating procedures, (4) developing data transfer procedures from the CT scanner to post-processors, and (5) developing post-processing software for image reconstruction. This report only summarizes some of the work performed to date.

Figure 1 shows the core mounting and end-cap design. The core mounting procedure consisted of fitting the core with end-caps, paint the core with epoxy, and wrap it with fiberglass tape. Figure 2 is a schematic of the flow system. The main component is a Micrometrics HPLC pump which is usually operated at about 5 cc/min.

In each test, an aqueous solution containing NaI is used to displace a solution containing NaCl. See individual quarterly reports for details. In the first test we used a 4 inch diameter by 1 foot long, cylindrical sandstone core. The core porosity was approximately 19%, its permeability was approximately 190 md. and its pore volume was about 469 cc. This test helped to refine our flow system design and CT scanner operating procedures. It also identified several serious data post-processing limitations. Originally we attempted to carry out post-processing and image reconstruction using Prime and Macintosh computers. Neither of these computers proved useful for post-processing because of either hardware and host software limitations. Since this time we have improved our post-processing capabilities by purchasing a Sun workstation (Feb., 1991). We note that the addition of the Sun workstation has greatly enhanced our progress with post-processing and image reconstruction. More specifically the Sun workstation permits easy data transfer from the CT scanner and utilizes much more powerful image reconstruction software. The progress using the image reconstruction software will be discussed more later.

One purpose of this first test was to obtain meaningful saturation measurements. Our efforts were complicated by random noise in the CT signals. The random noise resulted in appreciable errors in the saturation measurements. The error can be mitigated by using a pixel averaging method whereby we group several pixels together instead of using individual pixels. The disadvantage of this approach is that we lose resolution of our measurement. We have developed computer programs to process the saturation data using this pixel averaging technique. This problem of random noise complicating the saturation measurement is not well-documented in the literature. Our experience confronting this problem may be of interest for future CT scanner users.

Figure 1 - Core containment device.

Based on our error analysis, there is an alternative method to mitigate the error in the saturation measurements. This approach requires using a different concentration of NaI as our dopant. Though this approach may reduce the error, it alone may not be sufficient to reduce the error to an acceptable level.

Two subsequent core tests were carried out to obtain improved CT number and saturation measurements. In the first test we used a small Berea core having dimensions 1 in. X 1.5 in. X 4 in. We used an aqueous solution of 1 molar NaI to displace a solution containing 2% (wt) NaCl. This NaI concentration was higher than that in previous tests in order to improve the saturation measurement resolution. The results of this test showed good CT number resolution. A unique aspect of this test was that, because the core was small enough, the core was scanned longitudinally along the flow direction instead of transverse to flow. One advantage of scanning in this manner is that it requires less data processing to reconstruct the cross-sectional image. This maybe an attractive feature inasmuch as developing image reconstruction software is time-consuming. A disadvantage of this type of scanning, however, is that it is limited to core lengths less than about six inches. Since we wish to study core lengths greater than six inches, this limitation is

probably too restrictive. This test resulted in good CT number resolution between the fluids.

Figure 2 - Schematic of flow system.

In a second test we used a 4 inch diameter by 1 ft long Berea core and flooded it with the same fluids listed above except glycerine was added to the fluids to improve the density match. This test also yielded good CT number resolution between the fluids.

Concurrent and subsequent to carrying out these later two core tests, we have concentrated on developing a viable image reconstruction process. To achieve this, we have utilized Shell's image reconstruction software, CATPIX. This is an important part of Subtask 4 inasmuch as viscous fingers are 3-D projections which grow and change shape as a function of time and position and we require some method of representing these projections. We have selected Shell's CATPIX software mainly because it has been donated by Shell and because this type of software is prohibitively expensive for us to purchase. A prerequisite of image reconstruction software is that it must, at least, be able to reconstruct 2-D (longitudinal) images from the 2-D (transverse) images normally procured during scanning. In addition, we may eventually require the reconstruction of fully 3-D images from the 2-D transverse images. This is indeed a challenging task.

We have successfully used Shell's CATPIX software on the Sun workstation to generate 2-D (longitudinal) cross-sectional CT number profiles. We are now able to generate these 2-D longitudinal profiles along any longitudinal plane from the 2-D transverse slice data. This work represents a major accomplishment for this project because we require such data processing in order to study viscous fingering using the CT scanner. We note that the Shell personnel were instrumental in helping the graduate students utilize the software.

Presently the Sun workstation has no printing capabilities so we are unable to present any hardcopy images at this time. We are presently addressing this limitation and hope to have hardcopy images in the near future.

Mathematical Modeling Work

Kenji Seto is carrying out the mathematical modeling work and is refining a finite-difference, miscible displacement model procured from one of Dr. Slattery's past students. Once this model is adapted for use on Texas A&M's vector computer, it will be used to guide the fingering experiments.

Chang and Slattery (1990) originally developed the computer model to simulate the miscible displacement of one fluid by another in a 3-D porous matrix. Their simulations proved successful in modeling the different physical phenomena that occur in miscible displacements. Unfortunately, the model exhibited poor execution times, even on a vector computer.

The initial focus thus far has been to increase execution speed and efficiency of the reservoir simulator. To determine the computationally intensive areas of the program, the simulator was analyzed by CPU accounting software resident on the Cray-YMP computer. We decided that the pressure/velocity field calculation was the most likely to benefit from a numerical method revision. The original calculation was performed using a ADI-SOR method as outlined by Peaceman and Rachford (1962). This method, being highly iterative in nature, not only gave rise to questions of its efficiency, but also accuracy.

To reconcile the accuracy question, we began by programming a "direct" solution of the pressure/velocity field. This entailed explicitly solving a large system of linear equations. The size of our problem and the limited memory capacity available on most computers prohibited the use of traditional linear equation solvers. An out-of-core linear equation solver residing in the Boeing Computer Services Library Software was employed. This software, though too slow to permit its regular use, did allow us to check the accuracy of the ADI-SOR code and the other indirect solver considered.

From our runs of the "direct solution" software, it became obvious that an iterative solver would provide the best chance of increasing the efficiency of our simulator. The Conjugate Gradient (CG) method is commonly employed to iteratively solve large linear systems. The software package, CgCodes, produced under the joint supervision of the University of Chicago at Urbana-Champaign and Los Alamos National Laboratories, was selected to perform this calculation. It has the benefit of providing very efficient routines, ease of use, and different preconditioning options. The iterative nature of the CG method makes its efficiency directly dependent upon the type of preconditioning methods used with it.

At present, we have attained reasonable success with the use of diagonal scaling in conjunction with the Chebyshev adaptive polynomial preconditioning algorithm that was supplied with CgCodes. We are exploring more extensive preconditioning methods. The use of the "direct" solution software has proved invaluable by confirming the accuracy of the iterative solution and providing estimations of the error tolerances for both the ADI-SOR and CG algorithms.

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