BULK AND SPATIALLY RESOLVED NMR OF SATURATED RESERVOIR ROCK

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ABSTRACT

This thesis forms part of a continuing programme of research to investigate the application of NMR to fluid saturated rock. The work falls into four sections;

(i) The development of a novel broad line NMR imaging technique for the study of short $T_2$ fluid components in reservoir rock

The technique is a repetitive pulse variant of an established gradient echo method which employs oscillating magnetic field gradients. The variant uses low flip angle r.f. pulses to reduce image rounding artefacts and provide naturally $T_1$ weighted data.

(ii) The selective imaging of fluids within preserved reservoir rock and the first broad line NMR imaging study of immiscible fluid flow.

The selective imaging of reservoir fluids within preserved rock core samples has been achieved using $T_1$ weighted MRI methods. To account for the natural heterogeneity of the rock and the observed mixed wettability, $T_1$ suppression has been enhanced by lowering the temperature of the rock cores, thus exploiting the difference in dominant relaxation mechanisms of the two core fluids. A model has been developed to explain this temperature dependence in terms of pore surface relaxation theory.

Fluid flow processes within reservoir rock have been investigated using chemical substitution and $T_1$ weighted imaging. Due to the short transverse relaxation times expected at irreducible saturation, short $T_2$ imaging protocols have been adopted and represent the first such study. This has provided quantitative data from which the individual phase saturations can be directly obtained.
(iii) The first broad line NMR imaging study of liquid and vapour phase diffusion processes in partially saturated rock.

Excellent agreement is found between the NMR diffusion profiles of partially saturated rock and a model based on a combination of vapour and liquid phase transport. Estimates of the surface water diffusion coefficient and vapour percolation threshold have thus been obtained.

(iv) A detailed study of proton relaxation times of water-saturated rock as a function of saturation.

The saturation levels range from 0.06%, equivalent to monolayer water coverage, to 100%. The results have been used to test fast diffusion relaxation theory in rock over the full saturation range for the first time. The relaxation measurements at monolayer coverage have led to the first unambiguous estimates of rock plug pore surface relaxivity. Evidence has been obtained for the effect of pore throats on the relaxation times and pore throat size estimates have been made.
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CHAPTER ONE

NMR THEORY
1.1 INTRODUCTION

The phenomenon of nuclear magnetic resonance (NMR) is observed when nuclei which possess a net spin angular momentum, interact with static and time varying magnetic fields to induce transitions between nuclear spin energy levels.

Since its discovery in 1946 by two research groups headed by Purcell and Bloch, NMR has become well established and well documented (Abragam 1961, Farrar and Becker 1971, Harris 1986 and Slichter 1978, for example). The first NMR spectrometers were developed in the 1950's after the discovery of the chemical shift effect by Proctor and Yu (1950), but it was not until 1973 that magnetic resonance imaging (MRI) was first suggested by Lauterbur and independently by Mansfield and Graneil. NMR has now become a very sophisticated technique with applications in chemistry, solid state physics, medicine, food science and petroleum engineering, making it a powerful analytical tool.

This chapter gives a brief outline of the classical and quantum mechanical description of NMR theory and includes some of the techniques employed with regard to the study of reservoir rock cores.

1.2 QUANTUM MECHANICAL DESCRIPTION

Only nuclei with a net spin angular momentum, the magnitude of which depends on the spin quantum number $I$, are detectable by NMR. The value of this spin quantum number is determined by the mass and charge number of the nuclei (table 1.1). For example, the proton, neutron and $^1\text{H}$ all have a spin quantum number $I$ of $1/2$. 
The relationship between angular momentum $P$ and nuclear spin $I$ is given by

$$P = I \hbar$$

(1.1)

where $\hbar$ is Planck's constant divided by $2\pi$.

As nuclei are positively charged, the possession of charge and spin gives rise to a magnetic moment $\mu$ which is collinear with the angular momentum vector and related to it by

$$\mu = \gamma P$$

(1.2)

$\gamma$ is the magnetogyric ratio which is a constant for any given nucleus.

The quantum mechanical approach states that as the total angular momentum of an isolated particle is quantised, only its magnitude and one spatial component can be specified. Taking the z direction component gives

$$|P| = \hbar[I(I+1)]^{1/2}$$

(1.3)

$$P_z = m_I \hbar \quad (m_I = I, I-1, ..., -I)$$

(1.4)

$m_I$ is a quantum number with $2I+1$ values which specifies the direction of the angular momentum. Thus $I \hbar$ is the largest measurable component of the angular momentum with $I$ either integer or half integer.
Table 2.1 lists some typical nuclei which exhibit NMR with their relative sensitivity to $^1$H.

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Natural Abundance (%)</th>
<th>Relative Sensitivity To $^1$H</th>
<th>Resonant Frequency At 2.35 Tesla (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>99.98</td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>$^2$H</td>
<td>0.016</td>
<td>$9.7 \times 10^{-3}$</td>
<td>15.4</td>
</tr>
<tr>
<td>$^{13}$C</td>
<td>1.11</td>
<td>$1.6 \times 10^{-2}$</td>
<td>25.4</td>
</tr>
<tr>
<td>$^{19}$F</td>
<td>100</td>
<td>$8.3 \times 10^{-1}$</td>
<td>94.1</td>
</tr>
<tr>
<td>$^{23}$Na</td>
<td>100</td>
<td>$9.3 \times 10^{-2}$</td>
<td>26.5</td>
</tr>
<tr>
<td>$^{31}$P</td>
<td>100</td>
<td>$6.6 \times 10^{-2}$</td>
<td>40.5</td>
</tr>
</tbody>
</table>

Table 1.2 Properties Of Certain Nuclei Sensitive To NMR

If a nucleus with a net magnetic moment is placed in a magnetic field $B_0$, there is an interaction energy with that field resulting in a Hamiltonian of

$$\mathcal{H} = -\mu \cdot B_0$$  \hspace{1cm} (1.5)

From equations 1.1 and 1.2 this can then be rewritten as

$$\mathcal{H} = -\gamma \hbar B_0 \cdot I$$  \hspace{1cm} (1.6)

Taking the magnetic field to be static and along the z direction with magnitude $B_0$, the energy eigenvalues of this Hamiltonian are given by

$$E = -\gamma \hbar m_1 B_0$$  \hspace{1cm} (1.7)

The allowed energy levels for the case of a spin $1/2$ nucleus are illustrated in figure 1.1 with the energy gap given by

$$\Delta E = \gamma \hbar B_0$$  \hspace{1cm} (1.8)
The separation of the two energy levels is due to the interaction of $\mu$ with the main field $B_0$ and is known as Zeeman splitting. Inducing transitions between energy levels can be achieved by applying electromagnetic radiation of energy $\Delta E$. This is governed by the Bohr condition

$$\Delta E = h \nu$$

where $\nu$ is the frequency of the electromagnetic radiation.

The coupling most commonly used to produce magnetic resonance is an alternating magnetic field applied perpendicular to the static field. Writing the alternating field in terms of amplitude $B_0^0$, there is a perturbing term in the Hamiltonian

$$H_{\text{pert}} = -\frac{\gamma h B_0^0 I_x}{\hbar} \cos \omega t$$

The operator $I_x$ has matrix elements between states $m_I$ and $m'_I$, $( m'_I | I_x | m_I )$, which vanish unless $m'_I = m_I \pm 1$. Therefore the allowed transitions are between levels adjacent in energy. Substituting equation 1.9 into 1.8 leads to the resonance equation
\[ \omega_0 = \gamma B_o \]  

(1.11)

where \( \omega_0 = 2\pi v \). Planck's constant is missing from this equation, suggesting that the result is closely related to the classical picture.

Due to the size of the magnetogyric ratio, the stimulated radiation tends to be in the radio frequency (r.f.) part of the electromagnetic spectrum.

The behaviour of the proton (spin \( \frac{1}{2} \)) magnetic moment in quantum mechanics is described in terms of probability of the proton occupying a given state at any one time. It can occupy either of the two states, which can vary from observation to observation. It can be shown (Abragam, 1961) that the expectation value taken over the wave function of a free spin is consistent with classical equations. The relationship is linear, so large assemblies of independent nuclei will also behave classically allowing the net magnetic moment to be described in a classical manner.

In the absence of a \( B_o \) field there is degeneracy in spin states so spin up and spin down cannot be defined. The application of a field causes the spins to be distributed between the two states and eventually reach equilibrium, with the spin up state being more favoured. The population difference between the two states is described by the Boltzmann distribution

\[
\frac{n^-}{n^+} = \exp\left(\frac{-\Delta E}{kT_s}\right) 
\]

(1.12)

\( k \) is the Boltzmann constant and \( T_s \) is the absolute temperature of the spin system. \( n^- \) and \( n^+ \) correspond to the number of spins in \( m_I = -1/2 \) and \( m_I = +1/2 \) respectively.

At room temperature and in a field of flux density one Tesla, there is an excess of protons in the spin up state of about \( 3 \times 10^{-6} \). This explains the relatively low sensitivity of NMR, which can be increased slightly by either reducing the temperature or raising the field strength \( B_o \).
1.3 CLASSICAL DESCRIPTION

If a nucleus with a net magnetic moment is placed in a field $B_o$, it experiences a torque which produces a change in its angular momentum $P$,

$$\frac{dP}{dt} = -\mu \wedge B_o$$  \hspace{1cm} (1.13)

As stated before (equation 1.2), the angular momentum $P$ and magnetic moment $\mu$ are related by the magnetogyric ratio $\gamma$ and inserting this into 1.13 gives

$$\frac{d\mu}{dt} = -\mu \wedge \gamma B_o$$  \hspace{1cm} (1.14)

If the field $B_o$ is in the z direction, solutions to the above equation can be obtained by expanding the cross product and integrating with respect to time to give

$$\mu_x = |\mu| \sin \alpha \cos (-\gamma B_z t + \beta)$$

$$\mu_y = |\mu| \sin \alpha \sin (-\gamma B_z t + \beta)$$  \hspace{1cm} (1.15)

$$\mu_z = |\mu| \cos \alpha$$

$\alpha$ is the constant angle that the magnetic moment makes with the field $B_o$ and $\beta$ is a constant which is determined from the initial position of $\gamma$ when $B_o$ was first applied. The magnetic moment can be thought to rotate at a rate $\omega_\alpha$, where

$$\omega_\alpha = -\gamma B_o$$  \hspace{1cm} (1.16)

This is equivalent to the quantum mechanical solution (equation 1.11). The angular frequency $\omega_\alpha$ is sometimes referred to as the Larmor frequency (figure 1.2).
A system which contains a large number of nuclei with magnetic moments has a vector sum of individual components \( \mathbf{M} \) called the bulk magnetisation and given by

\[
\mathbf{M} = \sum_i \mathbf{\mu}_i
\]  

(1.17)

Thus equation 1.14 can be rewritten as

\[
\frac{d\mathbf{M}}{dt} = \mathbf{M} \wedge \gamma \mathbf{B}_0
\]  

(1.18)

At equilibrium, the magnetisation is in the same direction as \( \mathbf{B}_0 \) and its magnitude (denoted by \( M_0 \)) is related to the Boltzmann distribution (equation 1.12).

The behaviour of \( \mathbf{M} \) can often be more simply described by considering a reference frame which is rotating at angular frequency \( \omega \) with co-ordinates \( x', \gamma', z' \). This transforms the above equation to

\[
\frac{d\mathbf{M}}{dt} = \mathbf{M} \wedge (\gamma \mathbf{B}_0 + \omega)
\]  

(1.19)
and results in an effective field $B_{\text{eff}}$ in the rotating frame

$$B_{\text{eff}} = B_0 + \frac{\omega}{\gamma} \quad (1.20)$$

If the rotating frame is at such a frequency that $\omega = -\gamma B_0$, the field $B_{\text{eff}}$ will become zero and the magnetisation $M$ will appear stationary. Thus, $\omega = \omega_0$ and the rotating frame $(x', y', z')$ is at the Larmor frequency.

To observe resonance, the magnetisation must be tipped into an orthogonal direction to $B_0$. This can be achieved by applying an oscillating field $B_1$ perpendicular to $B_0$. Equation 1.19 now becomes

$$\frac{dM}{dt} = M \wedge [\gamma B_0 + \omega + \gamma B_1(t)] \quad (1.21)$$

The oscillating field $B_1$ will appear stationary if it rotates at the same frequency as the reference frame. If this frequency is the Larmor frequency, $\omega_0$, the above equation simplifies to

$$\frac{dM}{dt} = M \wedge \gamma B_1 \hat{i} \quad (1.22)$$

$B_1$ is the amplitude of the oscillating field and $\hat{i}$ is the $x'$ direction unit vector.

Equation 1.22 implies that in the rotating frame, the magnetisation $M$ is acted on by a stationary field $B_1$ which causes $M$ to rotate along the $z'$-$y'$ plane onto the $y'$ axis (figure 1.3). The angle through which $M$ rotates $\phi$ is given by

$$\phi = \gamma B_1 t_\text{p} \quad (1.23)$$

$t_\text{p}$ is the time for which the field $B_1$ is applied.
If the magnetisation is allowed to rotate through $90^\circ$ to lie along the $x'$-$y'$ plane, the duration of the $B_1$ field is said to be a $90^\circ$ pulse length. When the magnetisation lies totally in the $x'$-$y'$ plane it results in the maximum observable signal. Inverting the magnetisation is achieved by applying the $B_1$ field for double the duration ($180^\circ$ pulse length).

![Diagram](image)

Figure 1.3 Effect Of The $B_1$ Field In The Rotating Frame

1.4 RADIO FREQUENCY PULSES

Until the 1970's, NMR experiments were carried out under continuous wave (cw) stimulation where the r.f. frequency was swept across the desired frequency range. With the development of multichannel spectrometers and Fourier analysis, small delta function like r.f. pulses could be used to stimulate nuclei. An r.f. pulse of duration $t_p$ contains a bandwidth of frequencies given by $t_p^{-1}$.

Resonance is caused by the interaction of the magnetic moments with the main field $B_0$ and observed as an EMF signal induced in a receiver coil. With no other interaction, this signal would continue indefinitely. However, there is a reduction in signal intensity (figure 1.4), known as the free induction decay (FID). This decay is
due to field inhomogeneities and natural relaxation effects (section 1.5). Transformation of this time domain signal to the frequency domain results in a characteristic frequency spectrum. The time and frequency domains are related by the Fourier transformation

\[ f(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} F(\omega) \exp(i\omega t) \, d\omega \]  

(1.24)

The frequency spectrum has an NMR line shape with the width given by

\[ \nu_1 = \frac{1}{\pi T_2^*} \]  

(1.25)

\( T_2^* \) is the time constant associated with the dephasing of the transverse magnetisation. Figure 1.4 shows the decay of transverse magnetisation as a function of time and includes the subsequent Fourier transformed line shape.

![Figure 1.4 Transverse Decay Of The Bulk Magnetisation As A Function Of Time In A Frame Rotating At The Larmor Frequency, With Subsequent Fourier Transform](image-url)
1.5 RELAXATION

Relaxation occurs through the exchange of energy between nuclei or the molecular lattice. The two main processes are known as T₁ (spin-lattice) and T₂ (spin-spin).

T₁ is often referred to as longitudinal relaxation and is a measure of the rate at which the spin system comes into equilibrium with its environment. T₁ relaxation occurs through the exchange of energy between nuclei and the molecular lattice.

T₂ is often referred to as transverse relaxation and is responsible for line broadening or dephasing of the magnetisation in the x-y plane. T₂ relaxation occurs through the exchange of energy between nuclei. Figure 1.5 illustrates the effect of T₁ and T₂ relaxation on the magnetisation in the rotating reference frame.

Figure 1.5 (a) Transverse And (b) Longitudinal Relaxation
1.5.1 THE BLOCH EQUATIONS

Bloch (1946) formulated a set of equations which successfully describe the motion of the macroscopic magnetisation in the presence of an applied magnetic field $B_0$. The theory is based on equation 1.18 and incorporates $T_1$ and $T_2$ relaxation times to allow the magnetisation to reach an equilibrium value $M_0$. Solutions to these equations can provide an accurate description of the NMR behaviour of a bulk spin system.

The introduction of a second field $B_1$ oscillating in the x-y plane causes the magnetisation to rotate into x-y plane and hence reduce the z component. Following the absorption of energy, the magnetisation relaxes back to an equilibrium value $M_0$ in the direction of $B_0$ and described by

$$\frac{dM_z}{dt} = -\frac{(M_z - M_0)}{T_1}$$  \hspace{1cm} (1.26)

The components of the magnetisation $M_x$ and $M_y$ decay under the dephasing effect of local field variations and are described by

$$\frac{dM_y}{dt} = -\frac{M_y}{T_2} \quad \frac{dM_x}{dt} = -\frac{M_x}{T_2}$$  \hspace{1cm} (1.27)

The magnetic interaction, absorption of energy and relaxation processes can all be combined to give

$$\frac{dM}{dt} = \gamma (M \times B) - \frac{(M_x \hat{i} + M_y \hat{j})}{T_2} - \frac{(M_z \hat{k} - M_0 \hat{k})}{T_1}$$  \hspace{1cm} (1.28)

where $\hat{i}$, $\hat{j}$ and $\hat{k}$ are the unit vectors in the laboratory frame. $B_1$ can be expressed in terms of its components in the x-y plane

$$B_1 = \hat{i} B_1 \cos \alpha - \hat{j} B_1 \sin \alpha$$  \hspace{1cm} (1.29)
Allowing the components of $\mathbf{M}$ to be described as below

$$\frac{dM_x}{dt} = \gamma(M_y B_0 + M_z B_1 \sin \omega t) - \frac{M_x}{T_2}$$

$$\frac{dM_y}{dt} = \gamma(M_z B_1 \cos \omega t - M_x B_0) - \frac{M_y}{T_2}$$

$$\frac{dM_z}{dt} = \gamma(M_x B_1 \sin \omega t + M_y B_1 \cos \omega t) - \frac{(M_z - M_0)}{T_1}$$

(1.30)

These are the Bloch equations.

**1.5.2 MAGNETIC DIPOLAR INTERACTIONS**

The dipole-dipole interaction between neighbouring nuclei can cause a large broadening in the width of the NMR resonance line. The amount of broadening is dependent on the size of the magnetic moment, the proximity of the nuclei and the frequency distribution of the molecular motion. For two classical magnetic moments $\mu_1$ and $\mu_2$, the interaction energy is given by

$$E = \frac{\mu_1 \cdot \mu_2}{r^3} - \frac{3(\mu_1 \cdot \mathbf{r})(\mu_2 \cdot \mathbf{r})}{r^5}$$

(1.31)

where $\mathbf{r}$ is the radius vector from $\mu_1$ to $\mu_2$. If $\mu_1$ and $\mu_2$ are treated as quantum mechanical operators

$$\mu_1 = \gamma_1 \mathbf{I}_1 \quad \mu_2 = \gamma_2 \mathbf{I}_2$$

(1.32)

the general dipolar contribution to the Hamiltonian for N spins becomes
By expressing the \( x \) and \( y \) terms of the Hamiltonian with raising and lowering operators \( I_{1}^{+} \) and \( I_{1}^{-} \) and transforming to spherical co-ordinates \( (r, \theta, \phi) \), Van Vleck (1948) showed that the Hamiltonian may be written as

\[
\mathcal{H} = \frac{\gamma_{1} \gamma_{2} \hbar^2}{r^3} [A + B + C + D + E + F] \tag{1.34}
\]

where

\[
A = I_{1z} I_{2z} (1 - 3 \cos^2 \theta)
\]

\[
B = -\frac{1}{4} (I_{1}^{+} I_{2}^{-} + I_{1}^{-} I_{2}^{+}) (1 - 3 \cos^2 \theta)
\]

\[
C = -\frac{3}{2} (I_{1}^{+} I_{2z} + I_{1z} I_{2}^{+}) \sin \theta \cos \theta \exp(-i\phi)
\]

\[
D = -\frac{3}{2} (I_{1}^{-} I_{2z} + I_{1z} I_{2}^{-}) \sin \theta \cos \theta \exp(i\phi) \tag{1.35}
\]

\[
E = -\frac{3}{4} I_{1}^{+} I_{2}^{+} \sin^2 \theta \exp(-2i\phi)
\]

\[
F = -\frac{3}{4} I_{1}^{-} I_{2}^{-} \sin^2 \theta \exp(2i\phi)
\]

\[I_{1}^{+} = I_x + i I_y \quad I_{1}^{-} = I_x - i I_y\]

These terms contain information about the allowed transitions and the likelihood of a transition at a particular frequency. Figure 1.6 gives a diagrammatic representation of these Van Vleck terms.
Term A corresponds to the interaction with the static component of the local magnetic field due to neighbouring magnetic moments. This interaction does not raise the degeneracy.

Term B can only flip one spin up with the subsequent lowering of the other coupled spin. This process broadens the line by shortening the life-time of the spin states. Terms A and B do not contribute to T\textsubscript{1} relaxation as there is no change in degeneracy, but they do change the phase and so contribute to T\textsubscript{2} relaxation.

Terms C and D both flip one spin only and therefore induce transitions across the energy gap $\hbar \omega_o$. Terms E and F flip two spins either up or down which corresponds to a transition of the order of $2\hbar \omega_o$. 
The latter four terms change the energy of the system and therefore contribute to $T_1$ relaxation. All six terms cause a phase change and therefore contribute to $T_2$ relaxation. This indicates that $T_2$ relaxation is a more effective process. The $T_2$ relaxation time of the spin system will therefore be equal to or shorter than the $T_1$ relaxation time.

In a liquid, molecular motions cause $r, \theta, \phi$ to change rapidly so that $(1 - 3\cos^2\theta)$ averages to zero in the time scale of an NMR experiment. This effect is known as motional narrowing and cancels out terms A and B from the equation 1.35. In a pure liquid, $T_1$ and $T_2$ relaxation times are therefore approximately equal.

If the motion of the spins is slowed down, the A and B terms become more dominant and the line shape changes from a thin peak to a more broad Lorentzian line shape. In this rigid lattice limit where $\theta$ is fixed, local field contributions can be very large leading to rapid $T_2$ relaxation.

1.5.3 MOLECULAR MOTION AND EFFECT ON RELAXATION

Bloembergen, Purcell and Pound first proposed the link between molecular motion and relaxation (BPP theory, 1948). They introduced the concept of a correlation time $\tau_c$ as a measure of the time that two nuclei remain in a given orientation

$$\frac{1}{T_1} \propto \frac{2\gamma^2 B_{loc}^2 \tau_c}{(1 + \omega_0^2 \tau_c^2)}$$

(1.36)

$$\frac{1}{T_2} \propto \gamma^2 B_{loc}^2 \left[\tau_c + \frac{\tau_c}{1 + \omega_0^2 \tau_c^2}\right]$$

(1.37)

Where $B_{loc}$ is the local fluctuating magnetic field.
For very rapid molecular motion (liquid) \( \frac{1}{\tau_c} \gg \omega_0 \), equation 1.36 reduces to

\[
\frac{1}{T_1} \propto \tau_c \tag{1.38}
\]

For very slow molecular motion (solid) \( \frac{1}{\tau_c} \ll \omega_0 \), equation 1.36 reduces to

\[
\frac{1}{T_1} \propto \frac{1}{\tau_c} \tag{1.39}
\]

Figure 1.7 shows the dependence of \( T_1 \) and \( T_2 \) with the correlation time. It can be seen that the most effective \( T_1 \) relaxation occurs when \( \frac{1}{\tau_c} = \omega_0 \).

\[\tau_c = \omega_0^{-1} \]

Figure 1.7 Relaxation Times Versus Correlation Time
1.5.4 CHEMICAL SHIFT EFFECT

Magnetic fields originating from the motion of the surrounding electron cloud, partially shield a nucleus such that it does not experience the total magnetic field generated by the laboratory magnet \( B_0 \), but rather a reduced field \( B_{\text{nucleus}} \), governed by

\[
B_{\text{nucleus}} = B_0 - \sigma B_0 = B_0 (1 - \sigma) \tag{1.40}
\]

\( \sigma \) is the shielding factor (about \( 10^{-5} \) for protons). The magnitude of the shielding (or chemical shift) at a nucleus is dependent upon the orientation of the molecule in the magnetic field. In the liquid state, the rapid molecular motion averages out the shielding to give an average value of \( \sigma \).

As the resonant frequency is proportional to the local magnetic field at the nucleus, the resonance condition (equation 1.11) becomes

\[
\omega_0 = \gamma B_0 (1 - \sigma) \tag{1.41}
\]

Since nuclei with different chemical shifts precess with different frequencies, the shielding produces a modulation in the FID and subsequent Fourier transformation reveals the corresponding peaks which are unique for each chemical species. The discovery of this effect by Proctor and Yu (1950) led to the development of the NMR spectrometer.

1.5.5 PARAMAGNETIC EFFECTS AND SUSCEPTIBILITY

Paramagnetic materials contain unpaired electrons which provide fluctuating dipolar magnetic fields and greatly enhance the relaxation of nearby systems. This is due to the large magnetogyric ratio of an electron, which is 657 times that of proton. Paramagnetic materials such as copper sulphate and manganese chloride can be used as doping agents in systems with long \( T_1 \) relaxation times to allow
faster repetition rates in magnetic resonance experiments. Paramagnetic impurities are common in reservoir rock cores and tend to dominate surface relaxation rates.

The magnetic susceptibility $\chi$ is defined as

$$\chi = \frac{M}{H_o}$$

where $M$ is the total number of magnetic moments per cubic metre of a system of $N$ nuclei with spin $I$ and $H_o$ is the applied magnetic field.

For a system in thermal equilibrium, with a temperature $T_s$

$$\chi = \frac{N \gamma^2 h^2 I (I+1)}{3 k T_s}$$

In a homogenous sample with a mixture of molecules, any susceptibility differences may be averaged out by molecular motion. Heterogeneous samples have susceptibility differences which cannot be averaged out. These produce local field gradients and broaden the NMR resonance line. Reservoir rock cores are very heterogeneous with a large number of boundaries. Susceptibility effects can thus be very large and severely reduce observed relaxation times.

1.5.6 MEASUREMENT OF RELAXATION

$T_1$ and $T_2$ relaxation times are not only dependent on the system being investigated, but also the local environment in which they exist. Accurate measurements of relaxation times can thus lead to quantitative information about important physical parameters such as porosity, permeability and pore size distribution in reservoir cores. To measure relaxation times it is necessary to apply a sequence of r.f. pulses.
1.5.6.1 MEASUREMENT OF T\textsubscript{1} RELAXATION

In physical terms, T\textsubscript{1} is the time constant for the exponential decay in the recovery of magnetisation in the B\textsubscript{0} direction. The recovery of magnetisation is achieved by the transfer of energy from the spin system to the molecular lattice. To measure T\textsubscript{1} it is therefore necessary to monitor the rate at which the magnetisation M reaches equilibrium. One such technique which measures magnetisation recovery is the inversion recovery sequence (figure 1.8).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{inversion_recovery_sequence}
\caption{The Inversion Recovery Sequence}
\end{figure}

A 180° pulse inverts the equilibrium magnetisation to -M\textsubscript{0} which then recovers along the z' axis (direction of B\textsubscript{0}) towards M\textsubscript{0}. This will not induce a detectable signal until it is tipped into the x'-y' plane. If after an interval τ, a 90° pulse is applied along the x' axis, the magnetisation M\textsubscript{x} will lie along the y' axis inducing a
signal proportional to $M_z$. The value of $M_z$ in the absence of any $B_1$ is described by

$$\frac{dM_z}{dt} = -\left(\frac{M_z - M_\alpha}{T_1}\right)$$

(1.44)

This can then be solved for $M_z(0) = -M_\alpha$, assuming the decay to be a monoexponential to give

$$M_z(t) = M_\alpha[1 - 2\exp(-\frac{t}{T_1})]$$

(1.45)

The magnetisation must recover fully before the next set of pulses can be applied. The repetition time $T_r$ is usually in the order of $5T_1$. Once equilibrium has been re-established, the sequence can be repeated with a different inter pulse gap $\tau$. A plot of $\ln(M_\alpha - M_z)$ versus $\tau$ gives a straight line of gradient $-1/T_1$.

### 1.5.6.2 MEASUREMENT OF $T_2$ RELAXATION

$T_2$ relaxation is the loss of magnetisation from the x-y plane due to energy transfer between nuclei. In practice, factors other than $T_2$ relaxation cause loss of transverse magnetisation. These additional features together with $T_2$ relaxation effects lead to a decay in the envelope of the FID with a time constant $T_2^*$. The main contribution to this extra relaxation is from magnetic field inhomogeneities in the $B_0$ field, giving rise to a spread of frequencies and a loss of coherence. $T_2^*$ is given by

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{\gamma \Delta B_0}{2}$$

(1.46)

$\Delta B_0$ is the variation in the magnetic field. Due to this extra relaxation, $T_2$ cannot be measured directly from the shape of the FID. The spin echo method proposed by
Hahn (1950) which consists of a 90° - τ - 180° pulse sequence overcomes this field inhomogeneity problem as shown in figure 1.9.

![Figure 1.9 The Hahn Echo](image)

The 90° pulse is applied along the x' axis and tips the magnetisation onto the y' axis. Field inhomogeneity and natural T₂ effects cause the spins to have slightly different precessional frequencies and fan out in the x'-y' plane. The 180° pulse is applied a time τ later also along the x' axis causing the spins to rotate around the x' axis. Natural T₂ relaxation still takes place but the field inhomogeneities have now effectively been reversed and cause the magnetisation to rephase in the form of an echo 2τ after the 90° pulse. The signal from this echo now has an amplitude proportional to the time constant T₂ and by making a number of measurements of peak echo amplitude versus τ, the transverse relaxation can be determined

\[
M(2\tau) = M_0 \exp\left[\left(-\frac{2\tau}{T_2}\right) - \frac{2}{3} \gamma^2 G^2 D \tau^2 \right]
\]  

(1.47)

The extra term in the above equation is due to molecular diffusion through the gradient G caused by \( B_0 \) field inhomogeneity. D is the self diffusion coefficient.
which Carr and Purcell (1954) showed could have a reduced effect by a simple modification to the Hahn echo. The Carr-Purcell sequence involves a train of 180° pulses after the initial 90° pulse. The 180° pulses are placed at times τ, 3τ, 5τ...etc. and form Hahn echoes at times 2τ, 4τ, 6τ...etc. along the y' axis. The resulting echo envelope decays exponentially with a time constant $T_2$ and the diffusion term can be reduced by using short τ values. This sequence relies on accurate 180° pulses to ensure the spins remain in the x'-y' plane and modifications were proposed by Meiboom and Gill (1958) to eliminate any cumulative effect. Their sequence known generally as the CPMG sequence uses the same pulse layout as Carr and Purcell but the 180° pulses are applied sequentially along the positive and negative y' axis. Although the odd echoes are still affected by inaccurate 180° pulses, the effect is no longer cumulative and the envelope of the even numbered echoes decays exponentially with the time constant $T_2$. Figure 1.10 illustrates the pulse layout and echo train for the CPMG sequence.

Figure 1.10  The CPMG Sequence And Echo Train
1.6 PULSE FIELD GRADIENT METHOD

To measure the self diffusion coefficient $D$, a method commonly employed is the pulse field gradient technique. The pulse sequence is shown in figure 1.11 and is based around the Hahn echo experiment. A magnetic field gradient pulse of duration $\delta$ is applied either side of the 180° pulse which has the effect of dephasing spins that have undergone diffusion. Taking account of transverse relaxation, diffusion and flow, the echo amplitude is given by

$$M(2\tau) = M_o \cos(\gamma G v \delta \Delta) \exp\left[\frac{-2\tau}{T_2} - \gamma^2 G^2 D \delta^2 (\Delta - \frac{\delta}{3})\right]$$  \hspace{1cm} (1.48)

$G$ is the linear gradient strength, $v$ is the flow velocity, $\Delta$ is the gap between the start of the gradient pulses and $2\tau$ is the echo time. If $M_a(2\tau)$ is the echo amplitude with the pulse gradient switched off and $M_b(2\tau)$ is the echo amplitude including the gradients, the relaxation effects can be eliminated and $D$ can be calculated.
\[ \ln \left[ \frac{M_b(2\tau)}{M_a(2\tau)} \right] = -\gamma^2 D \delta^2 G^2 (\Delta - \frac{\delta}{3}) \]  

(1.49)

The values of \( D \) which can be measured depend on the gradient strength \( G \) and can be as low as \( 10^{-8} \) cm\(^2\) sec\(^{-1}\). The echo attenuation can be varied by alterations to either \( \delta \), \( \Delta \) or \( G \), but in practice \( \delta \) is usually the variable.

A standard way of avoiding the accurate measurement of \( G \) is to carry out a separate experiment on a sample of known \( D \) (such as water), keeping everything else constant. From equation 1.49 a simplified expression emerges relating the slopes from plots of \( \ln[M_b(2\tau)/M_a(2\tau)] \) versus \( \delta^2(\Delta - \delta/3) \) to the \( D \) values for the unknown (*) and control samples (c)

\[ \frac{S_\bullet}{S_c} = \frac{D_\bullet}{D_c} \]  

(1.50)

Limitations and errors typically associated with this sequence are: Stability, sample movement, short \( T_2 \) relaxation rates and non-linear gradients. In the case of short \( T_2 \) samples, the stimulated echo technique can be employed (Tanner, 1970). The stimulated echo depends on \( T_1 \) rather than \( T_2 \) (figure 1.12).

\[ \text{Figure 1.12 The Stimulated Echo P.F.G. Technique} \]
1.6.1 RESTRICTED DIFFUSION

Diffusion measurements made on the water filled pores (for example) show a non-linearity inconsistent with equation 1.49. This is due to restricted diffusion of bounded heterogeneous systems. The effect can be exploited to probe pore sizes or distributions of such porous systems. If the range of diffusion in time $t$ is restricted to a distance $R$, the dephasing of the spins and hence echo attenuation due to the gradients will be reduced. Extending the gradient pulse gap $\Delta$ beyond $t$ will result in an apparent diffusion $D = D_{\text{app}} = R^2/5\Delta$.

1.7 NMR IMAGING

The fundamental objective of NMR imaging is to identify individually the nuclear signals coming from each location in space. This is achieved by the application of magnetic field gradients. These field gradients cause a spatial variation in the magnitude of the magnetic field but not a variation in the direction. The most common gradients used in NMR imaging are linear (figure 1.13).

If the main magnetic field $B_0$ acts in the $z$ direction but varies linearly in the $x$ direction, the field at any point along the co-ordinate system can be described by

$$B_z = B_0 + xG_x$$  \hspace{1cm} (1.51)

where $G_x$ is the magnetic field gradient. Putting this into the resonance equation (equation 1.11), the Larmor frequency is now given by

$$\omega = \gamma B_0 + \gamma xG_x$$  \hspace{1cm} (1.52)

Following a pulse of r.f. irradiation, any magnetisation normal to the $z$ direction will precess around $z$ at a frequency proportional to its position along the $x$ direction. The frequency spectrum obtained by Fourier transformation is effectively a one-dimensional projection of the spin density onto the $x$ axis, with the amplitude
proportional to the amount of nuclear species at each position along x. In order to identify two different groups of spins within a sample, the Rayleigh criterion can be used. Two peaks can be separated if

$$\frac{(\omega_1 - \omega_2)}{2\pi} = \frac{1}{\pi T_2} \text{ Hz} \quad (1.53)$$

where $\omega_1$ and $\omega_2$ are the Larmor frequencies of the two peaks. Equation 1.53 can be expressed in terms of resolution along the x axis

$$\Delta x = \frac{2}{\gamma T_2 G_x} \quad (1.54)$$

![Figure 1.13 A Linear Field Gradient Along The x Axis](image)

1.7.1 BACK PROJECTION RECONSTRUCTION

Back projection reconstruction was the first method of obtaining two-dimensional NMR images, as used by Lauterbur in 1973. The technique consists of a series of one-dimensional projections which are obtained by varying the field gradient vector in the x-y plane. The gradient is varied in steps (18 or 36) going from dB$_x$/dx...
through $dB_y/dy$ to nearly $-dB_x/dx$. Typically, the image reconstruction takes place on a 128 x 128 grid of picture elements (pixels). The back projection process is illustrated in figure 1.14.

The two-dimensional picture is reconstructed by spreading the measured one-dimensional density distribution profiles uniformly back across the image plane. Using $\phi$ as the projection angle and $r$ as the distance along the projection, the back projection technique can be described mathematically

$$p(x,y) = \sum_{j=1}^{m} P(x \cos \phi_j + y \sin \phi_j, \phi_j) \Delta \phi_j$$  \hspace{1cm} (1.55)

$p(x,y)$ is the spatial distribution of spins, $P(r,\phi)$ is the projection data, $m$ is the number of projections and $\Delta \phi$ is the projection angular separation. The problem
with this method is that the density is over estimated resulting in a $1/r$ halo surrounding each point in the image. The effect is known as the 'star artefact' (Brooks, Di Chiro, 1976) and can be overcome by using a filtered back projection algorithm. The filtered projection data $P'(r,\phi)$ is formed by convoluting $P(r,\phi)$ with the filter function $h(r)$

$$P'(r,\phi) = P(r,\phi)h(r) \quad \quad (1.56)$$

The filter function $h(r)$ is usually given by

$$h(q) = \begin{cases} \frac{\pi^2}{4} & q = 0 \\ \frac{-1}{q^2} & q = \text{odd} \\ 0 & q = \text{even} \end{cases} \quad \quad (1.57)$$

where $q$ is an integer and $r$ goes from $-q/2$ to $+(q/2)-1$. The negative $1/r^2$ term in the function produces a negative $1/r$ halo which cancels out the positive $1/r$ halo around the image points.

### 1.7.2 THE 2DFT IMAGING TECHNIQUE

Although projection reconstruction is still commonly used in imaging research (broad line techniques, for example), the standard liquid state (long $T_2$) technique is the two dimensional Fourier transform (2DFT) sequence. The method was proposed by Kumar et al (1975) and later improved by Edelstein (1980). Sequences consist of a gradient to define a slice through the sample followed by two pulsed orthogonal gradients to encode the signal. The method provides a uniform error distribution across the complete frequency range (in contrast to earlier techniques) which implies that coarse and fine detail are obtained with the same accuracy. The main principles behind 2DFT imaging are explained below.
1.7.2.1 SLICE SELECTION

A radio frequency pulse applied in the \( x' \) direction causes the magnetisation to rotate along the \( z'-y' \) plane towards the \( y' \) axis. If a magnetic field gradient is applied at the same time, the frequency of each individual spin precession becomes proportional to position (equation 1.52). Putting \( B(r) = (G_r \cdot r) \) \((G_r \) is the gradient strength along the \( r \) direction), solutions to the Bloch equations (section 1.5.1) can be derived.

To selectively irradiate a rectangular slice of spins, the time domain wave form must be shaped such that its frequency spectrum has a rectangular profile. A sinc function has a 'top hat' Fourier transform and would appear the ideal r.f. wave shape. In practice, a three or five node truncated sinc shape provides an acceptable compromise between slice profile and pulse length. The shaped r.f. pulse is usually weighted with a Gaussian to prevent unwanted 'ripples' in the slice profile (figure 1.15).

![Diagram of R.F. Pulse Shape And Resultant Slice Profile](image-url)
For a slice selective r.f. pulse of frequency bandwidth $\Delta \omega$, the slice thickness $\Delta r$ is given by

$$\Delta r = \frac{\Delta \omega}{\gamma G_r}$$ (1.58)

The selective pulse length ($t$) is usually kept constant in an imaging sequence with the amplitude varied to tip the magnetisation through $90^\circ$

$$\frac{\pi}{2} = \int_0^t \gamma B_1(t) \, dt$$ (1.59)

After excitation, the selected spins have a range in phase due to the gradient. The phase can be refocussed by reversing the slice gradient for a time equal to half the selective pulse length.

This selective irradiation technique was first proposed by Garroway, Grannel and Mansfield (1974) and has become standard in virtually all MRI pulse sequences.

### 1.7.2.2 FREQUENCY ENCODING

The process of frequency encoding is analogous to obtaining a one dimensional projection in the back projection technique (section 1.7.1).

A linear gradient which is orthogonal to the slice gradient is applied during the acquisition of the signal to spatially encode the spin distribution. A Fourier transform of the signal with respect to time results in a frequency spectrum which is essentially a one dimensional profile of the sample in the direction of the magnetic field gradient. If $dt_r$ is the sample period of the digitised signal and $\rho(r)$ represents the spin density along the $r$ direction, the signal and its Fourier transform are given by

$$S(t) = \int \rho(r) S(r,t) \, dr$$ (1.60)
\[ S(\omega) = \int S(t) \exp(-i\omega t) \, dt \tag{1.61} \]

As the gradient is applied during data acquisition it is sometimes referred to as the read gradient.

1.7.2.3 PHASE ENCODING

The application of a linear magnetic field gradient pulse causes a range of spin precessional frequencies along the gradient direction. This leaves the spin system with a linear phase shift. The gradient is said to have imposed a 'spatial frequency' along the gradient direction. The phase shift can be detected using a phase sensitive detector and encodes the spin distribution in a technique known as phase encoding. With a gradient strength \( G_r \) in the \( r \) direction, the phase shift is given by

\[ \phi(r) = -\gamma \int_0^t G_r \cdot r \, dt \tag{1.62} \]

The phase encoding gradient is usually a rectangular pulse or half sine wave and is applied in an orthogonal direction to both the slice and read gradients. The gradient strength is usually incremented from \(-G_r\) to \(+G_r\) in small steps separated by \( \delta G_r \)

\[ \delta G_r = \frac{2\pi}{\gamma L t} \tag{1.63} \]

\( L \) is the sample length and \( t \) is the gradient duration (which is usually kept constant). The phase encoding technique is mathematically analogous to frequency encoding except the Fourier transform is made with respect to the gradient amplitude \( G_r \) and not \( t \).
1.7.2.4 K-SPACE REPRESENTATION

The idea of k-space is a useful formalism for describing and manipulating the magnetic resonance data collected in 2DFT scanning methods. A 2DFT imaging sequence applied to a system of spin density \( \rho(x,y) \) in the x-y plane may be written as

\[
F(k_x, k_y) = \int\int \rho(x,y) \exp[2\pi i (k_x x + k_y y)] dx \, dy
\]

(1.64)

\( F(k_x, k_y) \) represents the two dimensional spectrum of spatial frequencies in the system (ignoring relaxation effects). \( k_x/2\pi \) and \( k_y/2\pi \) are the spatial frequencies, related to the gradient strengths and encoding times by

\[
k_x(t_x) = \gamma \int_0^{t_x} G_x(t') \, dt'
\]

(1.65)

\[
k_y(t_y) = \gamma \int_0^{t_y} G_y(t') \, dt'
\]

(1.66)

To convert from \( F(k_x, k_y) \) to \( \rho(x, y) \), an inverse Fourier transform must be made with respect to the frequency encoding time \( t_x \) and the phase gradient amplitude \( G_y \) (which is sometimes referred to as pseudo time).

For a gradient encoded spin system, the response in k-space contains all the information required to produce an image (density distribution). The principle difference between all the NMR imaging techniques is the way k-space is scanned. If k-space is not completely or evenly sampled, various artefacts may appear in the final image. A two dimensional imaging method has a two dimensional k-space diagram, as shown in figure 1.16. In the spin warp technique, k-space is sampled as a series of horizontal lines, one for each value of \( k_y \) (i.e. for each value of phase or warp due to the \( G_y \) gradient). The diagram indicates clearly how the 2DFT sequence covers k-space evenly and hence obtain coarse and fine detail with the same accuracy. This contrasts to the back projection k-space diagram (figure 34).
1.16b) where information is predominantly obtained at smaller values of k, leading to a non-uniform error distribution across the complete frequency range.

Figure 1.16  k - Space Diagram For (a) The Spin Warp Sequence And (b) The Back Projection Sequence

If only two quadrants of k-space are covered in a sequence, the rest can be calculated by taking complex conjugates. This is because \( p(x, y) \) is real and thus \( p(-k) = p^*(k) \).

1.7.3 MRI PULSE SEQUENCES

This section gives an overview of the variety of magnetic resonance imaging (MRI) techniques employed in liquid state (long \( T_2 \)) magnetic resonance studies. There is an emphasis on sequences commonly applied to reservoir rock core analysis.
1.7.3.1 THE SPIN WARP TECHNIQUE

Established by Edelstein (1980), this is one of the many spin echo imaging techniques and is illustrated below in figure 1.17.

![Spin Warp Sequence Diagram]

Figure 1.17 The Spin Warp Sequence

The sequence is based on the Hahn echo technique (section 1.5.6.2) whereby a 180° pulse follows the initial 90° pulse to form a spin echo. The dephasing and subsequent rephasing of the spin system with gradient pulses also forms an echo, known as the gradient echo. The sequence is designed such that the spin and gradient echo form at the same time by varying either the r.f. pulse gap or the rephase gradient amplitude.

More recent variants of this sequence use two slice selective r.f. pulses to perform a technique known as multislicing. This technique allows many slices to be obtained in one go.
Without the 180° r.f. pulse, the gradients will still form an echo at a time $2\tau$ (where $\tau$ is the time from the beginning of the sequence to the centre of the rephase gradient). Due to the absence of the 180° pulse, the spins are not inverted and the phase gradient lobe must be in the opposite sense to the read gradient direction. This simple technique allows for shorter acquisition echo times and is known as the gradient echo method.

### 1.7.3.2 THE INVERSION RECOVERY SPIN ECHO TECHNIQUE

The standard spin echo sequence can be used to indicate $T_1$ dependence by simply changing the repetition time between each sequence of pulses (known as $T_1$ weighting). Also, $T_2$ contrast can be made by varying the spin echo time ($T_2$ weighting), but to exploit relaxation properties effectively, special sequences usually have to be employed. The inversion recovery spin echo technique is based around the spin-warp method, except a 180° pulse is applied to invert the magnetisation a time $T_l$ before the selective 90° pulse. As described in section 1.5.6.1, the recovery time $T_l$ can be varied, giving an initial magnetisation which is proportional to $T_1$. The general expression describing the signal amplitude at the echo is given by

$$M_{TR} = M_0 [1 - 2 \exp\left(-\frac{T_l}{T_1}\right) + \exp\left(-\frac{T_E}{T_2}\right)]$$  \hspace{1cm} (1.67)

$T_E$ is the spin echo time. As the resulting image is a magnitude of the signal, there may be complications in interpreting the data with signals from regions of very short and very long $T_1$ appearing similar. The null point of a specific $T_1$ can be used to suppress unwanted signal from the image. The value of $T_l$ which gives this null is given by

$$T_l = \frac{T_1 \ln 2}{[1 + \exp(-TR/T_1)]}$$  \hspace{1cm} (1.68)
For signal elimination, $T_1$ must be 0.69 $T_1$ and the repetition time $TR$ greater than
3$T_1$. Contributions from $T_2$ relaxation can complicate the contrast, but these
effects can be reduced by using a short TE.

1.7.3.3 CHEMICAL SHIFT IMAGING

Chemical shift imaging (C.S.I.) allows the separate identification of spins in
different chemical environments based on their chemical shift (section 1.5.4).
Conventional 2DFT techniques do not permit the measurement of chemical shift
spectra, as the frequency encoding gradient broadens the spectral lines. This
problem is overcome by using two phase encoding gradients as in figure 1.18. For
a $N \times N$ array of k-space points, the phase gradients must be sequentially varied
$N^2$ times, which lengthens the image acquire time and data size considerably.

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{chemical_shift_imaging.png}
\caption{The Chemical Shift Imaging (C.S.I) Technique}
\end{figure}
C.S.I techniques obtain chemical spectra from each volume element (voxel). The resultant spectra from each voxel can be used to quantify the relative number of spins in each chemical environment. C.S.I sequences are commonly used in distinguishing oil and water (within rock cores, for example), provided the spectral peak separation (3.5 ppm) is resolvable.

1.7.3.4 ECHO PLANAR IMAGING

Echo planar imaging (E.P.I) is a rapid imaging 'one shot' technique first proposed by Mansfield (1977). Unlike conventional imaging sequences which have to be repeated many times, E.P.I. covers the whole of k-space in just one scan. This is achieved by applying one slice selective 90° pulse followed by a small continuous phase gradient with rapidly alternating pulses of the frequency encoding gradient. k-space is thus covered in a 'zig-zag' trajectory and special routines have to be used to account for this non-linear sampling. Various improvements have been made to this technique, including the use of phase encoding 'blips', to sample k-space more evenly.

1.7.4 BROAD LINE NMR IMAGING

NMR imaging of liquid state systems (long T2) has progressed very rapidly since its discovery in 1973, but despite one of the first papers in MRI dealing specifically with the imaging of solid materials (Mansfield, Grannell, 1973), solid state (short T2) or broad line NMR imaging still remains a specialist area. This is largely due to the technical difficulties involved in overcoming the broadening caused by strong homonuclear dipolar interactions. Listed below are typical difficulties encountered in solid state imaging.
1. Very large gradients (>30 G/cm) are required if traditional methods, such as gradient echo, are to be used.

2. For typical gradient sets, the coil inductance may lead to gradient rise times which are longer than the $T_2$ of the sample.

3. The large gradients themselves lead to a reduced $T_2$, so that the spatial encoding time is very short.

4. A large fraction of the signal can be lost in the NMR receiver dead time.

Various imaging techniques have been used to study 'solid' systems and three of these are included in the remainder of this chapter.

### 1.7.4.1 BROAD LINE GRADIENT ECHO IMAGING

The gradient echo method (section 1.7.3.1) can be used for imaging solids, provided the gradient strength $G$ satisfies the equation

$$G \cdot \Delta r = \Delta B$$

(1.69)

where $\Delta B$ is the line width and $\Delta r$ is the desired resolution. The problem usually encountered with such an approach is the long gradient rise time required to obtain an acceptable $G$. A technique developed by Cottrell et al (1989) overcomes this problem by using oscillating gradients of frequency $\tau^{-1}$ to refocus the spins a time $\tau$ following a 90° r.f. pulse. The gradients can thus be applied n-cycles before the application of the r.f. pulse to account for the gradient rise time. With a sinusoidal gradient period of about 80 μs, the technique is ideal for imaging materials with $T_2$ relaxation times of the order of a few hundred microseconds. The pulse sequence layout is quite simple with the r.f. pulses placed at the zero crossing of the gradients (figure 1.19).
Due to the oscillating nature of the gradients, k-space is not sampled linearly and special reconstruction routines have to be employed to account for this (section 3.3.5.3). Two dimensional images can be obtained by using two orthogonal oscillating gradients with the amplitudes varying according to the back projection technique.

The broad line gradient echo technique and variants of it, have been used extensively in this thesis for the study of short $T_2$ fluid components within reservoir rock cores (chapters 5, 6 and 7). A more thorough review of these pulse sequences is given in chapter 3.

![Figure 1.19 The Broad line Gradient Echo Imaging Sequence](image)

**1.7.4.2 MULTIPLE PULSE IMAGING**

Multipulse imaging techniques use radio frequency pulses to manipulate the nuclear spin Hamiltonians and coherently average the dipolar interaction to zero. This has the effect of simulating molecular motion in the spin system and removes the associated line broadening. The technique was first proposed by Mansfield and Granell (1975), with a sequence known as MREV-8. Variants of this technique use
either blipped or oscillating gradients to encode the spins. The blipped techniques suffer from gradient rise time which limits the available gradient strength. The oscillating gradient techniques (Miller et al, 1989 and McDonald et al, 1989) can be affected by r.f. pulse-gradient interaction at the gradient zero crossing, and this also limits the maximum gradient strength.

Multipulse techniques are useful in very short \( T_2 \) systems. However the image contrast can be poor and the resolution is low, due to the available gradient strength. The sequences are usually difficult to operate and require very accurate timings and large amounts of r.f. power.

1.7.4.3 STRAY FIELD IMAGING

Stray field imaging (STRAFI) overcomes problems associated with the gradient rise time by using the fringe field of a high field superconducting magnet (Kinchesh et al, 1992). The sample is moved mechanically through the linear point in the stray field and a sequence of r.f. pulses applied. The large gradient has the effect of excluding all the NMR signal, except a very small slice at the appropriate resonant frequency. The magnitude of the resultant echoes can be reconstructed to form a one dimensional profile composed of all the resonant slices. Further dimensions can be obtained by rotating the sample about its axis.

With typical gradient strengths of 5000 G/cm, STRAFI has the advantage of extremely high resolution (\( \Delta x < 50 \mu m \)). STRAFI is useful for imaging materials that produce large susceptibility effects due to its extremely slice selective nature.
CHAPTER TWO

AN OVERVIEW OF PETROLEUM ENGINEERING TECHNIQUES AND THE APPLICATION OF NMR IN POROUS MEDIA.
2.1 BACKGROUND

Crude oil is found deep underground in strata of porous 'reservoir' rock, capped by an impervious layer. The pores of reservoir rock form an intricate three-dimensional network with channels of the order of 1 to 100 μm wide. The total pore volume can occupy up to 30% of the rock bulk volume and is filled with crude oil, gas and an irreducible amount of saline water, known as 'connate water'. Connate water is usually present as a thin film coating the surfaces of the rock and tightly bound in some of the smaller pores.

Reservoir rock is of a sandstone or limestone origin, laid down in a marine sedimentary environment. The grains are usually irregular and cemented in various places, leading to possible reductions in inter-pore connection and porosity (figure 2.1).

![Figure 2.1 Representation Of A Typical Sandstone Rock.](image)

Reservoir oil is often recovered by displacing it with some other fluid, usually gas or water. The displacing fluid is pumped into the reservoir and 'swept' across the oil bearing strata to make contact with as many oil-containing pores as possible. Although the displacing fluid is usually immiscible with the oil, the displacement is not piston-like, except at the irreducible or residual saturation of one of the fluids.
During the displacement process, much of the oil is left behind and not recovered. This is partially due to droplets forming in the microscopic pores, or large areas of the reservoir being totally bypassed. The quantity of oil remaining can amount to more than half of the initial oil-in-place. The residual oil saturation can be reduced with 'enhanced oil recovery' (EOR) techniques, whereby the displacing fluid is modified with the addition of polymers and surfactants. Depending on the structure of the reservoir, EOR processes may be used early in the production of oil. A thorough review of EOR techniques is given by Dawe and Egbogah (1978).

Considerable research has been devoted to the study of mechanisms by which one fluid is displaced by another in a porous medium. A majority of the work is concerned with studying the displacement of oil by water, since many reservoirs are produced by water flooding. Laboratory displacement experiments are frequently conducted with core plugs in 'Special Core Analysis' studies.

Applications of NMR in special core analysis has grown steadily since the 1950's with experiments conducted under static and dynamic conditions. Using both bulk and spatially resolved techniques, magnetic resonance has led to quantitative information about fluid flow processes and the structure of pores within reservoir cores.

### 2.2 POROSITY

In porous media, the porosity (\( \phi \)) is defined as the ratio of void volume to bulk volume. Reservoir rocks usually have irregularly shaped pore spaces, which due to grain cement may become blocked, thus reducing the effective porosity.

To measure porosity, the bulk volume is normally determined by calliper measurement or mercury displacement. Various methods exists for measuring the pore volume. The easiest method is to evacuate the core and allow water in. When re-pressurised, the increase in mass determines the pore volume. The porosity is given by
\[ \phi = \frac{M}{\pi r^2 L \rho_w} \]  

(2.1)

where \( M \) is the mass of water added, \( \rho_w \) is the density of water, \( L \) and \( r \) are the core length and radius respectively. For more accurate measurements, mercury can be injected into the core at various pressures. Although this is usually a destructive technique, this method allows the pore size distribution to be estimated, as higher pressures are needed for smaller pores.

2.3 ABSOLUTE PERMEABILITY

For a rock, fully saturated with a single phase (i.e. water), the flow rate is directly related to the pressure drop across the sample by the absolute permeability (\( k \)). In the simplest case, the permeability or specific flow capacity is given by Darcy's law

\[ q = \frac{k A \Delta P}{\mu} \frac{1}{L} \]  

(2.2)

where \( q \) is the flow rate (\( \text{cm}^3\text{s}^{-1} \)), \( k \) is the permeability (millidarcy), \( \Delta P \) is the pressure drop (atmospheres), \( \mu \) is the viscosity (centistokes), \( L \) is the sample length (cm) and \( A \) is the sample cross sectional area (cm\(^2\)).

The most significant limitations to this equation are that the flow is non-turbulent and there is no chemical reaction between the fluid and the porous surface (Crichlow 1977).

To measure absolute permeability, the core must undergo a single phase flood test. The core, encased to prevent unwanted fluid escape, has an external pressure applied. The volume flow rate, pressure drop and output volumes can then be measured for the injected fluid.
2.4 MULTIPHASE FLUID FLOW

For a porous system, the physical laws governing equilibrium and flow of several immiscible fluids at the pore level are simple and well known. In practice, however only the global behaviour of the system is of interest. Unfortunately, due to the complexity of pore geometry, macroscopic behaviour is not easily deduced from pore level behaviour. Nevertheless, investigating multiphase flow in pores can give some insight into the physical phenomena involved, providing some qualitative indications that are macroscopically useful.

2.4.1 CAPILLARY PRESSURE AND WETTABILITY

Consider a cylindrical capillary of radius $r$ containing an oil-water interface (figure 2.2). At the interface there are net surface forces causing a tension which acts parallel to the surface. These interfacial forces, curve the oil-water interface. If the radius of curvature is $R$ and the surface tension is $\gamma$, a pressure difference across the interface will occur, known as the capillary pressure $p_c$ and given by

$$p_o - p_w = p_c = \frac{2\gamma}{R} = \frac{2\gamma \cos \theta}{r}$$

(2.3)

where $\theta$ is the angle of contact, controlled by the intermolecular forces and is a measure of the wettability of the system. The larger the value of $\theta$, the less the fluid wets the solid and the tendency to form a bead is greater than spread on the surface. The shape and direction of curvature of the meniscus is determined by the wettability. In multiphase flow experiments, the water phase is usually considered to be the wetting phase within the rock core. As such, throughout this thesis, water will be taken to be the wetting phase, unless otherwise stated.
2.4.2 EFFECTIVE PERMEABILITY

When two immiscible fluids are flowing simultaneously, it is found that the permeability of the rock to each fluid is not a simple function of saturation. The permeabilities to the individual phases are reduced, and are referred to as effective permeability ($k_e$). The sum of the effective permeabilities for the two fluids is always less than the absolute permeability. The explanation is not properly understood, but is thought to be related to wettability effects and the general hydrodynamics of the system.

2.4.3 RELATIVE PERMEABILITY

The ratio of effective permeability to absolute permeability is known as relative permeability ($k_r$).

$$k_r = \frac{k_e}{k}$$  \hspace{1cm} (2.4)
For a water wet system, figure 2.3 shows a typical plot of oil and water relative permeability curves obtained by flowing the fluids simultaneously through a particular rock as a function of water saturation. Points A and B represent 100% oil and water saturations respectively, where the absolute permeability applies. At 25% water saturation only oil is found to flow, but the permeability is reduced to about 60% of the absolute value (point D). If the water saturation is slightly increased, water will start to flow. This value of saturation is known as the critical or irreducible saturation. As the water saturation increases, the oil relative permeability decreases, until at point F the oil ceases to flow as hydraulic continuity is broken. This is the residual oil saturation ($S_{or}$), the value below which the oil will not flow through the pores.

If the rock is oil wet, the arguments can be used in reverse and the shape of the relative permeability curves will be reversed.

Figure 2.3 Relative Phase Permeability Curves Versus Water Saturation
During flow, the invasion of the nonwetting fluid is referred to as drainage and the invasion of the wetting fluid as imbibition.

To measure relative permeability, both oil and water displacements are required. The various methods used to determine relative permeability can be divided into steady state and unsteady state. Steady state techniques offer the most sensitive results, but for each measurement the outflow rates must be stable. Unsteady state techniques make measurements just after breakthrough, based on the Buckley-Leverett (1942) displacement equation, which was later modified by Welge (1952).

### 2.4.4 VISCOSOUS FORCES AND THE CAPILLARY NUMBER

Flow rates in capillaries are restricted by viscous forces, where the pressure drop is given by Poiseuille's equation.

\[
\Delta P = \frac{8 Q \mu L}{\pi r^4}
\]

Q is the volume flow rate in the capillary, L is the length and r the radius.

As viscous forces become larger for smaller capillaries, the interplay of viscous and capillary forces is dominated by the flow rate. If a large pressure difference is applied, viscous forces dominate and the flow is predominantly in the larger capillaries. For small pressure drops, capillary forces dominate and flow is faster in the smaller capillaries.

The ratio of these forces at the pore scale determine the outcome of macroscopic oil recovery and are termed by the capillary number, $N_c$, (Melrose and Brandner 1974).
\[ N_c = \frac{V_w \eta_w}{\gamma_{ow} \phi} \] (2.6)

\( V_w \) is the water phase flow velocity per unit cross-sectional area, \( \eta_w \) is the coefficient of viscosity of the water phase, \( \gamma_{ow} \) is the oil-water interfacial tension and \( \phi \) is the rock porosity. For ordinary water flooding conditions, \( N_c \) is of the order of \( 10^{-6} \) and typically up to 50% residual oil may occur.

### 2.4.5 MECHANISMS OF MICROSCOPIC FLUID ENTRAPMENT

During an immiscible flood, the physical forces acting on a rock core are mainly capillary, viscous and gravitational in origin and result in fluid entrapment. Residual oil can occur macroscopically when areas are cut-off owing to bypassing (perhaps due to different permeability layers), and microscopically, when droplets can be left in individual pores. Two microscopic entrapment mechanisms are listed below.

#### 2.4.5.1 THE CONVERGENT - DIVERGENT CAPILLARY MODEL

The first model, which is based around spherical pores connected by smaller throats, is illustrated in figure 2.4. As the oil-water interface flows through the capillary, the interfacial curvature changes from point to point. The capillary pressure across the interface also necessarily changes. The meniscus is subject to local expansions and contractions, and is compelled to adopt instantaneous non-equilibrium shapes. As the oil filament thins, break-off can occur, leaving isolated spherical oil drops. With many type of reservoir rock having pore throats much smaller than the average pore size, this type of entrapment mechanism can be very common during immiscible floods.
2.4.5.2 THE PORE DOUBLET MODEL

The pore doublet model consists of a pair of interconnected cylindrical capillaries with different diameters and illustrates how the amount of trapped oil varies as displacement conditions change (figure 2.5). The oil-water interfaces in the two arms of the doublet will generally move with different velocities as the fluids respond to the combined effects of viscous and capillary forces. One of the two interfaces will reach point B first and trap the remaining oil in the other arm of the doublet.

The pressure drop across each capillary of the doublet is $P_A - P_B$, and is the algebraic sum of the capillary pressure (equation 2.3) across that interface and the viscous pressure drop (equation 2.5).

If the applied pressure is large, viscous forces dominate and there is a more rapid flow of water through the larger capillary. This traps oil in the smaller capillary. If the applied pressure is small, capillary forces become more significant and control the rate and direction of movement of the oil-water interfaces. Flow will therefore
be faster in the smaller capillary and oil in the larger capillary will become trapped. For very low flow rates, the viscous forces can be negligible compared to the capillary forces and the phenomenon of counterflow may occur. This is where the interface of the larger capillary recedes as the smaller capillary advances. Oil in the larger capillary will therefore become trapped.

Under reservoir conditions, where driving pressure gradients are small (of the order of 0.1 bar m$^{-1}$), the capillary pressure difference in the doublet dominates. Therefore, trapping of oil is expected to occur primarily in the larger pores.

![Figure 2.5 Pore Doublet Model To Illustrate Oil Entrapment](image)

### 2.4.6 Surfactants and Polymers

Laboratory data has shown that in order to recover significant amounts of residual oil, the capillary number must be increased by a factor of at least $10^4$. This can be achieved by lowering the oil-water interfacial tension. Surfactant flooding involves the addition of surface-active chemicals to water which effectively reduces the oil-
water interfacial tension. This is an expensive process and in commercial reservoirs, only a small slug of surfactant is used at the front of the water flood.

Polymers may also be added at the front of a water flood to protect the surfactant slug and increase the viscosity of the injected water. The polymers are of high molecular weight such as polyacrylamides and polysaccharides. The polymers can improve the overall sweep efficiency and thereby improve oil recovery.

2.5 PERCOLATION THEORY

Percolation processes were first developed by Flory (1941) and Stockmayer (1943) to describe how small branching molecules react and form large macromolecules. In mathematical literature, percolation was introduced by Broadbent and Hammersley (1957) to deal with the concept of the spread of hypothetical fluid particles through a random medium. Recently with the aid of computer modelling, percolation theory has been successfully used to study multiphase flow in porous systems.

By converting complicated porous structures into a matrix consisting of interconnected nodes, percolation theory can tell whether a system is macroscopically connected or not. This macroscopic connectivity is of fundamental importance to many phenomena involving disordered systems. The transition from a macroscopically disconnected structure to a connected one is known as the percolation threshold and plays a fundamental role in any transport process in percolating systems. For instance, if a rock core is partially filled with a fluid which blocks the pores such that there is no clear path from one side to the other, it is said to have reached the percolation threshold.

A comprehensive review of percolation theory and applications to petroleum engineering is given by Sahimi (1994).
NMR has proven to be a valuable non-invasive technique for probing porous media. A proton NMR experiment provides information on the amount of hydrogen in the pore space and is thus a measure of porosity. Further, the rate of decay (or build-up) of the proton magnetisation depends on the characteristic length scales of the pores and on the pore-fluid-grain interactions. The principle challenge, is to interpret the NMR information to obtain physically interesting characteristics of the porous medium.

2.6.1 PORE SCALE NMR RELAXATION

Fluid transverse and longitudinal relaxation rates in porous systems appear quite different from that observed in bulk fluid studies. In particular, relaxation rates are considerably shorter than those in bulk fluids and the relaxation cannot be described by a single-exponential process.

The fundamental paper by Brownstein and Tarr (1979), attributes the enhanced relaxation rates to two main effects: The interaction of the protons at the pore-grain interface (surface relaxation) and the hindered motion of the fluid molecules in a layer adjacent to the pore-grain interface. A brief review of the theory behind these enhanced relaxation processes is included here.

2.6.1.1 THEORY OF PORE SCALE LONGITUDINAL RELAXATION

Consider an isolated pore, filled with water, of volume $V$, surface area $S$ and radius $a$. The fluid in the centre of the pore relaxes with a characteristic longitudinal relaxation time $T_{1B}$. An enhanced relaxation rate is assumed for molecules within a certain distance $\lambda$ from the surface. The mechanism for the enhancement varies for different porous media, but is usually due to either a nuclear-nuclear dipole coupling between the liquid and the pore surface, or to the presence of
paramagnetic sites on the solid surface (section 2.6.1.5). The strength of the
surface relaxation is characterised by a parameter $\rho$ (surface relativity) with units
of velocity. $\rho$ is the product of a fluid-surface relaxation rate and the thickness of
the fluid layer interacting with the surface.

In general, the decay of nuclear magnetisation due to surface relaxation depends
upon both $\rho$ and the self-diffusion coefficient $D$ of the fluid. The equations
describing the decay of magnetisation are

$$\frac{\partial M}{\partial t} = D \nabla^2 M - \frac{M}{T_{1B}}$$

(2.7)

with the boundary condition

$$[D \hat{n} \cdot \nabla M + \rho M]_{\text{surface}} = 0$$

(2.8)

where $\hat{n}$ is a unit vector pointing towards the surface at the pore-surface interface.
The solution of the diffusion problem can be expressed as a sum of normal modes

$$M(t) = \sum_{n=1}^{\infty} A_n e^{-t/T_n}$$

(2.9)

with the constraint that $M(0) = \sum_n A_n$. Brownstein and Tarr (1979) solved these
equations for simple geometries (spherical, planar and cylindrical) and to an
excellent approximation, showed that the decay is dominated by the surface
relaxation rate ($T_{1S}$)

$$T_{1S} = \frac{a^2}{D} \quad \text{for} \quad \rho \frac{a}{D} \gg 1 \quad \text{(strong killing regime)}$$

(2.10a)

$$T_{1S} = \frac{a}{\rho} \quad \text{for} \quad \rho \frac{a}{D} \ll 1 \quad \text{(weak killing regime)}$$

(2.10b)
Depending on the value of the dimensionless parameter \( \frac{p}{a/D} \), diffusion either limits the decay (slow diffusion limit), or supplies the walls with enough protons that \( a/p \) dominates (fast diffusion limit). In the strong killing (slow diffusion) regime, higher modes contribute, and the relaxation of a single isolated pore is multiexponential. In the weak killing (fast diffusion) regime, the lowest mode dominates completely, and for a single isolated pore, the relaxation is a single exponential. The relaxation rate in the extreme weak killing regime is therefore directly related to the pore size and thus the pore surface to volume ratio. The smaller the pore, the shorter the relaxation time.

The pore radius \( a \) is sometimes an ambiguous definition because of the fractal nature of the pore. However, the surface to volume ratio and pore size may be related.

\[
a = m \left[ \frac{S}{V} \right]^{-1}
\]

where \( m \) is a measure of the pore shape, of the order of 2-3, Halperin (1989). The longitudinal surface relaxivity usually includes the constant \( m \) and is denoted by \( \rho_1 \).

The surface relaxation mechanism acts independently of the usual bulk relaxation process so that in the weak killing regime, the observed relaxation rate is given by

\[
\frac{1}{T_1} = \frac{1}{T_{1B}} + \rho_1 \frac{S}{V}
\]

As the fluid-solid interaction has its basis in either dipole-dipole or paramagnetic interaction, it is very short ranged, so \( \lambda \) should not be much more than a few \( \text{A} \). By reducing the pore fluid saturation to one molecular layer, the pore surface relaxivity \( (\rho_1) \) is related to the observed relaxation rate by

\[
\frac{1}{T_{1\text{monolayer}}} = \frac{\rho_1}{\lambda}
\]
This can lead to direct measurement of the surface relaxivity, providing the NMR instrumentation is fast enough (typically, $T_{1\text{monolayer}} \ll 1 \text{ ms}$).

### 2.6.1.2 THEORY OF PORE SCALE TRANSVERSE RELAXATION

In porous media, internal magnetic field gradients exist due to the different susceptibility values of the solid matrix and the pore fluid. The form of the gradient depends on the geometry of the pore structure, with the magnitude being directly proportional to the applied magnetic field strength. The situation is further complicated as the diffusion is restricted in the pore space. For a fluid in a single pore, the observed transverse relaxation rate (using a standard CPMG sequence) is strongly affected by the presence of diffusion through these internal magnetic field gradients. Without the internal gradients, the theory of pore scale transverse relaxation is directly analogous to the longitudinal relaxation theory (section 2.4.1.1), except the surface relaxivity is given by $\rho_2$. A theory which accounts for the effect of surface relaxation, the internal field gradients and restricted diffusion has been presented by Kleinberg and Horsfield (1990).

Studies performed by Kleinberg and Horsfield on a range of fully saturated sandstone cores have shown that the transverse rate is related to the applied magnetic field strength and the CPMG inter-pulse gap $\tau$. At the lowest field strengths and pulse gaps, the transverse relaxation rate is independent of $\tau$. This indicates that surface relaxation effects dominate. With longer pulse gaps or field strengths, there is clear evidence of the effect of molecular diffusion in the presence of static magnetic field gradients.

Neuman (1974) derived equations for describing the decay of transverse magnetisation due to restricted molecular diffusion in a uniform field gradient. For spherical pores, the magnetisation is given by
\[ M(t) = M_0 \left[ -2\gamma^2 G^2 a^4 t \sum_{i=1}^{\infty} \left( \frac{1}{\alpha_i^4(\alpha_i^2 - 2)} \right) (1 - \frac{3 - 4 \exp(-q/2) + \exp(-q)}{q}) \right] (2.14) \]

where
\[ q = \frac{2t_{cp} \alpha_i^2 D}{a^2} \] (2.15)

\[ G \] is the field gradient strength, \( a \) is the pore radius, \( t_{cp} \) is the CMPG echo spacing, \( D \) is the self-diffusion coefficient and \( \alpha_i \) is a numerical coefficient given by
\[ \tan(\alpha_i) = \frac{2\alpha_i}{(2 - \alpha_i^2)} \] (2.16)

For a region close to the pore surface, Glasel and Lee (1974) have calculated the average field gradient to be
\[ G = \frac{\mu_0 H_0 \Delta \chi}{4a} \] (2.17)

where \( \mu_0 \) is the magnetic permeability of vacuum, \( H_0 \) is the applied field strength and \( \Delta \chi \) is the difference between the volume magnetic susceptibilities of the pore and the external medium.

Combining the diffusion-related effects with the work carried out by Brownstein and Tarr (section 2.6.1.1), the observed transverse relaxation rate for a single spherical pore is given by the unified equation
\[ M(t) = M_0 \left[ \exp\left(\frac{-mp_2^2}{a} t\right) \exp\left(\frac{-1}{T_{2B}} t\right) \exp\left[\frac{-2\gamma^2 G^2 a^4 t}{D}\right] \right. \]
\[ \times \left. \sum_{i=1}^{\infty} \left( \frac{1}{\alpha_i^4(\alpha_i^2 - 2)} \right) (1 - \frac{3 - 4 \exp(-q/2) + \exp(-q)}{q}) \right] \] (2.18)

where \( T_{2B} \) is the bulk transverse relaxation rate.
For a porous medium containing a range of pores of varying size, Kenyon et al (1988) have shown the total pore volume to be given by

\[ V = c \int_{0}^{a} da \exp\left(-\left(\frac{a}{a_0}\right)^2\right) \]  \hspace{1cm} (2.19)

where \( a_0 \) is the characteristic length scale and \( c \) is a constant having dimensions of length squared. Equation 2.19 can be put into 2.18 to obtain a unified theory accounting for a porous medium with a range of pore sizes.

An alternative theory has recently been proposed by Jerosch-Herold et al (1994) which describes transverse relaxation in a porous medium where diffusion effects overwhelmingly dominate the surface effects. For small CPMG pulse gaps, the macroscopically observed transverse magnetisation is described by an expression for free diffusion. For longer pulse gaps, the effects of restriction become more prominent and the observed transverse relaxation rate decreases.

In the free diffusion limit (short pulse gaps), the \( n \)th echo of the CPMG sequence is given by

\[ M(t = n\tau) = M_0 \exp[-(\gamma G \tau)^2 D t / 12] \]  \hspace{1cm} (2.20)

where \( \tau \) is the CPMG echo spacing. For free diffusion in a linear field gradient, the observed transverse relaxation should decrease as \( 1/\tau^2 \).

A model which extrapolates between the limits of free and restricted diffusion was proposed by Mitra et al (1992). The cross-over from unrestricted to restricted diffusion is characterised by

\[ D_{\text{eff}} = \frac{l_{\text{NMR}}^2}{\tau} \left[ 1 - \exp\left(-D_{\tau}/l_{\text{NMR}}^2\right) \right] \]  \hspace{1cm} (2.21)
$l_{\text{NMR}}$ is the NMR length scale and should be of the order of the volume-to-surface ratio of a pore. Using this time dependent effective diffusion coefficient, the $\tau$ dependence for transverse relaxation is given by

$$T_2^{-1}(\tau) = \frac{(\gamma G)^2 l_{\text{NMR}}^2}{12} \tau [1 - \exp(-D_o \tau / l_{\text{NMR}}^2)]$$ (2.22)

The length $l_{\text{NMR}}$ has been observed to be well correlated with a length $l_M$, derived from mercury injection experiments at the percolation threshold. The choice of pore geometry determines the proportionality between $l_{\text{NMR}}$ and $l_M$.

The $\tau$ dependence of $T_2$ can be taken as a signature of whether the surface effects dominate and the Kleinberg, Horsfield model should be applied, or diffusion effects dominate and the Jerosch-Herold model is appropriate.

### 2.6.1.3 THE EFFECT OF PORE CONNECTIVITY

The work carried out by Brownstein and Tarr (1979) is concerned with magnetisation evolution in independent pores, but in real porous systems, the pores are usually interconnected by throats. McCall et al (1991) have proposed a theory which accounts for pore connectivity with either weak or strong coupling.

Consider a porous system (figure 2.6), where $V$ is the pore volume, $A$ the pore surface area, $S$ the cross-sectional area of a throat and $l$ the distance between the centre of adjacent pores. The pore size $a$ is defined as $a = \sqrt[3]{V/A}$. The behaviour of magnetisation in a pore space is controlled by four rates.

1. $\omega_B = 1/T_{1B}$, the bulk relaxation rate, an intrinsic property of the pore fluid.
2. $\omega_p = \rho/a$, the relaxation rate in the vicinity of the fluid-matrix interface.
3. $\omega_P = D/a^2$, the rate of molecular diffusion to the fluid-matrix interface.
4. $\omega_c = SD/Vl$, the rate of molecular diffusion between pores (coupling rate).
Figure 2.6 Schematic Of A Porous Medium

The work of Brownstein and Tarr on a single pore corresponds to the weak coupling limit, $\omega_c \to 0$. In the fast diffusion limit, the surface relaxation rate is slow compared to the rate of diffusive magnetisation equilibrium; the magnetisation is approximately uniform across a pore and the decay is single exponential. Coupling between the pores can be important in the fast diffusion regime.

Figure 2.7 shows a rate space diagram for magnetisation decay in a pore system. The Brownstein and Tarr analysis corresponds to the path along $1 \to 2$. Previous studies (Kenyon et al., 1986) have shown that reservoir rocks correspond to a point somewhere along $2 \to 3$. Individual pores would therefore be in the fast diffusion limit were they uncoupled from their neighbours. If the pore coupling $\omega_c$ is in the strong regime, the entire pore space becomes a single pore in the fast diffusion limit. The decay spectrum therefore narrows to a delta-function at the rate given by $\omega_p = \rho A/V$, where $A$ and $V$ are the total area and pore volume of the system. The decay in this limit is strictly single exponential.
McCall et al (1991) have developed equations governing the magnetisation evolution in fluid-filled connected porous systems using three methods; perturbation theory, effective-medium theory and matrix diagonalisation. The results of all three methods are in good agreement and show that the cross-over from uncoupled to strongly coupled behaviour occurs over approximately two decades in the coupling strength.

Measurements made on reservoir sandstone cores (Kenyon et al, 1986) have shown that at room temperature, the coupling strength is given by $\omega_c / \omega_p < 0.1$. This weak coupling suggests that for reservoir cores, the Brownstein and Tarr approximations can be applied when the pores are in the fast diffusion limit. Equivalent studies on porous silica glasses (D'Orazio et al, 1989), which are highly coupled systems, have given a coupling strength of $\omega_c / \omega_p < 10^3$. Studies on such a system, would lead to a delta-function distribution of relaxation.
2.6.1.4 RELAXATION ANALYSIS

In the weak killing (fast diffusion) regime, where surface effects dominate, work by Brownstein and Tarr (1979) has shown that relaxation in a single fluid filled pore, decays with a single exponential, with the decay rate being proportional to the pore size. In a real porous sample, there will usually be a complex distribution of pore sizes and shapes, so the observed relaxation behaviour will be a sum over all the contributing pores.

A variety of methods for the analysis of such relaxation curves have been developed. The simplest approaches, are to fit relaxation data to a predetermined number of exponential functions

\[ M(t) = \sum_{i=1}^{N} M_{0i} \exp \left[ \frac{-t}{T_i} \right] \]  \hspace{1cm} (2.23)

where \( N \) is an integer number of exponential fits, usually between 1 and 4. This can be rather a crude approach, especially in the study of reservoir rock cores, where there is a large distribution of pore sizes.

Assuming that the observed relaxation decay rate can be written as the superposition of single-exponential decays, Kenyon et al (1986) proposed a fitting technique with only three variables, known as the stretched exponential.

\[ M(t) = M_0 \exp \left[ -\left( \frac{t}{T} \right)^\alpha \right] \]  \hspace{1cm} (2.24)

\( \alpha \) is a dimensionless number known as the stretching exponent. The value of \( \alpha \) determines the multiexponential nature of the decay. For an \( \alpha \) value of 1, the decay is a single exponential. With an \( \alpha \) value of 0.66, the decay forms a Gaussian distribution about a central point given by \( T \). Lower values of \( \alpha \), correspond to broader relaxation rate distributions. With only three fitting parameters, this method can be very useful when only the average relaxation rate and an estimate of the distribution are required.
An alternative approach is to describe the observed relaxation by a weighted sum of independent relaxations in each pore, multiplied by the volume probability density $P(a)$. Assuming that the pore system is in the weak killing regime.

$$M(t) = \sum_a P(a) \exp\left[ -\frac{t}{T(a)} \right]$$  \hspace{1cm} (2.25)

Typically, 20 logarithmically spaced $T(a)$ values are selected, and the corresponding probability density $P(a)$ estimated. The estimation problem is linear, except that $P(a) \geq 0$. The inverse of the Laplace transform of the magnetisation is then directly related to the pore size distribution function, Halperin (1989).

Seevers (1966), proposed a link between longitudinal relaxation and porosity for rock core permeability estimation ($k = \phi T_1^2$). An improvement provided by Kenyon et al (1986), suggested the permeability to be better estimated by $\phi^4 T_1^2$. With fewer fitting parameters, the stretched exponential fitting routine provides the most robust permeability estimates.

2.6.1.5 MECHANISMS OF RELAXATION IN RESERVOIR ROCKS

It is generally believed that surface relaxation processes in reservoir rock cores are associated with the presence of paramagnetic ions, such as iron or manganese, on or near the pore surfaces (Korringa et al, 1962). A model proposed by Kleinberg et al (1994), takes into account recent studies performed on rock cores and explains the expected mechanisms behind rock core surface relaxation effects. Listed below are a few of the recent findings from which the model was based.

Howard et al (1990), first obtained estimates of the longitudinal surface relaxivity $\rho_1$, using prior knowledge of the pore size distribution. For 'clean' sandstones, they found $\rho_1 = 3 \times 10^{-3}$ cm/s.
Latour et al (1992), measured the temperature dependence on about a dozen rock cores and found the relaxation times relatively independent of temperature between 25°C and 175°C. This showed conclusively that the rocks were in the fast diffusion regime and that the surface relaxation mechanism was temperature independent, or nearly so.

Kleinberg et al (1993), determined the $T_1/T_2$ ratio on a selected number of cores to be in the range 1 to 2.6, with a median value of 1.6. They also measured the frequency dependence of $T_1$ at 5 MHz, 40 MHz and 90 MHz and showed only a modest variation with frequency, rather than the frequency squared behaviour commonly encountered in NMR investigations.

There is a large amount of literature on the relaxation of fluids on silica and other surfaces. The most recent work has been done by D'Orazio et al (1990). This group found that for water on pure silica, the longitudinal surface relaxivity $\rho_1 = 5 \times 10^{-7}$ cm/s, orders of magnitude smaller than $\rho_1$ found in rocks. They also found $T_1/T_2 = 58$, in distinct contrast to values reported for rock cores. This suggests that the process studied by D'Orazio et al, nuclear-nuclear dipolar coupling, does not dominate NMR relaxation in rocks. Mineralogy handbooks report that rocks generally contain approximately 1% iron. At this concentration, paramagnetic relaxation mechanisms can be expected to dominate at the pore surfaces.

The basic principles of surface relaxation by paramagnetic impurities were first suggested by Korringa, Seevers and Torrey (KST), 1962. Assuming paramagnetic impurities dominate relaxation, the KST equation for longitudinal surface relaxation, for a single pore is given by

$$\frac{1}{T_1} = \left(\frac{S \lambda}{V}\right) \frac{n_M}{T_{1M} + \tau_M} = \rho_1 \frac{S}{V}$$

where $n_M$ is the proportion of surface sites occupied by paramagnetic metal ions, $T_{1M}$ is the relaxation time of protons in molecules co-ordinated with paramagnetic
ions, and \( \tau_M \) is the residence time of the fluid molecules. Providing the CPMG echo spacings are short (Kleinberg et al, 1990), an analogous equation to 2.26 exists for transverse relaxation. The decay of magnetisation at a surface site may itself be nonexponential (Tse and Hartmann 1968). However, since the fraction of fluid molecules at surface sites is usually very small, the overall decay of magnetisation will not reflect the detailed time dependence at a surface site, but will be sensitive only to the mean lifetime of decay at surface sites. Equation 2.26 assumes that all relaxing surface sites are identical; the extension to multiple site properties (e.g., multiple paramagnetic ion species) is trivial. Appendix 1 demonstrates that an equation of the same form results when the site relaxation is nonexponential.

Using the experimental results mentioned earlier, Kleinberg and Kenyon postulated that \( \lambda \) must not be more than 3 Å. This excludes the possibility that paramagnetic ions buried under the grain surface are effective in relaxing proton spins. From the given \( T_1/T_2 \) ratio and using previously established paramagnetic theory, Kleinberg and Kenyon also derived equations for \( T_{1M} \) and \( T_{2M} \)

\[
\frac{1}{T_{1M}} = \frac{\gamma_1^2 \gamma_S^2 \hbar^2 S(S+1)}{15 \tau^6} 6\tau_{CI} \tag{2.27a}
\]

\[
\frac{1}{T_{2M}} = \frac{\gamma_1^2 \gamma_S^2 \hbar^2 S(S+1)}{15 \tau^6} 7\tau_{CI} + \frac{1}{3} S(S+1) \left( \frac{A}{\hbar} \right)^2 \tau_{CI} \tag{2.27b}
\]

where \( \gamma_1 \) and \( \gamma_S \) are the gyromagnetic ratios of the nucleus and the electron respectively, \( S \) is the spin of the magnetic ion, \( \tau \) is the electron-nucleus distance, \( A/\hbar \) is the scalar coupling constant and \( \tau_{CI} \) is the correlation time, corresponding to the amount of time a fluid molecule spends in contact with the paramagnetic ion.

The theory proposed by Kleinberg and Kenyon, suggests the dominant interactions are scalar and dipolar couplings between electron and nuclear spins at the grain surfaces. Also, the effect is very short ranged, as oil in water wet rock is known to
relax more slowly (Latour et al, 1992) due to a monolayer of water blocking the surfaces and preventing the contribution of paramagnetic effects.

2.6.2 PULSE FIELD GRADIENT STUDIES IN POROUS MEDIA

The time-dependent diffusion coefficient of fluid molecules in confining geometries has been the subject of a number of recent studies. It has long been realised that the time dependence contains information about pore geometry restrictions (Woessner, 1963). The short-time behaviour of the diffusion constant is independent of the microscopic details of the restricting geometry and depends only on the surface-to-volume ratio ($S/V$) of the pore space (Mitra et al, 1992). The time-dependent diffusion constant $D(t)$ is usually defined as

$$D(t) = \langle r^2(t) \rangle / 6t$$  \hspace{1cm} (2.28)

where $\langle r^2(t) \rangle$ is the mean-square displacement of spins in time $t$. It has been shown that for porous media with smooth boundaries, $D(t)$ is given at short times by

$$\frac{D(t)}{D_0} = 1 - \frac{4}{9\pi^{3/2}} \frac{S}{V} \sqrt{D_0 t} - \frac{S}{12V} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) D_0 t$$

$$+ \frac{1}{6V} \rho S D_0 t + [(D_0 t)^{3/2}]$$  \hspace{1cm} (2.29)

$S$ and $V$ are the pore surface area and pore volume, $R_1$ and $R_2$ are the principal radii of curvature of the pore walls and $\rho$ is the surface relaxivity. Using this equation or variants of it, pulse field gradient experiments can be used to probe the surface-to-volume ratio of porous systems.

2.6.3 THE APPLICATION OF MRI TO PETROLEUM ENGINEERING

The ability to visualise the location of specific fluids such as oil and water in a reservoir core is extremely important for the study of multiphase flow and the various factors that influence it. While X-ray CT imaging has been quite useful for determining the distributions of such fluids, these images are complicated by the response of the rock matrix and typically require the addition of high levels of contrast agent (Withjack, 1987). Proton NMR images of core fluids are only indirectly affected by the rock matrix and do not usually require the use of contrast agents.

The indirect effects of the rock matrix on the NMR properties of the fluids can be severe (Case et al, 1987). One principal effect is on the width of the proton NMR signal for the water or oil phase. The line broadening effect arises from the difference in the bulk magnetic susceptibilities of the fluid and the rock matrix and is proportional to the static magnetic field strength. Depending on the nature of the rock, the broadening can be sufficient to prevent the spectral resolution of NMR signals for immiscible pore fluids and can severely limit image resolution. The rock matrix also acts as a paramagnetic relaxation sink, causing enhanced fluid relaxation at the surface. If the effect is severe, pore fluid transverse relaxation times can be very short ($T_2 < 3\ ms$), and standard liquid state imaging techniques may be inappropriate.

Reservoir cores with low NMR signal broadening effects (i.e. most carbonates), can have immiscible fluids separately imaged using some variation of chemical-shift-selective imaging (Edelstein et al, 1988 and Dechter et al, 1991). The technique involves applying a pre-saturation pulse at the beginning of a standard spin warp sequence to selectively saturate either the oil or water phase. A more sophisticated technique is C.S.I. (section 1.7.3.3), which uses two phase encoding gradients to preserve chemical shift information. Although C.S.I is technically difficult and time consuming, successful results have been published by Williams et al (1990) and Horsfield et al (1990), among others.
In certain rock cores, the difference in $T_1$ between water and oil can be sufficient to obtain fluid-selective images using a $T_1$ weighted imaging sequence. Hall et al (1987) demonstrated this technique on Berea sandstone, which due to extensive line broadening, cannot be imaged using chemical-shift-selection. More recently, Davies et al (1994) used a $T_1$ weighted imaging sequence to selectively image crude oil and brine in preserved chalk samples.

When the rock matrix prevents standard selective imaging techniques, doping agents (such as manganese chloride) can be added to the water (Baldwin et al, 1988) or the water can be replaced with deuterium oxide (isotropic substitution). In these cases, only the oil signal can be detected using proton NMR imaging techniques. Multinuclear imaging is also possible, where different nuclides ($^{19}$F, $^{23}$Na) are used in tracers for selective images of the different fluids. $^{13}$C spectroscopy has also been suggested for oil determination in shaley rocks (Edelstein et al, 1988).

2.7 CONCLUSION

The natural mechanisms by which an oil reservoir is depleted will not produce all the oil initially present in the reservoir. A combination of pore size and geometry coupled with capillary and viscous forces prevent this. The actual physical mechanism whereby oil is entrapped in a natural porous system is still not properly understood and more research into the basic physics of two-phase flow is needed.

Magnetic resonance studies of rock cores have led to estimates of pore size, shape and distribution, using relaxation and diffusion analysis. Also, with the advent of magnetic resonance imaging techniques, single and multiphase flow studies have been successfully performed on rock core 'plugs' under laboratory conditions.

Due to large susceptibility effects, certain rock cores cannot be imaged effectively using standard liquid state NMR techniques and doping agents have to be
employed to selectively image different immiscible phases. A new method which includes changing the temperature of the pore fluid to separately image brine and oil based on $T_1$ suppression, is included in chapter 4 of this thesis.

A review of current pore scale relaxation theory clearly shows the complex nature of surface relaxation effects and the difficulty of interpreting NMR data in such heterogeneous systems. A clearer understanding of surface relaxation can be gained by removing the bulk fluid from the pores. This greatly reduces the relaxation times of the remaining fluid and requires the use of specialist solid state NMR techniques to obtain quantitative data. Using such techniques, chapter 7 of this thesis includes the first ever broad line NMR relaxation study of reservoir rock cores with connate and monolayer coverage saturations.
CHAPTER THREE

INSTRUMENTATION AND TECHNIQUES
3.1 INTRODUCTION

This chapter gives a brief outline of the hardware and software employed in this research, including novel broad line imaging pulse sequences.

3.2 THE WHOLE BODY MRI SYSTEM

The whole body MRI scanner consists of a 486 host computer, data processing cards and pulse sequence controller, all supplied by S.M.I.S. Ltd (Guildford, UK.). The large homogeneous region of static magnetic field allows this system to study samples up to 30 cm in diameter. The system is well suited to many medical and industrial applications, but is limited in the study of very short $T_2$ samples with only a small available magnetic field gradient to spatially encode the spins.

3.2.1 SYSTEM HARDWARE

The host computer runs in a windows environment and allows the user easy access to pulse sequence set-up and data acquisition. All pulse programs are written in a C-like language (PPL) which are compiled into Forth prior to run time. The pulse sequence controller (MR3020) stores the compiled pulse sequence at run time and controls up to three MR3031 waveform boards, which produce the gradient and r.f. wave shapes.

Transmission pulse wave shapes are gated and modulated in the 3330 r.f. unit with the frequency source provided by a PTS frequency synthesiser. The r.f. wave shape is amplified according to software specifications before entering the final stage of amplification, provided by a 1 kW solid state r.f. power amplifier.

Gradient wave forms undergo two stages of software controlled amplification before entering the pre-emphasis unit. This unit produces offsets in the gradient
shapes to account for eddy current effects caused by the time dependent gradients in the magnet. Power amplifiers provide the final stage of gradient amplification. There are two amplifiers per gradient axis, each capable of producing a peak current of 38 amps for a 10 ms duration. The amplified wave shapes travel to the gradient coils through shielded coaxial cable and via a low pass filter to reduce gradient noise. The gradient coils consist of 19 turns of wire per gradient axis and produce a maximum magnetic field strength of 0.7 G/cm.

3.2.2 THE MAGNET

The Oxford Instruments Ltd super-conducting magnet has a 85 cm diameter bore producing a uniform static magnetic field of 0.5 Tesla. The super-conducting temperature of the magnet is maintained at 4 K by recycled liquid helium with an average boil off rate of 0.25 litres per hour. The magnet is shimmed using Oxford Instruments passive shims and has been shown to give a homogeneity of better than 5 ppm over a 30 cm diameter.

3.2.3 THE R.F. PROBE

The r.f. probe is a bird cage resonator design (figure 3.1). This consists of eight uniformly spaced copper legs placed around a perspex tube of 14 cm internal diameter. Fixed ceramic capacitors placed at the top of each leg, tune the probe to the desired frequency (21.24 MHz) and variable capacitors attached to the end of the probe permit fine tuning and impedance match to 50 Ω.

The bird cage r.f. probe is capable of both transmitting r.f. pulses and receiving the induced EMF signal by a specially designed circuit layout built around the pre-amplifier (figure 3.2). The circuit consists of three λ/4 transmission lines (where λ is the wavelength of the r.f. radiation) which cause a transformation from low impedance to high impedance or visa versa. During transmission, the crossed diodes near the pre-amplifier act as an open circuit causing the majority of r.f.
radiation to enter the probe. The slight voltage leak to the pre-amplifier which does occur, leads to a characteristic 'dead time' in the receiver. The induced NMR signal, which is prevented from travelling down the transmitter line by series crossed diodes, travels along the $\lambda/2$ line to the pre-amplifier.

![Figure 3.1 Bird Cage Coil Electrically Equivalent Circuit](image)

![Figure 3.2 Pre-amplifier Protection Circuit](image)
3.2.4 PULSE SEQUENCES

Most of the experiments carried out on the whole body MRI system use standard pulse sequences: CPMG, inversion recovery, gradient and spin echo imaging. Due to the weak available field gradient, standard imaging sequences can only be applied to the study of samples with long transverse relaxation times ($T_2 > 20$ ms). A modified spin echo imaging sequence has been written to permit the study of shorter $T_2$ samples (figure 3.3). The sequence (SF31T1.PPL) is an inversion recovery variant of the spin warp imaging technique (section 1.7.3.2) and incorporates many time saving features to allow the study of samples with transverse relaxation times as short as a few milliseconds. To obtain short echo times with acceptable pixel resolution, the gradient ramps have been reduced to 500 $\mu$s with a 2 ms (3000 Hz) slice selective $90^\circ$ pulse and non-slice selective $180^\circ$ pulses. Along with a 50 kHz sample rate, the echo time has been reduced to 6 ms, with 128 data points in the read direction (1mm pixel resolution). The combination of a relatively high bandwidth slice selective pulse and weak magnetic field gradients has increased the minimum slice thickness to 15 mm.

![Figure 3.3 SF31T1.PPL - Inversion Recovery Spin Echo Sequence](image)

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3.3 THE BROAD LINE NMR IMAGING SPECTROMETER

The MRI console combines a modified S.M.I.S. Ltd pulse sequence controller and a Magnex Scientific Ltd actively shielded gradient set to effectively study short $T_2$ samples using a variety of broad line imaging techniques. The following text describes the relevant instrumentation used in the study of short $T_2$ fluid components in reservoir rock plugs.

3.3.1 SYSTEM HARDWARE

The MRI system (figure 3.4) is based around a 0.7 Tesla super-conducting magnet with modified S.M.I.S. Ltd hardware. Pulse sequence control is performed by a 386 sx computer along with the MR3020 pulse programmer board, which stores pulse sequences at run time and sends gradient wave shapes to the two MR3031 waveform boards.

3.3.1.1 R.F. PULSE TRANSMISSION

During r.f. pulse transmission, a constant 30 MHz frequency source is supplied by the PTS 040 frequency synthesiser. The 3330 r.f. unit uses the frequency source to modulate r.f. wave shapes sent by the MR3031 waveform boards. The resultant r.f. pulse is sent to a Merrimac 6-bit digital phase shifter which uses the 30 MHz frequency source and a control line from the interface board to shift the pulse phase according to table 3.1.

The phase shifted r.f. pulse is amplified by a Heatherlite 400 W r.f. amplifier and sent to a home-made pre-amplifier box with cross diode protection. The r.f. pulse travels along a copper shielded $\lambda/2$ transmission line to the r.f. probe within the magnet.
Figure 3.4 Block Diagram Of The Broad line NMR system
### Table 3.1 Response Of Merrimac PTM-64A Phase Shifter

<table>
<thead>
<tr>
<th>Bit</th>
<th>Phase Increment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(LSB) 1</td>
<td>5.6°</td>
</tr>
<tr>
<td>2</td>
<td>11.2°</td>
</tr>
<tr>
<td>3</td>
<td>22.5°</td>
</tr>
<tr>
<td>4</td>
<td>45°</td>
</tr>
<tr>
<td>5</td>
<td>90°</td>
</tr>
<tr>
<td>(MSB) 6</td>
<td>180°</td>
</tr>
</tbody>
</table>

**3.3.1.2 THE RECEIVER SYSTEM**

The induced EMF within the probe travels as a voltage signal down the λ/2 line to the pre-amplifier. Before entering the console, the signal is attenuated to be within the maximum voltage range of the data capture boards (± 0.0815 volts). The attenuation needed to prevent signal saturation is typically between 10 and 35 db.

A phase sensitive detector (P.S.D.) within the console uses the 30 MHz reference to demodulate the NMR signal and split it into real and imaginary components. A manually controlled phase shifter varies the phase of the reference source to change the effective receiver phase of the system. The demodulated and phase shifted signal is sent simultaneously to the data capture boards and a Hameg 20 MHz HM205-3 digital storage scope. The scope is used as a visual aid in accurate pulse phase and frequency settings.

The Loughborough Sound Images (L.S.I.) data capture boards are designed for rapid data acquisition and run in conjunction with the standard S.M.I.S. digital signal processing board (D.S.P.). The real and imaginary components are acquired on separate L.S.I. boards with a maximum sample rate of 10 MHz in a 8-bit digital form. Both L.S.I. boards can sample 4 KB of data in either a one shot process or by collecting multiple windows. The resultant digital information is sent to the D.S.P board, processed and converted into an ASCII data format before being written to the computer's hard drive.

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3.3.2 THE MAGNET

The Magnex Scientific Ltd super-conducting magnet has a 20 cm diameter bore which provides a static uniform magnetic field of 0.7 Tesla. The super-conducting temperature of the magnet is maintained with a liquid helium inner core surrounded by a liquid nitrogen jacket. The liquid nitrogen is designed to reduce helium boil off due to radiation effects and has to be refilled every other day. With an average helium boil off rate of approximately 0.05 litres per hour, the liquid helium chamber is refilled at four or five weekly intervals.

3.3.3 THE GRADIENTS

Gradient wave shapes are stored in the MR3020 pulse programmer at run time and clocked out through the MR3031 boards when required. These wave shapes travel to Techron 7700 gradient power amplifiers. There are five amplifiers in total (one for the z gradient and two for the x and y gradients) and each is capable of producing up to 180 amps when running in current mode.

The Magnex Scientific Ltd gradient set is actively shielded with an 8 cm diameter bore and 4 cm range of linear magnetic gradient field. The gradient coils are wound from copper wire onto a GRP former and potted in epoxy resin to provide mechanical stability.

The broad line NMR imaging sequences employed on this system use oscillating magnetic field gradients with cycle periods of either 216 µs or 80 µs. This corresponds to gradient cycling frequencies of 4.62 kHz and 12.5 kHz respectively. Treating the system as a standard RCL series circuit, capacitor values can be found for each gradient driving frequency where the circuit impedance is a minimum. This results in maximum current transfer from the Techrons to the gradient coils. Tables 3.2a and 3.2b give the capacitor values needed for each gradient axis with the corresponding maximum achievable gradient strength at the two input frequencies.
## 3.3.4 THE R.F. PROBE

The NMR r.f probe is a bird cage resonator design consisting of eight uniformly spaced copper legs placed around a glass tube of 2.5 cm internal diameter (figure 3.5). Small high voltage 556 pF capacitors placed between the outer ring of copper and the top of each leg, tune the probe and variable tuning and matching capacitors fine tune the system and impedance match to 50 Ω. The probe produces a sine distribution of current around the outer rings which form nodes and antinodes of current flow along the coil legs. This results in a homogenous magnetic field within the probe. With the 400 W r.f. amplifier, the probe has a 90° pulse length of 8 μs and a receiver dead time of 10μs.

A temperature controller has recently been fitted to the probe (figure 3.6), allowing temperatures in the range 13°C to 60°C (where 13°C is the average bore temperature).

<table>
<thead>
<tr>
<th>Gradient Cycling Frequency (kHz)</th>
<th>Capacitance (μF)</th>
<th>Maximum Gradient Strength (G/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.62</td>
<td>11.8</td>
<td>121</td>
</tr>
<tr>
<td>12.5</td>
<td>1.38</td>
<td>90</td>
</tr>
</tbody>
</table>

*Table 3.2a  Capacitance Values And Maximum Gradient Strength Of The Z Gradient At The Two Gradient Cycling Frequencies.*

<table>
<thead>
<tr>
<th>Gradient Cycling Frequency (kHz)</th>
<th>Capacitance (μF)</th>
<th>Maximum Gradient Strength (G/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.62</td>
<td>4.6</td>
<td>52</td>
</tr>
<tr>
<td>12.5</td>
<td>0.814</td>
<td>24</td>
</tr>
</tbody>
</table>

*Table 3.2b  Capacitance Values And Maximum Gradient Strength Of The X And Y Gradients At The Two Gradient Cycling Frequencies.*
Figure 3.5  The Birdcage Resonator Probe With Typical Size Sample And Appropriate PTFE Sample Holder

Figure 3.6  The Broad line Imaging System With Temperature Control Attachment
3.3.5 SYSTEM SOFTWARE

The integration of the modified imaging console and the Merrimac phase shifter has rendered the system incompatible with all standard reconstruction programs and NMR pulse sequences. This has required the implementation of new software to utilise the rapid nature of the system.

3.3.5.1 NON-Spatially Resolved Pulse Sequences

FID***.PPL - A simple r.f. pulse and acquire sequence with variable ring down delay and an option to use any one of four transmitter phases (x y -x or -y). The L.S.I. data capture boards have four software controlled sensitivity levels and can acquire between 9 and 4096 data points in each shot.

Table 3.3 gives a list and brief description of the various FID pulse programs used on the system. These sequences have either a 4 MHz or 10 MHz sample rate and some contain a baseline option which acquires a small amount of data 100 ms after the r.f. pulse. This option is essential for samples with long transverse relaxation times (> 50 ms) to establish a sensible signal baseline.

<table>
<thead>
<tr>
<th>Sequence Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>FID4M.PPL</td>
<td>Pulse and acquire with 4 MHz sample rate</td>
</tr>
<tr>
<td>FID4MB.PPL</td>
<td>As above except with baseline option</td>
</tr>
<tr>
<td>FID10M.PPL</td>
<td>Pulse and acquire with 10 MHz sample rate</td>
</tr>
<tr>
<td>FID10B.PPL</td>
<td>As above except with baseline option</td>
</tr>
</tbody>
</table>

*Table 3.3 The Pulse And Acquire Sequences*
FID4MT1.PPL - Based around the standard inversion recovery technique (section 1.5.5.1) to calculate longitudinal relaxation times. The 180° and 90° r.f. pulses are separated by a variable delay and a 4 MHz sample rate is used to acquire up to 4096 data points on the L.S.I. boards.

The variable array command automatically collects data into a file by varying the pulse gap from 1 to 32000 ms in predetermined steps. If pulse gaps shorter than 1 ms are required, a second program (FID4MT1B.PPL) can be used in conjunction with this one. The pulse sequence layout is similar, except the pulse gap range is from 15 μs up to 1000 μs.

CPMG*.PPL - Based around the standard CPMG sequence (section 1.5.5.2) used to calculate transverse relaxation rates (table 3.4). The 90°(x) pulse is followed by a train of 180° pulses of either y phase or alternating y and -y phases. Depending on probe pulse lengths, pulse gaps as short as 50 ps can be used with 30 points acquired for each echo. All programs allow the echo acquisition window to be shifted around the pulse gap as a way of avoid pulse ring down and some also acquire part of the FID following the 90° pulse to monitor very short component decays.

<table>
<thead>
<tr>
<th>Sequence Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPMGA.PPL</td>
<td>110 echoes all with y phase 180° pulses</td>
</tr>
<tr>
<td>CPMGB.PPL</td>
<td>As above except with alternating y and -y phases</td>
</tr>
<tr>
<td>CPMGC.PPL</td>
<td>100 echoes with y phase and baseline option</td>
</tr>
<tr>
<td>CPMGD.PPL</td>
<td>As above except with alternating y and -y phases</td>
</tr>
<tr>
<td>CPMGE.PPL</td>
<td>80 echoes with y phase, baseline and FID</td>
</tr>
<tr>
<td>CPMGF.PPL</td>
<td>As above except with alternating y and -y phases</td>
</tr>
</tbody>
</table>

*Table 3.4 The CPMG Pulse Sequences*
3.3.5.2 BROAD LINE GRADIENT ECHO PULSE SEQUENCES

For samples with spin-spin relaxation times of the order of a few hundred microseconds, the ideal imaging sequence is the gradient echo method developed by Cottrell, Halse and Strange (1990). This method is based around an oscillating magnetic field gradient of frequency $\tau^{-1}$, which refocuses magnetisation at a time $\tau$ following an r.f. pulse applied at the gradient zero crossing. The full echo is recorded, linearised (section 3.3.5.4) and Fourier transformed to give a one dimensional profile of the spin system.

By varying the arrangement of r.f. pulses, spatial relaxation maps can be obtained. Many variants of the original technique have been successfully implemented, some of which are listed below and illustrated in figure 3.7.

GE216.PPL - Based around the conventional broad line gradient echo method, with a single r.f. pulse placed at the gradient zero crossing. The gradient cycle period is 216 $\mu$s and a 4 MHz sample rate is used to acquire 860 points for each echo. To account for the high gradient coil inductance, 20 gradient 'warm-up' cycles are needed before applying the r.f. pulse. A variable delay can be used to shift the gradient phase and acquisition window relative to the r.f. pulse.

Due to the change of gradient direction over the echo, two data sets are acquired to correctly reconstruct the profile. The phase of the gradient is shifted by $180^\circ$ for the second data set which has the effect of inverting the imaginary signal.

To perform two dimensional imaging, all the broad line gradient echo sequences allow for individual control over two orthogonal gradients. The relative amplitudes of these gradients follow the sine and cosine arrangement needed for the back projection technique (section 1.6.1).
Figure 3.1 Variants Of The Broad line Gradient Echo Imaging Sequence

GE80.PPL - Based around the conventional broad line gradient echo method with a gradient period of 80 µs. 50 gradient 'warm-up' cycles are needed before the r.f. pulse is applied. The acquisition sample rate is 10 MHz, resulting in 800 data points for each echo.
GE216T1.PPL - An inversion recovery variant of the gradient echo technique to obtain $T_1$ weighted data sets (figure 3.7). The $180^\circ$ r.f. pulse is applied before the gradient 'warm up' cycles. Due to the rise time of the gradient field, the shortest inversion pulse gap achievable is 3 ms. Fully inverted signals cannot therefore be obtained. The gradient cycle period is fixed at 216 $\mu$s, but an equivalent program (GE80T1.PPL) can be used with a 80 $\mu$s gradient period to image or profile shorter $T_2$ samples.

SE216_*.PPL - A CPMG variant of the gradient echo imaging technique to obtain $T_2$ weighted data sets (figure 3.7). The $90^\circ$ r.f. pulse applied at the gradient zero crossing is followed by a train of $180^\circ$ pulses at 432 $\mu$s intervals (two gradient cycles). Due to pulse bandwidth limitations, severe rounding artefacts can occur from the interaction of the gradient field with the r.f. field. These artefacts arise when the maximum gradient field at the sample ends and at the ends of the pulse is significant compared to the pulse amplitude. The required condition to reduce these artefacts is given by

$$\frac{\pi}{\gamma t_{180}} \gg \frac{L G_0}{2} \sin\left(\frac{\pi t_{180}}{\tau}\right)$$

(3.1)

where $t_{180}$ is the $180^\circ$ pulse length, $L$ is the sample length, $G_0$ is the maximum gradient strength and $\tau$ is the gradient cycle period (216 $\mu$s).

With a 4 MHz sample rate, only four echoes can be acquired on the L.S.I. boards in one go. As at least twelve echoes are required to achieve an acceptable $T_2$ fit, three separate programs have been written. These programs, denoted by the suffix 1, 2 and 3, obtain the first four, second four and last four echoes respectively. Special reconstruction routines (section 3.3.5.3) have been written to extract each individual echo.
3.3.5.3 REPETITIVE PULSE VARIANT OF BROAD LINE GRADIENT ECHO IMAGING

This section describes a variant of broad line gradient echo imaging which improves image quality by using a rapid train of sub-90° r.f. pulses at the gradient zero crossing. The pulse sequence, which has now been published (McDonald, Perry and Roberts, 1993), is based on rapid acquisition liquid state techniques and the idea of steady state free precession (Carr, 1958). It differs from these liquid state sequences in that the aim is mainly to improve imaging quality rather than acquisition speed.

In the broad line gradient echo technique, the pixel resolution is governed by the gradient strength $G_0$ and the gradient period $\tau$, given by

$$\delta r = \frac{\pi}{2 \gamma G_0 \tau} \quad (3.2)$$

The assumption with this technique, is that the length of the r.f. pulse is very small when compared to the period of the gradient. As the pulse is of finite width, there may be signal degradation due to gradient interaction. For a 90° pulse of length $t_{90}$, the ends of the sample at positions $\pm L/2$ ($L$ is the sample length), experience a maximum gradient strength of

$$B_g = \frac{L G_0}{2} \sin \left( \frac{\pi t_{90}}{\tau} \right) \quad (3.3)$$

The magnitude of the r.f. field for a 90° pulse is given by

$$B_p = \frac{\pi}{2 \gamma t_{90}} \quad (3.4)$$

The assumption that $B_p >> B_g$ places a restriction on the number of pixels $N_{\text{max}}$ in the field of view. Rearranging equations 3.2 to 3.4 gives
\[
N_{\text{max}} = \frac{L}{\delta r} \ll \frac{2\tau}{t90 \sin(\pi t90 / \tau)}
\] (3.5)

With a 10 µs pulse length and \( \tau \) equal to 80 µs, \( N_{\text{max}} \) is less than 42 and sensible spatial resolution is not possible. With the repetitive pulse technique, the concept is to use a sub-90° pulse length \( \tau_p \) and thus increase the pulse bandwidth. For a small \( \tau_p \) to \( \tau \) ratios, the increase in the number of pixels goes approximately as the square of the pulse width reduction as

\[
N_{\text{max}} \approx \frac{2\tau^2}{\pi \tau_p^2}
\] (3.6)

With the reduction in pulse length, there is an obvious reduction in the signal to noise (S/N) ratio

\[
\frac{S}{N} \propto \sin\left(\frac{\pi \tau_p}{2t90}\right)
\] (3.7)

This signal to noise can be recovered by using a train of rapidly repeating pulses as in steady state free precession technique (Carr, 1958). Most steady state techniques are concerned with the rapid imaging of long \( T_2 \) systems. This contrasts with short \( T_2 \) sequences, where the aim is to improve the signal to noise and image quality by whatever means possible.

By varying the gap \( n \tau \) between each r.f. pulse in the pulse train, the signal can be \( T_1 \) weighted as the signal intensity is proportional to

\[
\frac{[1 - \exp(-n \tau / T_1)]}{1 - \cos(\pi \tau_p / 2t90)\exp(-n \tau / T_1)} \sin(\frac{\pi \tau_p}{2t90})
\] (3.8)

This has led to the implementation of a fast \( T_1 \) weighted broad line imaging sequence, which is listed below, along with other minor variants of the repetitive pulse technique.
Subsequent modifications to the broad line gradient echo technique have been made, which involve shifting the r.f pulses relative to the gradient zero crossing and thus reduce phase induced image artefacts (Benson et al., 1993). This r.f pulse shifting is not discussed in further detail here, but has been implemented in all the broad line techniques employed in this thesis.

GE216SS.PPL - The standard repetitive pulse variant of the broad line gradient echo technique, which improves image quality by using a rapid train of sub-90° r.f. pulses. Within the program, a SLICE_BLOCK command is set-up to maintain the gradient and acquire echoes every 19 gradient cycles. Due to limitations in system hardware, this pulse sequence cannot obtain shorter echo spacings. Echoes are accumulated in a single buffer and reconstructed in the normal manner (section 3.3.5.4). The program has a 216 μs gradient period and 4 MHz sample rate to acquire 860 points per echo. A 2 μs r.f. pulse is usually applied at the gradient zero crossing with a gradient strength of at least 27 G/cm to achieve acceptable spatial resolution. Allowing for typical gradient duty cycles (2%), up to 200 averages can be acquired per gradient burst.

A similar program (GE80SS.PPL) with a 80 μs gradient period and a 10 MHz sample rate can be used on samples with shorter T₂. 50 gradient cycles are left between the application of each r.f. pulse in the pulse train, allowing up to 80 averages per gradient burst.

To demonstrate the improvements of this technique over the conventional broad line gradient echo sequence, a phantom has been constructed, consisting of six rubber slices each 1 mm thick, separated by 1 mm Teflon spacers. Using a 90° pulse length and acquiring 2 averages, the resultant profile from the conventional imaging sequence is shown in figure 3.8a. With the repetitive pulse technique and using a 2 μs pulse and a train of 200 averages, the improvement of profile quality (figure 3.8b) is clearly evident, even though the acquisition time for both experiments is the same. Both experiments were performed with a gradient cycle period of 80 μs.
Figure 3.8 (a) Profile Of Rubber Phantom Using Conventional Imaging Technique With 90° Pulse. (b) Equivalent Profile Using Repetitive Pulse Technique With 2 μs Pulse

GE216ST.PPL - A modified version of GE216SS.PPL which overcomes the pulse gap limitation problem. The sequence allows for r.f. pulse gaps as short as 216 μs by acquiring echoes at or after 20 gradient cycles. For example, with a pulse gap of 432 μs, r.f. pulses are applied at the gradient crossing of every other gradient cycle, but only every tenth echo is acquired on the data capture boards. A pulse gap range of 216 μs to 86.4 ms is thus achievable and T₁ weighted profiles can easily be obtained.

Steady state free precession theory states that to obtain true T₁ weighted data, the pulse gap must be longer than T₂*. This is to avoid transverse relaxation interference from preceding echo trains. The advantage of this technique over the inversion recovery variant (GE216TI.PPL) is there is no need to wait 5T₁ between
each r.f. pulse. The acquisition time is therefore greatly reduced. Pulse gaps can also be much shorter, allowing samples with faster longitudinal relaxation rates to be monitored. An equivalent program (GE80ST.PPL) can be used with a 80 μs gradient period and a pulse gap range of 80 to 10000 μs. For this sequence, echoes are acquired at or after every 50 gradient cycles.

Using the rubber slices phantom, T₁ weighted data has been obtained using the repetitive pulse technique (figure 3.9) with 2 μs sub-90° r.f pulses applied at the gradient zero crossing. As expected, the attenuation in signal intensity is uniform across the rubber slices. The resultant reconstructed 'spatial' relaxation curves have been fitted to an exponential function giving a T₁ of 35 ± 5 ms across the phantom. This compares well with the bulk relaxation value of 32 ms, obtained using the standard inversion recovery sequence. Data acquisition times using this technique are approximately five times faster than an equivalent study using the inversion recovery broad line gradient echo technique.

Figure 3.9 T₁ Weighted Profiles Of The Rubber Phantom Using The Repetitive Pulse Technique With A Pulse Gap Range Of 432 μs To 43.2 ms

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3.3.5.4 RECONSTRUCTION SOFTWARE

Data acquired on the S.M.I.S. console is written in an ASCII format with alternate real and imaginary points. The data file names are denoted by the label MRD and contain a header and tail with information about the pulse sequence and parameters used in the acquisition of the data. For display purposes and analysis, it is desirable to have the data in a floating point format and various programs have been written to reconstruct data from the pulse sequences discussed in sections 3.3.5.2 and 3.3.5.3.

FIDR - Written in C and running in a DOS environment, this program reconstructs FID data into separate real and imaginary curves with appropriate time base.

REDUCE - A variant of FIDR with an option to reduce the size of the data set by averaging over a specified number of points. For example, with a reduction factor of 4, the program will average over 4 points and reduce the data set to a quarter of its original size. This program is mainly used when the display package does not have enough memory to display the data.

CPMGR - This program is used to reconstruct CPMG data sets. All CPMG experiments acquire 30 points per echo and these are averaged and written to disk with the appropriate tau value. The relaxation curves can be fitted to exponential functions using commercial software packages.

MRDR - Gradient echo data sets undergo initial reconstruction using this program. The real and imaginary data points are converted into floating point numbers and written into separate files, ready for further data reconstruction using one of the REC programs. The first data set file includes the number of samples and number of views parameters, taken from the header of the MRD data.
These reconstruction routines have been written to account for the variation of magnetic field gradient during image data acquisition. The programs also perform a one dimensional Fourier transform, to obtain a profile of the sample spin distribution.

The two data sets which have been reconstructed using MRDR are read in and the conjugate of the second is added to the first. The real and imaginary data points are placed into separate buffers and a baseline correction is made by averaging over the first and last twenty data points. To correct for phase offset errors, the real and imaginary data points are rotated by a value phi, calculated from the arctan of the central imaginary data point over the central real data point.

A sine to square conversion is made to account for the non-linear sampling which shifts the data points according to their position along the echo. The data is thus reordered as if it had been sampled under a constant linear field gradient. The data is converted into 256 points and sent to a sub-program (FFT9.PAS) where it is Fourier transformed to obtain a 512 point frequency map. Finally, the data is written to disk as real, imaginary and modulus floating point data where it can be displayed using a commercial software package.

To test the accuracy of this reconstruction procedure, a simulation program has been written (ECHO.PAS) which calculates the theoretical (ideal) signal obtained from the six rubber slices (figures 3.10a). The resultant Fourier transformation after linearisation (figure 3.10b) illustrates clearly the effectiveness of the sine to square reordering routine, with no apparent profile degradation due to the reconstruction.

Table 3.5 lists the REC programs used to reconstruct gradient echo data. The $T_2$ weighted data reconstruction routine separates and Fourier transforms the four echoes obtained using the spin echo programs. The profiles are then written to four separate files denoted by the suffix 1, 2, 3 or 4 for the first, second, third and fourth echoes respectively.
Figure 3.10 (a) Theoretical Signal From Six Rubber Slices (b) Resultant Fourier Transform After Linearisation

<table>
<thead>
<tr>
<th>Reconstruction Program</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>REC1D</td>
<td>Single Echo Reconstruction For Profile Display</td>
</tr>
<tr>
<td>REC1D_4</td>
<td>As Above, Except To Be Used With T₂ Weighted Data</td>
</tr>
<tr>
<td>REC2D</td>
<td>Multi-Echo Reconstruction For Back Projection</td>
</tr>
<tr>
<td>RED2D_4</td>
<td>As Above, Except To Be Used With T₂ Weighted Data</td>
</tr>
</tbody>
</table>

Table 3.5 Gradient Echo Reconstruction Programs
Two dimensional imaging data is reconstructed using one of the REC2D programs. Each echo is stored in the VIEW_BLOCK loop and is individually reordered and Fourier transformed. The real and imaginary points are then written to a file as a long floating point list with a header containing the number of samples and views.

BP - The two dimensional data is finally reconstructed using the filtered back projection technique (section 1.7.1). The profiles firstly undergo delta function suppression where the central points are linearised to reduce the characteristic central spike. After a normalisation procedure to equalise profile areas, the profiles are then back projected onto a 110 x 110 grid to form a two dimensional map of the sample. For 256 grey scale image display, the data is normalised according to its highest and lowest points to be within the range 0 to 256. The image can then be displayed using a commercial software package.
CHAPTER FOUR

THE VISUALISATION OF RESERVOIR FLUIDS WITHIN PRESERVED ROCK CORES USING CONVENTIONAL MRI METHODS
4.1 INTRODUCTION

This chapter explores the potential of magnetic resonance imaging (MRI) as a tool for visualising the spatial distribution of reservoir fluids in very heterogeneous preserved rock core samples. Various NMR techniques are described to attempt to separately image the brine and crude oil within ten preserved sandstone rock cores. The 10 cm diameter cores are from an oil producing reservoir and have been encased in wax to preserve most of the reservoir fluid. The NMR relaxation measurements have been related to a model based on diffusion and pore surface relaxation theory.

4.1.1 BACKGROUND

The traditional approach to the study of a preserved reservoir rock core is simple distillation to determine crude oil and brine content. The physical properties of the core are usually studied only after cleaning.

NMR has considerable potential as a non-destructive probe of preserved reservoir rock samples, offering the possibility of direct determination of fluid distributions within the core. Discrimination of fluids in preserved cores by X-ray techniques is not feasible, as there is no contrast between the fluids.

Analysis of reservoir core samples by proton NMR, requires the separation of the response into oil and brine components. For cores with narrow NMR line widths, this can be achieved by chemical shift discrimination (Williams et al, 1991), or in some instances, spin-lattice relaxation time distributions can be used to distinguish the two fluids (Davies et al, 1994).
4.2 BULK NMR MEASUREMENTS

The ten preserved rock core samples were studied using the 0.5 tesla (21.3 MHz) whole body MRI scanner (section 2.2). A $^1$H birdcage imaging probe, designed to provide optimum performance for imaging fluid distributions within the whole core samples, was employed throughout.

Bulk NMR measurements were obtained for the two reservoir bulk fluids and two smaller (38 mm diameter) reservoir core plugs taken from the same oil bearing zone as the preserved rock cores. The smaller reservoir plugs were fully saturated, using vacuum techniques, with either the reservoir crude oil or a simulated formation brine (S.F.B) made according to the formulation shown in table 4.1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>NaCl</th>
<th>CaCl$_2$</th>
<th>KCl</th>
<th>MgCl$_2$</th>
<th>BaCl$_2$</th>
<th>FeCl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity (g/L)</td>
<td>93.7</td>
<td>10.47</td>
<td>3.45</td>
<td>1.43</td>
<td>1.52</td>
<td>0.29</td>
</tr>
</tbody>
</table>

*Table 4.1 Compounds Used For S.F.B. In g/L of Distilled Water*

4.2.1 CHEMICAL SHIFT STUDY

The NMR resonance line shape obtained for the two bulk fluids shows a separate peak for each fluid due to differences in their chemical shift (section 1.5.4). The separation of these peaks is approximately 80 Hz which corresponds closely to the expected chemical shift between oil and water (3.5 ppm). However, for the two saturated rock cores, only one broad peak is detectable. This is due either to variations in the rocks magnetic susceptibility distorting the magnetic field, or fluid-rock interactions severely reducing the T$_2$ of the fluid and hence broadening the NMR resonance line. In either case, it is not possible to separately identify the peaks arising from the two fluids within the cores and chemical shift imaging techniques could not be applied to separately image the two fluids.
4.2.2 RELAXATION TIME MEASUREMENTS

$T_1$ and $T_2$ relaxation time measurements were acquired at room temperature ($18^\circ{}C$), for the bulk fluids and the smaller cores, using inversion recovery and CPMG pulse sequences respectively. The relaxation data was fitted to stretched exponential functions (section 2.6.1.4), with $\alpha$ determining the multiexponential nature of the decay (table 4.2). Figures 4.1 and 4.2 show the bulk fluid relaxation curves with appropriate fits, indicating clearly the difference in relaxation between the two bulk fluids.

<table>
<thead>
<tr>
<th>Type</th>
<th>$T_1 \alpha$ (ms)</th>
<th>$\alpha$</th>
<th>$T_2 \alpha$ (ms)</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Brine</td>
<td>2270</td>
<td>1.00</td>
<td>1740</td>
<td>0.99</td>
</tr>
<tr>
<td>Bulk Crude</td>
<td>590</td>
<td>0.71</td>
<td>230</td>
<td>0.67</td>
</tr>
<tr>
<td>Core Brine</td>
<td>167</td>
<td>0.71</td>
<td>95</td>
<td>0.70</td>
</tr>
<tr>
<td>Core Crude</td>
<td>203</td>
<td>0.63</td>
<td>100</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Table 4.2 Relaxation Measurements (±3%) At Room Temperature ($18^\circ{}C$)

The relative $T_1$ relaxation times of the two bulk fluids are such that spin-lattice discrimination could be used to distinguish the bulk brine and crude oil. When introduced into the rock cores, interactions between the rock surfaces and the fluid, significantly change the fluid relaxation behaviour (section 2.6.1). This enhanced relaxation, prevents accurate spin-lattice discrimination of the crude oil and brine within the rock cores at room temperature.

The ratio of oil and brine relaxation times within the rock cores is small compared to previous studies on 'cleaned' rock core plugs, known to be water wet (Latour et al., 1992). This could suggest that the reservoir cores are in a mixed wettability state. Such observations have been made before (Brown et al., 1956). In cases of mixed wettability, both the crude oil and brine experience rapid relaxation at the pore surfaces.
Figure 4.1 $T_2$ Relaxation Curves For The Bulk Fluids

Figure 4.2 $T_1$ Relaxation Curves For The Bulk Fluids
The calculated alpha values for the fluid-saturated cores suggest a Gaussian distribution of relaxation. Assuming that at room temperature, the sandstone cores are in the fast diffusion limit (section 2.6.1.1), the range of relaxation times is directly related to the range of pore sizes. The alpha values therefore suggest a Gaussian distribution of pore sizes within the sandstone samples.

Previous studies on homogenous preserved carbonate samples (Davies et al, 1994) have used spin-lattice discrimination to separately image the different reservoir fluids. These carbonate samples were known to be strongly water wet with a very small range of pore sizes. The heterogeneous sandstone samples in this study though (figure 4.3) are agglomerates made up of porous clast, non-porous clast and matrix. The non-porous clasts consist of large quartz fragments which do not contribute to the detected NMR signal. The porous clast and the matrix however have a large range in porosity, permeability and pore size, and combined with the suggestive mixed wettability, could account for the inability to separately identify the pore fluids using standard NMR techniques.

Figure 4.3 Typical Structure Of The Preserved Rock Cores
4.2.2.1 RELAXATION ANALYSIS AS A FUNCTION OF TEMPERATURE

Latour et al (1992) have shown that the relaxation times of water-saturated sandstones depend weakly on temperature in the range 25°C to 175°C. Conversely, relaxation time measurements made on sandstone cores saturated with oil, have a large temperature dependence in the same temperature range. These observations suggest that temperature variations may affect the relative relaxation times of reservoir fluids within preserved rock cores. With the preserved cores used in this study encased in wax, high temperatures could not be obtained without melting the outer coating. It was therefore proposed to study the relaxation dependence of the reservoir cores at temperatures below 18°C. To prevent the brine freezing (damaging the cores), a temperature range of 18°C to -5°C was studied.

Low temperature viscosity measurements of the bulk fluids, show a rapid change in crude oil viscosity (table 4.3). The bulk fluid self diffusion coefficients are known to be important in pore surface relaxation analysis and have been calculated from the viscosity measurements using a Stokes-Einstein-like relation (Douglass et al 1958)

\[
\frac{\eta D}{kT \left( \frac{V}{N} \right)^{1/3}} = c
\]

(4.1)

where \( \eta \) is the viscosity, D is the self diffusion coefficient, T is the absolute temperature, k is Boltzmann's constant \((1.38 \times 10^{-23} \text{ J/K})\), V/N is the molecular volume and c is an empirical constant on the order of unity (for oils, c = 0.17). The cube root of the molecular volume for oils is well approximated by \(7 \times 10^{-8} \text{ cm} \).
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Oil Viscosity (kg s⁻¹ m⁻¹)</th>
<th>D (oil) (cm² s⁻¹)</th>
<th>Brine Viscosity (kg s⁻¹ m⁻¹)</th>
<th>D (brine) (cm² s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>4.9 x 10⁻³</td>
<td>2 x 10⁻⁶</td>
<td>1.2 x 10⁻³</td>
<td>2.3 x 10⁻⁵</td>
</tr>
<tr>
<td>5</td>
<td>12.5 x 10⁻³</td>
<td>8 x 10⁻⁷</td>
<td>1.5 x 10⁻³</td>
<td>1.8 x 10⁻⁵</td>
</tr>
<tr>
<td>0</td>
<td>16.3 x 10⁻³</td>
<td>6 x 10⁻⁷</td>
<td>1.8 x 10⁻³</td>
<td>1.4 x 10⁻⁵</td>
</tr>
<tr>
<td>-5</td>
<td>20.8 x 10⁻³</td>
<td>4 x 10⁻⁷</td>
<td>1.9 x 10⁻³</td>
<td>1.3 x 10⁻⁵</td>
</tr>
</tbody>
</table>

*Table 4.3  Viscosity Measurements (± 5%) And Self Diffusion Estimates*

CPMG and inversion recovery data was acquired for the small reservoir rock cores at 5°C, 0°C and -5°C (tables 4.4a to 4.4c). The relaxation measurements indicate a clear temperature dependence for the oil saturated rock core. The brine saturated rock core has a much smaller temperature dependence. Figure 4.4 shows the inversion recovery curves obtained for the two cores at 18°C and -5°C. At -5°C, the T₁ relaxation times of the two core fluids are sufficiently different to permit individual fluid suppression using T₁ weighted NMR techniques.

<table>
<thead>
<tr>
<th>Type</th>
<th>T₁ α  (ms)</th>
<th>α</th>
<th>T₂ α  (ms)</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Brine</td>
<td>1410</td>
<td>0.98</td>
<td>1040</td>
<td>0.99</td>
</tr>
<tr>
<td>Bulk Crude</td>
<td>290</td>
<td>0.72</td>
<td>162</td>
<td>0.68</td>
</tr>
<tr>
<td>Core Brine</td>
<td>162</td>
<td>0.72</td>
<td>94</td>
<td>0.72</td>
</tr>
<tr>
<td>Core Crude</td>
<td>130</td>
<td>0.61</td>
<td>62</td>
<td>0.59</td>
</tr>
</tbody>
</table>

*Table 4.4a  Relaxation Measurements (± 3%) At 5°C*

<table>
<thead>
<tr>
<th>Type</th>
<th>T₁ α  (ms)</th>
<th>α</th>
<th>T₂ α  (ms)</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Brine</td>
<td>1115</td>
<td>0.96</td>
<td>860</td>
<td>0.99</td>
</tr>
<tr>
<td>Bulk Crude</td>
<td>230</td>
<td>0.70</td>
<td>140</td>
<td>0.67</td>
</tr>
<tr>
<td>Core Brine</td>
<td>159</td>
<td>0.71</td>
<td>92</td>
<td>0.70</td>
</tr>
<tr>
<td>Core Crude</td>
<td>107</td>
<td>0.63</td>
<td>54</td>
<td>0.61</td>
</tr>
</tbody>
</table>

*Table 4.4b  Relaxation Measurements (± 3%) At 0°C*
<table>
<thead>
<tr>
<th>Type</th>
<th>$T_1$ α (ms)</th>
<th>α</th>
<th>$T_2$ α (ms)</th>
<th>α</th>
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</thead>
<tbody>
<tr>
<td>Bulk Brine</td>
<td>880</td>
<td>0.94</td>
<td>650</td>
<td>0.99</td>
</tr>
<tr>
<td>Bulk Crude</td>
<td>160</td>
<td>0.71</td>
<td>98</td>
<td>0.68</td>
</tr>
<tr>
<td>Core Brine</td>
<td>156</td>
<td>0.73</td>
<td>85</td>
<td>0.71</td>
</tr>
<tr>
<td>Core Crude</td>
<td>82</td>
<td>0.67</td>
<td>46</td>
<td>0.64</td>
</tr>
</tbody>
</table>

*Table 4.4c  Relaxation Measurements (±3%) At -5°C*

*Figure 4.4  $T_1$ Relaxation Curves From The Two Fluids Within The Small Cores At Temperatures Of (a) 18°C And (b) -5°C*
4.3 ROCK CORE IMAGING

This section discusses the application of standard liquid state MRI techniques to visualise the spatial distribution of reservoir fluid within the rock core samples. The two immiscible fluids within the cores were separately imaged using T₁ suppression techniques, with the cores at low temperature. This suppression, combined with the long spin echo time (6 ms) required by the MRI spectrometer, has prevented the acquisition of fully quantitative data. Instead, the resultant images provide an indication as to the location of the two fluids within the cores.

4.3.1 IMAGE FEASIBILITY STUDY ON SMALL ROCK CORES

Using an inversion recovery variant of the spin warp imaging technique (section 3.2.4), images were obtained for the two small reservoir rock cores. The inversion ‘null times’ of the two core fluids were obtained by varying the inversion 180° pulse gap, so that either the oil or brine NMR signal was suppressed. Table 4.5 lists the measured ‘null times’ for the two cores at various temperatures and the resultant transverse images for the two cores are shown in figure 4.5. At room temperature, there is a large overlap of T₁ between the two rock core fluids and neither of the fluids can be individually suppressed. Cooling the rock cores changes the core fluid properties such that individual suppression can be made. This has been successfully demonstrated at -5°C, with almost perfect suppression of the desired pore fluid.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Crude Oil Signal ‘Null Time’ (ms)</th>
<th>Brine Signal ‘Null Time’ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>140</td>
<td>120</td>
</tr>
<tr>
<td>5</td>
<td>90</td>
<td>115</td>
</tr>
<tr>
<td>0</td>
<td>75</td>
<td>112</td>
</tr>
<tr>
<td>-5</td>
<td>55</td>
<td>108</td>
</tr>
</tbody>
</table>

*Table 4.5 Inversion ‘Null Time’ Versus Temperature*
Figure 4.5 Transverse Images Of the Small Rock Cores At 18°C And -5°C Using The Inversion Recovery Imaging Technique.

4.3.2 PRESERVED ROCK CORE IMAGES

The T₁ selective suppression imaging technique has been applied successfully to the preserved rock cores at low temperature and the results compare favourably with the feasibility study performed on the smaller cores of known fluid saturation. This section includes images from three of the preserved cores which show typical fluid distributions found in the preserved samples.
Figure 4.6  Brine Suppressed, Oil Suppressed And Whole Proton
          Transverse Images From Core 1

Figure 4.7  Brine Suppressed, Oil Suppressed And Whole Proton
          Transverse Images From Core 2
Brine suppressed images from many of the preserved cores, indicate high crude oil saturations around the edges of the samples (figure 4.6). This could be due to the extreme pressure release the cores undergo when being brought to the surface, causing much of the oil or liquefied gas to be expelled, or the invasion of mud during the drilling process. A few of the cores appear to contain larger quantities of oil and the suppressed images show very clearly regions of high oil concentration and regions of high brine concentration. A region containing a large localised quantity of crude oil is shown in figure 4.7. The corresponding oil suppressed image shows this region to contain very little brine. Longitudinal slice images have also been obtained for all the preserved cores (figure 4.8).
4.4 PORE FLUID RELAXATION MODEL

To help understand the observed temperature dependence of pore fluid relaxation (section 4.2.2.1), a model has been developed, based on current pore surface relaxation theory (Brownstein and Tarr, 1979). The model uses the measured change in viscosity and $T_1$ relaxation of the bulk reservoir fluids, along with estimates of pore size and pore surface relaxivity, to extrapolate between the fast and slow diffusion limits. The observed core fluid relaxation times suggest a mixed wettability state and this assumption has been made in the model, allowing paramagnetic impurities on the pore surfaces to enhance relaxation of both the brine and crude oil. The model uses an interconnected space of spherical pores as an approximation for the pore space.

For a single pore of size $a$, the longitudinal relaxation is given by

$$\frac{1}{T_1^a} = \frac{1}{T_{1B}} + \frac{6(D^\beta \rho_1^{1-\beta})}{a^{1+\beta}}$$

(4.2)

where $T_{1B}$ is the bulk fluid relaxation time, $D$ is the diffusion coefficient and $\rho_1$ is the longitudinal pore surface relaxivity. $\beta = 0$ in the fast diffusion regime, $\beta = 1$ in the slow diffusion regime and crosses over from 0 to 1 in the intermediate diffusion regime. The equations governing these diffusion limits are included in section 2.6.1.1.

The computer model uses equation 4.2 to calculate the $T_1$ relaxation time of the pore fluid at each temperature. This is done by calculating the magnetisation for each pore as a function of time and summing over the whole pore space. The calculated magnetisation versus time can then be fitted to the stretched exponential function in the same way as the NMR data.

Previous studies (Howard et al, 1990) on a variety of sandstone cores have found the longitudinal pore surface relaxivity ($\rho_1$) to have an average value of $3 \times 10^{-3}$ cm/s. Using this value of $\rho_1$ and the calculated $T_1$ relaxation time of the
brine saturated core, the average pore size within the preserved cores has been estimated at 30 μm. The measured $T_1$ alpha values indicate a Gaussian distribution of relaxation, and hence pore size. This has been incorporated into the model to achieve a more realistic fit.

Using the model and data acquired at room temperature, the pore surface relaxivity for the crude oil in contact with the pore surfaces has been estimated at $1.2 \times 10^{-3}$ cm$^2$/s. This value of $r_1$(oil) is an order of magnitude larger than previous estimates (Latour et al, 1992) performed on sandstone cores, known to be water wet and is again suggestive of a mixed wettability state within the cores.

The measured longitudinal relaxation rates of the core fluids and corresponding fits using the computer model are shown in figure 4.9. The graph shows excellent correlation between the NMR data and the analytical approximation. This suggests that the pore surface relaxation model is applicable, even with the assumptions made.

![Figure 4.9](image)

*Figure 4.9 Core Fluid Relaxation Versus Temperature, With Corresponding Analytical Fit Using Pore Surface Relaxation Model*
The brine saturated pores remain in the fast diffusion regime, even at low temperature, and the relaxation time is dominated by pore surface effects. This leads to the relatively small temperature dependence observed in the brine saturated rock. The oil filled pores tend to be in either the fast diffusion or intermediate diffusion regime. This is because the reduced diffusion coefficient is partially compensated for by the reduced pore surface relaxivity. The reduction in $p_1(\text{oil})$, coupled with the short bulk fluid relaxation times, suggest that at low temperatures, the dominant relaxation mechanism for oil filled pores is the bulk fluid relaxation rate. This accounts for the large temperature dependence observed in the oil saturated rock. The differences in dominant relaxation mechanism for the two immiscible fluids, suggest that the model is applicable to individual pores containing both brine and crude oil. The quality of the fluid suppressed images from the preserved rock cores verifies this.

4.5 CONCLUSION

Preserved sandstone reservoir rock cores are generally very heterogeneous and can contain large amounts of line broadening impurities. This prevents the use of standard NMR fluid discrimination techniques such as chemical shift imaging.

Relaxation studies of sandstone cores saturated with crude oil show a large temperature dependence in the range $18^\circ\text{C}$ to $-5^\circ\text{C}$, whereas the relaxation times of brine-saturated sandstones depend weakly on temperature in the same range. With the preserved samples used in this study cooled to $-5^\circ\text{C}$, the $T_1$ relaxation times of the core fluids are sufficiently different to allow the use of $T_1$ suppression imaging to separate the brine and crude oil components.

A model has been developed to explain the relaxation time temperature dependence in terms of pore surface relaxation theory. The model indicates that brine filled pores remain in the fast diffusion regime and the relaxation is dominated by pore surface effects. The oil filled pores are either in the fast or intermediate
diffusion regime and due to the small $\rho_1$(oil), the pore relaxation is dominated by the bulk fluid relaxation rate. This leads to the observed temperature dependence of relaxation in oil filled pores. The difference in dominant relaxation mechanisms indicates that the model is applicable to pores containing both brine and crude oil.

The pore fluid relaxation model has been applied to longitudinal relaxation, but is also applicable to the transverse relaxation, providing that the surface relaxation effects dominate susceptibility broadening of the magnetic resonance line at the pore-grain interface (section 2.6.1.2).
CHAPTER FIVE

CORE FLOOD IMAGING USING BROAD LINE MRI TECHNIQUES
5.1 INTRODUCTION

This chapter explores the potential of MRI for visualising reservoir rock residual fluids, with the first ever broad line MRI study of reservoir fluid flow during miscible and immiscible rock plug flooding experiments. Three encapsulated rock plugs, known to be water wet, were studied using variants of broad line gradient echo imaging (section 3.3.5.2). The rapid nature of these sequences ensures the detection of residual fluids, which due to surface effects, cannot always be detected with conventional MRI methods. The flooding experiments were conducted using a variety of fluids, including deuterium oxide and fluorinated oil, which are ‘invisible’ to hydrogen NMR. This has allowed easy visualisation of the drainage and imbibition stages. Relaxation measurements obtained at various immiscible phase saturations have been used to determine the dominant relaxation mechanism of each pore fluid.

5.1.1 BACKGROUND

For the petrochemical industry, the removal of small additional fractions of oil from large reservoir fields can be worth billions of dollars. There is therefore great interest in experiments which directly probe the dynamic processes of liquids in rock cores. NMR has been shown to be extremely valuable in this respect and a large number of MRI experiments and relaxation studies have been carried out on laboratory size rock plugs (Edelstein et al, 1988).

The effect of the rock matrix on pore fluids can result in an increase of the NMR spectral line width. This line broadening effect arises from molecular diffusion through susceptibility gradients near the pore-grain interface, and enhanced fluid relaxation at the pore surface. If the effect is severe, pore fluid transverse relaxation times can be very short and standard liquid state imaging techniques may be inappropriate. Even rock plug samples with long transverse relaxation times can have pore fluid bound to the pore surfaces or trapped in very small pores during
immiscible flooding experiments. The use of broad line MRI techniques has long been proposed as a possible way of detecting residual fluid saturations. The very rapid nature of line narrowing broad line techniques, such as multipulse imaging, can be technically difficult to implement and the image quality tends to be inferior to conventional imaging sequences. The broad line gradient echo technique (Cottrell et al, 1990) is therefore an ideal compromise between the rapid line narrowing sequences and standard liquid state techniques for imaging residual fluids in porous systems. As such, variants of broad line gradient echo imaging have been employed throughout this study to obtain quantitative one dimensional profiles of fluid distribution within reservoir rock plugs.

5.2 EXPERIMENTAL PROCEDURE

The three sandstone core plugs used in this study are from the same oil producing reservoir and have been chosen due to their visual homogeneity and similar petrophysical parameters.

The rock plugs were cleaned by miscible cold flushing and embedded in epoxy with end pieces and fittings attached. The rock plug porosities were measured using vacuum saturation with the aid of gravimetric analysis and the permeabilities were measured by flowing brine through the plugs at a rate of 5 ml/h. Using standard NMR pulse sequences (section 3.3.5.1), the bulk proton $T_1$ and $T_2$ relaxation times were obtained for the rock plugs at full brine saturation. The petrophysical and NMR parameters for the three rock plugs are listed in table 5.1.

The core flood experiments were set-up as shown in figure 5.1. The core fluid flow rates were maintained at 5 ml/h, using a peristaltic rotary pump. This corresponds to a mean fluid speed of 26 cm/day within the rock plugs and is comparable with flood rates in commercial reservoirs. The pressure drop ($\Delta P$) across the rock plugs was measured using a digital manometer.
To obtain quantitative measurement of the fluid distribution during immiscible flooding, two sandstone plugs were investigated in parallel, and in each case, either the brine or the oil was substituted with a chemical which is 'invisible' to hydrogen NMR. The resultant one-dimensional NMR profiles therefore reveal the location of the 'non-substituted' fluid. The brine in the first sandstone plug was replaced with deuterated brine and the oil in the second plug was replaced with a fluorinated oil ($C_{15}F_{33}N$). During the first drainage stage, dodecane was chosen as the invading fluid. This was due to its similar viscosity to the fluorinated oil ($= 6 \times 10^{-3} \text{ kg s}^{-1}\text{m}^{-1}$, at $20^\circ\text{C}$). The bulk relaxation times of these fluids are listed in table 5.2.
Table 5.2 Bulk Fluid Relaxation Times (±3%) At 20°C

<table>
<thead>
<tr>
<th>Bulk Fluid</th>
<th>$T_1 (\alpha)$ (ms)</th>
<th>$T_2 (\alpha)$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brine</td>
<td>2150 (0.97)</td>
<td>1640 (0.96)</td>
</tr>
<tr>
<td>Dodecane</td>
<td>760 (0.85)</td>
<td>420 (0.82)</td>
</tr>
<tr>
<td>Reservoir Crude Oil</td>
<td>600 (0.70)</td>
<td>250 (0.68)</td>
</tr>
</tbody>
</table>

5.3 MISCELLOUS FLUID DISPLACEMENT

During miscible displacement, the capillary forces are eliminated and in principle, total recovery of the initial pore fluid is possible. The miscible displacement process forms a mixture zone which can increase in size during the course of the flood. If the mixture zone is small compared to the size of the reservoir (or rock plug), the displacement is piston-like and all the initial fluid is recovered after one pore volume of the injected fluid. For larger mixture zones, it may require many pore volumes to remove all the initial fluid.

To monitor the miscible displacement of brine, the first sandstone plug was fully saturated with brine ($S_w = 1.0$) and then flooded with deuterated brine in stages. After each stage, the end attachments were thoroughly dried to remove surface water and the plug profiled along its length. The resultant profiles are shown in figure 5.2.

The displacement is clearly not piston-like with a large mixture zone clearly visible. This mixture zone takes up at least 70% of the plug length, as expected with miscible fluids of similar density. The initially high brine content at the inlet end indicates a slightly inefficient sweep. This brine is probably located around the edges of the sample and is eventually removed after the injection of 1 PV of the displacing fluid. Even after 5 PV of flooding there is still a small uniform concentration of brine within the core. Assuming that with short echo times, the profile intensity is directly proportional to the saturation, this remaining brine content is approximately 3% of the total pore volume (NMR empty cavity measurements have shown the empty cavity signal to be negligible). The NMR
relaxation times of this remaining brine are within 5% of the measured values at full saturation. This suggests that the brine is trapped in cut-off pores rather than being confined to the pore surfaces, where relaxation times are dramatically reduced.

\[ 6 \times 10^4 \]

\[ 4 \times 10^4 \]

\[ 2 \times 10^4 \]

\[ 0 \]

\[ -20 \]

\[ 0 \]

\[ 20 \]

\[ 40 \]

\[ \text{Magnetisation} \]

\[ \text{mm} \]

Figure 5.2 Miscible Brine Displacement In Plug 1, With The Deuterated Brine Injected From The Left

5.4 IMMISCIBLE FLUID DISPLACEMENT

When a fluid (such as brine) displaces another fluid (such as oil) which is not miscible, the displacement is never total since the capillary forces retain part of the displaced fluid. With the sandstone plugs used in this study known to be preferentially water wet, the invasion of oil (drainage) will leave an irreducible fraction of brine \( (S_{wi}) \). The subsequent invasion of brine (imbibition) will leave a residual fraction of oil \( (S_{or}) \). NMR relaxation measurements at various saturations during the displacement can be used to determine the dominant relaxation mechanism of each pore fluid.
5.4.1 DRAINAGE

To monitor drainage, the first rock plug, already saturated with deuterated brine, was flooded with dodecane and the second rock plug, already saturated with brine, was flooded with the fluorinated oil. The two sets of profiles are shown in figures 5.3 and 5.4 respectively and clearly show the invading oil with good correlation between the brine profiles (showing a reduction in magnetisation) and the oil profiles (showing an increase in magnetisation). After injecting 5 PV of the non-wetting fluid, it is expected that the irreducible wetting saturation ($S_{wi}$) will be reached. Using the full brine saturation profile as a reference, $S_{wi}$ for plug 1 and plug 2 have been estimated at 0.24 and 0.22 respectively. These values are typical for rock plug floods under ambient conditions. The effective permeability at $S_{wi}$ is approximately 20 mD in both rock plugs. This corresponds to one of the end points in the oil permeability curve and is about 40% of the absolute value. The slight drop in oil saturation at the outlet end is a result of capillary discontinuity. This ‘end-effect’ is due to the flow of fluids from regions of finite capillary pressure to a region of zero capillary pressure.

5.4.2 IMBIBITION

To monitor imbibition, the first rock plug was flooded with deuterated brine and the second plug with normal brine. Profiles were acquired at regular intervals and are shown in figures 5.5 and 5.6 respectively. Both data sets clearly show the invading brine, with the oil saturation tending towards a residual level. After injecting 5 PV of the wetting fluid, it is expected that the residual non-wetting saturation ($S_{or}$) will be reached. $S_{or}$ for plug 1 and plug 2 have been estimated at 0.37 and 0.39 respectively. These values are typical for rock plug floods under ambient conditions and clearly illustrate the need for enhanced recovery techniques in commercial reservoirs. The effective permeability at $S_{or}$ is approximately 25 mD in both rock plugs. This corresponds to one of the end points in water saturation permeability curve and is approximately 50% of the absolute value.
Figure 5.3 Oil Saturation In Plug 1 During Drainage

Figure 5.4 Brine Saturation In Plug 2 During Drainage
Figure 5.5 Oil Saturation In Plug 1 During Imbibition

Figure 5.6 Brine Saturation In Plug 2 During Imbibition
5.4.3 RELAXATION ANALYSIS

Relaxation measurements at various immiscible phase saturations have been used to determine the dominant relaxation mechanisms of the two pore fluids. The calculated $T_1$ and alpha values are listed in table 5.3.

Following the injection of 0.5 PV of either deuterated brine or fluorinated oil, $T_1$ weighted profiles were acquired using the inversion recovery variant of the broad line gradient echo technique (section 3.3.5.2). The appropriate spatial saturations of the remaining dodecane or brine were calculated from the observed magnetisation at various points along the profiles. Bulk $T_1$ relaxation time measurements were also obtained at full and irreducible saturations, using conventional NMR techniques.

<table>
<thead>
<tr>
<th>Dodecane In Plug 1</th>
<th>Brine In Plug 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_o$</td>
<td>$T_1$ ((\alpha)) (ms)</td>
</tr>
<tr>
<td>0.37</td>
<td>726 (0.79)</td>
</tr>
<tr>
<td>0.54</td>
<td>728 (0.79)</td>
</tr>
<tr>
<td>0.59</td>
<td>728 (0.80)</td>
</tr>
<tr>
<td>0.64</td>
<td>730 (0.79)</td>
</tr>
<tr>
<td>0.67</td>
<td>727 (0.78)</td>
</tr>
<tr>
<td>0.70</td>
<td>732 (0.81)</td>
</tr>
<tr>
<td>0.74</td>
<td>732 (0.80)</td>
</tr>
<tr>
<td>0.82</td>
<td>736 (0.81)</td>
</tr>
<tr>
<td>0.90</td>
<td>734 (0.82)</td>
</tr>
<tr>
<td>0.94</td>
<td>733 (0.81)</td>
</tr>
<tr>
<td>1.00</td>
<td>735 (0.80)</td>
</tr>
</tbody>
</table>

Table 5.3 Oil And Brine $T_1$ Relaxation Times During Immiscible Flooding
The dodecane $T_1$ relaxation times obtained from plug 1 are comparable to the bulk fluid value and show only a small dependence on saturation in the range 37 to 100%. Conversely, the brine $T_1$ relaxation times obtained from plug 2 are greatly reduced compared to the bulk fluid value and show a large saturation dependence in the range 22 to 100%. Such observations are common in strongly water wet rock, where enhanced relaxation at the pore surface dominates brine relaxation, but has an almost negligible effect on oil relaxation.

The dodecane $T_1$ alpha value shows no dependence on saturation in the given range and is comparable to the bulk fluid value. However, the brine $T_1$ alpha value does show a small dependence on saturation in the given range, and indicates a broader distribution of relaxation at lower saturation. In porous systems where the fluid saturation is reduced uniformly for all size pores, the $T_1$ alpha parameter tends towards a higher value. This is due to the reduced effect of pore size and geometry at low saturation. As the opposite is true for the brine alpha values obtained in this study, it suggests that the invasion of fluorinated oil does not uniformly remove the brine. Instead it is more likely that certain size pores are preferentially invaded, leaving other pores fully saturated with brine. This leads to a large range of relaxation times across the rock plug, as shown by the alpha value of 0.55 obtained at $S_{wi}$. With the low flow rate used in this study, capillary forces dominate the viscous forces and under such conditions, imbibition and drainage can be described by the rules of invasion percolation (Sahimi, 1994). It is therefore expected that during drainage, the non-wetting fluid (fluorinated oil) will preferentially invade the largest accessible pores.

5.5 IMMISCIBLE DISPLACEMENT OF RESERVOIR FLUIDS AT HIGH TEMPERATURE

Immiscible displacement images obtained by chemical substitution (section 5.4), provide quantitative information about the relative fluid distribution within reservoir rock plugs. Unfortunately, the chemicals tend to be very expensive and may not always match the viscosity of the fluid they replace. NMR imaging
techniques have the potential of separating reservoir fluids based on their chemical shift or spin-lattice relaxation rates. These techniques have a clear cost advantage over chemical substitution and can separately image both fluids in a single flood experiment. Due to poor magnetic field homogeneity, chemical shift imaging techniques cannot be performed on the broad line imaging system. The feasibility of $T_1$ suppression imaging during immiscible displacement was therefore investigated.

The immiscible displacement of reservoir crude oil and brine was monitored within the third encapsulated sandstone plug (table 1). The crude oil viscosity is known to have a large temperature dependence (section 4.4), and as fluid viscosities play an important role in multiphase flow processes, the rock plug flood was performed in a temperature controlled environment at 60°C. This temperature is more representative of reservoir conditions. Unfortunately, the high pressures also associated with reservoir rock at great depth could not be reproduced.

The inversion recovery broad line gradient echo technique was used to individually suppress the crude oil and brine NMR signals. The effective suppression of the brine NMR signal was achieved by systematically varying the inversion pulse during the rock plug flood according to the $T_1$ relaxation data obtained in section 5.4.3. This pulse gap variation changes the magnitude of the non-suppressed crude oil signal. To account for this variation, the observed crude oil signal was modified according to

$$A(\tau_1) = \frac{A(\tau_n)}{1 - 2 \exp \left( -\frac{\tau_1}{T_{1\text{OIL}}} \right) \alpha} \left( 1 - 2 \exp \left( -\frac{\tau_n}{T_{1\text{OIL}}} \right) \alpha \right)$$

(5.1)

where $A(\tau_1)$ and $A(\tau_n)$ are the NMR signal amplitudes of the crude oil with pulse gaps of $\tau_1$ and $\tau_n$ respectively. The amplitude of the NMR signal following the nth
inversion pulse gap can thus be calibrated with the 1st inversion pulse gap amplitude.

At 60°C, the crude oil within the sandstone plug has a $T_{1\text{OIL}}$ ($\alpha$) of 650 (0.74) ms and exhibits no variation of relaxation with saturation. The inversion pulse gap for crude oil signal suppression therefore remained constant throughout the displacement experiment and no calibration of the resultant brine signal was required.

Following drainage, the resultant NMR profiles with brine and crude oil suppression are shown in figures 5.7 and 5.8 respectively. There is generally good agreement between the two data sets, with the invasion of crude oil clearly visible. The brine suppressed profile at $S_w = 1.0$ should correspond to total suppression of the NMR signal. This is clearly not the case and illustrates the difficulty of totally suppressing the magnetisation of a pore fluid which exhibits a large relaxation dependence on pore size. After the injection of 2 PV of crude oil, the brine saturation is approximately at the irreducible level ($S_w^i = 0.28$). The capillary ‘end-effect’ due to changes in capillary pressure is clearly visible.

The brine and crude oil suppressed profiles, following imbibition, are shown in figures 5.9 and 5.10 respectively. Again, there is reasonable agreement between the two data sets, although a large saturation gradient is apparent across the length of the plug. This gradient is probably due to some form of bypassing, which prevents the brine sweeping the entire rock plug and leaves large regions of the rock at full crude oil saturation. After the injection of 2 PV of brine, $S_{or} = 0.48$. This value of $S_{or}$ is not untypical in reservoirs, where bypassing due layers of high rock permeability is common.
Figure 5.7 Brine Suppressed Profiles During Drainage

Figure 5.8 Oil Suppressed Profiles During Drainage
Figure 5.9 Brine Suppressed Profiles During Imbibition

Figure 5.10 Oil Suppressed Profiles During Imbibition
5.6 CONCLUSIONS

The feasibility of broad line NMR imaging as a non-invasive method for monitoring fluid distributions in reservoir rock plugs during displacement experiments has been clearly demonstrated. Such techniques are especially applicable to rock plugs with ultra small pore sizes (< 1 μm) or large quantities of line broadening impurities (such as iron), where transverse relaxation rates can be less than a millisecond.

Chemical substitution has been successfully employed to separately image either the brine or oil during the rock plug floods. The quantitative nature of the data has allowed the irreducible and residual fluid saturations to be directly measured from the spatial magnetisations. The values of $S_{wi}$ and $S_{or}$ thus obtained are in good agreement with previous rock plug studies under ambient conditions and indicate that about 40% of the oil remains after brine flooding. This large remaining fraction of oil clearly shows the need for enhanced recovery techniques in commercial reservoirs. Chemical substitution also allows the individual measurement of fluid relaxation times as a function of saturation and hence establish the dominant mechanisms of relaxation within the rock. The resultant $T_1$ weighted profiles obtained during drainage and imbibition show a strong dependence on saturation for the brine relaxation time, but the oil relaxation time is relatively independent of saturation. Such observations are common in strongly water wet rock, where enhanced relaxation at the pore surface dominates the brine relaxation time, but has an almost negligible effect on the oil relaxation time.

$T_1$ suppression imaging has been successfully demonstrated during reservoir fluid immiscible displacement. The flow of brine and reservoir crude oil was performed at 60°C and individual suppression was made according to the spatial relaxation data obtained earlier. Subsequent calibration of the brine suppressed profiles has allowed quantitative measurement of the fluid distribution during drainage and imbibition. There is clear evidence of bypassing during the brine flood and this has resulted in a residual oil saturation of nearly 50%. The saturation independence of the oil $T_1$ relaxation time permits very efficient suppression of the oil signal. In
water wet rock, the effective suppression of brine can only be obtained with prior knowledge of the saturation dependence. In this study, the saturation dependence has been shown to be almost linear, with the decreasing alpha value at low saturation. This indicates preferential pore size invasion of the non-wetting fluid during imbibition. For uncharacterised rock, quantitative T₁ suppression profiles can only be obtained by suppressing the non-wetting fluid, which is assumed to have a negligible dependence on saturation.

High temperature immiscible flood imaging has been demonstrated in this study, but to effectively understand flow processes under reservoir conditions, the addition of high pressure is also needed and should be included in any future work.
CHAPTER SIX

THE STUDY OF DIFFUSION PROCESSES IN PARTIALLY SATURATED SANDSTONE PLUGS USING BROAD LINE MRI TECHNIQUES
6.1 INTRODUCTION

This chapter discusses the first application of broad line MRI methods to the study of diffusion processes in partially saturated reservoir rock. The study has been performed on ten sandstone rock plugs, well characterised by other means. The samples were prepared using specially developed partial saturation techniques. These techniques rely on water vapour penetration and capillary action to initially saturate the plugs in a non-uniform manner.

The diffusion process at low saturation has been found to be in excellent quantitative agreement with a model based on parallel transport of water in the vapour phase and absorbed on the pore surfaces, with the vapour and pore surface water maintained in dynamic local equilibrium. The analysis has yielded estimates of the surface water diffusion coefficients, vapour percolation thresholds and of the critical depths of surface water, below which the vapour pressure is substantially reduced.

6.1.1 BACKGROUND

The ability to visualise water and oil in rock plugs is of substantial importance in the modelling of diffusion processes within rock and the subsequent development of enhanced oil recovery techniques. MRI is now widely established as one of the preferred methods for obtaining diffusion profiles and considerable literature now exists on the subject. However, due to the effects of pore surface relaxation, applications of MRI have concentrated on mapping relatively mobile fluid found at high rock plug saturation levels. In order to study diffusion processes at very low saturation levels, it is necessary to adopt broad line imaging protocols and the work in this chapter represents the first such study.
6.2 STANDARD DESATURATION TECHNIQUES

Standard desaturation techniques are employed in rock plug analysis to reduce the wetting phase saturation to an irreducible level and thus simulate reservoir conditions during drainage. These techniques usually involve rapid desaturation and are thought to leave small amounts of trapped bulk fluid within the rock. To monitor rock plug fluid distribution following a standard desaturation process, broad line MRI techniques were employed and represent the first such study of reservoir plugs at very low fluid saturation (Attard et al, 1994).

The study was performed on two reservoir rock plugs (a sandstone and a carbonate) with the mobile brine removed by porous plate desaturation, using humidified nitrogen gas at pressures up to 1.24 MPa. At this pressure it was known that the irreducible brine saturation was reached ($S_wi$). The brine content for both rock plugs was estimated to be about 2% of the pore volume and plug integrity was maintained by subsequent saturation with a fluorinated oil. Two dimensional non-slice select images were obtained for both rock plugs using the repetitive pulse broad line gradient echo technique (section 3.3.5.3). Bulk and spatially resolved relaxation time measurements were also obtained and fitted to stretched exponential functions (section 2.6.1.4).

The two dimensional images clearly show non-uniform fluid distribution within the plugs, which suggests the presence of localised regions of higher saturation (figure 6.1). The image data is supported by the relaxation time measurements, which although showing a large reduction in longitudinal and transverse relaxation times, display alpha values in the range 0.3 to 0.2. Low alpha values indicate a very broad range of relaxation times and suggest large variations of fluid saturation within the plugs. These NMR measurements clearly indicate the uncontrolled non-uniform manner in which rapid desaturation techniques remove the wetting fluid.
Ten sandstone plugs have been specially selected for the diffusion (section 6.4) and relaxation (chapter 7) studies. The 2.5 cm diameter plugs are from the South Morecombe reservoir field, located in the east Irish Sea Basin. The reservoir consists of the Triassic sandstone group laid down in a rapidly subsiding basin under continental semi-arid conditions (Stuart and Cowan, 1991). This has provided rock varying widely in composition, porosity and permeability throughout the reservoir and the ten plugs have been chosen to reflect this range. To prevent unwanted damage to the plugs, the petrophysical data was obtained from neighbouring plugs and is listed in table 6.1. All the rock plugs are known to be preferentially water wet. The rock plug pore size distributions were calculated by back scatter electron imaging of a thin slice of the rock saturated in epoxy. The measurements indicate a broad range of pore sizes (4 to 100 μm) but the pore throat sizes are not included. A typical example of the pore size distribution data is shown in figure 6.2, for plug 2.
<table>
<thead>
<tr>
<th>Core Number</th>
<th>Illite Affected</th>
<th>Length (mm)</th>
<th>Porosity (%)</th>
<th>Permeability (mD)</th>
<th>Av. Pore Size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>yes</td>
<td>22.4</td>
<td>14.0</td>
<td>0.6</td>
<td>16.1</td>
</tr>
<tr>
<td>5</td>
<td>yes</td>
<td>23.0</td>
<td>9.0</td>
<td>5.1</td>
<td>22.6</td>
</tr>
<tr>
<td>6a</td>
<td>yes</td>
<td>22.5</td>
<td>9.8</td>
<td>1.4</td>
<td>18.9</td>
</tr>
<tr>
<td>7a</td>
<td>yes</td>
<td>21.6</td>
<td>12.4</td>
<td>8.3</td>
<td>20.6</td>
</tr>
<tr>
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<td>13.4</td>
<td>0.3</td>
<td>5.1</td>
</tr>
<tr>
<td>12</td>
<td>no</td>
<td>22.3</td>
<td>11.8</td>
<td>5.9</td>
<td>9.0</td>
</tr>
<tr>
<td>13</td>
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<td>19.4</td>
<td>603</td>
<td>12.9</td>
</tr>
</tbody>
</table>

Table 6.1 Petrophysical Data For The Ten Sandstone Plugs

![Pore Size Distribution](image)

Figure 6.2 Pore Size Distribution For Plug 2 Using Back Scatter Electron Imaging Of A Thin Slice Of The Rock
The rock plugs fall into two groups - illite affected and illite unaffected. From back scattered electron imaging (figure 6.3), the illite is known to form platy layers on the pore surfaces. This results in a very uneven texture on the pore surfaces and can have a severe affect on the rock plug permeability.

*Figure 6.3 Electron Back Scatter Images Showing a) The Formation of Illite On The Pore Surfaces b) An equivalent Rock With No Illite Formation*
The ten sandstone plugs are shown in figure 6.4. The plugs are well cemented with the exception of plug 18a which is friable and care had to be taken to prevent unwanted weight loss during the course of experiments. Plug 5 had been damaged previously and the cemented repair is clearly visible.

Figure 6.4 The Ten Sandstone Plugs
6.4 ROCK PLUG PARTIAL SATURATION TECHNIQUES

The rapid desaturation technique applied in section 6.2 clearly demonstrates the problems of removing rock plug bulk fluid in cut-off or dead-end channels. Trapping is a direct consequence of the desaturation procedure and can be prevented by slow drying at elevated temperature. In this study, the lowest saturation was reached by drying the rock plugs in a vacuum oven at 150°C for 48 hours and returning them to room temperature in a pure nitrogen gas environment. The 'dry' plugs were then saturated in a controlled manner by diffusion and capillary processes and this section covers two such techniques.

6.4.1 USING THE HUMIDITY CHAMBER

To obtain rock plug partial saturations in the range 0.3 to 20%, the initially 'dry' plugs were placed in a temperature controlled humidity chamber with all but one surface sealed against vapour penetration. Water diffusion resulted in a controlled non-uniform partial saturation of the rock plugs along the plug length. The water uptake was monitored using NMR profiling supported by gravimetric analysis. Two rock plugs which exhibit typical partial saturation behaviour are shown in figures 6.5 and 6.6, for plugs 2 and 6a respectively (the magnetisations have been converted to saturation). The profiles clearly show water vapour diffusing into the rock plug samples, even after 168 hours of surface exposure. The profiles indicate that the rock plugs eventually establish a spatially constant saturation level and it appears that continued exposure in the humidity chamber does not significantly increase water uptake after uniform distribution is reached. This level is substantially less than full saturation and is thought to be due to the blocking of the pore throats with bulk water which stops the rapid vapour diffusion process. The saturation level at which the pore throats become blocked and pore connectivity is lost is known as the vapour percolation threshold and is different for each rock plug. The vapour percolation thresholds, calculated using gravimetric analysis for each sandstone plug, are shown in table 6.2.
Figure 6.5 Partial Saturation Profiles For Plug 2
Using The Humidity Chamber

Figure 6.6 Partial Saturation Profiles For Plug 6a
Using The Humidity Chamber
6.4.2 USING THE WATER BATH

For rock plug saturations in the range 20 to 70%, the plugs were placed in a temperature controlled water bath instead of the humidity chamber, such that the exposed end was 1 mm below the surface. The plugs were then allowed to saturate by capillary processes. As before, the water uptake was monitored using NMR profiling supported by gravimetric analysis. Figures 6.7 and 6.8 show the resultant partial saturation profiles for plugs 7a and 10a respectively. The capillary saturation process is clearly more rapid than the vapour diffusion process, with an equilibrium saturation reached within 10 hours. This equilibrium saturation is less than full saturation and is thought to be due the presence of larger pore sizes, which cannot be fully saturated by capillary action alone. It is found that vacuum techniques are required if these larger pores are to be fully saturated. The threshold saturation of the capillary transport process for each rock plug is included in table 6.2.

<table>
<thead>
<tr>
<th>Rock Plug</th>
<th>Vapour Percolation Threshold Saturation (%)</th>
<th>Capillary Transport Threshold Saturation (%)</th>
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<td>2</td>
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</tr>
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</tr>
<tr>
<td>7a</td>
<td>11.8</td>
<td>68.4</td>
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<td>10a</td>
<td>15.2</td>
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<td>36.9</td>
</tr>
<tr>
<td>18a</td>
<td>10.6</td>
<td>22.8</td>
</tr>
</tbody>
</table>

Table 6.2 Vapour Percolation And Capillary Transport Thresholds For The Ten Sandstone Plugs Using The Partial Saturation Techniques
Figure 6.7 Partial Saturation Profiles For Plug 7a Using The Water Bath

Figure 6.8 Partial Saturation Profiles For Plug 10a Using The Water Bath
6.4.3 SPATIAL EQUILIBRATION

The partial saturation techniques are shown to initially produce a non-uniform distribution of water along the length of the rock plugs. By totally sealing the rock plugs to prevent unwanted water evaporation, the water within them can be allowed to spatially equilibrate according to natural diffusion and capillary processes. The water equilibration during both partial saturation techniques was monitored in plug 2 using NMR profiling (figure 6.9). In both cases, the plug was sealed for 240 hours, with less than 2% total water evaporation over the course of both experiments. The effectiveness of this simple technique is clearly evident and has been used to obtain uniform partial water saturation for the bulk relaxation experiments (chapter 7).

Figure 6.9 Broad line NMR Profiles Of Plug 2 Showing a) Non-uniform Water Distribution b) Subsequent Water Distribution After Equilibration
6.5 DIFFUSION ANALYSIS

This section describes an analytical model used to simulate the diffusion processes observed in the rock plugs during the humidity chamber partial saturation technique (section 6.4.1). Typically, the rock plugs were out of the humidity chamber for 10 minutes for each NMR measurement. Due to the relatively slow nature of the diffusion process, this procedure is not expected to have significantly affected the results.

Diffusion studies deal with the change in location of solute with time. Experimental studies of diffusion show that a proportionality exists between the rate of flow across a unit cross sectional area and the concentration gradient \( \frac{\partial C}{\partial x} \) at that cross section. The diffusion direction is that in which the concentration decreases, and the proportionality can be written as an equality by the introduction of a constant \( D \), so that

\[
\frac{\partial C}{\partial t} = -D \frac{\partial C}{\partial x}
\]

(6.1)

where \( C \) is the concentration and \( D \) is the diffusion coefficient. This equality is known as Fick's first law. It is often more convenient to have a description of the effect of diffusion on the concentration in a volume element.

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right)
\]

(6.2)

This is Fick's second law and is the basis for the deduction of most of the consequences of diffusion. In real systems, such as water diffusion in porous media, there may be a deviation from Fickian behaviour due to interactions of the diffusing species with the medium.
6.5.1 CONCENTRATION DEPENDENT DIFFUSION MODEL

A brief visual inspection suggests, and more detailed quantitative analysis confirms, that the diffusion of water in the rock plugs below the vapour percolation threshold is not governed by Fickian dynamics with a constant diffusion coefficient. This is clearly shown in figure 6.10, with a diffusion profile obtained for plug 2, together with a series of fits based on a constant $D$.

![Figure 6.10 Theoretical Fits With Constant D (cm$^2$s$^{-1}$) For The Plug 2 Water Diffusion Profile After 48 Hours Surface Exposure](figure)

The diffusion process is thought to be governed by a diffusion equation in which the constant $D$ is replaced with $D_{\text{eff}}$, which is a function of concentration. There are many possible ways in which $D$ can depend on $C$, some of which have been clearly illustrated by Pfeiffer (1976) and their effects on the diffusion profiles described by Crank (1975). For the rock plugs it is found empirically that excellent fits to the data are obtained for $D_{\text{eff}} = D_0 + D_1 \exp(C/C_0)$. Such observations have been made before during solute diffusion studies within zeolites (Barrer, 1943). More recently, the concentration dependent diffusion model has been successfully used to fit water...
diffusion profiles in beds of zeolite 4A powder (Hughes et al, 1994). In the latter case, the water is transported either in the vapour phase or in the liquid phase, according to normal diffusion (constant D in each case) and local dynamic equilibrium is maintained between the vapour pressure and the liquid concentration. A similar model is thought to apply to water diffusion in the rock plugs at low saturation, where water transport occurs by vapour diffusion in the pore space and by liquid phase transport along the pore surfaces.

Two coupled partial differential diffusion equations can be written for the vapour in the pore space and for the water on the pore surfaces. The equations are

\[
\frac{\partial C_v}{\partial t} = \frac{\partial}{\partial x} \left( D_v \frac{\partial C_v}{\partial x} \right) - \frac{\partial S}{\partial t}
\]

(6.3)

\[
\frac{\partial C_s}{\partial t} = \frac{\partial}{\partial x} \left( D_s \frac{\partial C_s}{\partial x} \right) + \frac{\partial S}{\partial t}
\]

where \(C_v\) and \(C_s\) are the water concentrations in the vapour and on the pore surfaces respectively. \(D_v\) and \(D_s\) are the corresponding diffusion coefficients and are considered constants. \(\frac{\partial S}{\partial t}\) is the rate of transfer of molecules from the vapour to the pore surface which maintains local equilibrium between \(C_v\) and \(C_s\). At very low rock plug saturation, the vapour pressure is low due to the preferential wetting nature of the pore surfaces. The diffusion at low saturation is therefore dominated by the liquid phase along the pore surfaces. As the surface coverage increases, so does the vapour pressure. The precise form of the relationship is unknown, but is assumed to be of the form

\[
C_v = C_v^0 \exp \left( \frac{C_s}{C_s^0} \right)
\]

(6.4)

This form displays the right characteristics and is analogous to the vapour isotherm of water diffusion in zeolite. The exchange term in the diffusion equation can be eliminated by addition. Thus
\[
\frac{\partial (C_y + C_g)}{\partial t} = \frac{\partial}{\partial x} \left( D_y \frac{\partial C_y}{\partial x} + D_s \frac{\partial C_g}{\partial x} \right) \tag{6.5}
\]

Noting that
\[
\frac{\partial C_y}{\partial x} = \frac{dC_y}{dC_g} \frac{\partial C_g}{\partial x} \tag{6.6}
\]
and that \( C_g \gg C_y \), equations 6.4, 6.5 and 6.6 lead to
\[
\frac{\partial C_g}{\partial t} = \frac{\partial}{\partial x} \left[ D_y \frac{\partial}{\partial x} C_y^0 \exp \left( \frac{C_y}{C_y^0} \right) + D_s \frac{\partial C_g}{\partial x} \right]
\]
\[
= \frac{\partial}{\partial x} \left[ D_y \frac{C_y^0}{C_g^0} \exp \left( \frac{C_g}{C_g^0} \right) \frac{\partial C_g}{\partial x} + D_ps \frac{\partial C_g}{\partial x} \right] \tag{6.7}
\]
\[
= \frac{\partial}{\partial x} \left[ D_{\text{eff}} \left( \frac{\partial C_g}{\partial x} \right) \right]
\]
where
\[
D_{\text{eff}} = \left( \frac{D_y C_y^0}{C_g^0} \exp \left( \frac{C_y}{C_y^0} \right) + D_s \right) \tag{6.8}
\]

Equation 6.7 can be numerically integrated to yield a set of diffusion profiles as a function of time, given the appropriate starting and boundary conditions. The form of the effective diffusion coefficient is the same as that which is found to fit the data. From this equation it is possible to calculate the various parameters and in particular the surface water diffusion coefficient \( D_s \) and the parameter \( C_g^0 \).
Ideal gas kinetics can be used to estimate $D_v$ (Kennard, 1938). The appropriate equation for the diffusion coefficient of water molecules in air is

$$D_v = \frac{3}{8} \sqrt{\frac{\pi}{2}} \frac{1}{C_{\text{air}} \pi \sigma^2} \left( \frac{R \theta}{M} \right)^{1/2} \tag{6.9}$$

where $C_{\text{air}}$ is the total number of air molecules per cc, $\sigma$ is the effective molecular diameter of an air molecule, $R$ is the gas constant, $M$ is the reduced molecular weight of water molecules in air and $\theta$ is the absolute temperature. Assuming typical values for the above parameters, the vapour diffusion coefficient at $20^\circ C$ is approximately $0.25 \text{ cm}^2 \text{s}^{-1}$. In the confined geometry of the pore space this value will be reduced by a tortuosity factor and by a porosity factor which together are expected to be of order 3. For the diffusion profiles obtained at room temperature, the vapour diffusion coefficient within the pore space is therefore assumed to be $0.1 \text{ cm}^2 \text{s}^{-1}$.

### 6.5.1.1 FITTING PROCEDURE

For each rock plug, the profile amplitude at the percolation threshold (table 6.2) was defined as $C_0$ and subsequent profiles for the same rock plug fitted with $C_0$ fixed at $x = 0$. The diffusion equation was then solved numerically for various values of $D_s$, $C_s^0$ and $t$, to obtain the best fit. The constant $C_v^0$ was fixed at $5 \times 10^{-8}$ % and is discussed further below. For each rock plug data set, the values of $D_s$ and $C_s^0$ were obtained for the diffusion profile after 48 hours surface exposure and fixed for the remaining partial saturation profiles. Theoretical profiles for different $t$ values according to the different experimental times were identified and compared to the NMR data. In each case, the diffusion profile was convoluted with a Gaussian broadening function, equivalent to the profile resolution and given by

$$c(x_n, t) = \sum_{j=1}^{m} c(x_j, t) \frac{1}{x_0 \sqrt{\pi}} \exp \left( -\frac{(x_j - x_n)^2}{x_0^2} \right) \tag{6.10}$$
where \(x_0\) is the convolution parameter, \(m\) is the total number of points for each theoretical profile and \(c\) is the concentration at point \(x\) and time \(t\). This convolution accounts for the 'rounding' of the NMR profiles due to spread of frequencies at each spatial point. This effect can be very prominent in short \(T_2\) systems. With \(x\) converted to a millimetre scale, the value of \(x_0\) was fixed at 0.95 mm.

The improvement in the quality of the theoretical profiles using the concentration dependent diffusion model is shown in figure 6.11. The fits are compared to the NMR diffusion profile obtained for plug 2 after 48 hours surface exposure at 20°C. For each theoretical profile, the value of \(D_s\) was fixed at \(4.5 \times 10^{-6} \text{ cm}^2\text{s}^{-1}\) and \(C_s^0\) was systematically varied. This clearly demonstrates the sensitivity of the fitting parameter \(C_s^0\).

![Figure 6.11 Theoretical Fits To A Water Diffusion Profile For Plug 2, With Fixed \(D_s (4.5 \times 10^{-6} \text{ cm}^2\text{s}^{-1})\) And Variable \(C_s^0\) (%)](image)

As stated earlier, the constant \(C_s^0\) was fixed at \(5 \times 10^{-8}\) %. This value gives the best fits to the NMR data, although reasonable fits can be achieved with other values. For instance, figure 6.12 shows the best fit to a plug 2 diffusion profile.
obtained using $C^0_v = 5 \times 10^{-8}$ %, together with the optimum fit obtained with $C^0_v = 1 \times 10^{-8}$ %. This is a reduction by a factor of 5. However, the corresponding change required in $C^0_v$ to obtain the best fit is a reduction from 1.85 to 1.65%. This is a reduction by a factor of only 1.15, whilst the change in $D_g$ is negligible. These findings suggest that the fits are relatively insensitive to $C^0_v$, that is to the vapour pressure at zero surface coverage. This provides added confidence to the estimates of the physically more significant parameters, $D_g$ and $C^0_g$.

![Figure 6.12](image)

*Figure 6.12  Theoretical Fits To A Plug 2 Diffusion Profile, With $C^0_v$ Fixed At $5 \times 10^{-8}$ And $1 \times 10^{-8}$ %

The saturation percentage, $C_s$, can be written in terms of numbers of molecules per cubic centimetre (cc) of water $n_s$, given that $C_s = 100\%$ corresponds to bulk water, $n_s = 3.3 \times 10^{22}$ cc$^{-1}$. Similarly, it is possible to convert the vapour saturations. Thus, the vapour concentration at zero surface coverage, $C^0_v = 5 \times 10^{-8}$ %, corresponds to $1.65 \times 10^{13}$ cc$^{-1}$. As a comparison, the absorption isotherm for water in zeolite 4A gives the corresponding value of $4 \times 10^{10}$ cc$^{-1}$. The difference is large, although the latter value might be expected to be smaller due to the strong affinity of the water molecules to the sodium ions in the zeolite. Moreover, as already stated, the NMR data fits are relatively insensitive to $C^0_v$. 
6.5.2 ESTIMATES OF $D_s$ AND $C_s^0$

Figure 6.13 shows the NMR data and corresponding theoretical profiles for plug 2 after various exposure times in the humidity chamber at $20^\circ$C. The quality of these fits is clearly evident, especially at the low saturations, where the diffusion is more Fickian in behaviour. The values of $D_s$ and $C_s^0$ were fixed throughout and $t$ was scaled according to the appropriate experimental time. The fitting procedure has been applied to all ten rock plugs with partial saturation profiles obtained at $20^\circ$C. The calculated values of $D_s$ and $C_s^0$ for each rock plug are listed in table 6.3. The average value of the surface water diffusion coefficient is smaller than the self diffusion coefficient of free water by a factor of about 5, as might be expected for water in a confined geometry and subject to restricted motion.

<table>
<thead>
<tr>
<th>Rock Plug</th>
<th>$D_s$ ($10^{-6}$ cm$^2$ s$^{-1}$)</th>
<th>$C_s^0$ (%)</th>
<th>$h_s^0$ (No. Of Monolayers)</th>
</tr>
</thead>
<tbody>
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<td>63</td>
</tr>
<tr>
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<td>25</td>
</tr>
<tr>
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<td>5.0</td>
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</tr>
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</tr>
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<tr>
<td>14</td>
<td>5.0</td>
<td>0.95</td>
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<tr>
<td>18a</td>
<td>7.0</td>
<td>1.00</td>
<td>23</td>
</tr>
</tbody>
</table>

Table 6.3 Parameters Used In Fitting The Experimental Diffusion Profiles With The Humidity Chamber At $20^\circ$C
Figure 6.13 Diffusion Profiles For Plug 2 At 20°C With Corresponding Theoretical Fits
Figure 6.14 shows the best fit for the plug 13 diffusion profile after 48 hours surface exposure. The macroscopic heterogeneities in the pore size distribution are reflected in the anomalous shape of the water diffusion profile. Nonetheless it has still been possible to smooth the structure by eye and obtain reasonable fits to the data. Rock plugs 5 and 7a are affected in a similar way.

![Figure 6.14 Best Fit To The Plug 13 Diffusion Profile After 48 Hours Surface Exposure](image)

Using the rock plug pore size distribution data (combined with pore throat size estimates obtained by NMR and discussed in chapter 7) and assuming spherical pores and uniform water coverage on the pore surfaces (section 7.4.1), it is possible to relate the water saturation $S_w$ to the depth of the surface water, $h$, according to

$$S_w = \frac{\sum_i V_i}{\sum_i \frac{4}{3} \pi r_i^3} \times 100\%$$  \hspace{1cm} (6.11)
where \( r_i \) is the radius of the \( i \)th pore and

\[
V_i = \frac{4}{3} (3r_i^2 h - 3r_i h^2 + h^3)
\]  
(6.12)

is the volume of surface water in the \( i \)th pore. These expressions have been used to calculate the critical depth of water \( h_0 \), corresponding to the critical saturation \( C_s^0 \). This is the depth at which the vapour pressure increases by a factor \( e = 2.718 \) above its value at zero water coverage and is typically found to be a few tens of Angstroms. Values in terms of molecular layers of water, assuming a molecular diameter of \( 3 \) Å for water, for each plug are given in table 6.3. At first inspection, these values appear slightly large. Powles et al (1992) have suggested that at depths in excess of a few molecular layers (≈ 5), the liquid can be treated as free liquid and behaves independently of the ‘smooth’ pore surface. However, for the sandstone plugs used in this study, the electron back scattered images have shown that the pore surfaces are not smooth. Rather, surface irregularities on the Angstrom scale lead to ‘peaks’ and ‘troughs’ along the pore surfaces. After monolayer coverage, it is expected that the water will collect in the troughs due to surface tension effects and leave the peaks devoid of surface water. These exposed portions of the pore surface will act as traps for additional vapour, thus keeping the vapour pressure low at greater depths. In support of this argument is the fact that the illite affected plugs, which are known to have very uneven pore surfaces, have a significantly greater value of \( C_s^0 \) than the illite unaffected plugs (table 6.3).

It is clear the \( C_V \) cannot increase indefinitely with \( C_s \) as suggested by equation 6.4. However, there is no evidence in the data for an upper limit to \( C_V \), presumably because all the data has been collected at low saturation, below the vapour percolation threshold.

### 6.5.2.1 TEMPERATURE DEPENDENCE OF \( D_s \)

The surface water diffusion coefficient has been measured as a function of temperature within plug 2. This was achieved by profiling the water uptake after
4 hours surface exposure, thereby reducing the effect of the enhanced vapour phase. From equation 6.9 it seen that the vapour diffusion coefficient is relatively independent of small temperature variations and may only change by about 8% in the range 5 to 60°C. The liquid phase diffusion coefficients were deduced using the model and show an exponential temperature dependence, rising from $2.0 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ at 5°C to $4.7 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$ at 60°C (figure 6.15). This suggests that the surface water diffusion coefficient is thermally activated and governed by an Arrhenius law. By fitting $D_s$ to the expression

$$D_s = D_s^0 \exp\left(\frac{-\theta_o}{\theta}\right)$$  

(6.13)

where $D_s^0$ and $\theta_o$ are constants and $\theta$ is the absolute temperature, the activation energy for the surface water diffusion has been estimated at 49 kJmol$^{-1}$. This value compares well with typical activation energies obtained from other porous systems.

![Figure 6.13 The Temperature Dependence Of $D_s$ For Plug 2, With The Solid Line Representing The Best Fit](image)
6.6 CONCLUSION

Broad line imaging methods have been successfully employed in the first study of diffusion processes in partially saturated reservoir rock. The diffusion process has been found to be in excellent quantitative agreement with a model based on parallel transport of water in the vapour phase and absorbed on the pore surfaces. The analysis has yielded estimates of the surface water diffusion coefficient for all ten rock plugs, with an average value of $5 \times 10^{-6}$ cm$^2$s$^{-1}$. This value is approximately 5 times smaller than the value for free water and is due to the combined effects of confined geometry and restricted diffusion.

At low saturation, below the vapour percolation threshold, the NMR data indicates that the vapour pressure has an exponential dependence on surface water saturation, due to the preferential wetting nature of the pore surfaces. Previous studies on porous materials have suggested that the vapour pressure should only depend on surface saturation up to a few molecular layers of surface coverage. This is not the case from the results obtained in this study, with measurements indicating a vapour pressure increase well above a few molecular layers. This has been attributed to the ‘roughness’ of the pore surfaces, especially in the illite affected rock plugs. This roughness of the pore surfaces has been related to a critical saturation parameter $C_s^0$, which is the exponential constant in the vapour pressure surface water saturation dependence. For the illite affected plugs $C_s^0 = 1.6\%$ and for the illite unaffected plugs $C_s^0 = 1.1\%$. Assuming spherical pores and uniform water coverage across the pore size range, these critical saturations have been converted to number of monolayers, giving 40 and 18 respectively.

A temperature controlled humidity chamber was used to partially saturate the rock plugs. This produced a controlled non-uniform distribution of water along the length of the plugs, which has been shown to spatially equilibrate with time. Combined with a partial saturation technique which relies on capillary water uptake, these procedures form the basis of sample preparation required for the relaxation time saturation dependence study (chapter 7).
Below the vapour percolation threshold there is no evidence of an upper limit to the vapour pressure. The vapour pressure will undoubtedly reach an upper limit at higher saturation and future studies should concentrate on the modelling of water uptake within rock plugs with water saturations in the range 10 to 60%. Unfortunately, such studies will be complicated by the addition of capillary effects, which are negligible at very low saturation, but are thought to dominate the water uptake at higher saturation.

Finally, it is worth reiterating that the measurements of water diffusion in these plugs at low saturation could not have been made using more conventional means, such as pulsed field gradient magnetic resonance (section 1.6). This is because the short spin-spin relaxation time found at low saturation ($T_2 < 1$ ms) precludes the generation of PFG spin echoes with sufficiently large pulse gaps. PFG experiments performed with sub-millisecond pulse gaps would not reflect the bulk transport over macroscopic distances, but rather would reflect shorter range self diffusion within the pores.
CHAPTER SEVEN

NMR RELAXATION STUDY OF SANDSTONE ROCK PLUGS AS A FUNCTION OF SATURATION
7.1 INTRODUCTION

This chapter represents the first rigorous test of fast diffusion relaxation theory (section 2.6.1) in water-saturated rock over the full saturation range. The study was performed on a series of ten well characterised sandstone plugs (section 6.3). Bulk and spatially localised $T_1$ and $T_2$ measurements were obtained with saturations in the range 0.06 to 100%. Since relaxation is surface dominated, measurements have led to unambiguous estimates of pore surface relaxivity ($p_1$ and $p_2$). At intermediate saturations, the preferential filling of pore throats is evident and this has led to estimates of pore throat size.

Spatial resolution is required to assess the uniformity of water distribution during the partial saturation procedures and thus account for the natural heterogeneity of the rock plugs. Due to the short relaxation times, especially at low saturation, short $T_2$ imaging protocols have been used rather than conventional imaging methods. As such, all bulk and spatially resolved NMR measurements were obtained using the broadline imaging spectrometer (section 3.3) with a 2.5 cm diameter birdcage resonator coil for the r.f. excitation.

7.1.1 BACKGROUND

It is well known that the NMR homonuclear dipolar relaxation of fluids is enhanced when the fluid occupies the pore space of reservoir rock cores (section 2.6.1), with the degree of enhancement dependent on the pore size and geometry. The enhanced relaxation of the pore fluid is particularly severe when the fluid 'wets' the pore surfaces and is due to susceptibility broadening of the magnetic resonance line at the pore-grain interface, restricted diffusion within the vicinity of the pore surface and nuclear spin relaxation by paramagnetic ions on the pore surface. Previous studies have shown that under appropriate conditions of fast diffusion, surface effects tend to dominate the observed relaxation rate (section 2.6.1.2).
The fast diffusion (weak killing) model has been developed to relate relaxation to pore size. It is based on theory first proposed by Zimmerman and Brittin (1957) and adapted for porous media by Brownstein and Tarr (1979). In the fast diffusion (weak killing) regime, all the fluid molecules encounter pore surface relaxation sinks (e.g. paramagnetic impurities) due to rapid self diffusion across the pore space in the time scale of the NMR experiment. The observed relaxation rate is the average for the bulk fluid and the near surface fluid, weighted by the time spent by an average molecule in each environment. Interpretation of the results depends critically on knowing the pore surface relaxivities ($\rho_1$ and $\rho_2$).

Measurements made on porous silica glasses (D'Orazio et al, 1990) have shown that at low saturation, the pore fluid relaxation becomes independent of the pore geometry and unambiguous measurements of pore surface relaxivity can be made. In general it is found that the pore surface relaxivity for porous silica glass is orders of magnitude smaller than estimates obtained from saturated rock plugs (Howard et al, 1990), where the surface relaxivity has been obtained using knowledge of the pore size distribution obtained by other means.

### 7.2 RELAXATION MEASUREMENTS AT FULL SATURATION

Bulk proton $T_1$ and $T_2$ data sets were acquired for the ten water-saturated sandstone plugs (chapter 6) using inversion recovery and CPMG pulse sequences respectively. The data was fitted to stretched exponential functions (section 2.6.1.4)

\[ M(t) = M_0 \left[ 1 - 2 \exp \left( \frac{-t}{T_1} \right)^{\alpha} \right] \]  

and

\[ M(t) = M_0 \exp \left( \frac{-t}{T_2} \right)^{\alpha} \]  

(7.2)
for $T_1$ and $T_2$ relaxation times respectively. The alpha parameter accounts for the multi-exponential decay expected in heterogeneous porous systems. This type of fitting procedure is robust and appropriate to rock plug relaxation analysis when only the average relaxation time and an estimate of the distribution is required. The calculated relaxation times and alpha values are shown in table 7.1.

The ten sandstone plugs show a wide spread in relaxation times, which is essential in making an effective study of pore surface relaxation processes. The alpha values indicate a gaussian or near-gaussian distribution of relaxation times and the $T_1$ and $T_2$ alpha values are comparable for each plug. This indicates that similar processes, presumed to be surface relaxation, are responsible for both spin-spin and spin-lattice relaxation.

<table>
<thead>
<tr>
<th>Rock Plug</th>
<th>$T_1 (\alpha)$ (ms)</th>
<th>$T_2 (\alpha)$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>38 (0.57)</td>
<td>26 (0.56)</td>
</tr>
<tr>
<td>5</td>
<td>248 (0.45)</td>
<td>73 (0.43)</td>
</tr>
<tr>
<td>6a</td>
<td>220 (0.49)</td>
<td>79 (0.47)</td>
</tr>
<tr>
<td>7a</td>
<td>234 (0.58)</td>
<td>94 (0.57)</td>
</tr>
<tr>
<td>10a</td>
<td>62 (0.56)</td>
<td>35 (0.57)</td>
</tr>
<tr>
<td>12</td>
<td>256 (0.62)</td>
<td>140 (0.61)</td>
</tr>
<tr>
<td>13</td>
<td>423 (0.55)</td>
<td>139 (0.53)</td>
</tr>
<tr>
<td>14</td>
<td>449 (0.65)</td>
<td>204 (0.61)</td>
</tr>
<tr>
<td>15a</td>
<td>529 (0.67)</td>
<td>263 (0.64)</td>
</tr>
<tr>
<td>18a</td>
<td>164 (0.68)</td>
<td>91 (0.64)</td>
</tr>
</tbody>
</table>

Table 7.1 Bulk Relaxation Data For The Water-Saturated Sandstone Plugs (±3%), With The Bore Temperature At 13°C

Spatially resolved $T_1$ weighted data sets were acquired for each sandstone plug using the inversion recovery variant of the broadline gradient echo technique (section 3.3.5.2). The resultant relaxation curves were fitted to the stretched
exponential function (equation 7.1) in the same way as the bulk $T_1$ data. Table 7.2 lists the calculated spatial $T_1$ relaxation times for each rock plug, which generally show a good correlation with the bulk $T_1$ data. There is however, a small amount of spatial variation in $T_1$ across some of the plugs, most notably plugs 5, 7a, 13 and 15a. This indicates that the spread of pore sizes may not be totally uniform across the length of these plugs.

<table>
<thead>
<tr>
<th>Position (mm)</th>
<th>Plug 2 $T_1$ ($\alpha$) (ms)</th>
<th>Plug 5 $T_1$ ($\alpha$) (ms)</th>
<th>Plug 6a $T_1$ ($\alpha$) (ms)</th>
<th>Plug 7a $T_1$ ($\alpha$) (ms)</th>
<th>Plug 10a $T_1$ ($\alpha$) (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>36 (0.54)</td>
<td>293 (0.51)</td>
<td>210 (0.49)</td>
<td>209 (0.57)</td>
<td>62 (0.59)</td>
</tr>
<tr>
<td>3</td>
<td>38 (0.53)</td>
<td>278 (0.49)</td>
<td>216 (0.51)</td>
<td>236 (0.55)</td>
<td>63 (0.59)</td>
</tr>
<tr>
<td>6</td>
<td>41 (0.59)</td>
<td>233 (0.53)</td>
<td>240 (0.48)</td>
<td>250 (0.58)</td>
<td>58 (0.54)</td>
</tr>
<tr>
<td>9</td>
<td>40 (0.57)</td>
<td>248 (0.45)</td>
<td>224 (0.49)</td>
<td>265 (0.53)</td>
<td>63 (0.56)</td>
</tr>
<tr>
<td>12</td>
<td>41 (0.58)</td>
<td>249 (0.50)</td>
<td>234 (0.46)</td>
<td>230 (0.54)</td>
<td>56 (0.52)</td>
</tr>
<tr>
<td>15</td>
<td>38 (0.58)</td>
<td>231 (0.49)</td>
<td>230 (0.50)</td>
<td>224 (0.55)</td>
<td>66 (0.58)</td>
</tr>
<tr>
<td>18</td>
<td>39 (0.57)</td>
<td>237 (0.48)</td>
<td>208 (0.52)</td>
<td>232 (0.54)</td>
<td>65 (0.56)</td>
</tr>
<tr>
<td>21</td>
<td>38 (0.57)</td>
<td>270 (0.49)</td>
<td>196 (0.52)</td>
<td>248 (0.55)</td>
<td>66 (0.55)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Position (mm)</th>
<th>Plug 12 $T_1$ ($\alpha$) (ms)</th>
<th>Plug 13 $T_1$ ($\alpha$) (ms)</th>
<th>Plug 14 $T_1$ ($\alpha$) (ms)</th>
<th>Plug 15a $T_1$ ($\alpha$) (ms)</th>
<th>Plug 18a $T_1$ ($\alpha$) (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>241 (0.64)</td>
<td>413 (0.59)</td>
<td>445 (0.66)</td>
<td>473 (0.70)</td>
<td>147 (0.67)</td>
</tr>
<tr>
<td>3</td>
<td>259 (0.64)</td>
<td>439 (0.56)</td>
<td>453 (0.71)</td>
<td>511 (0.68)</td>
<td>150 (0.64)</td>
</tr>
<tr>
<td>6</td>
<td>237 (0.61)</td>
<td>458 (0.54)</td>
<td>461 (0.69)</td>
<td>541 (0.68)</td>
<td>156 (0.66)</td>
</tr>
<tr>
<td>9</td>
<td>257 (0.60)</td>
<td>486 (0.51)</td>
<td>470 (0.67)</td>
<td>515 (0.71)</td>
<td>150 (0.65)</td>
</tr>
<tr>
<td>12</td>
<td>253 (0.57)</td>
<td>460 (0.55)</td>
<td>464 (0.66)</td>
<td>544 (0.68)</td>
<td>154 (0.66)</td>
</tr>
<tr>
<td>15</td>
<td>254 (0.62)</td>
<td>420 (0.60)</td>
<td>440 (0.65)</td>
<td>548 (0.70)</td>
<td>153 (0.65)</td>
</tr>
<tr>
<td>18</td>
<td>257 (0.67)</td>
<td>392 (0.62)</td>
<td>507 (0.71)</td>
<td>150 (0.65)</td>
<td>150 (0.65)</td>
</tr>
<tr>
<td>21</td>
<td>258 (0.62)</td>
<td>416 (0.57)</td>
<td>511 (0.72)</td>
<td>150 (0.65)</td>
<td>150 (0.65)</td>
</tr>
</tbody>
</table>

Table 7.2 Spatial $T_1\alpha$ Data For The Sandstone Plugs At Full Saturation
7.2.1 RELAXATION TIME MEASUREMENTS AT ELEVATED TEMPERATURE

Previous studies (Latour et al, 1992) have shown that water-saturated sandstone rock plugs depend weakly on temperature, an observation which strongly indicates that water-saturated rock plugs tend to be in the fast diffusion (weak killing) regime (section 2.6.1). Relaxation time measurements as a function of temperature were therefore obtained for the ten fully saturated sandstone plugs as a way of verifying fast diffusion behaviour.

The relaxation measurements of the ten fully saturated sandstone plugs generally show very little temperature dependence in the range 20 to 60°C (table 7.3). This indicates that the sandstone plugs are in the fast diffusion regime. Plugs 2, 5, 10a and 18a do show more than average variation over the temperature range, indicating that some of the larger pores may be in the intermediate diffusion regime. These results are discussed in more detail in section 7.5.3.
7.2.2 NMR POROSITY ESTIMATES

The NMR signal detected from a fully saturated rock plug is proportional to the total water content. Hence it is possible, with calibration for the constant of proportionality, to estimate rock plug porosity. Problems arise from inconsistent r.f. coil loading, spectrometer deadtime and differing sample transverse relaxation rates, which all have to be overcome in order to obtain consistent measurements.

The ten fully saturated sandstone rock plugs were individually placed in the magnet and allowed to equilibrate with the bore temperature (13°C). A simple pulse and acquire sequence with a 10 MHz sample rate was then used to measure the signal intensity from each plug. Data was acquired with 9 μs and 3 μs r.f. pulses to monitor the effect of reducing the spectrometer dead-time and to account for the differing sample transverse relaxation times. The free induction decay curves were back extrapolated to time zero, thus giving the true magnetisation. With the magnetisation recorded for each rock plug, a calibration sample of known porosity was used to convert the signal into the equivalent mass of pore fluid. The volume of each rock plug was measured using vernier callipers, allowing the NMR porosity to be easily calculated (section 2.2). To check for reproducibility, the experiment was repeated with the bore temperature raised to 20°C. A scatter plot of all the data is given in figures 7.1 and 7.2 for the 3 μs and 9 μs pulse lengths respectively.

The calculated porosities from the two data sets compare very well with the nitrogen gas absorption porosity data provided by British Gas. The data acquired with the 3 μs inspection r.f. pulse appears to be marginally more accurate. This is undoubtedly due to the reduction in spectrometer dead-time and pulse length, which makes for a better estimate of $M_0$, overriding any loss in signal to noise.
Figure 7.1 Scatter Plot Of NMR Porosity Versus Nitrogen Gas Absorption Porosity For The Ten Sandstone Plugs, Using A 3 μs Inspection Pulse

Figure 7.2 Scatter Plot Of NMR Porosity Versus Nitrogen Gas Absorption Porosity For The Ten Sandstone Plugs, Using A 9 μs Inspection Pulse
7.2.3 NMR PERMEABILITY ESTIMATES

Seevers (1966) proposed a link between the longitudinal relaxation time of a water-saturated rock plug and the porosity for permeability estimation \( k = \phi T_1^2 \). An improvement provided by Kenyon et al (1986), suggested the permeability to be better estimated by \( \phi^4 T_1^2 \).

Using the bulk \( T_1 \) data obtained for the water-saturated sandstone plugs (table 7.1) and the NMR porosity estimates calculated in section 7.2.2, NMR permeability estimates have been calculated using the above relationship. The estimates have been compared to permeability measurements obtained by fluid flow at a constant velocity (table 6.1) and are shown as a scatter plot in figure 7.3. The data compare very well, except for plug 18a, where the permeability is severely underestimated. This discrepancy is probably due to the fact that the fluid flow permeability estimates were performed on neighbouring plugs and in the case of plug 18a, the neighbouring plug has a much higher permeability.

![Figure 7.3 Scatter Plot Of NMR Permeability Versus Standard Technique Permeability For The Ten Sandstone Plugs, Using \( k = \phi^4 T_1^2 \)]
7.3 RELAXATION MEASUREMENTS AT LOW SATURATION

Previous relaxation time measurements on partially saturated rock plugs (section 6.2) indicate that standard desaturation techniques may leave bulk water trapped in dead-end or cut-off channels. This bulk water can dramatically affect the observed relaxation times and prevent accurate determination of the effect of pore surface relaxation. Therefore, to obtain the lowest saturation, the sandstone plugs used in this study were placed in a vacuum oven at 150\(^\circ\)C for 48 hours and allowed to return to room temperature in a pure nitrogen gas environment. Previous studies (Tittmann et al, 1980) on rock material have shown that even under these conditions, there is still monolayer water coverage on the rock pore surfaces.

NMR relaxation measurements were obtained for four of the rock plugs (12, 13, 14 and 15a) at the lowest saturation. Due to the very rapid decay rates, transverse relaxation rates were acquired directly from the free induction decay, following a sub-90\(^\circ\) r.f. pulse. A sub-90\(^\circ\) pulse length was required to ensure that the signal was not lost in the dead time following the r.f. excitation. Due to the extremely low signal to noise ratio, 50,000 averages were required for each bulk relaxation measurement, taking 5 hours in total for each rock plug.

Assuming that the water saturation in the four rock plugs is monolayer coverage, the observed NMR relaxation rates are directly related to the surface relaxivity by (section 2.6.1)

\[
\frac{1}{T_{1,2}} = \frac{\rho_{1,2}}{\lambda}
\]

(7.3)

where \( \lambda \) is the thickness of one monolayer of water on the pore surfaces (\( \lambda = 3 \text{\AA} \)). This allows \( \rho_1 \) and \( \rho_2 \) to be unambiguously estimated. The calculated surface relaxivities for these ‘monolayer’ measurements are shown in table 7.4.
The 'monolayer' pore surface relaxivity estimates are comparable with measurements made on fully saturated rock plugs, where prior knowledge of the pore size distribution was required (Howard et al, 1990). Unfortunately, at this low saturation it was not known if the NMR signal was partially due to protons within the actual sandstone grains, or if the water coverage was indeed a monolayer and equation 7.3 is applicable. The results are therefore discussed in more detail in section 7.5.3, where they are compared with NMR measurements made on the same sandstone plugs at intermediate saturations.

### 7.4 RELAXATION MEASUREMENTS AT INTERMEDIATE SATURATIONS

Intermediate rock plug saturations were reached using the partial saturation techniques discussed in chapter 6. At each saturation stage, bulk T1 and T2 measurements were obtained using the CPMG and inversion recovery sequences, with r.f. pulse gaps appropriate to the expected relaxation times.

For rock plug saturations in the range 0.3 to 20%, the initially 'dry' plug were placed in the humidity chamber (section 6.4.1) and the partially sealed samples allowed to saturate by vapour diffusion processes. This technique was applied until the vapour percolation threshold for each plug was reached (section 6.2). Rock plug saturations in the range 20 to 80% were obtained using the water bath

<table>
<thead>
<tr>
<th>Rock Plug</th>
<th>$\rho_1$ 'monolayer' (x 10^3 cm/s)</th>
<th>$\rho_2$ 'monolayer' (x 10^3 cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>13</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>15a</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 7.4 Pore Surface Relaxivity Estimates (±30%) From 'Monolayer' Relaxation Data
(section 6.4.2), with the samples allowed to saturate by capillary processes. At various stages during both saturation techniques, the samples were sealed and the water within them allowed to spatially equilibrate. The water uptake and subsequent equilibration was monitored using NMR profiling supported by gravimetric analysis. Following water equilibration, the NMR profiles obtained for plug 2 (figure 7.4a) show a fairly uniform increase of spatial magnetisation, which is typical for most of the sandstone plugs, whereas plug 7a (figure 7.4b) exhibits a distinct non-uniformity of spatial magnetisation over the same saturation range. This non-uniformity is more apparent at the higher rock plug saturations (including full saturation) and as such, is thought to be due to localised regions of differing pore sizes and porosity, rather than a failure in the partial saturation technique to uniformly saturate similar size pores. This spatial non-uniformity is also found in plugs 5 and 13.

The longitudinal and transverse relaxation times calculated at each saturation stage show a steady increase of $T_1$ and $T_2$ with increasing saturation, although the dependence is not linear. This is undoubtedly due to preferential filling of the smaller pores and pore throats at the lower saturations. Figures 7.5 to 7.8 show the observed relaxation data versus saturation of the ten sandstone plugs (including the relaxation data obtained at full saturation in section 7.2). The data is plotted against log-log scales to allow ease of viewing and the solid lines are theoretical fits, which are discussed in more detail in section 7.5. The relaxation data for plugs 2 and 18a are shown in more detail as they display typical behaviour for the ten sandstone plugs, with a sharp kink in the relaxation time saturation dependence clearly visible. This change in the gradient is thought to represent the filling of the smaller pores and pore throats, which are known to dominate relaxation at low saturation (pendular state). Some of the rock plugs (12, 15a and 18a) show further variations in the gradient at higher saturation, which is thought to be due to the filling of the intermediate size pores. The ratio of longitudinal and transverse relaxation ($T_1/T_2$) remains fairly constant and the corresponding alpha values are comparable throughout the saturation range. The small ratio of $T_1$ and $T_2$ ($T_1/T_2 \approx 2.3$) is common in the study of saturated reservoir plugs and is thought to indicate that paramagnetic impurities, rather than dipole-dipole effects, dominate.
surface relaxation (section 2.6.1.5). At higher saturation, water molecules exist in pores with a variety of sizes which leads to a wide distribution of relaxation times. This corresponds to a low alpha value, typically 0.6. The alpha values increase towards unity as the saturation is decreased. At low saturation, the pore size and geometry is not expected to affect the relaxation rate so that a single relaxation time should be observed. This corresponds to an alpha value of one. It is curious however that in no case does alpha reach unity, and this is discussed further in the model described in section 7.5.

Figure 7.4 Saturation Profiles Following Water Equilibration In
a) Plug 2 And b) Plug 7a
Figure 7.5 Plug 2 Bulk Relaxation Data With Theoretical Fit

Figure 7.6 Plug 18a Bulk Relaxation Data With Theoretical Fit
Figure 7.7 Bulk Relaxation Data With Theoretical Fits
For Plugs 5, 6a, 7a And 10a
Figure 7.8 Bulk Relaxation Data With Theoretical Fits
For Plugs 12, 13, 14 And 15a
7.4.1 SPATIALLY RESOLVED RELAXATION MEASUREMENTS

As a comparison to the bulk relaxation data, $T_1$ relaxation weighted profiles have been acquired during the partial saturation techniques, with non-uniform rock plug spatial saturations. Using gravimetric analysis and by integrating under each profile, the observed spatial magnetisations have been converted into spatial saturations across each plug. This has allowed the calculated $T_1$ relaxation times to be correlated with saturation. The spatially resolved data has advantages over the bulk relaxation study, in that many relaxation measurements are obtained from each $T_1$ weighted data set, and there is no need to wait for the water within the plugs to spatially equilibrate between experiments. It has not been necessary to obtain $T_2$ weighted profiles (which are technically more difficult), as the constant $T_1/T_2$ ratio shown in the bulk relaxation study, suggests they would be directly related to $T_1$ and no additional information would be gained.

For spatial saturations in the range 2 to 12%, the initially 'dry' rock plugs were placed in the humidity chamber for 45 hours. Rock plug spatial saturations in the range 12 to 60%, were obtained using the water bath saturation technique for 2 hours. Depending on the expected range of relaxation times, $T_1$ weighted profiles were acquired along the length of each plug using either the repetitive pulse or inversion recovery broadline gradient echo techniques (section 3.3.5.2).

There is generally good agreement between the spatial and bulk $T_1$ relaxation data (figures 7.9 to 7.13), although a few of the rock plugs show regions along the saturation gradient of higher than expected saturation (figure 7.12 for plug 13). These regions have correspondingly smaller values of $T_1$ and have led to the conclusion that the water covers the pore surface in a layer of uniform thickness, independent of pore size and the locally high saturations correspond to regions of smaller pores. If this were not the case and the regions of high local saturation were due to excessive local filling of average size pores, then the $T_1$ values would not be correspondingly reduced and, at low saturation, the alpha values would not remain close to unity, but would rather decrease towards values seen at full saturation.
Figure 7.9 Spatial $T_1$ Relaxation Data For Plugs 2 And 5 With Theoretical Fits And Corresponding NMR Profiles
Figure 7.10 Spatial $T_1$ Relaxation Data For Plugs 6a And 7a With Theoretical Fits And Corresponding NMR Profiles
Figure 7.11 Spatial $T_1$ Relaxation Data For Plugs 10a And 12 With Theoretical Fits And Corresponding NMR Profiles
Figure 7.12 Spatial $T_1$ Relaxation Data For Plugs 13 And 15a With Theoretical Fits And Corresponding NMR Profiles
Figure 7.13 Spatial $T_1$ Relaxation Data For Plugs 14 And 18a With Theoretical Fits And Corresponding NMR Profiles
7.5 THE FAST DIFFUSION MODEL

To explain the dependence of relaxation on saturation observed in both the bulk and spatially resolved studies, a model has been developed incorporating current fast diffusion relaxation theory, which includes the known pore size distribution and allows for a range of surface relaxation strengths. It is generally accepted that in the fast diffusion limit where pore surface relaxation effects dominate the total NMR spin relaxation, the $T_1$ and $T_2$ relaxation rates are given by

$$\frac{1}{T_{1,2}} = \left[1 - \frac{\lambda S}{V}\right] \frac{1}{T_{\text{Bl},2}} + \rho_{1,2} \frac{S}{V} \quad (7.4)$$

where $S/V$ is the surface (S) to volume (V) ratio of the pore space, $T_{\text{Bl},2}$ is the bulk spin-lattice (1) and spin-spin (2) fluid relaxation rate, $\lambda$ is the thickness of the surface relaxing layer (generally a monolayer of water, $3\,\text{Å}$) and $\rho_{1,2}$ is the appropriate surface relaxivity. Equation 7.4 has been used to model the current data assuming an interconnected space of spherical pores as an approximation for the pore space. If $h$ is the thickness of the water layer covering the surface of the rock, and $r_i$ is the radius of the $i$th pore, then the volume of water in the pore is $v_i = 4/3\pi(3r_i^2h - 3r_ih^2 + h^3)$. The surface area in contact with the rock is $s_i = 4\pi r_i^2$. Hence for the pore in question

$$\frac{1}{T_{1,i}} = \left[1 - \frac{\lambda s_i}{v_i}\right] \frac{1}{T_{\text{Bl},2}} + \rho_{1,2} \frac{s_i}{v_i}$$

$$= \left[1 - \frac{3\lambda r_i^2}{(3r_i^2h - 3r_ih^2 + h^3)}\right] \frac{1}{T_{\text{Bl},2}} + \left[\frac{3\rho_{1,2} r_i^2}{(3r_i^2h - 3r_ih^2 + h^3)}\right] \quad (7.5)$$

The water layer thickness, $h$, is independent of pore size and depends only on the local saturation, $S_w$, so that

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where the summations are over all the pores. The pore size distribution has been calculated by thin slice back scatter electron imaging (figure 6.2). The magnetisation observed at time t after a 90° r.f. pulse and for a surface layer thickness h, is given by

\[
M_h(t) = M_0 \sum_i v_i(h) \exp \left[ -\frac{t}{T_2^i(h)} \right]
\]

(7.7)

where \(M_0\) is proportional to the proton density per unit volume of water. \(T_2^i\) is given by equation 7.5. The observed magnetisation has been calculated as a function of t and for various h, and hence \(S_w\). The theoretical decay curves thus obtained have been fitted to stretched exponential functions to yield theoretical \(T_2\) and alpha values as a function of saturation. An analogous procedure in which

\[
M_h(t) = M_0 \sum_i v_i(h) \left( 1 - \exp \left[ -\frac{t}{T_1^i(h)} \right] \right)
\]

(7.8)

has been used to give theoretical \(T_1\) and alpha values.

7.5.1 PORE THROAT SIZE ESTIMATES

The first attempts to model the relaxation data proved unsuccessful. The discrepancy between the data and the model was thought to be due to the lack of pore throats in the pore size distribution data. Pore throats saturate first and dominate relaxation at low saturation. An iterative approach was therefore taken to fit rock plug relaxation data by varying an estimated average pore throat size and pore throat total volume.
Figure 7.14 shows experimentally measured values of $T_1$ and alpha as a function of saturation for plug 2, together with fits according to the model with and without the inclusion of pore throats. The improved quality of the fits with the pore throats is clearly evident, particularly for the alpha parameter, and the quality is maintained even at very low saturation. In obtaining these fits, the pore throats were assumed to be equal to 5% of the total pore volume and of mean diameter 1.6 μm.

![Figure 7.14 Bulk $T_1$ Relaxation Data And Alpha Values For Plug 2, Without The Estimated Pore Throat Size (Dashed Line) And With The Estimated Pore Throat Size (Bold Line)](image)

It should be noted that the diffusion study and petrophysical data included in chapter 6, indicate that the pore surfaces are not smooth (especially the illite affected plugs). This may lead to an underestimate of the pore surface area and could result in a slight underestimate of the pore throat size. The illite affect plugs
do not show correspondingly low pore throat sizes. This indicates that the effect of pore surface 'roughness' on the relaxation data is small.

Considering all ten rock plugs, the estimated average pore throat sizes show good correlation with the saturations measured at the vapour percolation threshold (Figure 7.15). At this threshold saturation (table 6.2), the rapid vapour phase transport ceases. The threshold is thought to be due to the blocking of the pore throats with the build-up of surface water and a check can be made on the estimate of pore throat size from the fitting procedure. The pore size should be $2h_{vpt}$, where $h_{vpt}$ is the water layer thickness corresponding to the saturation at the vapour percolation threshold. It is found that values at $2h_{vpt}$ are in excellent agreement with the pore throat sizes, as shown in table 7.5. The correlation of pore throat size with permeability is not as good and suggests that although the pore throats have an effect on permeability, the pore connectivity, pore size and porosity also contribute, and the measured permeability is a function of all of these. Across the ten rock plugs, the pore throat volume was estimated to have a mean value of 4.5% of the total volume, with a standard deviation of 0.9% and a mean pore throat diameter of 0.75 μm.

![Figure 7.15 Correlation Between Vapour Percolation Threshold Saturation And Estimated Average Pore Throat Size](image-url)
Table 7.5 Pore Throat Size Estimates Using NMR Relaxation Data And The Calculated Water Thickness At The Vapour Percolation Threshold

### 7.5.2 EFFECT OF VARYING SURFACE RELAXIVITY

The surface relaxivities ($\rho_1$ and $\rho_2$) are essentially multipliers to the longitudinal and transverse relaxation rates, except at the very high saturations, where the bulk fluid relaxation rates (which remain constant) become more dominant (figure 7.16). The surface relaxivities have therefore been systematically varied to achieve the best fit to the bulk NMR relaxation data. The observed alpha values throughout the saturation range and for all the sandstone plugs never reach unity (single exponential decay). This is thought to be due to the dominating effect of individual surface sites on the pore surfaces at low saturation, combined with variations of paramagnetic impurity concentration within the plugs. The decay of magnetisation at a surface site may itself be nonexponential (section 2.6.1.5), but is usually averaged out when the total number of fluid molecules in a pore is large compared to the number of molecules on the pore surface (appendix 1). At low saturation this is not the necessarily the case. To account for the multi-exponential decay of
magnetisation at low saturation, it must therefore be assumed that there is some small variation of surface relaxivity within the rock plugs. Within the model, this has been achieved by assuming a small gaussian distribution of pore surface relaxivity values. This natural variability accounts for the effect of localised surface sites within each individual pore and allows different pores of the same size to have different surface relaxivities due local variations in paramagnetic impurity concentration. The best width of the gaussian was found to be 30% of the central value of $\rho$ and was kept constant for all the rock plugs.

**Figure 7.16** Effect Of Varying $\rho_2$ On Theoretical Fit To Plug 10a

### 7.5.3 PORE SURFACE RELAXIVITY ESTIMATES

The average pore surface relaxivities for the rock plugs have been calculated using the fast diffusion model and are listed in table 7.6. The results compare very well with previous studies on fully saturated rock plugs (Howard et al, 1990) with an average value of $\rho_1 = 3.1 \times 10^{-3}$ cm/s. There is generally good agreement with the bulk and spatially resolved relaxation estimates.
The values of pore surface relaxivity obtained directly from the relaxation time measurements at low water saturation (table 7.4) compare very well with the relaxivity estimates included here. This suggests that the low water saturation does indeed correspond to near monolayer water coverage on the pore surfaces and that equation 7.3 is applicable. The results also suggest that for the sandstone plugs used in this study, the NMR signal arising directly from protons within the actual sand grains is negligible or its transverse decay rate is too rapid to be detected.

Care has to taken in the interpretation of the monolayer relaxation measurements, due to the possible nonexponential decay of the magnetisation from paramagnetic surface sites. At monolayer coverage, alpha values have not been obtained, but measurements at slightly higher saturation do indicate that the decay is nonexponential.

<table>
<thead>
<tr>
<th>Rock Plug</th>
<th>$\rho_1$ 'bulk' (x 10^{-3} cm/s)</th>
<th>$\rho_1$ 'spatial' (x 10^{-3} cm/s)</th>
<th>$\rho_2$ 'bulk' (x 10^{-3} cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>11.9</td>
<td>11.0</td>
<td>18.7</td>
</tr>
<tr>
<td>5</td>
<td>2.4</td>
<td>2.8</td>
<td>7.7</td>
</tr>
<tr>
<td>6a</td>
<td>2.5</td>
<td>2.7</td>
<td>6.5</td>
</tr>
<tr>
<td>7a</td>
<td>2.7</td>
<td>3.4</td>
<td>6.8</td>
</tr>
<tr>
<td>10a</td>
<td>4.6</td>
<td>4.4</td>
<td>8.4</td>
</tr>
<tr>
<td>12</td>
<td>1.9</td>
<td>1.9</td>
<td>3.7</td>
</tr>
<tr>
<td>13</td>
<td>1.2</td>
<td>1.3</td>
<td>3.4</td>
</tr>
<tr>
<td>14</td>
<td>0.9</td>
<td>0.9</td>
<td>2.2</td>
</tr>
<tr>
<td>15a</td>
<td>1.0</td>
<td>1.0</td>
<td>2.1</td>
</tr>
<tr>
<td>18a</td>
<td>3.9</td>
<td>4.0</td>
<td>7.7</td>
</tr>
</tbody>
</table>

Table 7.6 Pore Surface Relaxivity Estimates (±5%) From Bulk And Spatially Resolved NMR Relaxation Data
The values of surface relaxivity combined with the known pore sizes have been used to verify the fast diffusion assumption, the relevant condition is (section 2.6.1.1)

\[ \frac{\rho_{1,2} a}{D} \ll 1 \]  

(7.9)

where \( a \) is the pore size and \( D \) is the water self diffusion coefficient in the pore space (\( D = 2.5 \times 10^{-5} \, \text{cm}^2\text{s}^{-1} \), at room temperature). Using the calculated values of \( \rho_{1,2} \) and the known pore sizes, suggests that all but the very largest pores in three of the plugs (2, 10a, 18a) are in the fast diffusion regime. This finding is in very good agreement with the relaxation time measurements obtained in section 7.2.1, where the same three rock plugs were found to have a slight relaxation time dependence on temperature. Appropriate relaxation equations (equation 4.1) which account for intermediate diffusion in the larger pores of the three rock plug have been used and only change the calculated full saturation relaxation rates by about 5%. This suggests that the fast diffusion model is a good approximation, even in such cases.

### 7.6 CONCLUSION

The proton spin-lattice and spin-spin relaxation times have been measured over a broad range of saturations in ten otherwise well characterised sandstone rock plugs. The results have been shown to be in excellent agreement with the fast diffusion model of relaxation. The first measurements of surface relaxivity of sandstone rock plugs made at low saturation have been shown to be in agreement with values inferred from fully saturated cores but in disagreement with values from silica glasses. This last observation should not, perhaps, be unexpected since the systems are very different. It has been shown that at low saturations, the relaxation is very sensitive to small pores and indeed to pore throats. Thus, the results have permitted an estimate of pore throat size and total volume by NMR means. The throat size so obtained has been shown to correlate very well with the vapour percolation threshold.
DISCUSSION

The main objective of the work carried out in this thesis was to continue the programme of research in applications of NMR to fluid saturated rock, with special emphasis on the study pore fluid relaxation mechanisms and diffusion processes and the ability to relate such analysis to petrophysical parameters of interest to reservoir engineers. Secondary objectives were to develop NMR techniques for visualising short $T_2$ fluid components and to separately image immiscible fluids within preserved rock cores and during fluid flow experiments. These objectives are discussed in more detail below, along with proposed areas of future study.

Proton relaxation time measurements of water-saturated rock over a broad range of saturations were shown to be in excellent agreement with the fast diffusion model of relaxation. The model was shown to be robust even down at very low saturation, where direct measurements of surface relaxivity were obtained. The measurements were shown to agree with values inferred from fully saturated cores, but in disagreement with values from silica glasses. This was attributed to the dominant effect of paramagnetic impurities on the grains of sandstone cores. Even so, there is still no conclusive evidence that paramagnetic impurities are the dominant relaxation mechanism in rock. Future studies should therefore concentrate on investigating the effect of paramagnetic impurity concentration, with a detailed relaxation study on porous systems which have a known paramagnetic concentration.

Water diffusion studies on partially saturated rock were shown to be in excellent agreement with a model based on a combination of water phase and vapour phase transport. The vapour concentration was shown to increase exponentially with increasing saturation (below the vapour percolation threshold), due to the preferential wetting nature of the rock. From the model, measurements of the surface water diffusion coefficient and the exponential constant for the increase in vapour concentration were obtained. These measurements have been shown to be related to the ‘roughness’ of the pore surfaces. Future studies in this area should
concentrate on extending the diffusion model to rock plug water saturations above the vapour percolation threshold, where capillary effects have been shown to enhance the water ingress.

Selective imaging of reservoir fluids within preserved rock core samples was achieved using $T_1$ weighted MRI techniques. The $T_1$ suppression in these heterogeneous cores was enhanced by lowering the temperature of the rock, thus exploiting the difference in dominant relaxation mechanisms of the two core fluids. A model was developed which related this temperature dependence to fast and intermediate diffusion relaxation theory. Quantitative data was not obtained due to the long echo time required by the whole body spectrometer and the similar relaxation characteristics of the two reservoir fluids. Future studies of preserved rock material should therefore concentrate on the application of broadline imaging methods and the feasibility of fluid $T_1$ suppression at high temperature, where the temperature dependence of the oil relaxation time can be exploited more effectively.

Fluid flow processes within reservoir rock were investigated, using broad line imaging methods to obtain quantitative data from which individual phase saturations could be directly obtained. The study was performed on homogeneous sandstone samples which exhibited typical NMR relaxation behaviour expected in water wet rock. Future broadline imaging studies should concentrate on reservoir rock with short transverse relaxation times ($T_2 < 3$ ms, such as shaley rock), where conventional imaging techniques are totally inappropriate. High temperature immiscible flood imaging was successfully demonstrated, but to effectively understand flow processes under reservoir conditions, the addition of high pressure is also needed and should be included in any future work. The flow of polymers and surfactants which are used during enhanced oil recovery have been studied previously using standard liquid state NMR imaging techniques (Williams, 1992). Using broadline imaging methods, the study of such chemicals under flow could provide quantitative measurement of fluid distribution during enhanced oil recovery techniques.
APPENDIX 1

This appendix describes a simple model (proposed by Kleinberg et al, 1994) which shows that if the number of fluid molecules at relaxing surface sites is small compared to the total number of molecules, then the detailed behaviour of the magnetisation does not enter into the overall decay. The theory is applicable to the fast diffusion (weak killing) regime, but similar considerations hold for the slow diffusion (strong killing) regime, except that the additional complication of solving a diffusion equation must be considered.

In the model, there are two populations of molecules, labelled by subscripts s and b, corresponding to the surface relaxing sites and the bulk sites. Let \( m_s(t) \) and \( m_b(t) \) be the magnetisations of these two populations at time \( t \). The bulk decay of magnetisation has been neglected as it only has a small effect on the observed pore fluid relaxation time. In general, \( m_s(t) \) and \( m_b(t) \) will satisfy rate equations of the form

\[
\frac{d m_s(t)}{dt} = -\frac{1}{\tauM} m_s(t) + \frac{\varepsilon}{\tauM} m_b(t) - \int_{-\infty}^{t} R(t-t') m_s(t') \, dt' \quad (A1.1)
\]

\[
\frac{d m_b(t)}{dt} = \frac{1}{\tauM} m_s(t) - \frac{\varepsilon}{\tauM} m_b(t) \quad (A1.2)
\]

\( \varepsilon = n_M \lambda S/V \) is the ratio of the number of molecules at surface relaxing sites to the total number of molecules, where \( \lambda \) is the surface thickness, \( S \) is the pore surface area and \( V \) is the pore volume. For fully saturated rock, \( \varepsilon \) is on the order of \( 10^{-6} \); \( \tauM \) is the residence time at a surface site. \( R(t) \) is a relaxation function that characterises the decay process at a surface site. If the decay at a surface site is exponential, then the Laplace transform \( \bar{R}(s) \) is a constant. In general, the decay at a surface site is not exponential, but may be represented by having a spectrum of relaxation rates \( P(\Gamma) \), so that the decay site is given by
\[
\int_0^\infty P(\Gamma) e^{-\Gamma t} \quad (A1.3)
\]

In this case, \( \bar{R}(s) \) is given by

\[
\frac{1}{s + \bar{R}(s)} = \int_0^\infty \frac{P(\Gamma)}{s + \Gamma} \quad (A1.4)
\]

In particular, \( \bar{R}(0) = 1/T_M \), where \( T_M \) is the mean lifetime of a relaxing site.

After a Laplace transformation of the rate equations, with the initial conditions \( m_0(0) = \varepsilon, \ m_0(0) = 1 - \varepsilon \), linear equations are obtained which can be solved for the Laplace transform of the total magnetisation

\[
\bar{m}(s) = \frac{s + \tau_M^{-1} + \bar{R}(s)}{s^2 + s[\tau_M^{-1} + \bar{R}(s)] + \varepsilon \bar{R}(s) \tau_M^{-1}} \quad (A1.5)
\]

The Laplace transform of the above equation will in general lead to nonexponential decay. However, for \( \varepsilon \to 0 \), the decay will be exponential with negligible deviations. If \( \varepsilon = 0 \), then \( \bar{m}(s) = 1/s \), which consists of a single pole at the origin, corresponding to no decay in the absence of surface sites. If \( \varepsilon \ll 1 \), then the pole at the origin moves to slightly negative values of \( s \) in the Laplace domain. The position of the pole is given by

\[
s = \frac{\varepsilon \bar{R}(s) \tau_M^{-1}}{s + \tau_M^{-1} + \bar{R}(s)} \quad (A1.6)
\]

Assuming some reasonable analytic properties of \( \bar{R}(s) \), the position of the root near \( s = 0 \) can be found as an expansion in \( \varepsilon \),

\[
s_0 = -\frac{\varepsilon \bar{R}(0) \tau_M^{-1}}{\tau_M^{-1} + \bar{R}(0)} + O(\varepsilon^2) \quad (A1.7)
\]

or equivalently
The residue of this pole can similarly be shown to be $1 - O(\varepsilon)$. After Laplace transformation, this pole gives rise to a simple exponential decay, whose weight is almost one in the limit that $\varepsilon$ is very small. The decay of $m(t)$ therefore can be seen to have two parts: a simple exponential, with weight $1 - O(\varepsilon)$ and decay rate $|s_0|$ and an additional decay with weight $O(\varepsilon)$ that is in general nonexponential. Furthermore, the form of $\tilde{m}(s)$ shows that this nonexponential decay has a lifetime set by the lifetime at a surface site $T_M$ and the residence time $\tau_M$, which are both much smaller than $1/|s_0|$ in the $\varepsilon \to 0$ limit.

Thus, for $\varepsilon \to 0$, which corresponds to having very few surface sites compared to the number of bulk molecules, and regardless of the detailed behaviour at a surface site, the overall decay of the magnetisation is single exponential with decay rate

\[
\frac{1}{T_{1,2}} = \frac{n_M \lambda S}{V} \frac{1}{T_{1M,2M} + \tau_M} \tag{A1.9}
\]
REFERENCES


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