NMR IMAGING OF FLUID SATURATION DISTRIBUTIONS IN CORE SAMPLES USING A HIGH MAGNETIC FIELD

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Abstract Magnetic Resonance Imaging (MRI) now used in medical research should result in progress in the understanding of flows in porous media.
This paper describes several applications of the Magnetic Resonance Imaging technique to study fluid distributions in porous media using a high magnetic field of 9.4 Tesla.
The different applications studied are:
- determination of local porosity through the intensity of the NMR signal of a fluid in a porous medium,
- visualization of oil and water distribution by chemical-shift selective excitations.

Improvements obtained by using a high magnetic field for studies related to fluid distribution in porous media are shown. In addition the limitations of using such a magnetic field will be discussed.

INTRODUCTION

Nuclear Magnetic Resonance (NMR) has long been used in the oil industry as a research tool for the measurement of petrophysical rock properties: porosity, permeability. NMR imaging (MRI) adds the extra feature of the possibility of three-dimensional visualization of two immiscible fluids in porous media.

Unlike X-ray CT, which visualizes both the rock matrix and pore fluids, MRI can visualize mobile fluids and the interaction of these fluids with the surface of the pores.

We will begin by looking at the principles of these two techniques, NMR and MRI.

Secondly we will indicate the results given in the literature concerning the application of NMR and MRI to the study of fluids in porous media. The third part will describe the apparatus that we have used. Various results will then be presented concerning the study of fluids in porous media using a high magnetic field.

NMR AND NMR IMAGING

Nuclear Magnetic Resonance is mainly known as a Spectrometric Technique. When nuclei with magnetic moments are put in a static homogeneous magnetic field, populations are shared on discrete energy levels. An appropriated radio-frequency field is applied to induce transitions between the levels, thus changing the magnetization.

At the end of radio-frequency excitation, nuclei return to equilibrium and the decay of magnetization as a function of time is acquired. A Fourier transform is applied and gives the variation of magnetization as a function of frequency (υ) which constitutes the NMR signal.

$$M = f(t) \xrightarrow{FT} M = g(\upsilon) \qquad (1)$$

in which

$$\upsilon = (\gamma/2\pi) \cdot B \qquad (2)$$

with υ: signal frequency
B: magnetic field seen by the nucleus
γ: characteristic nucleus constant

The frequency of this decay depends on the strength of the magnetic field and is characteristic of both the nuclei species and of the chemical environment of the nucleus. This method is a very powerful tool for quantitative, qualitative and structural analysis.

To obtain an image of the distribution of a kind of nucleus, the hydrogen nucleus for instance, in a rock sample, a spatial discrimination is required instead of a chemical one. This discrimination is produced by superposition of three orthogonal linear magnetic field gradients on the main magnetic field. The three gradients are applied in the three x, y, z directions. In this way each point of the sample is subjected to a different magnetic field and then gives a signal at a different frequency, which is linked to a spatial position.

Generally one of the gradients is used to select a slice in the sample. The higher the gradient strength, the narrower the slice (in conjunction with the length of the radio-frequency pulse). The other two gradients determine the size of the pixel in the slice.

Resolution depends on the strength of the three gradients, on the density of nucleus and on the transverse relaxation rate.

There are two kinds of relaxation, longitudinal relaxation (T1) which governs the recovery of the system towards the equilibrium and the frequency of the repetition rate. The transverse relaxation (T2) characterizes the extinction of the signal and the width of the frequency signal, hence the resolution of the method. Likewise the time needed to apply and interrupt

gradients, especially in echo methods, can be long, and it is necessary to accord this time with the relaxation rate to obtain a signal.

This relaxation is governed by porosity, permeability, wettability and paramagnetic impurities, and in cores it might be necessary to use sequences of fast NMR imaging or, in extreme cases, the technique of Back Projection. This method enables signals to be received 1 ms or less after excitation instead of 4-6 ms for standard spin-warp sequences.

In high magnetic fields it is also possible to differentiate species with sufficient chemical resolution (Chemical Shift Selective Sequences): for instance, in core samples to obtain an image of oil or of water.

STATE OF THE ART

The use of the Nuclear Magnetic Resonance (NMR) of protons to study porous media began with spectroscopy research:
- to study the overall petrophysical characteristics: porosity (Timur (1969), Cowgill et. al. (March and May 1981)), absolute permeability (Headley (1973), Kenyon (0ctober 1986)), irreducible water saturation (Seevers (1966), Timur (1969), Cowgill et al. (March and May 1981)) and determination of the quantity of organic and inorganic carbon contained in cores from oil reservoirs coupled with ^{13}C NMR (Vinegar et al. (August and October 1989)),
- to determine the distribution of pore sizes (Seevers (1964), Kozlov et al. (1982), Brown et al. (1981), Gallegos et al. (1987 and 1988), Kenyon (1989)),
- to study wettability (Brown et al. (1956), Kumar et al. (1969), Williams et al. (1982)),
- to determine saturations in a sample (Saraf et al. (1966 and 1967)).

The use of NMR to study fluids in porous media is based on the observation that relaxation times of fluids in porous media are different from those of pure fluids. This difference is due to the presence of the porous medium.

These different applications use overall NMR measurements of nuclear spin density and various relaxation times.

The last application, the determination of saturations in a sample, has been extended to MRI.

In 1973, Lauterbur demonstrated that, by applying a magnetic field gradient the spatial distribution of the hydrogen contained inside the sample under study could be visualized. Thus was born the first magnetic resonance imager. The first image was then made by Mansfield in 1976. Several years later the first nonmedical applications of MRI were envisaged. Its application to porous media began in 1979 when Gummerson et al. (1979) used NMR to follow the capillary absorption of water in a plaster bar. They obtained one dimensional profiles indicating the quantity of water absorbed as a function of time. They used a magnetic field of 0.7 Tesla.

In 1985 Rothwell and Vinegar (December 1985) showed an image of Berea sandstone containing water. They used a Bruker imager of 0.84 Tesla, obtaining the images by back projection, since this method enables the study of samples having very small relaxation times T2, which is the case for fluids in porous media.

Blackband and Mansfield (February 1986) used a magnetic field of 0.7 Tesla produced by a resistive magnet. The signal was obtained by the SSFP method ("Steady-State Free Precession") which is the method that gives the best signal/noise ratio. The signal observed is proportional to T2/(T1 + T2). The images are obtained using a back projection algorithm. To visualize samples containing water and heavy oil, they used images depending more on T2. To visualize samples containing water and light oil, they used water acidified by sulfuric acid to take advantage of the difference in chemical shift between the protons of the acidified water and those of the oil.

Hall et al. (1986) used a greater magnetic field of 1.9 Tesla to exploit the chemical shift between the protons in water and those in oil. They showed the image of a composite sample of Berea sandstone made up of one part containing water (the lower part) and another part containing oil. One year later, the preceding method was applied to a sandstone sample containing both water and oil (Hall, Rajanayagam (1987)). The image of the oil was obtained by a particular sequence which canceled the water signal. The images obtained were 930 μm thick.

Baldwin and Yamanashi (1986) visualized the flow of water through an oil-saturated sample using a medical imager of 0.5 Tesla, a special coil adapted to the size of the samples, and water doped with Mn++ ions. They demonstrated a preferred path for the flow of water. Edelstein and Vinegar (1988) used a 2 Tesla imager to differentiate water and oil either by canceling the water signal by a suitable sequence, or by selectively exciting oil or water.

In 1988, Chen et al. (1988) studied drainage-imbibition experiments at 1.9 Tesla by doping water with Ni++ ions. That same year, Vinegar, Tutunjian (1988) registered a patent that indicated how to visualize a sample containing two fluids, by using two types of nuclei, ^{1}H and ^{19}F, since the sensitivities of the two nuclei are similar (1.0 for the ^{1}H and 0.85 for the ^{19}F).

In 1989, many papers appeared showing the use of MRI to visualize flows: chemical displacement data were used to selectively visualize water or oil (Horsfield et al., (1989), Dechter et al., (1989)), or one of the two phases was doped to cancel its signal (Baldwin et al., (May 1989), Guillot et al., (1989)). Dechter et al., (1989) presented a 3-dimensional visualization of a porous medium from slices obtained by MRI.

APPARATUS

We used a MSL 400 spectrometer built by Bruker. A field strength of 9.4 Tesla was obtained by a superconducting magnet with a wide bore (Ø 89 mm). It can be used in spectrometer and micro-imaging configuration.

Micro-imaging was performed only at 400 MHz (i.e. only Hydrogen nuclei could be observed) and different sizes of inserts can be adapted to the probe from 25 down to 2.5 mm diameter (the last one perpendicular to the field axis, the other ones parallel). For a 25 mm insert the height of the coil was 50 mm.

Theoretically the strength of the gradient can reach 50 Gauss/cm but to date we haven't used so much strength and have worked with a maximum of 22 Gauss/cm, for which we obtained slices 60 μm thick.

Different kinds of pulse sequences were used. For xy slices all of these were included in the Bruker Software package. We modified some of them slightly to obtain slices parallel to the Bo field.

EXPERIMENTAL

Resolution

All our experiments were performed with a 9.4 Tesla magnet described above. The most important advantage of a high magnetic field is that it increases the signal to noise ratio and thus the resolution of our images. The optimal elementary volume (VOXEL) defined by the best resolution conditions must contain a sufficient number of nuclei to be detected and the higher the field, the smaller the VOXEL can be . We will see below the possible disadvantages of such high fields.

The other parameters that act on the resolution are gradient strength and linearity, natural width of the signal, magnetic susceptibility and magnetic field homogeneity.

For the gradient strength, high gradients obviously yield a better resolution.

The natural width is linked to the value of the transverse relaxation rate. The width of the signal at half width ($\Delta\upsilon_{1/2}$) is:

$$\Delta \upsilon_{1/2} = 1/ (\pi \cdot T2^*) \qquad (3)$$

where T2* is the transverse relaxation time modified (decreased) by the inhomogeneities of the magnetic field. Generally fluids included in rock samples have a relatively short T2 and our first goal was to get a good resolution. There are two methods to achieve this goal:

- when the relaxation rate is about 4-5 ms and we undertook spin-echo methods, which take away inhomogeneity effects by refocusing the

signal. This reduces the signal-to-noise ratio because the time between the excitation and opening of the receiver is long and some of nuclei are relaxed.
- if the T2 relaxation rate is less than 2 ms and spin-echo methods are not operational, a fast method has to be used. This method gives a signal but one with a worse resolution because of the short T2 and the impossibility of performing spin-echo sequences.

Pulse Sequences

To determine the influence of the pulse sequence, we experimented with three different pulse sequences.

Generally, to get images of total hydrogen content, we applied the standard spin-warp sequence described in Figure 1.

All the samples were excited by a 90° radiofrequency pulse in a spin-echo sequence. The signal was refocused by a 180° selective pulse which, in conjunction with a Z gradient, selected the slice of interest. Discrimination in the XY plane was obtained by two gradients in Y-direction applied as phase encoding and one in X-direction during the acquisition. A two-dimensional Fourier transform produced the corresponding image.

For fluids with a high transverse relaxation rate, we used a fast sequence. A selective-pulse in conjunction with a Z gradient excited only one slice of the sample, and the signal was refocused by a reversal X gradient in such a way that the signal can be captured 1 or 2 ms after excitation. This is known as Flash method (fig. 2).

A third type of pulse sequence was used when two immiscible fluids, for instance oil and water, were both present in the core. This sequence is known as chemical shift selective sequence. The difference with the spin-warp method lies in the 90° pulse which here is a soft selective pulse that excites hydrogen in a very narrow frequency range. This range is changed by adjusting the frequency of the pulse either to the water proton frequency or to the oil proton one (fig. 3).

Core samples

Two porous materials were used:
. Fontainebleau sandstone (pure silica - quartz)
. limestone (bioclastic limestone).

For each kind of material, two core samples were investigated. For Fontainebleau sandstone, the porosity was 15% and the gas permeability was 2 Darcy.

For limestone, the porosity was 30% and the gas permeability was 300 mD.

One sample was 100% saturated with distilled water. The second sample was 100% saturated with a refined oil (Soltrol 130). In the

limestone sample saturated with water, an injection of about ten pore volumes of oil was performed.

The dimensions of the rock samples were 3 cm (1.18 in) in length and 1 cm (0.39 in) in diameter.

The rock samples were laterally coated with an epoxy resin. Two PTFE end-pieces were used to saturate the samples with various saturations of oil and water.

RESULTS

Different results were obtained on the previously described samples. On two limestone samples, one saturated with water and one saturated with oil, the spin-warp method enables us to obtain 512x512 images for a 50 μm-thick slice (fig. 4 and 5).

The distribution of oil and water inside the rock in the direction of the flow was observed by using the chemical shift sequence applied to a plane parallel to Bo (fig. 6 and 7).

A satisfactory image was also obtained on a sample with a lower porosity: Fontainebleau sandstone (fig. 8).

The FLASH sequence was tested on the limestone sample saturated with water. It was not possible to obtain any image. One reason could be the heterogeneity of local magnetic susceptibility. This heterogeneity is not totally compensated for by this kind of pulse sequence. Such problems may be related to the use of high magnetic fields.

CONCLUSIONS

In this paper we presented our first results. These results show:

- the feasibility of using NMR with high magnetic fields to visualize two immiscible fluids inside porous media. Until now, such high magnetic fields had not been used for this kind of application,
- the possibility to obtain an image from a 50 μm-thick slice. To our knowledge, no image of such a small thickness had yet been obtained.
- the discrimination between oil and water inside a porous medium by using chemical shift selective sequence.

Previous studies using MRI to visualize fluids inside porous media gave slices with a resolution similar to that obtained from CT-Scanner. Indeed, CT-Scanner gives slices 1.5 mm thick. We show that with a high magnetic field, it is possible to obtain a resolution 30 times better.

Moreover, the use of such high fields enables the visualization of water or oil inside the same porous medium without any addition of a doping agent.

To continue this work, we intend to investigate:

- the use of longitudinal or transversal selective pulse sequences,
- the quantitative study of applying NMR to fluids inside porous media.

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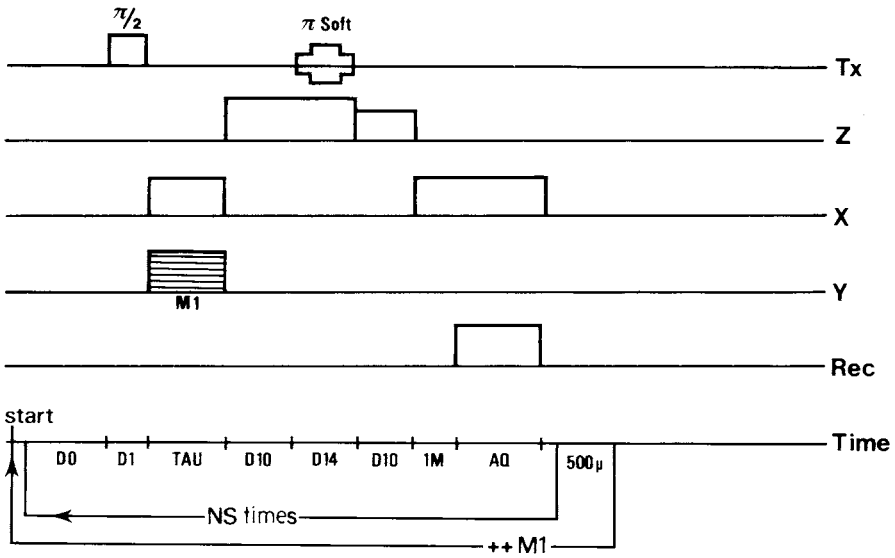

Figure 1 - SPIN WARP SEQUENCE

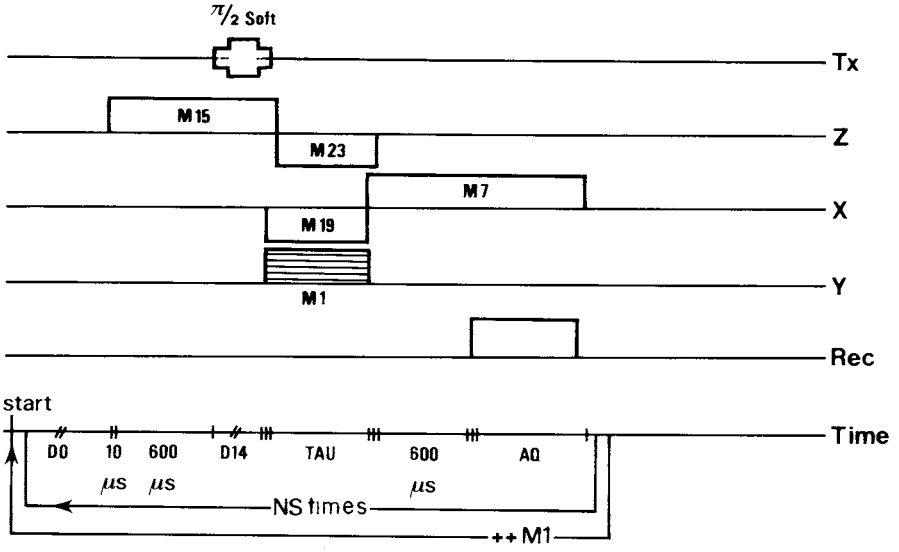

Figure 2 - FAST SEQUENCE

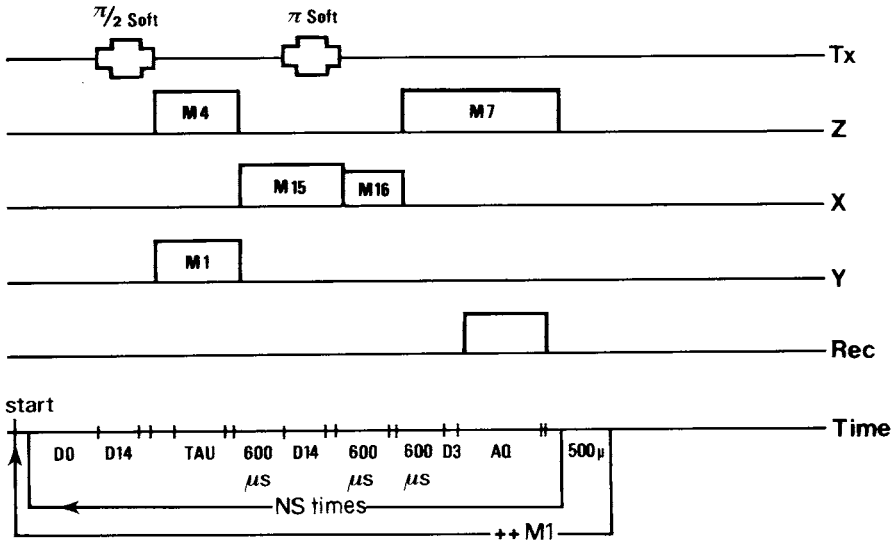

Figure 3 - SELECTIVE SHIFT SEQUENCE

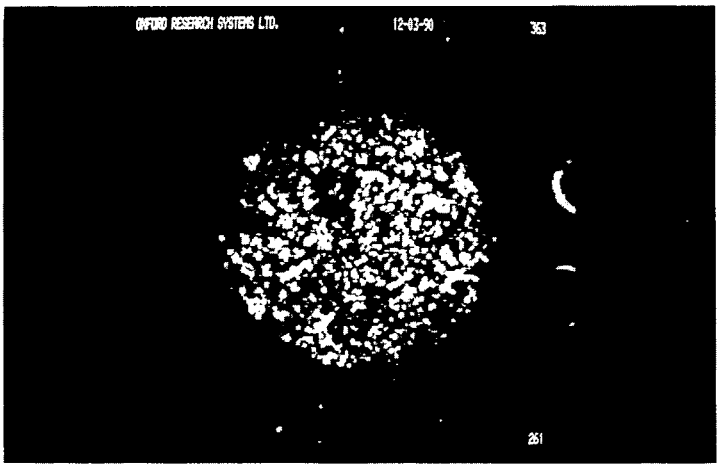

Figure 4 50μm-thick slice of a limestone sample saturated with water

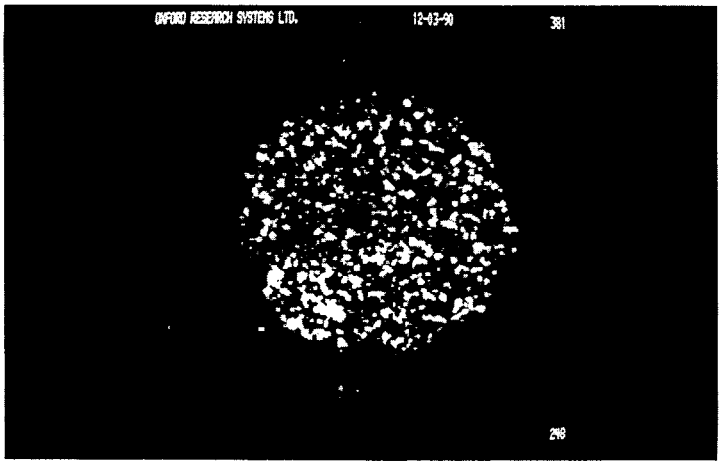

Figure 5 50μm-thick slice of a limestone sample saturated with oil

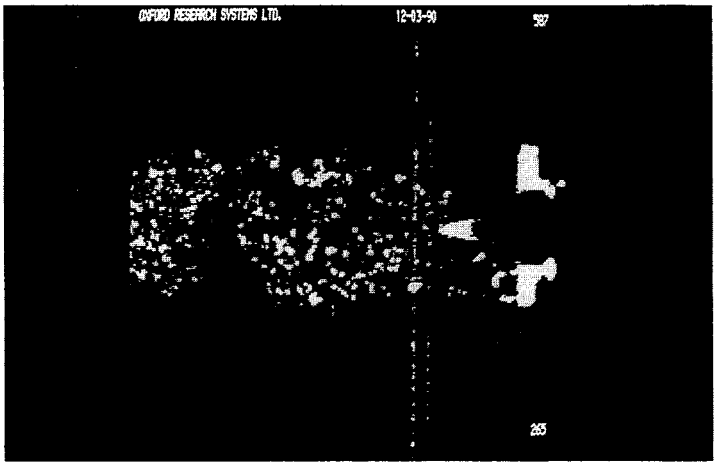

Figure 6 50μm-thick slice showing the distribution of oil inside the porous medium containing oil and water

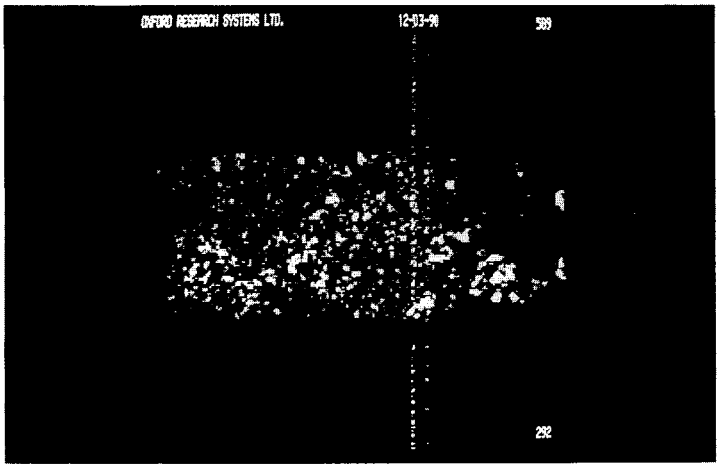

Figure 7 50μm-thick slice showing the distribution of water inside the porous medium containing oil and water

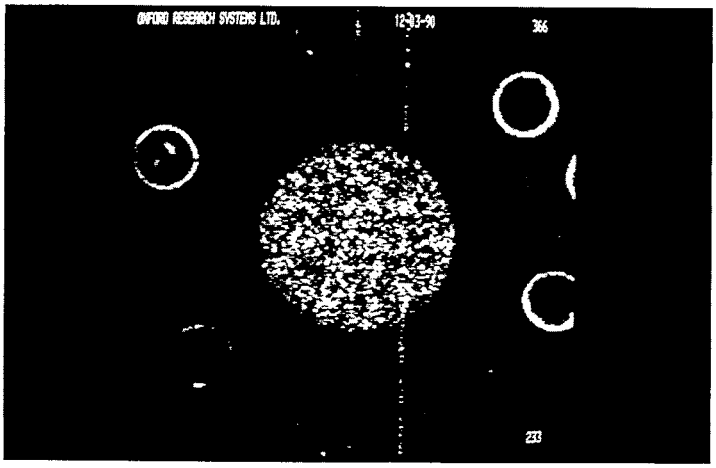

Figure 8 50μm-thick slice of a Fontainebleau sandstone saturated with water