

RICE UNIVERSITY

**Transverse Relaxation in Sandstones due to the
effect of Internal Field Gradients and
Characterizing the pore structure of Vuggy
Carbonates using NMR and Tracer analysis**

by

Neeraj Rohilla

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

APPROVED, THESIS COMMITTEE:

George J. Hirasaki, A. J. Hartsook Professor, Chair
Chemical and Biomolecular Engineering

Walter G. Chapman, William W. Akers Chair
Chemical and Biomolecular Engineering

Pedro Alvarez,
George R. Brown Professor of Engineering
Civil and Environmental Engineering

Houston, Texas

February, 2013

Contents

List of Illustrations	vi
List of Tables	xv
Abstract	1
1 Introduction	4
2 Basic Principles and Literature Review	9
2.1 Basic Principles	9
2.1.1 Pulse tipping and Free Induction Decay	10
2.1.2 Longitudinal (T_1) Relaxation	11
2.1.3 Transverse (T_2) Relaxation	12
2.1.4 Diffusion-Induced Relaxation	14
2.1.5 Surface Relaxation and Pore size distribution	15
2.2 Literature Review	16
2.2.1 Diffusion Coupling	17
2.2.2 Inhomogeneities of the applied magnetic field	20
2.2.3 Un-restricted or Free Diffusion	21

2.2.4	Restricted Diffusion	25
2.3	Clay minerals in sandstones	29
2.3.1	Formation of clay minerals in sandstones	30
2.3.2	Morphology of authigenic clays	31
2.3.3	Effect of grain coating chlorite on formation evaluation . .	36
3	Modeling Internal Field Gradients in clay-lined sand-	
	stones	40
3.1	Simulations for FID and CPMG pulse sequence	48
3.1.1	Governing equations	48
3.1.2	Boundary and Initial conditions	49
3.2	Dimensionless groups and their significance	50
3.3	FID results and discussion	53
3.4	CPMG results and discussion	56
3.5	Simulations for other geometrical parameters	68
3.6	Conclusions	73
4	Characterization of pore structure in vuggy carbon-	
	ates	74
4.1	NMR Experiments	78
4.2	NMR T_2 Relaxation and pore size distribution	79

4.3	Calculating specific surface area of the rock from NMR T_2 distribution	88
4.4	Tracer Analysis	92
4.5	Recovery Efficiency and Transfer Between Flowing And Stagnant Streams	98
4.6	Parameter estimation from experimental data of tracer concentration	99
4.7	Setup for the Tracer flow experiments and the data acquisition protocol	100
4.7.1	Reproducibility of tracer floods on core samples	101
4.8	Tracer Flow Experiments	102
4.8.1	Validation with sandpacks and homogeneous rock system .	102
4.9	Characterization of heterogeneous samples	103
4.9.1	Tracer flow experiments on 1.5 inch diameter samples . . .	104
4.10	Flow experiments on full sized cores	118
4.11	Static and Dynamic adsorption of surfactant	125
4.11.1	Static adsorption of surfactant on the crushed rock powder	126
4.11.2	Dynamic adsorption of the surfactant on the rock surface .	128
5	Conclusions and Future Work	133
5.1	Conclusions	133

5.1.1	Modeling internal field gradients for claylined pores	133
5.2	Pore structure of vuggy carbonates	134
5.2.1	NMR Chracterization	134
5.2.2	Characterization of the pore space by Tracer Analysis . . .	135
5.3	Future Work	136
5.3.1	Dynamic adsorption model for heterogeneous systems . . .	136
A Manual on using bromide ion sensitive electrode in		
laboratory experiments		139
 Bibliography		 153

Illustrations

2.1	Chlorite coating inhibiting quartz overgrowth	30
2.2	(A) Stacked plates of kaolinite in porous sandstone (face-to-face arrangement and pseudohexagonal outlines of individual plates) (B) Vermicular authigenic kaolinite in porous sandstone	32
2.3	SEM image of illite, showing lath-like projections which extend from one grain to another	33
2.4	SEM image of illite, showing delicate fiber like structure	34
2.5	SEM images of grain coating chlorite at different magnifications. The images on left and right are at 50 and 400 magnifications respectively	34
2.6	SEM images of grain coating chlorite at different magnifications. The images on left and right are at 1,000 and 10,000 magnifications respectively	35
2.7	Chlorite clay exhibiting delicate rosette like morphology	35
2.8	Field lines for the induced magnetic field for a clay lined macropore	38

2.9	Contours of dimensionless magnetic field gradient for a claylined macropore	39
3.1	T_1 and T_2 relaxation time spectrum for North Burbank core sample saturated with brine solution	41
3.2	Schematic of a macropore lined with clay flakes	42
3.3	Schematic of a clay-lined pore	43
3.4	Schematic of the simulation domain	44
3.5	(a) Field lines of the total magnetic field B due to the clay flake in a homogeneous field B_0 (b) Field lines of the induced magnetic field B_δ due to the clay flake in a homogeneous field B_0	45
3.6	(a) Contour lines of the z component of induced field (b) Contours of dimensionless gradient due to the presence of clay flake	45
3.7	Schematic of mesh used to resolve large values of gradients around the corner	47
3.8	Decay of the magnitude of magnetic moment versus dimensionless time for different value of $\zeta = \frac{\tau_R}{\tau_\omega}$	54
3.9	Comparison of FID decay of magnetization for different values of $\zeta = \frac{\tau_R}{\tau_\omega}$ and for the case when no diffusion is present	56

3.10	Plot for CPMG decay of magnitude of magnetization for dimensionless echo spacing, $\delta\omega\tau_E = 5.0$ and $\zeta = \delta\omega\tau_R = 100$. Geometrical parameters used are: aspect ratio of macropore (η) $= 1$, aspect ratio of the clay flake (λ) $= 1$ and microporosity fraction (β) $= 0.5$	57
3.11	Bi-exponential plot for $\zeta = 2681$, $\tau_E^* = 20.0$	59
3.12	Bi-exponential plot for $\zeta = 5180$, $\tau_E^* = 20.0$	59
3.13	Bi-exponential plot for $\zeta = 10000$, $\tau_E^* = 20.0$	60
3.14	Representation of different relaxation regimes as function of three timescales	61
3.15	A plot of secular relaxation rate versus $\delta\omega\tau_R$ for different values of dimensionless half-echo spacing ($\delta\omega\tau_E$). Geometrical parameters used are: aspect ratio of macropore (η) $= 1$, aspect ratio of the clay flake (λ) $= 1$ and microporosity fraction (β) $= 0.5$	64
3.16	Plot of secular relaxation rate as function of $\delta\omega\tau_E$ for different values of $\delta\omega\tau_R$. Geometrical parameters used are: aspect ratio of macropore (η) $= 1$, aspect ratio of the clay flake (λ) $= 1$ and microporosity fraction (β) $= 0.5$	65
3.17	Plot of secular relaxation rate as function of $\delta\omega\tau_E$ for different values of $\delta\omega\tau_R$ demonstrating various echo-spacing dependence in different regimes	66

- 3.18 Contours of secular relaxation rate as a function of $\delta\omega\tau_R$ for different values of $\delta\omega\tau_E$. Geometrical parameters used are: aspect ratio of macropore (η) = 1, aspect ratio of the clay flake (λ) = 1 and microporosity fraction (β) = 0.5 67
- 3.19 A plot of secular relaxation rate versus $\delta\omega\tau_R$ for different values of dimensionless half-echo spacing ($\delta\omega\tau_E$). Geometrical parameters used are: aspect ratio of macropore (η) = 10, aspect ratio of the clay flake (λ) = 10 and microporosity fraction (β) = 0.5 68
- 3.20 A plot of secular relaxation rate versus $\delta\omega\tau_R$ for different values of dimensionless half-echo spacing ($\delta\omega\tau_E$). Geometrical parameters used are: aspect ratio of macropore (η) = 20, aspect ratio of the clay flake (λ) = 20 and microporosity fraction (β) = 0.5 70
- 3.21 A plot of secular relaxation rate versus $\delta\omega\tau_R$ for different values of dimensionless half-echo spacing ($\delta\omega\tau_E$). Geometrical parameters used are: aspect ratio of macropore (η) = 50, aspect ratio of the clay flake (λ) = 50 and microporosity fraction (β) = 0.5 71
- 3.22 A plot of secular relaxation rate versus $\delta\omega\tau_R$ for different values of dimensionless half-echo spacing ($\delta\omega\tau_E$). Geometrical parameters used are: aspect ratio of macropore (η) = 100, aspect ratio of the clay flake (λ) = 20 and microporosity fraction (β) = 0.1 72

4.1	Core ID-1; Length = 9.0 inches, Diameter = 3.5 inches; Fractured, low porosity, No apparent vugs, uniform cylindrical shape	75
4.2	Core ID-2; Length = 5.5 inches, Diameter = 3.5 inches; Vuggy, well cored, uniform cylindrical shape	76
4.3	Core ID-3; Length = 3.5, 6 inches, Diameter = 3.5 inches; Very vuggy, well cored, uniform cylindrical shape	76
4.4	Core ID-4; Length = 4 inches, Diameter = 4.0 inches; Some big vugs, well cored	77
4.5	Core ID-5; Length = 4.0 inches, Diameter = 4.0 inches; Breccia, very vuggy and heterogeneous	77
4.6	A comparison of before (shown at left) and after (shown at right) cleaned pictures for a core-plug (Plug ID: 3V)	80
4.7	A comparison of before (shown at left) and after (shown at right) cleaned pictures for a core-plug (Plug ID: 2V)	81
4.8	T_2 relaxation time spectrum for 100 % brine saturated core-plug (Plug ID: 3V)	83
4.9	T_2 relaxation time spectrum for 100 % brine saturated core-plug (Plug ID: 2V)	84
4.10	T_2 relaxation time spectrum for 100 % brine saturated core-plug (Plug ID: 2VA)	84

4.11 T_2 relaxation time spectrum for 100 % brine saturated core-plug (Plug ID: 1H)	85
4.12 T_2 relaxation time spectrum for 100 % brine saturated core-plug (Plug ID: 1HA)	85
4.13 Permeability versus T_2 Log mean for various core samples	86
4.14 Permeability versus T_2 Log mean while using T_2 cut off of 750 msec for various core samples	87
4.15 T_2 relaxation time and S/V spectrum for 100 % brine saturated core-plug (Plug ID: 1H)	90
4.16 T_2 relaxation time spectrum for 100 % brine saturated crushed rock powder	91
4.17 A bar chart for the specific surface area of several core plugs	91
4.18 Schematic of the pore system containing interconnect flow channels, touching/isolated vugs and stagnant/dead end pores	92
4.19 Effluent concentration versus pore volume throughput for a set of dimensionless parameters	97
4.20 Plots of effluent concentration and recovery efficiency as a function of pore volume throughput illustrating importance of mass transfer between flowing and stagnant streams	108
4.21 A comparison of synthetic data with and without noise used for benchmarking parameter estimation algorithm	109

4.22	A comparison of transfer function for experimental data and fitted curve for parameter estimation	109
4.23	Comparison of fitted model parameters using the inversion routine when (A) Data at one flowrate is used and (B) When data at two flow rates is used	110
4.24	Effluent concentration versus pore volume throughput for 100 ppm and 10,000 ppm floods for similar values of the flowrates . .	111
4.25	Effluent concentration versus pore volume throughput for 100 ppm and 10,000 ppm floods for several values of the flowrates . .	111
4.26	Effluent concentration versus pore volume throughput for homogeneous and heterogeneous sandpacks	112
4.27	Effluent concentration and Recovery efficiency as a function of pore volume for homogeneous Silurian outcrop sample	113
4.28	(A) Transfer function for the fitted parameters (B) Effluent concentration and recovery efficiency for core plug 3V (diameter = 1.5 inch, length = 1.25 inch) at the flow rate of 15 ft/day and (C) The corresponding NMR T_2 distribution for the core plug 3V	114
4.29	(A) Transfer function for fitted parameters (B) Effluent concentration and recovery efficiency for core plug 1H (diameter = 1.5 inch, length = 2.25 inch) at the flow rate of 1.4 ft/day and (C) The corresponding NMR T_2 distribution for the core plug 1H	115

4.30 ((A) Transfer function for the fitted parameters (B) Effluent concentration and recovery efficiency for core plug 1.5D (diameter = 1.5 inch, length = 3 inch), (C) The corresponding NMR T_2 distribution for the core plug 1.5D	116
4.31 (A) Transfer function for the fitted parameters (B) Effluent concentration and recovery efficiency for core plug 1.5C (diameter = 1.5 inch, length = 3.5 inch), (C) The corresponding NMR T_2 distribution for the core plug 1.5B	117
4.32 Transfer functions for the fitted parameters for 3.5B, 3.5C and 3.5D rock samples	120
4.33 Effluent concentration and Recovery efficiency for the cases when strong mass transfer is observed. (A) Sample 3.5D with $1/M =$ 0.6 days and (B) Sample 4.0B with $1/M = 0.1$ days	121
4.34 Effluent concentration and Recovery efficiency for the cases when mass transfer is small. (A) Sample 3.5C with $1/M = 2.1$ days and (B) Sample 3.5B with $1/M = 4.3$ days	122
4.35 Calculated Effluent concentration and Recovery Efficiency for various interstitial velocities using parameters estimated from tracer flow experiments	124
4.36 Adsorption on NI blend on crushed powder rock with BET area of $1.5 \text{ m}^2/\text{gm}$	127

4.37	Adsorption of NI blend on a heterogeneous rock sample (A)	
	Comparison of the surfactant fast flood with tracer (B)	
	Comparison of the slow surfactant flood with tracer	130
4.38	A comparison of fast and slow surfactant floods showing	
	adsorption of NI blend on a heterogeneous rock sample	131

Tables

4.1	Comparison of porosity for different core-plugs	80
4.2	Summary of estimated model parameters from various tracer flow experiments for 1.5 inch diameter core samples	107
4.3	Summary of estimated model parameters from various tracer flow experiments for full core samples	125
4.4	Summary of both surfactant flood and loss of surfactant due to dynamic adsorption	132

ABSTRACT

Transverse Relaxation in Sandstones due to the effect of Internal Field
Gradients and Characterizing the pore structure of Vuggy Carbonates using
NMR and Tracer analysis

by

Neeraj Rohilla

Nuclear magnetic resonance (NMR) has become an indispensable tool in petroleum industry for formation evaluation. This dissertation addresses two problems.

- We aim at developing a theory to better understand the phenomena of transverse relaxation in the presence of internal field gradients.
- Characterizing the pore structure of vuggy carbonates.

We have developed a two dimensional model to study a system of claylined pore. We have identified three distinct relaxation regimes. The interplay of three time parameters characterize the transverse relaxation in three different regimes. In future work, useful geometric information can be extracted from SEM images and the pore size distribution analysis of North Burbank sandstone to simulate transverse relaxation using our 2-D clay flake model and study diffusional coupling in the presence of internal field gradients.

Carbonates reservoirs exhibit complex pore structure with micropores and macropores/vugs. Vuggy pore space can be divided into separate-vugs and touching-vugs, depending on vug interconnection. Separate vugs are connected only through interparticle pore networks and do not contribute to permeability. Touching vugs are independent of rock fabric and form an interconnected pore system enhancing the permeability. Accurate characterization of pore structure of carbonate reservoirs is essential for design and implementation of enhanced oil recovery processes. However, characterizing pore structure in carbonates is a complex task due to the diverse variety of pore types seen in carbonates and extreme pore level heterogeneity. The carbonate samples which are focus of this study are very heterogeneous in pore structures. Some of the sample rocks are breccia and other samples are fractured. In order to characterize the pore size in vuggy carbonates, we use NMR along with tracer analysis. The distribution of porosity between micro and macro-porosity can be measured by NMR. However, NMR cannot predict if different sized vugs are connected or isolated. Tracer analysis is used to characterize the connectivity of the vug system and matrix. Modified version of differential capacitance model of Coats and Smith (1964) and a solution procedure developed by Baker (1975) is used to study dispersion and capacitance effects in core-samples. The model has three dimensionless groups: 1) flowing fraction (f), 2) dimensionless group for mass transfer (N_M) characterizing the mass transfer between flowing and stagnant phase and 3) dimensionless

group for dispersion (N_K) characterizing the extent of dispersion. In order to obtain unique set of model parameters from experimental data, we have developed an algorithm which uses effluent concentration data at two different flow rates to obtain the fitted parameter for both cases simultaneously. Tracer analysis gives valuable insight on fraction of dead-end pores and dispersion and mass transfer effects at core scale. This can be used to model the flow of surfactant solution through vuggy and fractured carbonates to evaluate the loss of surfactant due to dynamic adsorption.

Chapter 1

Introduction

The ever increasing demand for energy worldwide is calling for accurate and sophisticated methods for evaluating petroleum formations. These approaches include seismic data analysis, various logging methods (such as wireline, acoustic, neutron density, gamma ray and nuclear magnetic resonance) and core analysis in laboratory. Nuclear magnetic resonance (NMR) has increasingly become an indispensable tool in the field of petroleum technology due to its numerous applications. NMR is applied for measurements of porosity, pore size distribution, permeability, viscosity, diffusion coefficient, residual oil and water saturation and free-fluid index (Kenyon 1997). The difference in NMR properties of different fluids is used as a basis for pore fluid identification. Different techniques based on Longitudinal (T_1) and Transverse (T_2) relaxation measurements are used for evaluating formation properties and reservoir fluid properties.

The estimation of bulk volume irreducible (BVI), free-fluid index (FFI), permeability and fluid type relies on the accurate interpretation of T_1 and T_2 relaxation. The NMR response in porous media is complicated due to various factors. The first of these is diffusional coupling between macropore and micropore. Fluid

molecules relax at the micropore surface and if the diffusion is fast (i.e. relaxation at the micropore surface is much slower compared to diffusional transport of molecules to the pore surface), whole pore relaxes at a single T_2 . Traditional methods for the interpretation of NMR data use the assumption of fast diffusion. However, if the surface relaxation is very fast or diffusion is slow, the diffusion is not sufficient to homogenize the relaxing molecules and both micro and macro pore decay at different T_2 (Anand and Hirasaki 2007a). In such cases, traditional methods to calculate free-fluid index like sharp cut off may give erroneous results (Straley, Morriss, Kenyon and Howard 1991). The extent of diffusional coupling and its effect on relaxation time spectrum is quantitatively analyzed by Anand and Hirasaki (2007a).

Inhomogeneities in the applied magnetic field significantly affect transverse relaxation. Magnetic field inhomogeneities can be either externally applied (by the logging tool) or internal field gradients. The applied magnetic field by the logging tool is only uniform near the center of the coils (Tarczon and Halperin 1985). Thus much of the sample volume could be exposed to a non-uniform magnetic field. Internal field gradients in the pore space are caused by the susceptibility contrast between solid matrix and the fluid filling the pore space. It is commonly assumed that these field gradients are caused by paramagnetic minerals such as iron, nickel or manganese which are frequently found in clays (Kleinberg, Kenyon and Mitra 1994).

Laboratory or field diffusion measurements by default assume that the spins can diffuse freely. This means that distribution of spins is Gaussian and that the diffusion is not limited by geometrical constraints. This is only true when the diffusion length ($l_d = \sqrt{D\tau}$) is smaller than the dephasing length ($l_g = (D\gamma g)^{1/3}$) and the size of the pore ($l_s = V/S$). Only in such instances, the formula of free diffusion regime developed by Neuman (1974) can be applied. When internal field gradients are higher or comparable to those applied by the logging tools, the use of free diffusion formula can overestimate the value of diffusion coefficient due to enhanced relaxation. In such cases, the diffusion based interpretation techniques for pore fluid identification could lead to erroneous results.

Another important consideration is that of restricted diffusion due to geometrical restrictions. At times short enough that most spins do not encounter the pore walls or experience a significant change in local gradient, we expect the protons to behave as if they are a part of infinite fluid medium. If the size of geometrical confinement is smaller than the diffusion length ($\sqrt{D\tau}$), the diffusion measurements are strongly affected by surface relaxation and the local field gradient resulting in a time-dependent value of effective diffusion coefficient.

In sedimentary rocks, a detailed understanding of transverse relaxation is not only the function of susceptibility contrast but also of the pore geometry. Hence, an accurate interpretation of transverse relaxation in principle, can give valuable insights about the pore fluid and the pore structure. In recent years,

the researchers have attempted to use the internal field gradients as a convenient way to deduce information about the micro-geometry of the formation such as pore connectivity, isolated pores and pore structure using the concept of decay due to diffusion in the internal field (DDIF) (Mitra and Sen 1992, Song et al. 2000, Song 2000, Song 2001, Chen and Song 2002, Song et al. 2002).

The interpretation of transverse relaxation is complicated when effects of spins self-diffusion in an inhomogeneous field and restricted geometry become dominant. So far, only simple cases of magnetic field inhomogeneities (linear, parabolic and cosine) have been taken into account in the context of restricted diffusion (Le Doussal and Sen 1992a, Grebenkov 2007). The combined effects of diffusion coupling, restricted diffusion and internal field gradients are not completely understood. A detailed understanding of combined effect of these phenomena will serve as a tool to better interpret NMR wells logs and enable us to accurately evaluate petroleum formations.

The second part of this study deals with characterizing vuggy carbonates. Carbonates account for more than 50 % of the world's hydrocarbons reserves (Palaz and Marfurt 1997). Carbonate formation exhibit wide range of pore sizes and types (Lucia 1999). Many carbonates are triple porosity system where the porosity is distributed among micro-pores, marco-pores and large vugs. Such heterogeneities come in variety of length scales from microscopic to macroscopic level. Therefore predicting the properties of a carbonate reservoir on a field scale is

extremely difficult. Understanding the pore structure of such carbonate systems is very essential for designing and implementation of enhanced oil recovery processes. We use laboratory NMR experiments along with tracer flow analysis to characterize the pore structure of carbonates. Hidajat, Mohanty, Flaum and Hirasaki (2004) studied vuggy carbonate samples using core analysis, NMR and X-ray CT scanning. They found that for vuggy carbonates CT scans and tracer effluent concentration profiles can help identify the preferential flow paths and the variation of the porosity within the cores.

This thesis is organized as follows. In chapter two we briefly review the relevant literature for transverse relaxation in the presence of diffusion with and without geometrical restriction and effect of grain-coating chlorite clay on transverse relaxation. Chapter three describes a two dimensional model to describe transverse relaxation in chlorite coated sandstones like North Burbank sandstone. Chapter four describe the NMR and tracer analysis for characterizing the pore structure in vuggy carbonates. Chapter five describes future scope of this work.

Chapter 2

Basic Principles and Literature Review

In this chapter we describe the basic principles of NMR and a brief literature review on the subject of internal field gradients. Later, relevant modeling approaches will be discussed in detail to outline the scope of present work.

2.1 Basic Principles

NMR loosely refers to the phenomena of behavior of atomic nuclei under the influence of externally applied magnetic fields. If the spins of protons and/or neutrons in a nucleus are paired, the overall spin of the nucleus is zero. When the spins of protons and/or neutrons are not paired, the overall spin of the nucleus generates a magnetic moment along the spin axis. NMR measurements can be made on any nucleus that has an odd number of protons or neutrons or both, such as the nucleus of hydrogen (^1H), carbon (^{13}C), and sodium (^{23}Na) etc. NMR studies presented in this work are based on responses of the nucleus of the hydrogen atom.

Under the influence of an externally applied magnetic field, B_0 , the individual magnetic moments align parallel (lower energy state) or antiparallel (higher en-

ergy state) to the field. There is slight preference of nuclei for aligning parallel to the applied field which gives rise to a net magnetization (M_0) along the direction of applied field.

The external magnetic field (B_0) produces a torque on the magnetic moment. If the external field is static, it causes magnetic moment to precess about the applied field at a fixed angle. The equation of motion for the macroscopic magnetization (M) is given by equating the torque due to the external field with the rate of change of M shown below.

$$\frac{dM}{dt} = M \times (\gamma B_0) \quad (2.1)$$

Where γ is gyromagnetic ratio, which is a measure of the strength of the nuclear magnetism. The frequency for the precession of magnetic moment about applied field is called Larmor frequency and is given by:

$$f = \frac{\gamma B_0}{2\pi} \quad (2.2)$$

2.1.1 Pulse tipping and Free Induction Decay

The magnetization (M) remains in equilibrium state until perturbed. If the static magnetic field is in the longitudinal direction and a magnetic field rotating at Larmor frequency is applied in the plane perpendicular to the static field, the

magnetization starts to tip from the longitudinal direction towards transverse plane. The angle θ through which the magnetization is tipped is given as:

$$\theta_p = \gamma B_1 t_p \quad (2.3)$$

Where t_p is the time over which the oscillating field is applied and B_1 is the amplitude of the applied magnetic field. In NMR measurements, usually a π ($\theta_p = 180^\circ$) or $\frac{\pi}{2}$ ($\theta_p = 90^\circ$) radio frequency (RF) pulse is applied. When the RF pulse is removed, the relaxation mechanisms cause the magnetization to return to equilibrium condition. If a coil of wire is set up around the axis perpendicular to B_o , oscillations of M induces a sinusoidal current in the coil which can be detected. This signal is called the Free Induction Decay (FID).

2.1.2 Longitudinal (T_1) Relaxation

Longitudinal relaxation is also called spin-lattice relaxation. In the absence of an external magnetic field, protons do not align in any preferred direction and the net magnetization is zero. When the external field is applied, protons respond to this field and net magnetization begins to build up. The time constant for this first order kinetic process is called T_1 . The equation describing the longitudinal relaxation is given as:

$$\frac{dM_z}{dt} = -\frac{[M_z - M_0]}{T_1} \quad (2.4)$$

Where, M_0 is the equilibrium magnetization and M_z is the z component of magnetization. A common pulse sequence used to measure T_1 relaxation time is the Inversion-Recovery (IR) pulse sequence. The IR sequence starts with a 180° pulse which flips the magnetization in the negative z direction. After a fixed amount of time t , a 90° pulse is applied which brings the magnetization to the $x - y$ plane. Free induction decay of the magnetization after the 90° pulse induces a sinusoidal voltage which is detected by the receiver coil. The amplitude of the FID immediately after the 90° pulse gives the value of M_z after the wait time t . A series of such experiments are performed for a range of values of t , which give the values of M_z increasing from $-M_0$ to $+M_0$. The T_1 relaxation time is determined by fitting an exponential fit to the measured values of M_z given as

$$M_z(t) = M_0 \left(1 - 2 \exp \left(\frac{-t}{T_1} \right) \right) \quad (2.5)$$

2.1.3 Transverse (T_2) Relaxation

Transverse relaxation is also called spin-spin relaxation. When a 90° pulse is applied, all the spins are in transverse plane. After the application of a 90° pulse, the proton population begins to dephase, or lose phase coherency. This means that the precession of the protons will no longer be in phase with one another. As dephasing progresses, the net magnetization decreases. This decay is usually exponential and is characterized by the FID time constant (T_2^*). FID is caused by

certain molecular relaxation processes and due to magnetic field inhomogeneities.

The equation describing transverse relaxation is given as:

$$\frac{dM_{x,y}}{dt} = -\frac{M_{x,y}}{T_2^*} \quad (2.6)$$

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \gamma\Delta B_0 \quad (2.7)$$

Where ΔB_0 is the inhomogeneity of the magnetic field.

Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence was designed to partially offset the effect of the inhomogeneous field. A CPMG spin echo train starts with a 90° RF pulse along the x-axis in the rotating frame that tips the magnetization onto the y axis. After the initial 90° pulse, the spins dephase due to the inhomogeneity of the field. Then, after a time τ (half echo spacing), a 180° pulse is applied along the y axis. The 180° pulse refocuses the spins on y axis at time 2τ to form a “spin echo”. Subsequent 180° pulses are applied at 3τ , 5τ , 7τ ... and the spin echoes are formed at time 4τ , 6τ , 8τ ... The peak amplitudes of the spin echoes are recorded to yield the decay curve from which the effect of the inhomogeneous dephasing has been partially removed. The decay, if single

exponential, can be expressed as:

$$M_{x,y}(t) = M_0 \exp\left(-\frac{t}{T_2}\right) \quad (2.8)$$

Where, $t = [2\tau, 4\tau, 6\tau\dots]$.

2.1.4 Diffusion-Induced Relaxation

When fluid molecules are subjected to magnetic field gradient and are free to move around, they exhibit significant diffusion induced transverse relaxation. If molecules move into regions of different magnetic field strength then the precession rate is different at different regions. This leads to additional dephasing and, therefore, increases the T_2 relaxation rate ($1/T_2$). Diffusion has no influence on the T_1 relaxation rate. If the diffusion is fast, the diffusion-induced relaxation rate is given by:

$$\frac{1}{T_{2,\text{diffusion}}} = \frac{D(\gamma g \tau)^2}{3} \quad (2.9)$$

Where, D is molecular self diffusion coefficient, g is the magnetic field gradient (either internally induced or externally applied) and τ is the half echo spacing. This equation applies to the simple case of a uniform gradient g , and unbounded diffusion, i.e., where pore walls do not restrict molecular diffusion (Kleinberg and Horsfield 1990).

2.1.5 Surface Relaxation and Pore size distribution

The NMR response of protons in pore space of the rocks is significantly different than that in the bulk due to interactions with the pore surface. Surface relaxation occurs at the fluid-solid interface, i.e. at the grain surface of rocks. In the limit of fast diffusion (i.e. relaxation at the surface of the pores is much slower compared to the transport of spins to the pore surface), the surface relaxation is characterized by surface relaxivities (ρ_1 and ρ_2) for longitudinal and transverse relaxation, and surface to volume (S/V) ratio of the pores (Brownstein and Tarr 1979).

$$\frac{1}{T_{1,\text{surface}}} = \rho_1 \left(\frac{S}{V} \right)_{\text{pore}} \quad (2.10)$$

$$\frac{1}{T_{2,\text{surface}}} = \rho_2 \left(\frac{S}{V} \right)_{\text{pore}} \quad (2.11)$$

Surface relaxivity varies with mineralogy. Carbonate formations exhibit weaker surface relaxivity than quartz surface.

For a rock sample having a pore size distribution, in the limit of fast diffusion all pores relax independent of each other. Each pore size is associated with a T_2 component and the net magnetization will no longer relax as a single exponential, but instead, relax as a multi-exponential decay. Thus, the observed T_2 distribution of all the pores in the system represents the pore size distribution of

the rock sample (Loren and Robinson 1970, Brownstein and Tarr 1979).

Relaxation mechanisms act in parallel and, therefore, the relaxation rates can be written as:

$$\frac{1}{T_1} = \frac{1}{T_{1, \text{bulk}}} + \frac{1}{T_{1, \text{surface}}} \quad (2.12)$$

$$\frac{1}{T_2} = \frac{1}{T_{2, \text{bulk}}} + \frac{1}{T_{2, \text{surface}}} + \frac{1}{T_{2, \text{diffusion}}} \quad (2.13)$$

2.2 Literature Review

Nuclear Magnetic Resonance (NMR) and Magnetic Resonance Imaging (MRI) are frequently used in petrophysics and in the field of medicine. Petrophysics and the field of medicine share some key problems for NMR/MRI. In medicine, the objective is to construct a sharp and accurate image for distinguishing between different types of tissues, bones and body fluids, all having different magnetic susceptibility. Sometimes in MRI, the contrasting agents containing paramagnetic particles are deliberately injected into the body to obtain a high resolution image. On the other hand in petrophysics, the object of interest is a rock sample or petroleum formation which has different magnetic susceptibility than the susceptibility of pore filling fluid.

In this section we summarize the key research contributions for diffusion coupling and understanding transverse relaxation in the presence of inhomogeneous

magnetic field. We also point out their key assumptions and limitations which will provide the motivation for the current work.

2.2.1 Diffusion Coupling

As described in section 2.1.5, pore size estimation from NMR measurements on fluid saturated porous media assumes that the T_2 distribution is directly related to the pore size distribution and the net magnetization decays as a multiexponential decay.

$$M(t) = \sum_i f_i \exp\left(-\frac{t}{T_{2,i}}\right) \quad (2.14)$$

where f_i is the amplitude of each $T_{2,i}$. Such interpretation assumes that different pores relax independent of each other. However, when surface relaxation is very fast or diffusion is slow, this assumption breaks down and fluid molecules in different sized pore communicate with each other through diffusion. This is true for the case of rocks where porosity is divided between two or more populations of very different length scales.

Ramakrishnan et al. (1999) observed that NMR T_2 measurements on water saturated peloidal grainstone exhibit a single peak suggesting a single pore size. However, the ESEM images of the sample showed a wide range of pore sizes exhibiting both micro and macro porosities. Ramakrishnan et al. (1999) explained this behavior using three-dimensional random walk simulations considering the

diffusion of fluid molecules between macro and micro pores. They proposed an analytical model of 3D array of spherical micropores surrounded by intergranular pores. This model can be simplified as two-dimensional periodic array of identical slab-like microporous grains separated by intergranular pores. This model is completely described by four parameters total porosity, ϕ , volume fraction of intergranular porosity, f_m , the pore volume to surface area ratio for macropores, V_{Sm} and the pore volume to surface area ratio for micropores $T_{2\mu}$. They found that when decay of magnetization in macropore happens on a much larger timescale in comparison to that of micropore, the relaxation can be expressed as a bi-exponential decay with amplitudes representing micro and macroporosity fractions as shown in the equation below.

$$M(t) = (\phi - f_m) \exp\left(-\frac{t}{T_{2,\mu}}\right) + f_m \exp\left(-\frac{\rho_a t}{V_{Sm}}\right) \quad (2.15)$$

Where, V_{Sm} is the macropore volume-to-surface ratio, ϕ and f_m are the total porosity and macroporosity respectively and ρ_a is the apparent relaxivity for the macropore. The above bi-exponential decay model is only valid when the diffusion length within the microporous grain is much smaller than the grain radius, i.e.

$$\sqrt{\frac{DT_{2,\mu}}{\phi_\mu F_\mu}} \ll R_g \quad (2.16)$$

Where, F_μ is the formation factor.

Toumelin et al. (2003) used a conditional Monte Carlo random-walk algorithm to simulation the NMR response for a three-dimensional array of spheres of different sizes representing porous media. The three-dimensional model can accomodate different pore sizes and can represent both micro and macroporosity. The model allows diffusional coupling between different pore modes. The model has four parameters, 1) average pore radii 2) porosities of different pore sizes 3) micro-porosity radius and 4) surface relaxivity. First two parameters are obtained by SEM analysis of core samples while other two are fitted to match simulation results with NMR measurements in laboratory. By keeping the same parameters and by preventing the diffusional coupling between pore modes, equivalent uncoupled models are constructed. Simulations through these uncoupled models yield the NMR response which would have been observed in laboratory in the absence of diffusion coupling. These results can be used to calculate the extent of diffusional coupling on estimation of BVI. They showed that in some cases using a $T_{2,cutoff}$ of 90 ms for carbonates can results in substantial error of 48 % in BVI calculations.

Anand and Hirasaki (2007a) explained diffusional coupling based on a coupling parameter (α) for a clay lined pore (Straley, Morriss, Kenyon and Howard 1995). The coupling parameter (α) is the ratio of characteristic relaxation rate of the pore to the rate of diffusional mixing of spins between the micro and macro-

pore. Depending on the value of coupling parameter (α), micro and macropores can communicate through total, intermediate or decoupled regimes of coupling. For values of α less than 1, the micropore is totally coupled with the macropore and the entire pore relaxes with a single relaxation rate. In intermediate coupling ($1 < \alpha < 250$) regime, the T_2 distribution consists of two distinct peaks for two pore types but the peak amplitudes are not representative of micro and macroporosity fractions. For values of α greater than 250, the two pores relax independent of each other and T_2 distribution correctly represents micro and macropore relaxation and the peak amplitudes are representative of the porosity fractions (β and $1 - \beta$ for micro and macroporosity respectively). They also found appropriate coupling parameter for grainstones using the spherical grain model developed by Ramakrishnan et al. (1999). They developed a new technique for calculating irreducible fluid saturation that is applicable in all coupling regimes.

2.2.2 Inhomogeneities of the applied magnetic field

Diffusion of fluid molecules in inhomogeneous fields causes enhanced relaxation of transverse magnetization due to loss of phase coherence. The enhanced relaxation is termed as “Secular relaxation” and is defined as the difference in transverse and longitudinal relaxation rates (Gillis and Koenig 1987).

$$\frac{1}{T_{2,\text{sec}}} = \frac{1}{T_2} - \frac{1}{T_1} \quad (2.17)$$

For the sake of clarity and completeness, the literature review for un-restricted (Free) and restricted diffusion is discussed in separate sections.

2.2.3 Un-restricted or Free Diffusion

Neuman (1974) derived the expression of the Hahn echo amplitude in a constant gradient (g) in unbounded space which is given as:

$$\ln \left[\frac{M(2\tau, g)}{M_0} \right] = -\frac{2D\gamma^2 g^2 \tau^3}{3} \quad (2.18)$$

Glaser and Lee (1974) studied transverse and longitudinal relaxation of protons for a series of deuterium oxide glass bead systems. For small beads, the approximate expression for magnetic field inhomogeneities is proportional to susceptibility contrast and applied magnetic field. Gillis and Koenig (1987) used microscopic outer sphere theory and developed expression for transverse relaxation in motionally narrowing/averaging regime.

Kleinberg et al. (1994) studied low field NMR response of several sandstones and reported that the T_1/T_2 ratio varied over a long range from 1 to 2.6, with a median value of 1.59. Several other researchers (Hurlimann 1998, Appel et al. 1999, Dunn et al. 2001, Zhang 2001, Brown and Fantazzini 1993, Borgia et al. 1995, Fantazzini and Brown 2005) performed experiments with fluid-saturated porous media and reported strong dependence of transverse relaxation on echo

spacing.

Brown and Fantazzini (1993, 2005) used a model of multiple correlation times to study echo spacing dependent increase in the value of $1/T_2$ obtained from CPMG measurements. They observed an initial quasi-linear dependence on echo spacing for CPMG with diffusion and susceptibility contrast in porous media and tissues. This dependence on echo spacing was different than the quadratic dependence predicted by classical expression given by Carr and Purcell (1954) and Neuman (1974).

Foley et al. (1996) studied the longitudinal and transverse relaxation of water saturated powder packs of synthetic calcium silicates with different concentrations of iron or manganese paramagnetic ions. They reported that the transverse relaxation rates are linearly proportional to the amount of paramagnetic ions in small concentrations.

Bergman and Dunn (1995b) used a Fourier expansion method to solve the diffusion eigenvalue problem associated with T_2 relaxation in a periodic porous medium. La Torraca et al. (1995) used the theory of Bergman to interpret internal field gradients on experimental T_2 measurements. They correlated the relaxation rate due to diffusion with half echo spacing (τ) using a hyperbolic tangent function:

$$\Delta\text{Rate} = A \left(1 - \frac{\tanh(\lambda_1 \tau)}{\lambda_1 \tau} \right) \quad (2.19)$$

Hurlimann (1998) attempted to explain the transverse relaxation in the presence of inhomogeneous magnetic field using the concept of Effective gradients. In simple geometries characterized by a single length scale, l_s , the decay of magnetization in a gradient, g , is governed by the interplay of three lengths.

1. the diffusion length, $l_d = \sqrt{Dt}$;
2. the size of the pore or structure, l_s ; and
3. the dephasing length, $l_g = \left(\frac{D}{\gamma g}\right)^{1/3}$.

The diffusion length gives a measure of the average distance that a spin diffuses during the time t . The dephasing length l_g may be thought of as the typical length scale over which a spin must travel to dephase by 2π radians. It depends on the gradient strength.

The idea of effective gradients is simple. The magnetic field gradients are not constant in a sedimentary rocks. However, if a given spin does not diffuse very far during the NMR measurement, the local field variation can be adequately modeled by some local effective field gradient. This effective field gradient is related to the field variations over the local dephasing length. The total signal decay is then a superposition of the signal decay due to different subsets of spins, each of which experiences a local effective gradient and can be in free diffusion or the motionally averaging regime, depending on the pore size (Hurlimann 1998).

While the complexity of the systems (irregular geometry, inhomogeneous fields etc.) make a general theory of relaxation difficult, some researchers (Brooks et al. 2001, Gillis et al. 2002) have come up with theories which apply in certain limits, depending on the relative magnitude of three time parameters. One of the time parameters is τ_E , defined as half the interval between successive 180° pulses in a CPMG sequence ($\tau_E = TE/2$). The other two time parameters are inherent in the system being studied; they are the diffusional correlation time ($\tau_R = \frac{a^2}{D}$) and the time for a significant amount of dephasing to occur (i.e., the inverse of the spread in Larmor frequency, $\tau_\omega = 1/\Delta\omega$). (Brooks et al. 2001, Gillis et al. 2002) studied enhanced transverse relaxation by magnetized particles using a refocusing and chemical exchange models. They summarized transverse relaxation by magnetized particles in different limiting cases using three time scales.

Weisskoff et al. (1994) performed Monte-Carlo simulations to study transverse relaxation due to the presence of spherical paramagnetic particles. Brooks et al. (2001) compared the results of various theories with those obtained by random walk simulations. Several other researchers (Gudbjartsson and Patz 1995, Valkenborg et al. 2002, Anand and Hirasaki 2007b) have performed random walk simulations to study transverse relaxation in uniform and non-uniform magnetic fields.

2.2.4 Restricted Diffusion

In the previous section we reviewed and discussed results for transverse relaxation for un-restricted diffusion, i.e. when nuclei diffused freely in an infinite reservoir. The presence of a restrictive boundary drastically influences the motion and the consequent signal decay in NMR. Woessner (1963) used the spin-echo technique to experimentally demonstrate the effect of a geometric restriction, measuring the signal attenuation for water molecules in a geological core and in aqueous suspensions of silica spheres (Woessner 1960, 1961, 1963). Woessner, in his experiments found a time-dependent value of the diffusion coefficient which is called the effective, time-dependent, or apparent diffusion coefficient.

The size of geometrical confinement is a natural length scale for restricted diffusion. Different regimes of restricted diffusion depend on the relative magnitude of the following lengths with respect to one another.

- Diffusion length $l_d = \sqrt{Dt}$
- Gradient length $l_g = (\gamma g t)^{-1}$, over which the spins are dephased of the order of 2π
- Relaxation length $l_h = D/\rho$, which is the distance a particle should travel near the boundary before surface relaxation effects reduce its expected magnetization

Robertson (1966) applied a quantum-mechanical operator formalism to study restricted diffusion between two parallel planes. Robertson derived results for short and long times. For long times, Robertson found a new behavior of the signal attenuation due to restricted diffusion in a slab geometry, which is now called the motionally averaging or motionally narrowing regime.

$$\frac{M(t)}{M(0)} = \exp \left[-\frac{\gamma^2 g^2 L^4 t}{120D} \right] \quad (2.20)$$

We observe from equation 2.20 that there is no dependence on the echo spacing unlike the case of free diffusion. A sharp dependence on the size of the confining domain appears here as a characteristic feature of the restricted diffusion. The same behavior was experimentally observed by Wayne and Cotts (1966).

Neuman (1974) extended Robertson's results by considering accumulation of phase shifts during diffusive motion. Neuman assumed that the spatial displacements on a spin can be seen as independent "jump" at random and thus the phases of diffusing spins follow a Gaussian distribution. This assumption is called "Gaussian phase approximation (GPA)".

However, for the large gradient intensity g , Gaussian phase approximation (GPA) breaks down. de Swiet and Sen (1994) discussed the consequences of the breakdown of GPA or so-called localization regime. Hurlimann et al. (1995) for the first time experimentally observed the localization regime.

de Swiet and Sen (1994) introduced three different length scales to characterize the transverse relaxation by bounded diffusion in a constant gradient. They developed the correction to Neuman's free diffusion formula for bounded diffusion.

$$\ln \left[\frac{M(2\tau, g)}{M_0} \right] = \left[-\frac{2D_{eff}\gamma^2 g^2 \tau^3}{3} + O \left(D_0^{5/2} \gamma^4 g^4 \tau^{13/2} \frac{S}{V} \right) \right] \quad (2.21)$$

With an effective diffusion coefficient $D_{eff} = D_0 [1 - \alpha \sqrt{D_0 \tau} (S/V) + \dots]$, where α is a numerical constant, D_0 is the molecular self-diffusion coefficient and S/V is the surface to volume ratio of the bounded region. The numerical constant α can be analytically computed for Hahn's echo and CPMG pulse sequence. At short times the breakdown from free diffusion to bounded diffusion formula is governed by the length scale $l_c = (\gamma g / D_0)^{-1/3}$ and the geometry of the region.

This concept can be used to obtain accurate pore size information in the porous media using the early time echo data. Zielinski and Hürlimann (2005) proposed the use of the CPMG sequence to probe short length scales in a static gradient. A tutorial about the time-dependent diffusion coefficient and its application to probe geometry is given by Sen (2004).

Tarczon and Halperin (1985) presented first theoretical study for the effect of non-linear magnetic fields on restricted diffusion. Tarczon and Halperin proposed

an approximate relation in the short-time limit:

$$\frac{M(t)}{M(0)} = \exp \left[-\frac{D\gamma^2 g_{eff}^2 t^3}{12} \right] \quad (2.22)$$

where $g_{eff}^2 = \langle (\nabla B(r))^2 \rangle$ is the spatial average of the squared of the magnetic field. Tarczón and Halperin argued that the signal attenuation in a non-linear magnetic field $B(r)$ can be characterized by an effective gradient g_{eff} which leads to the result now known as local gradient approximation.

Le Doussal and Sen (1992b) derived an exact solution of the Bloch-Torrey equation in the whole space for a quadratic magnetic field $B(z) = g_o + g_1 z + g_2 z^2$. In the short-time limit, the signal attenuation was similar to that of the effective linear gradient, in agreement with equation 2.22. In the long-time limit, Le Doussal and Sen (1992b) found that the attenuation was proportional to t rather than t^3 dependence.

Anand and Hirasaki (2007b) presented a generalized theory with random walk simulations to study transverse relaxation in the presence of internal field gradients. They identified three distinct relaxation regimes (motionally averaging, localization and free diffusion) characterized by the values of three time parameters. Anand and Hirasaki (2007b) conducted experiments on sand coated with magnetic nanoparticles to demonstrate that T_1/T_2 ratio can vary to a wide range depending on the concentration and size of nanoparticles. T_1/T_2 ratio varied

from 1.26 for clean sand to 13 for the case of sand coated with $2.4\ \mu\text{m}$ magnetite particles.

The subsequent sections discuss occurrence of clay minerals in sandstones and their effect on NMR measurements and interpretations.

2.3 Clay minerals in sandstones

Clays minerals are common constituents of sandstone formations. Depositional environment, composition/pH of formation waters and temperature or depth of burial determine the type and morphology of clay minerals in sandstones (Velde 1995). Kaolinite and dickite appear as pore filling clays and significantly reduce porosity and permeability of the formation. Chlorite and illite are grain coating/lining and help preserve anomalously high values of porosity and permeability in deeply buried ($> 4\ \text{km}$) sandstones by inhibiting diagenetic precipitation of quartz overgrowth (Bloch et al. 2002, Anjos et al. 2003, Claudine et al. 2001). Illite sometimes exhibits grain-bridging characteristics where illite fibers extend from one sand grain to another which leads to significant reduction in permeability. Chlorite occurs in a variety of morphologies although classic chlorite occurs as a grain coating boxwork, with the chlorite crystals attached perpendicular to the grain surface (Worden and Morad 2003). Chlorite coatings on the sand grains act as excellent inhibitor of quartz overgrowth which results in up to 20-25 %

porosity even at the burial depth of 4-7 Kms as shown in figure 2.1. Preservation of porosity in deeply buried sandstones is directly related to the extent of grain coats and in the absence of good grain coats the porosity is not well preserved (Bloch et al. 2002).

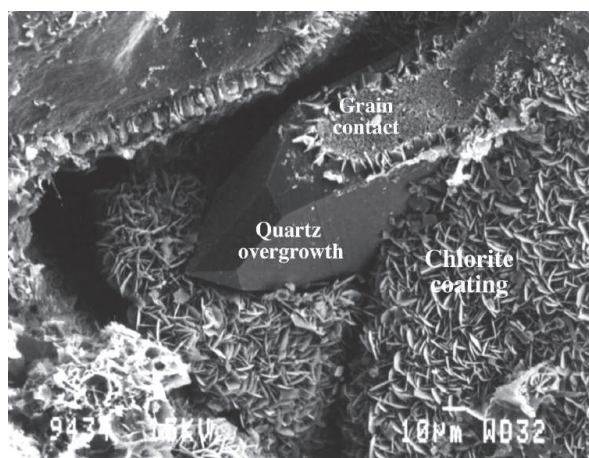


Figure 2.1: Chlorite coating inhibiting quartz overgrowth

2.3.1 Formation of clay minerals in sandstones

Most clays are formed as result of the interaction of aqueous solutions with rocks (Velde 1995). In sandstones, there are two modes of occurrence of clays. Allogenic (also referred as detrital) clays are formed prior to deposition and are mixed with the sand fraction during or immediately following deposition. Allogenic refers to clay minerals originating outside of a rock of which they now constitute a part. Authigenic clays develop subsequent to burial and include both new and

regenerated forms. Authigenic clay minerals are formed or regenerated in place. Authigenic clays form as a direct precipitate from formation waters (neof ormation) or through reactions between precursor materials and the contained waters (regenerated) (Wilson and Pittman 1977).

Clays generally are degraded during weathering, erosion and transport and generated or regenerated during burial diagenesis. Authigenic clays can be differentiated from Allogenic (detrital) clays on the basis of clay composition, structure, morphology and distribution and textural properties. For example, presence of delicate clay morphology (rosette or vermicular aggregates) hints at authigenic origin because delicate clay morphologies are very unlikely to be intact during sedimentary transport (Wilson and Pittman 1977). Authigenic grain coating clays are usually absent only at grain contacts (Wilson and Pittman 1977).

2.3.2 Morphology of authigenic clays

Authigenic clays can be easily identified based on their morphology. Three most common morphologies of authigenic clays are pore-fillings, pore-linings (also called clay films, or grain coating) and replacements. Kaolinite and dickite are most common pore-filling clays. Kaolinite forms in sediments by the action of low-pH ground waters on detrital aluminosilicate minerals such as feldspars, mica, rock fragments and heavy minerals (Velde 1995). Kaolinite almost always occurs as pseudo-hexagonal plates in the form of books (stacked plates) or as a deli-

cate vermicular growth, a sequence of stacked pseudohexagonal plates that may extend length of a pore as shown in the figure 2.2 (Wilson and Pittman 1977). With progressive increase in burial depth and temperature (2-3 km, $T=70-90^{\circ}\text{C}$), thin booklet-like kaolinite is progressively transformed into thick, well-developed crystals called dickite (Worden and Morad 2003). Pore-filling clays plug inter-

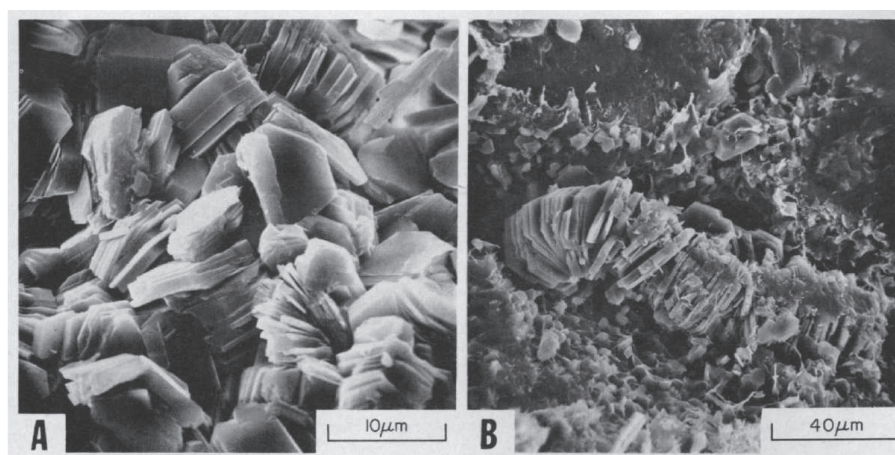


Figure 2.2: (A) Stacked plates of kaolinite in porous sandstone (face-to-face arrangement and pseudohexagonal outlines of individual plates) (B) Vermicular authigenic kaolinite in porous sandstone (Wilson and Pittman 1977)

stitial pores and individual flakes or aggregates of the flakes exhibit no apparent alignment relative to the detrital grain surfaces.

Pore linings are formed by clay coatings deposited on the surfaces of framework grains, except at points of grain-to-grain contact. Clay particles usually exhibit a preferred orientation normal to or parallel to the detrital grain surface. Illite is a grain coating clay but appears as irregular flakes with fiber or lath-like

projections. Occasionally, the sheets of illite may develop relatively long, delicate appearing, lath-like projections and may measure up to $30\text{ }\mu\text{m}$ long and range from 0.5 to $2\text{ }\mu\text{m}$ in width as shown in figures 2.3 and 2.4.

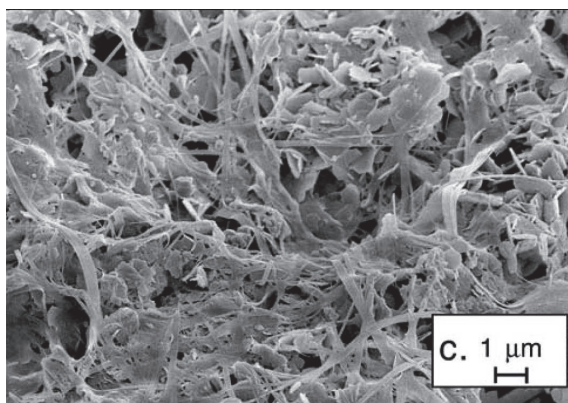


Figure 2.3: SEM image of illite, showing lath-like projections which extend from one grain to another (Storvoll et al. 2002)

Chlorite is an important pore lining clay. Authigenic chlorite occurs primarily as pore-lining pseudo-hexagonal flakes with a cardhouse, honeycomb or rosette arrangement (Hayes 1970). Figures 2.5 and 2.6 show grain coating chlorite clay at different magnifications. We observe that the crystals appear attached to sand grains along their longest dimension. Chlorite flakes are generally $2\text{-}10\text{ }\mu\text{m}$ across with a thickness of approximately $0.1\text{ }\mu\text{m}$. Figure 2.7 shows the delicate rosette like arrangement of chlorite crystals.

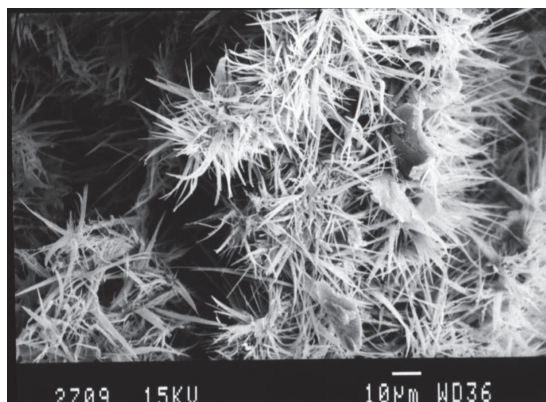


Figure 2.4: SEM image of illite, showing delicate fiber like structure (Storvoll et al. 2002)

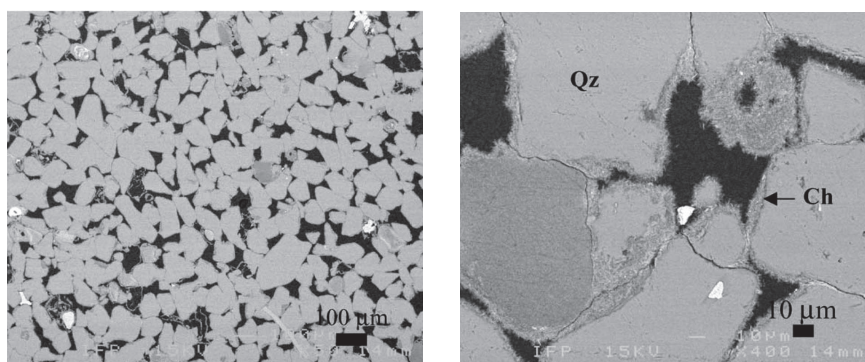


Figure 2.5: SEM images of grain coating chlorite at different magnifications. The images on left and right are at 50 and 400 magnifications respectively (Cerepi et al. 2002)

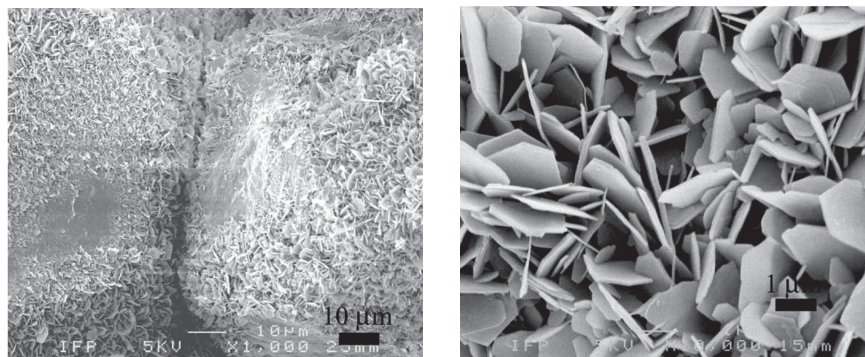


Figure 2.6: SEM images of grain coating chlorite at different magnifications. The images on left and right are at 1,000 and 10,000 magnifications respectively (Cerepi et al. 2002)

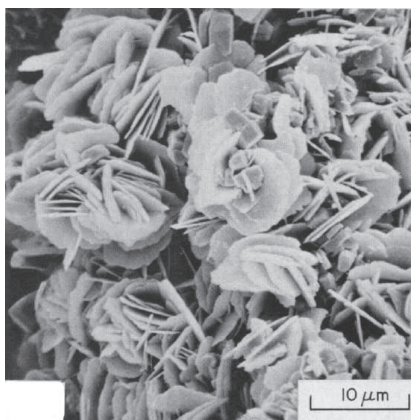


Figure 2.7: Chlorite clay exhibiting delicate rosette like morphology (Wilson and Pittman 1977)

2.3.3 Effect of grain coating chlorite on formation evaluation

Presence of chlorite clays affect wireline and NMR measurements (Claudine et al. 2001, Rueslåtten et al. 1998). Claudine et al. (2001) argued that chlorite bearing sandstones usually give low resistivity signals and can lead to overestimation of water saturations while interpreting the logs. Rueslåtten et al. (1998) validated NMR logs from sandstone oil reservoir offshore Mid Norway by taking into account pore lining iron rich chamosite and concluded that the faster T_2 decay is due to the magnetic field inhomogeneities caused by chlorite clays on pore scale. Pore-lining chlorite acts as micropores and if the diffusion of spins from macropore to micropore surface is not fast both micropore and macropore do not relax independent of each other. Diffusional coupling and internal field gradients become very important consideration when interpreting NMR logs from reservoirs which contain significant amount of pore lining clay.

Straley et al. (1995) compared FFI derived from borehole NMR logs with laboratory-measured values of the centrifugeable water for the core samples containing significant amount of pore-lining authigenic chlorite clay. They found that T_1 distribution for partially saturated cores shifts towards shorter T_1 components. They observed that the peak amplitude of shorter T_1 component for partially saturated cores is larger than that of for fully saturated cores. This observation can be explained by taking into account increased value of surface

to volume ratio (S/V) for partially saturated cores. When the sample is fully water saturated, macropores open into microchannel created by pore-lining clay flakes. For the fast diffusion limit, the whole micropore has a single relaxation time characterized by surface to volume ratio (S/V). For partially saturated core samples, the micropores are still saturated with water while the macropores are drained. This results in higher value of surface to volume ratio (S/V) because even though the relaxing surface area is the same, the volume of water has greatly decreased.

Zhang, Hirasaki and House (2001, 2003) used a simplified model to compute the magnitude of internal field gradients in a clay coated sandstones and compared with experimental data. They reported that in clay-lined sandstones the magnitude of internal field gradients can be as high as ~ 300 Gauss/cm which can be much greater than the gradient applied by the logging tool. They also studied a one dimensional system with constant gradient under restricted diffusion.

Next chapter describes a two dimensional model to explain transverse relaxation in a macropore which contains a clay flake.

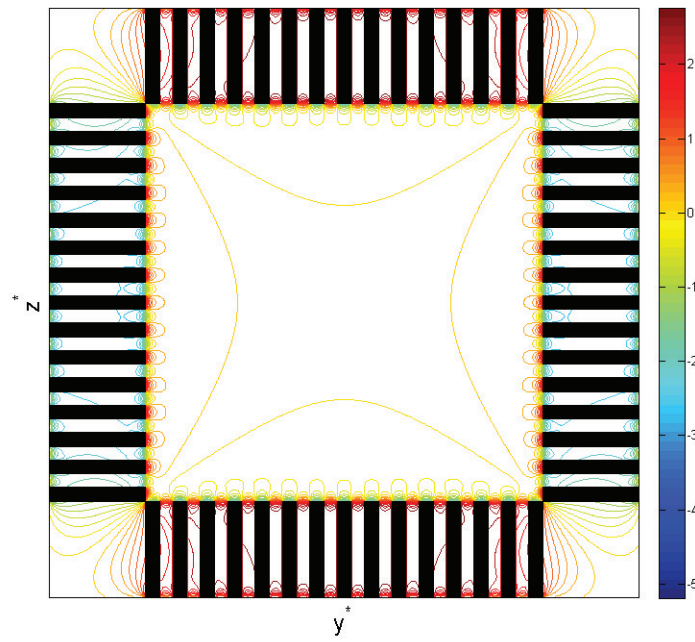


Figure 2.8: Field lines for the induced magnetic field for a clay lined macropore (Zhang et al. 2001)

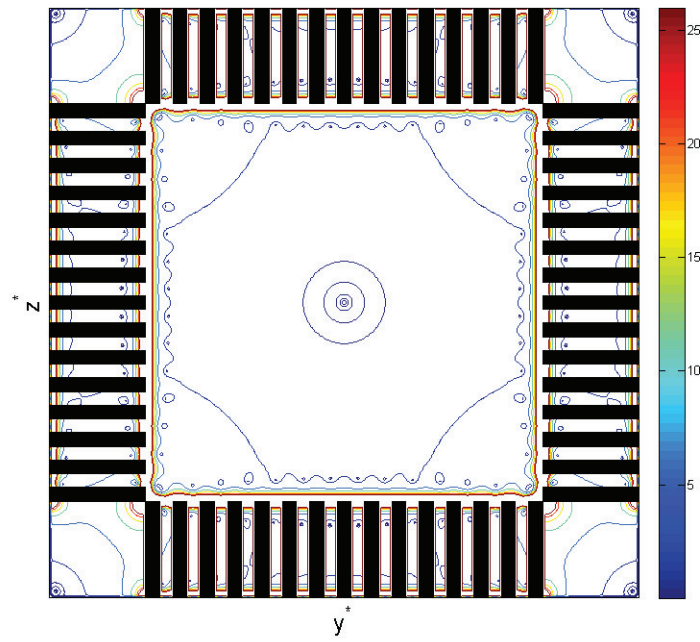


Figure 2.9: Contours of dimensionless magnetic field gradient for a claylined macropore (Zhang et al. 2001)

Chapter 3

Modeling Internal Field Gradients in clay-lined sandstones

The apparent similarity of the NMR surface relaxivity of sandstones has led to the adoption of a default value of T_2 irreducible water cut-off for all sandstones. Carbonate rocks do not exhibit strong echo spacing dependence of transverse relaxation. However, T_2 distribution is strongly dependent on echo spacing for chlorite clay-lined sandstones and sandstones which contains large amounts of paramagnetic minerals. Such sandstones should be treated differently and a generalized theory to understand the effect of internal field gradients on transverse relaxation is needed.

Figure 3.1 shows the T_1 and T_2 relaxation time spectrum for brine saturated North Burbank sandstone core sample. T_2 distribution is shown for four values of half echo spacings from 0.16 ms to 1 ms. We observe that the T_2 relaxation time distribution is strongly dependent on half echo spacing. Figure 3.1 shows the shift in the peak for T_2 relaxation time for different echo spacings. We also observe that the T_1/T_2 ratio is strongly dependent on echo spacing.

Chlorite coated North Burbank sandstone shows a much stronger diffusion

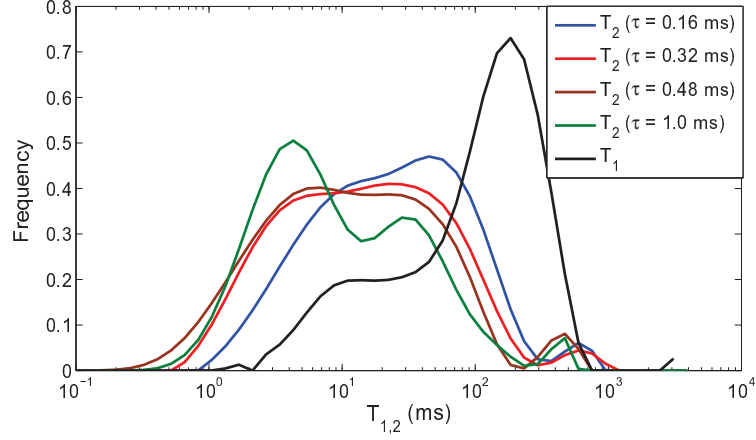


Figure 3.1: T_1 and T_2 relaxation time spectrum for North Burbank core sample saturated with brine solution

effect due to internal field gradients. North Burbank sandstone is chamosite coated (Trantham and Clampitt 1977). A common feature of the chamosite is that it is an iron rich chlorite and is pore lining (Zhang, Hirasaki and House 2003). North Burbank sandstone has a T_1/T_2 and ρ_2/ρ_1 ratio that is larger than most values reported in the literature (Zhang and Hirasaki 2003, Zhang et al. 2003).

Figure 3.2 shows a schematic of a claylined pore. Clay flakes form microchannels in the macropore which are called micropores. Clay flakes have a different magnetic susceptibility than that of pore filling fluid. In order to model the effect of internal field gradients on transverse relaxation due to the presence of

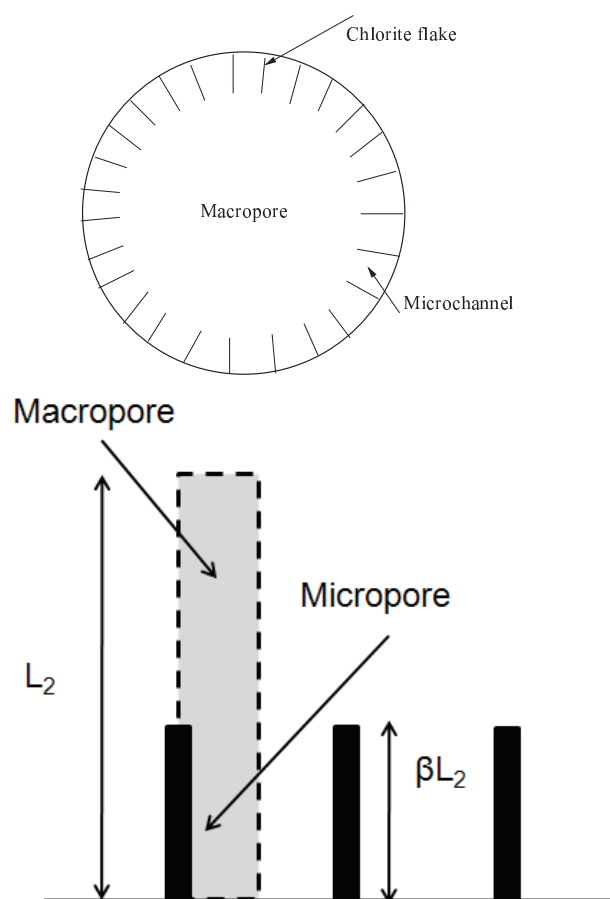


Figure 3.2: Schematic of a macropore lined with clay flakes

clay flakes in sandstones, we consider a clay-lined pore as described in figure 3.2. Figure 3.3 and 3.4 show the simplified geometry for simulation purpose. Only one-fourth of the pore is considered because of the presence of symmetry boundary planes as marked in figure 3.3 and 3.4. The clay flake is assumed to be infinitely long in $\pm x$ directions. This strikes out any dependence of x co-ordinate and effectively makes the model two dimensional. η and λ are the aspect ratio for the macropore and clay flake respectively, and β is the microporosity fraction.

The induced magnetic field due to the presence of clay flake can be calculated

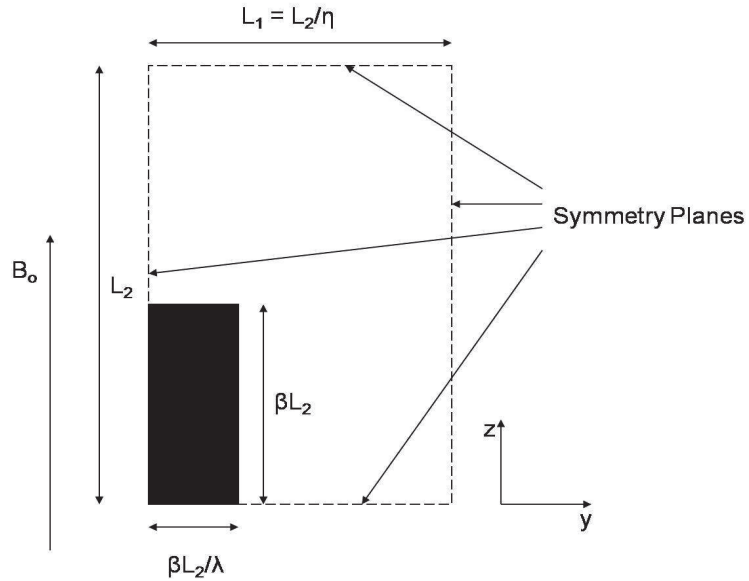


Figure 3.3: Schematic of a clay-lined pore

using Green's function in two dimensions (Zhang et al. 2003). The following is

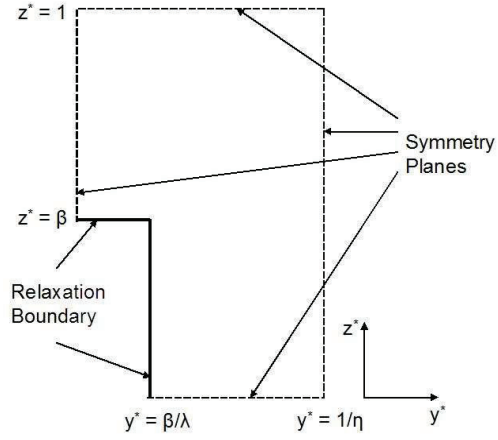


Figure 3.4: Schematic of the simulation domain

the expression for the induced magnetic field due to a clay flake.

$$\begin{aligned}
 B_{\delta z} = & \frac{B_0 \Delta \chi}{2\pi} \left[\tan^{-1} \left(\frac{\lambda (\beta - z^*)}{(y^* \lambda - \beta)} \right) + \tan^{-1} \left(\frac{\lambda (\beta + z^*)}{(y^* \lambda - \beta)} \right) \right. \\
 & \left. - \tan^{-1} \left(\frac{\lambda (\beta - z^*)}{(y^* \lambda + \beta)} \right) - \tan^{-1} \left(\frac{\lambda (\beta + z^*)}{(y^* \lambda + \beta)} \right) \right] \quad (3.1)
 \end{aligned}$$

Where $y^* = y/L_2$ and $z^* = z/L_2$ are dimensionless y and z coordinates.

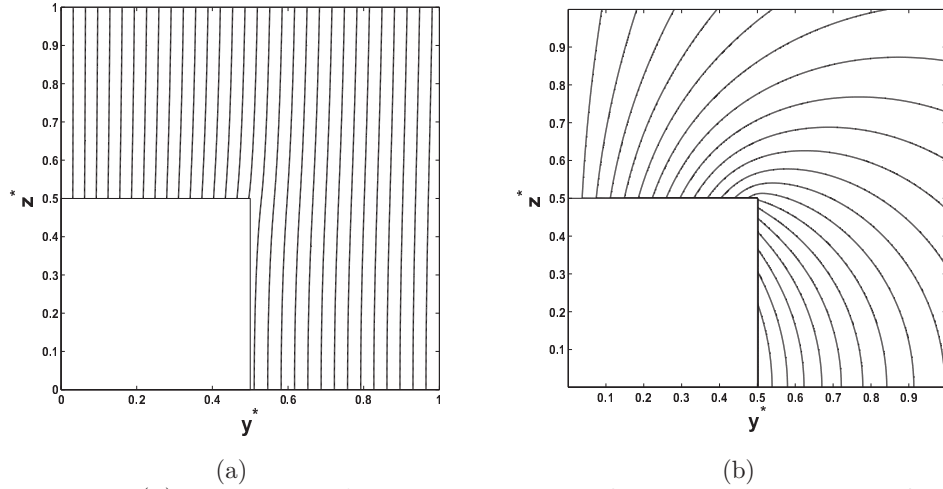


Figure 3.5: (a) Field lines of the total magnetic field B due to the clay flake in a homogeneous field B_0 (b) Field lines of the induced magnetic field B_δ due to the clay flake in a homogeneous field B_0

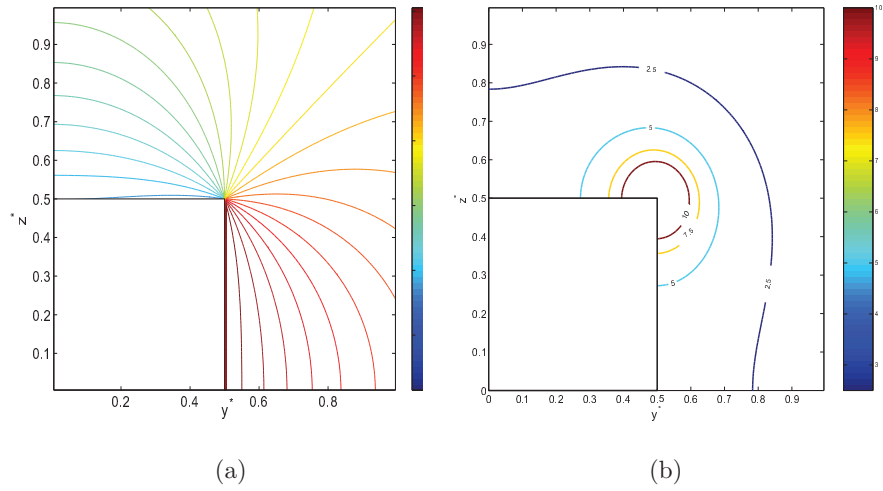


Figure 3.6: (a) Contour lines of the z component of induced field (b) Contours of dimensionless gradient due to the presence of clay flake

Figure 3.5 shows the field lines of the induced magnetic field due to the presence of a square shaped clay flake at the center of the pore. The field lines are shown for both, the total magnetic field B and difference between total and applied homogeneous field $B_\delta = B - B_0$. The magnetic field lines are similar to those caused by a bar magnet.

The gradient of induced magnetic field is made dimensionless using $\frac{B_0 \Delta \chi}{2\pi L_2}$ as the characteristic value of the gradient. In order to better visualize the induced magnetic field, we also plot the contours of the z component of the induced magnetic field and the dimensionless gradient of the induced magnetic field as shown in figure 3.6. We observe very high gradients of induced field around the corner of the clay flake. In order to accurately capture high values of gradients, we use adaptive mesh in the simulation. Figure 3.7 shows the structure of the grid blocks used in the simulation. We use smaller grid spacing near the corner of the clay flake and relatively large grid spacing for the rest of the domain. Using an adaptive mesh considerably reduces the simulation time.

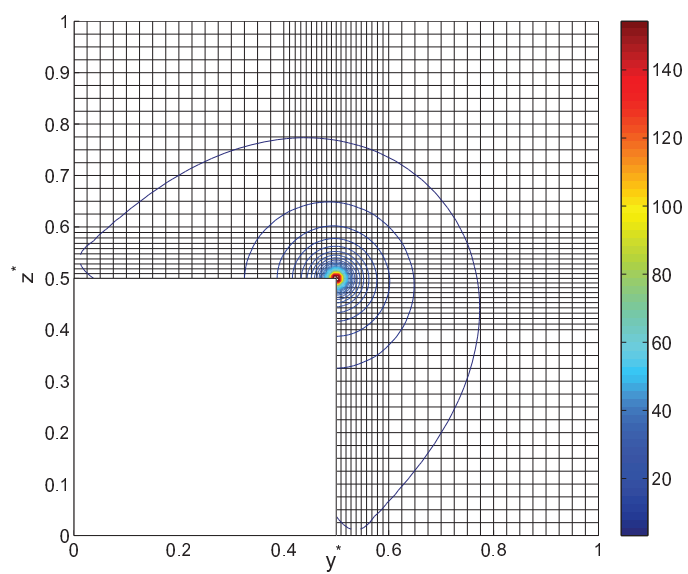


Figure 3.7: Schematic of mesh used to resolve large values of gradients around the corner

3.1 Simulations for FID and CPMG pulse sequence

This section describes the procedure for the simulation of Free Induction Decay (FID) and Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence for a macropore which contains a clay flake. The Transverse relaxation is simulated in y-z plane. We start with Bloch-Torrey equations for the transverse magnetization after the application of a 90° pulse. The applied magnetic field is in the z direction, B_0 .

3.1.1 Governing equations

The Governing equations are Bloch-Torrey equations which are described below (Torrey 1956).

$$\frac{\partial M_x}{\partial t} = \gamma M_y B_z - \frac{M_x}{T_{2B}} + D \nabla^2 M_x \quad (3.2)$$

$$\frac{\partial M_y}{\partial t} = -\gamma M_x B_z - \frac{M_y}{T_{2B}} + D \nabla^2 M_y \quad (3.3)$$

Where, M_x and M_y are the x and y components of the magnetization, γ is the gyromagnetic ratio of the proton, T_{2B} is the bulk transverse relaxation time and B_z is the z component of the magnetic field. If we assume $M = M_x + iM_y$, then the above equations can be described by a single equation (Bergman and Dunn 1995a).

$$\frac{\partial M}{\partial t} = -i\gamma M B_z - \frac{M}{T_{2B}} + D \nabla^2 M \quad (3.4)$$

When, $M = m \exp \left[-i\omega_0 t - \frac{t}{T_{2B}} \right]$ is substituted in equation 3.4, the equation is transformed into rotating co-ordinate frame and bulk relaxation term is factored out. The resulting equation is:

$$\frac{\partial m}{\partial t} = -i\gamma m B_{\delta z} + D\nabla^2 m \quad (3.5)$$

Where, $B_{\delta z} = B_z - B_0$ and m is a complex variable ($m = m_R + im_I$). The expression for $B_{\delta z}$ is given by equation 3.1.

For the sake the convenience, now onwards we shall refer $B_{\delta z} = \frac{B_0 \Delta \chi}{2\pi} F(y^*, z^*)$ so that the dependence of y^* and z^* is represented by $F(y^*, z^*)$. This yields a simple equation which is as follows.

$$\frac{\partial m}{\partial t} = -\frac{-i\gamma B_0 \Delta \chi}{2\pi} F(y^*, z^*) m + D\nabla^2 m \quad (3.6)$$

3.1.2 Boundary and Initial conditions

At symmetry planes zero flux condition for magnetization is applied. At the relaxation boundary, the Fourier boundary condition is used. At initial time a

uniform magnetization through out the pore space is assumed.

$$\hat{n} \cdot \nabla m = 0 \quad : \text{ at symmetry planes}$$

$$D\hat{n} \cdot \nabla m + \rho m = 0 \quad : \text{ at micropore surface}$$

$$m(t = 0) = m_0 \quad : \text{ uniform magnetization throughout the pore}$$

Where, D is the free diffusion coefficient and ρ is the surface relaxivity for transverse relaxation.

3.2 Dimensionless groups and their significance

The governing equations and boundary conditions are made dimensionless with characteristic scales, x^0 , t^0 and m^0 . x^0 is taken as half length of the macropore, L_2 , and m^0 as the initial uniform magnetization. The characteristic time scale is taken as the time for significant dephasing of spins, $\tau_\omega = \frac{1}{\delta\omega}$. $\delta\omega$ is the spread of Larmor frequency which is given as:

$$\tau_\omega = \frac{1}{\delta\omega} = \frac{1}{\gamma g L_2} \quad (3.7)$$

Where, g characterizes the internal field gradients. Using the concept of effective gradients developed by Hurlimann (1998), g and τ_ω can be described by the

following expressions.

$$g = |\nabla B| \simeq \frac{B_0 \Delta \chi}{L_2} \quad (3.8)$$

$$\tau_\omega = \frac{1}{\delta \omega} = \frac{1}{\gamma B_0 \Delta \chi} \quad (3.9)$$

Other timescales are diffusional correlation time $\tau_R = \frac{L_2^2}{D}$ and half echo spacing τ_E . The characteristic scales and respective dimensionless variables are described below.

$$x^0 = L_2 : \text{Half length of the macropore}$$

$$t^0 = \tau_\omega = \frac{1}{\delta \omega} = \frac{1}{\gamma B_0 \Delta \chi} : \text{Time for significant dephasing}$$

$$m^0 = m_0 : \text{Initial magnetization}$$

$$m^* = \frac{m}{m_0}$$

$$y^* = \frac{y}{L_2}, \quad z^* = \frac{z}{L_2}$$

$$t^* = \frac{t}{\tau_\omega}$$

$$\tau_E^* = \frac{\tau_E}{\tau_\omega} = \delta \omega \tau_E$$

$$\tau_R^* = \frac{\tau_R}{\tau_\omega} = \delta \omega \tau_R$$

Using dimensionless variables, the governing equations become:

$$\frac{\left(\frac{L_2^2}{D}\right)}{\left(\frac{1}{\gamma B_0 \Delta \chi}\right)} \frac{\partial m^*}{\partial t^*} = \frac{-i}{2\pi} \frac{\left(\frac{L_2^2}{D}\right)}{\left(\frac{1}{\gamma B_0 \Delta \chi}\right)} F(y^*, z^*) m^* + \nabla^{*2} m^* \quad (3.10)$$

Equation 3.10 can be further simplified by identifying the dimensionless groups.

$$\zeta \frac{\partial m^*}{\partial t^*} = \frac{-i}{2\pi} \zeta F(y^*, z^*) m^* + \nabla^{*2} m^* \quad (3.11)$$

Equation 3.10 contains the dimensionless group ζ which is defined below.

$$\zeta = \frac{\tau_R}{\tau_\omega} = \frac{\left(\frac{L_2^2}{D}\right)}{\left(\frac{1}{\gamma B_0 \Delta \chi}\right)} = \frac{\gamma B_0 \Delta \chi L_2^2}{D} \quad (3.12)$$

ζ is the ratio of two timescales present in the system. First is the diffusional correlation time ($\tau_R = \frac{L_2^2}{D}$) and another is the time for significant dephasing ($\tau_\omega = \frac{1}{\gamma B_0 \Delta \chi}$). For simulating CPMG pulse sequence, the third characteristic timescale is the dimensionless echo spacing, $\tau_E^* = \tau_E / \tau_\omega$.

The other dimensionless parameters are geometrical parameters namely aspect ratio of the macropore (η), aspect ratio of the clay flake (λ) and the microporosity fraction (β).

Equation 3.11 with given boundary and initial conditions is solved using finite difference method in residual form. Iterative Alternating Direction Implicit (ADI) method (Peaceman and Rachford Jr 1955) is used for integrating the difference

equations in time. The macroscopic magnetization is calculated by taking the magnitude of the sum of individual magnetization vectors over all the grid blocks. The dependence of timestep size was examined and the optimum value of the timestep size was used for all simulations.

In the following simulation results, the surface relaxivity (ρ) is taken as zero which means the decay of NMR signal is caused solely by the diffusion of spins under the influence of inhomogeneous magnetic field. The subsequent sections discuss the secular relaxation for free induction decay (FID) and CPMG pulse sequence.

3.3 FID results and discussion

Free induction decay (FID) can be easily simulated by starting with initial uniform magnetization. As spins diffuse under the influence of internal field gradients, they precess with different Larmor frequency and this causes the loss of phase coherence leading to the decay of the magnetization.

Figure 3.8 show the decay of magnetization for different values of $\zeta = \tau_R / \tau_w$. For small values of ζ , we see a single-exponential decay of magnetization. However, when the values of ζ is more than 20, free induction decay (FID) is not monotonically decreasing. The magnetization drops by two orders of magnitude and begins to rise again. These undulations finally die out in the noise level. It is

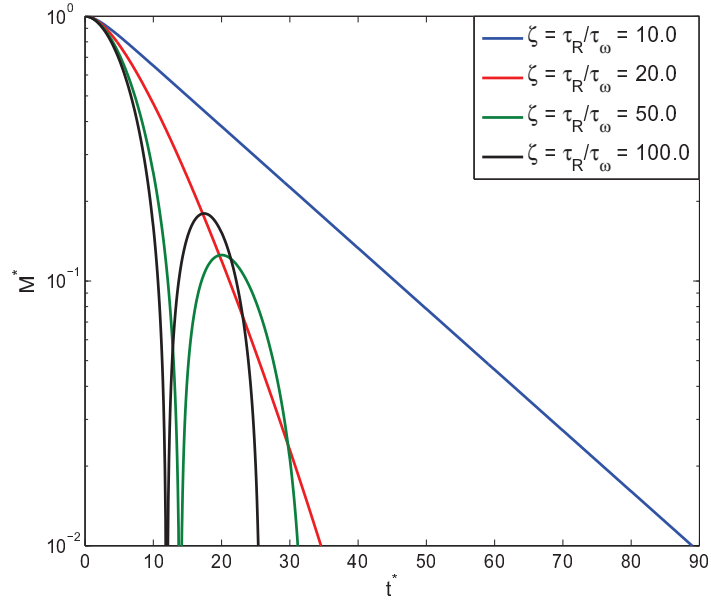


Figure 3.8: Decay of the magnitude of magnetic moment versus dimensionless time for different value of $\zeta = \frac{\tau_R}{\tau_\omega}$

interesting to see that the amplitude of these undulations is not small. For first undulation, magnetization reaches the magnitude of ~ 0.2 before starting to go down again.

The small value of ζ corresponds to large value of diffusion coefficient and fast diffusion of spins. Spins sample different Larmor frequencies at different locations and fast diffusion homogenizes the magnetization in the macropore and the magnetization for the macropore decays monotonically following a single exponential decay. Large value of ζ means slow diffusion and spins do not move around much and spins at different spatial position precess with different Larmor

frequencies. When spins are out of phase from one another, we see the decay of magnetization. However, when the spins are back in phase with one another, the magnitude of magnetization starts to build up again and finally decays due to the loss of phase coherence.

In order to test this hypothesis, we perform another set of simulations. We switch off diffusion term completely and let spins relax in an inhomogeneous field. This simplifies the equations significantly and we have a first order differential equation which can be solved using implicit Euler method.

We should recover this solution in the limit of large value of ζ because large value of ζ means slow diffusion. Figure 3.9 shows decay of magnetization for the case when diffusion is switched off and for different values of ζ . We observe that for higher values of ζ , the FID decay results match very well with the case for no diffusion. This confirms our hypothesis and suggests that in the presence of internal field gradients, we can actually observe FID data which does not decay monotonically.

Sukstanskii and Yablonskiy (2002) have observed periodicity in the FID signal for the case of constant gradient with restricted diffusion. They have used “Multiple propagator approach” to calculate the signal amplitude in one, two and three dimensional cases under constant gradient conditions. They defined a parameter p which is the ratio of two timescales in their system, dephasing time $t_g = \frac{1}{\gamma g a}$ and diffusion time $t_c = \frac{a^2}{D}$. Where, a is the system size, g is the applied

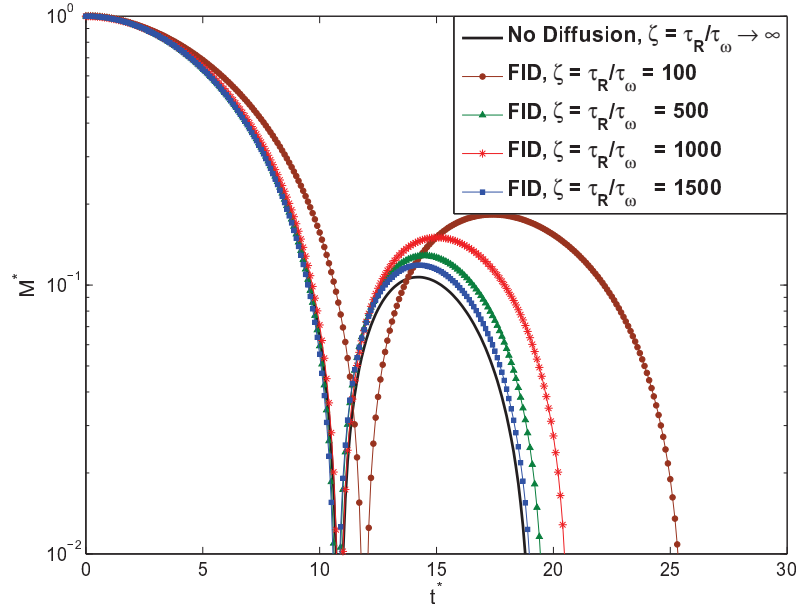


Figure 3.9: Comparison of FID decay of magnetization for different values of $\zeta = \frac{\tau_R}{\tau_\omega}$ and for the case when no diffusion is present

gradient and D is the self-diffusion coefficient. Periodic FID signal is observed when the value of parameter p is less than 0.3.

3.4 CPMG results and discussion

The program for FID decay can be easily modified for CPMG pulse sequence. For CPMG pulse sequence, at $t = \tau_E, 3\tau_E, 5\tau_E$ and so on, we apply a 180° pulse which is equivalent to $m(t = \tau_E^+) = \bar{m}(t = \tau_E^-)$, where $\bar{m}$ represents the transpose of the m . This effectively means that 180° pulse reverses the direction

of the precession of the spins. Application of the train of 180° pulse produces spin echoes at times $t = 2\tau_E, 4\tau_E, 6\tau_E$ and so on.

There are three geometrical parameters in the simulations; aspect ratio of the macro pore, η , aspect ratio of the clay flake, λ and microporosity fraction, β . The following results are for $\eta = 1$, $\lambda = 1$ and $\beta = 0.5$. In next section we discuss results for other sets of geometrical parameters.

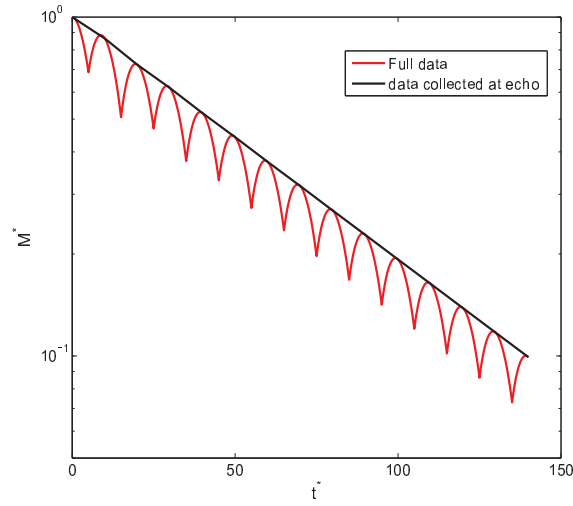


Figure 3.10: Plot for CPMG decay of magnitude of magnetization for dimensionless echo spacing, $\delta\omega\tau_E = 5.0$ and $\zeta = \delta\omega\tau_R = 100$. Geometrical parameters used are: aspect ratio of macropore (η) = 1, aspect ratio of the clay flake (λ) = 1 and microporosity fraction (β) = 0.5

Figure 3.10 shows the decay of magnitude of magnetization for CPMG pulse sequence with $\zeta = \tau_R/\tau_w = \delta\omega\tau_R = 100$, dimensionless echo spacing, $\delta\omega\tau_E = 5.0$ and a set of geometrical parameters ($\eta = 1$, $\lambda = 1$, $\beta = 0.5$). Figure 3.10 demonstrates

that a train of 180° pulses refocus the magnetization and secular relaxation follows a single exponential decay.

For a given set of geometrical parameters, we summarize our results in terms of two parameters. First is $\zeta = \delta\omega\tau_R$, which is the ratio of τ_R and τ_ω and second is dimensionless half-echo spacing, $\tau_E^* = \delta\omega\tau_E$ which is the ratio of τ_E and τ_ω . We fit a single-exponential curve for the decay of magnetic moment and calculate dimensionless secular relaxation rate for each parameter value.

The magnetization decay is bi-exponential for the simulations where $\zeta = \tau_R/\tau_\omega$ is more than 1000. A few of these cases are illustrated in figures 3.11, 3.12 and 3.13. For such cases, slower component of bi-exponential decay is taken as the relaxation rate. Using these values of the dimensionless transverse relaxation rate, we create a single plot which shows the relaxation rates for all parameter values which is illustrated in figure 3.15.

Based on the relative magnitudes of three timescales, three different characteristic relaxation regimes are defined (Anand and Hirasaki 2007b).

Motionally averaging regime: This regime is characterized by fast diffusion of protons such that the inhomogeneities in the magnetic field are motionally averaged. This occurs when the diffusional correlation time (τ_R) is the smallest timescale and is much shorter compared to half echo spacing and the time taken for significant dephasing due to presence of field inhomogeneities. In this regime, the secular relaxation rate does not show any dependence on echo spacing. The

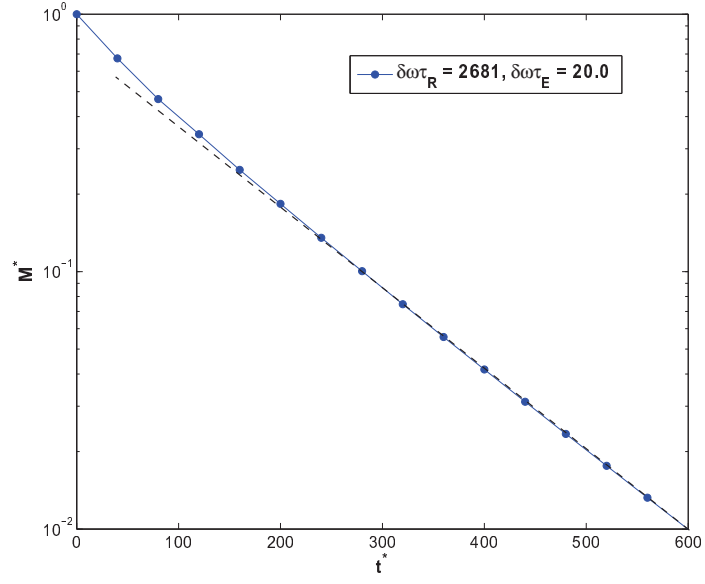


Figure 3.11: Bi-exponential plot for $\zeta = 2681$, $\tau_E^* = 20.0$

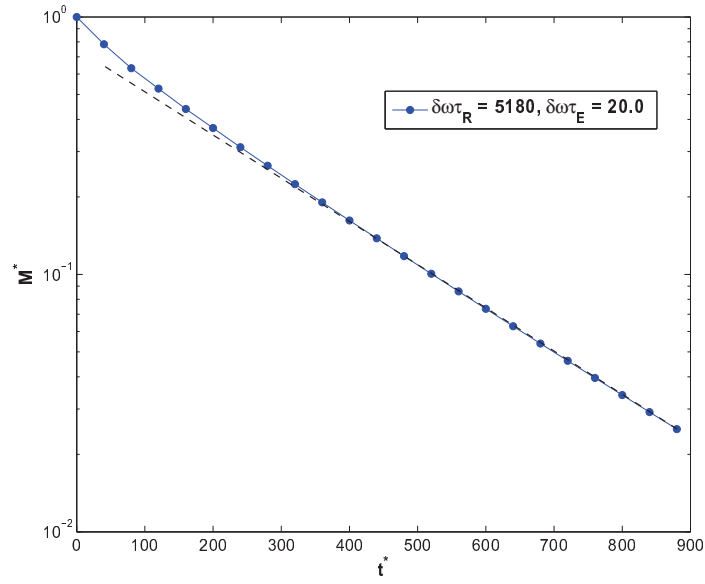


Figure 3.12: Bi-exponential plot for $\zeta = 5180$, $\tau_E^* = 20.0$

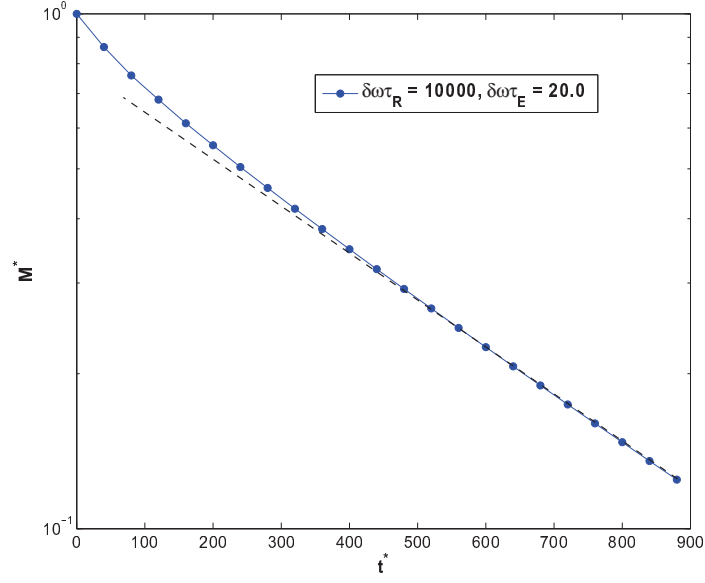


Figure 3.13: Bi-exponential plot for $\zeta = 10000$, $\tau_E^* = 20.0$

conditions for motionally averaging regime are:

$$\tau_R \ll \tau_\omega \quad (3.13)$$

$$\tau_R \ll \tau_E$$

Free diffusion regime: This regime is valid when half echo spacing is the shortest timescale. The effect of restriction as well as large field inhomogeneities are not felt by the spins in the time of echo formation. Thus, spins dephase as if

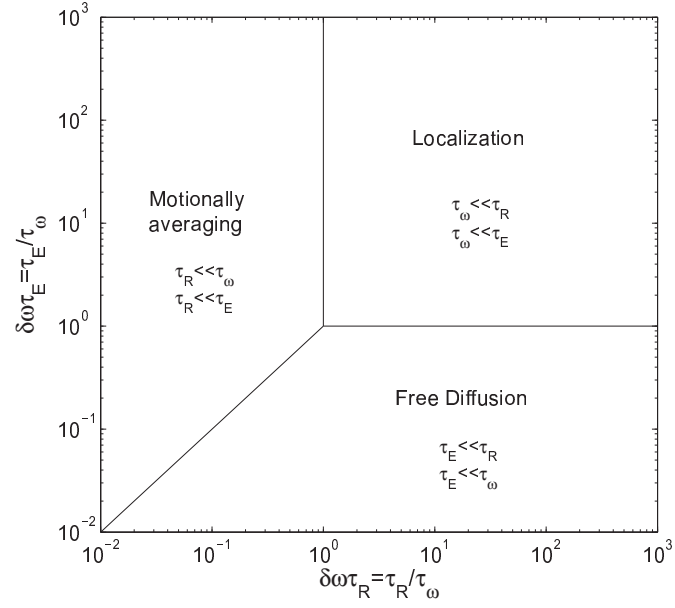


Figure 3.14: Representation of different relaxation regimes as function of three timescales (Anand and Hirasaki 2007b)

diffusing in an unrestricted medium. The conditions for free diffusion regime are:

$$\tau_E \ll \tau_\omega \quad (3.14)$$

$$\tau_E \ll \tau_R$$

Localization regime: This regime is characterized by large field inhomogeneities.

This occurs when the time taken for significant dephasing (τ_ω) is the smallest timescale and is much shorter than other two timescales. The conditions for

localization regime are:

$$\tau_\omega \ll \tau_R \quad (3.15)$$

$$\tau_\omega \ll \tau_E$$

These three relaxation regimes are shown in figure 3.4.

Figure 3.15 is a plot of secular relaxation rate for all values of $\delta\omega\tau_R$ and $\delta\omega\tau_E$ (dimensionless half-echo spacing). The different color series represent simulation results for different values of dimensionless half-echo spacing. We observe that for motionally average regime ($\delta\omega\tau_R < 1$), where τ_R is the smallest timescale, relaxation rates are independent of echo spacing. For localization regime ($\delta\omega\tau_E > 1$) and free diffusion regime ($\delta\omega\tau_E < 1$) relaxation rates are strongly dependent on echo spacing.

Figure 3.16 and 3.17 show the dependence of secular relaxation rate on half echo spacing for two different sets of parameter values of $\delta\omega\tau_R$. The parameters are selected such that free diffusion and localization regimes can be distinguished. Solid lines represents the analytical quadratic dependence of half echo spacing given by Neuman's formula for free diffusion. We observe that for free diffusion regime, the dependence of half echo spacing is quadratic. However, for localization regime the relaxation rates follow less than quadratic dependence on half echo spacing. Figure 3.17 shows that a similar to power-law dependence can also

be observed if during crossover from one regime to another.

In order to better visualize all three regimes on the same plot, we plot the contours of the secular relaxation rate. Figure 3.18 shows the plot of simulated dimensionless relaxation rates ($1/T_{2,\text{secular}}^*$) as a function of $\delta\omega\tau_R$ for different values of $\delta\omega\tau_E$. We observe that for motionally averaging regime, the contour lines are vertical and show no dependence on echo spacing. For free diffusion and localization regimes, contour lines are dependent on echo spacing.

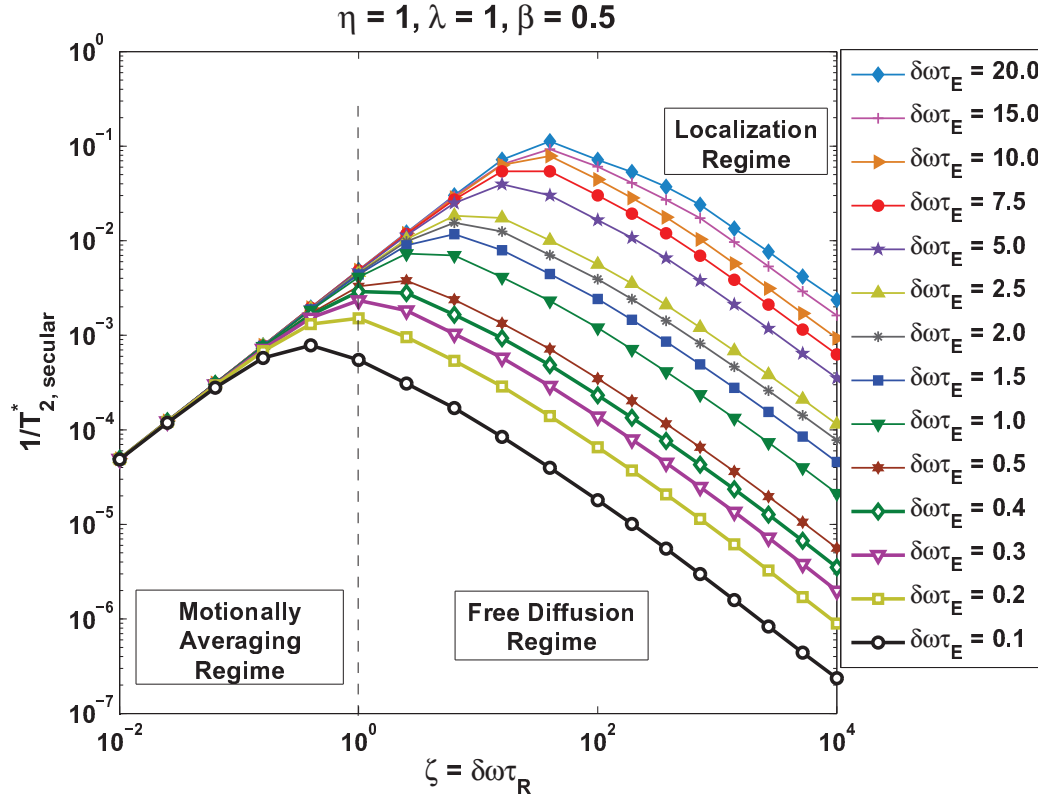


Figure 3.15: A plot of secular relaxation rate versus $\delta\omega\tau_R$ for different values of dimensionless half-echo spacing ($\delta\omega\tau_E$). Geometrical parameters used are: aspect ratio of macropore (η) = 1, aspect ratio of the clay flake (λ) = 1 and microporosity fraction (β) = 0.5

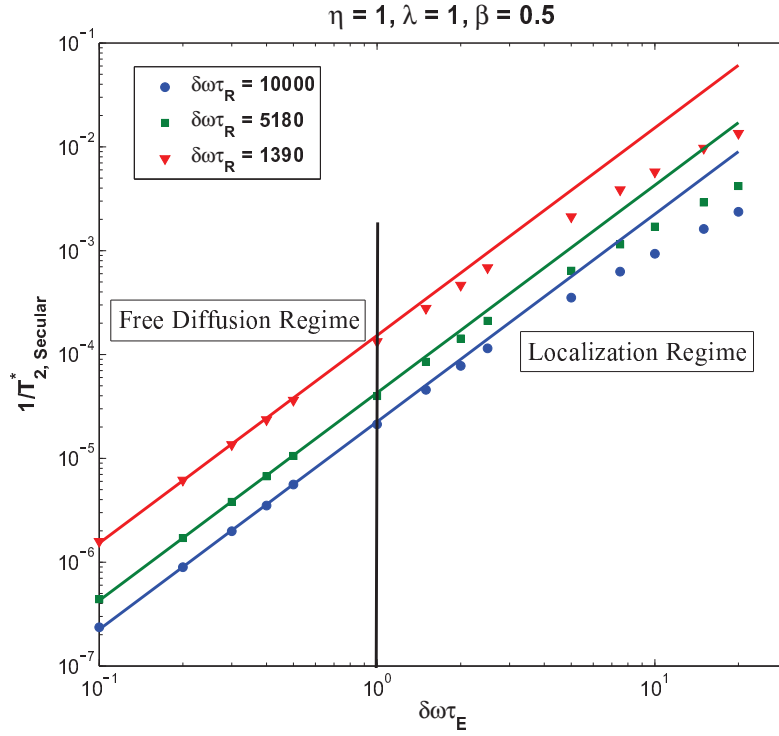


Figure 3.16: Plot of secular relaxation rate as function of $\delta\omega\tau_E$ for different values of $\delta\omega\tau_R$. Geometrical parameters used are: aspect ratio of macropore (η) = 1, aspect ratio of the clay flake (λ) = 1 and microporosity fraction (β) = 0.5

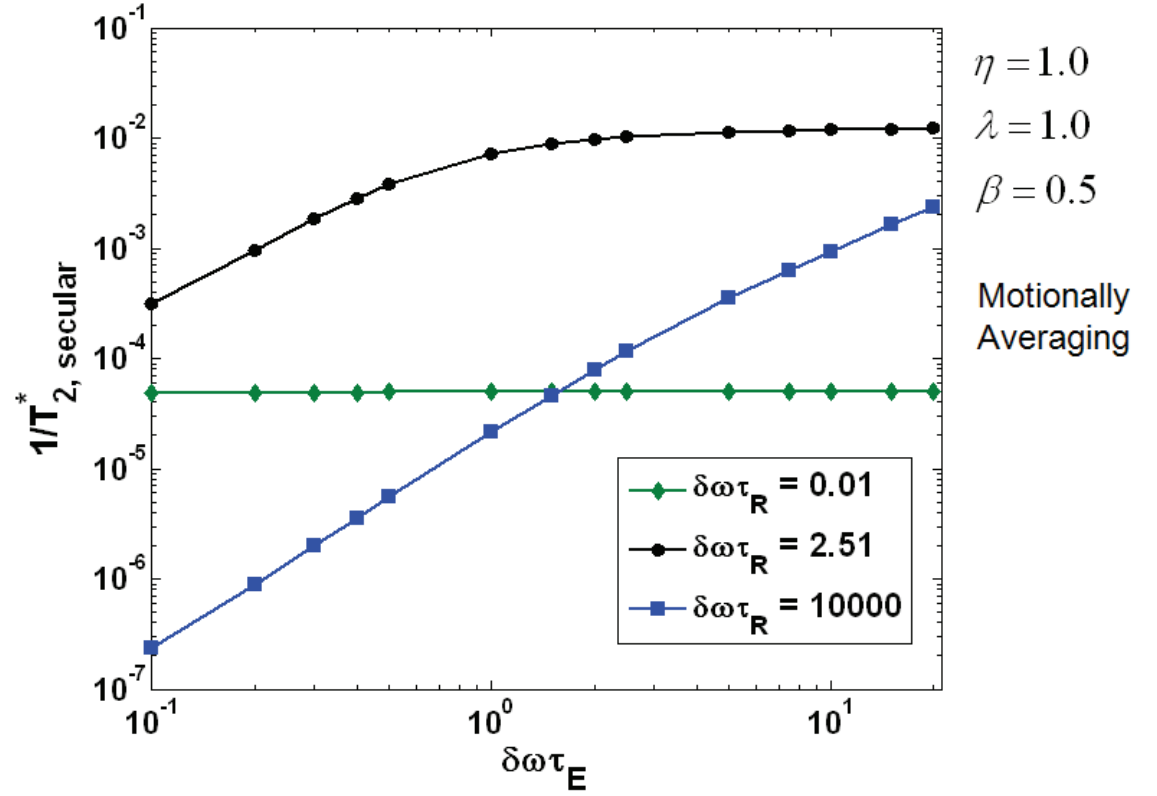


Figure 3.17: Plot of secular relaxation rate as function of $\delta\omega\tau_E$ for different values of $\delta\omega\tau_R$ demonstrating various echo-spacing dependence in different regimes

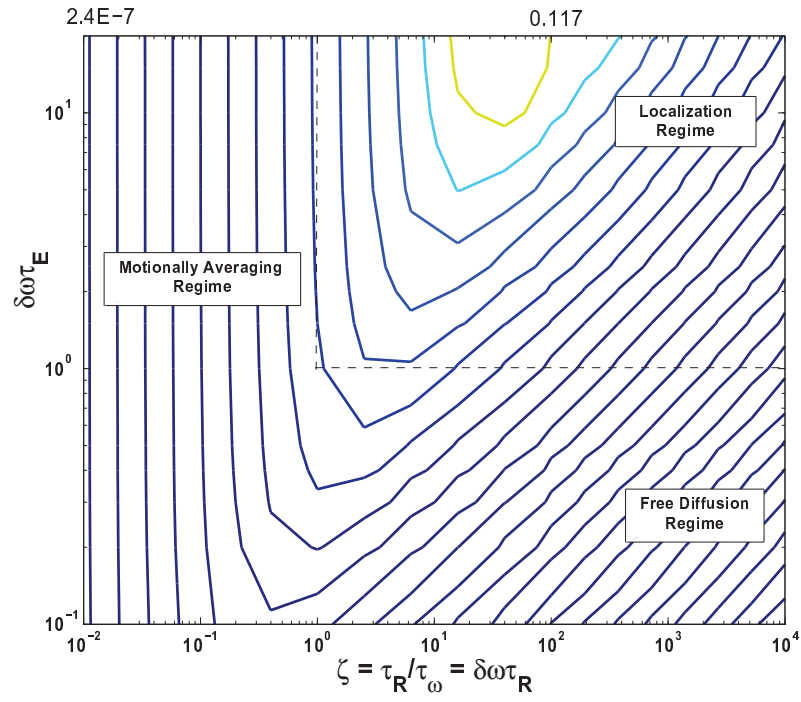


Figure 3.18: Contours of secular relaxation rate as a function of $\delta\omega\tau_R$ for different values of $\delta\omega\tau_E$. Geometrical parameters used are: aspect ratio of macropore (η) = 1, aspect ratio of the clay flake (λ) = 1 and microporosity fraction (β) = 0.5

3.5 Simulations for other geometrical parameters

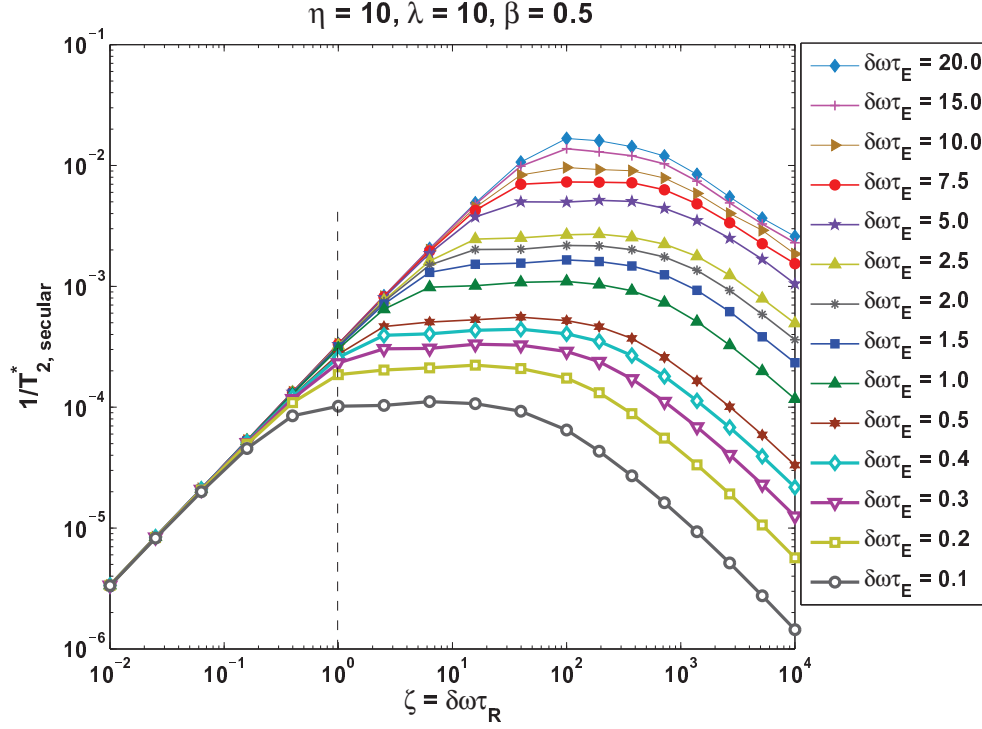


Figure 3.19: A plot of secular relaxation rate versus $\delta\omega\tau_R$ for different values of dimensionless half-echo spacing ($\delta\omega\tau_E$). Geometrical parameters used are: aspect ratio of macropore (η) = 10, aspect ratio of the clay flake (λ) = 10 and microporosity fraction (β) = 0.5

The results described in the previous section are valid only for one set of geometrical parameters and calculated relaxation rates cannot be used for other values of geometrical parameters. A value of 10 – 100 is more representative of

the aspect ratio of macropore. Similarly, photo micrographs of clay flakes reveal that aspect ratio of the pore lining clay flakes are in the range of 10 – 20 (Zhang and Hirasaki 2003).

Figures 3.19, 3.20, 3.21 and 3.22 describe secular relaxation rate for various values of geometrical parameters (η , λ and β). The following observations can be drawn from figures 3.15, 3.19, 3.20, 3.21 and 3.22.

1. We notice that the secular relaxation rate decreases as area fraction of the clay flake, $\frac{\beta^2\eta}{\lambda}$ decreases from 0.25 ($\eta = 1$, $\lambda = 1$ and $\beta = 0.5$) to 0.05 ($\eta = 100$, $\lambda = 20$ and $\beta = 0.1$).
2. The motionally averaging regime is well defined in all of the cases. For $\delta\omega\tau_R < 1$, we observe no dependence on echo spacing for a wide range of echo spacing.
3. The transition from motionally averaging regime to free diffusion or localization regime happens over a large range of parameter $\delta\omega\tau_R$ for large values of η .

The above observations show common features in the results for a wide range of geometrical parameters. This calls for the need to finding appropriate scaling parameters to obtain a single master plot for all values of geometrical parameters. The research work to find scaling parameters is currently under progress.

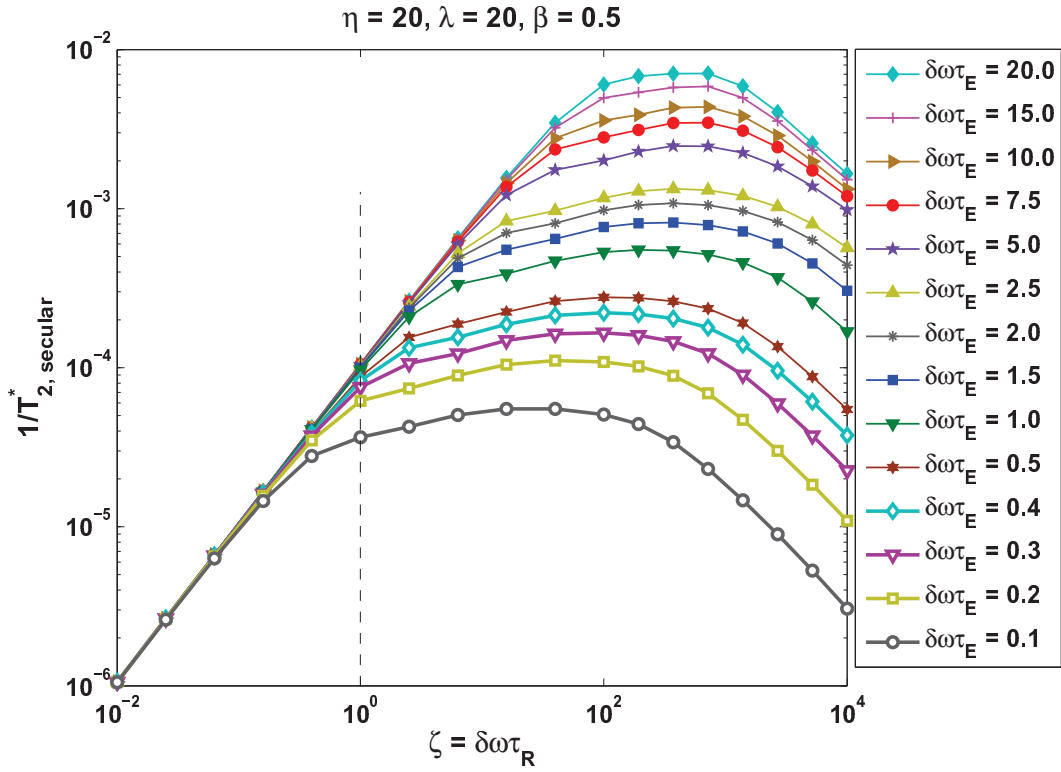


Figure 3.20: A plot of secular relaxation rate versus $\delta\omega\tau_R$ for different values of dimensionless half-echo spacing ($\delta\omega\tau_E$). Geometrical parameters used are: aspect ratio of macropore (η) = 20, aspect ratio of the clay flake (λ) = 20 and microporosity fraction (β) = 0.5

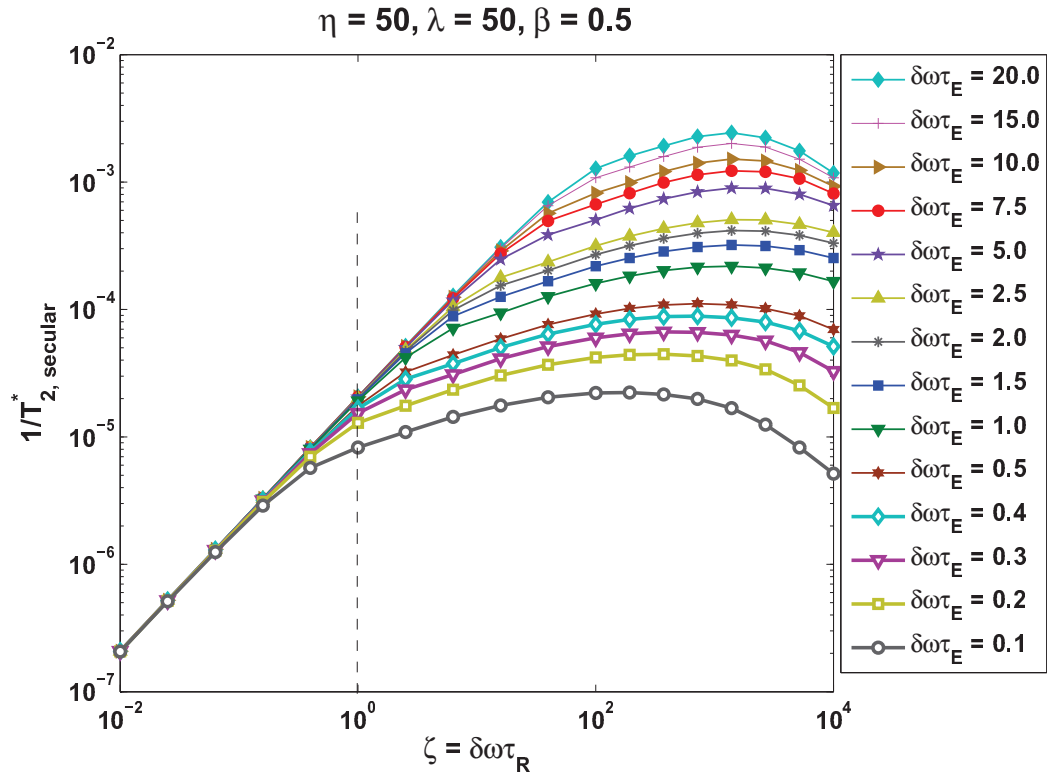


Figure 3.21: A plot of secular relaxation rate versus $\delta\omega\tau_R$ for different values of dimensionless half-echo spacing ($\delta\omega\tau_E$). Geometrical parameters used are: aspect ratio of macropore (η) = 50, aspect ratio of the clay flake (λ) = 50 and microporosity fraction (β) = 0.5

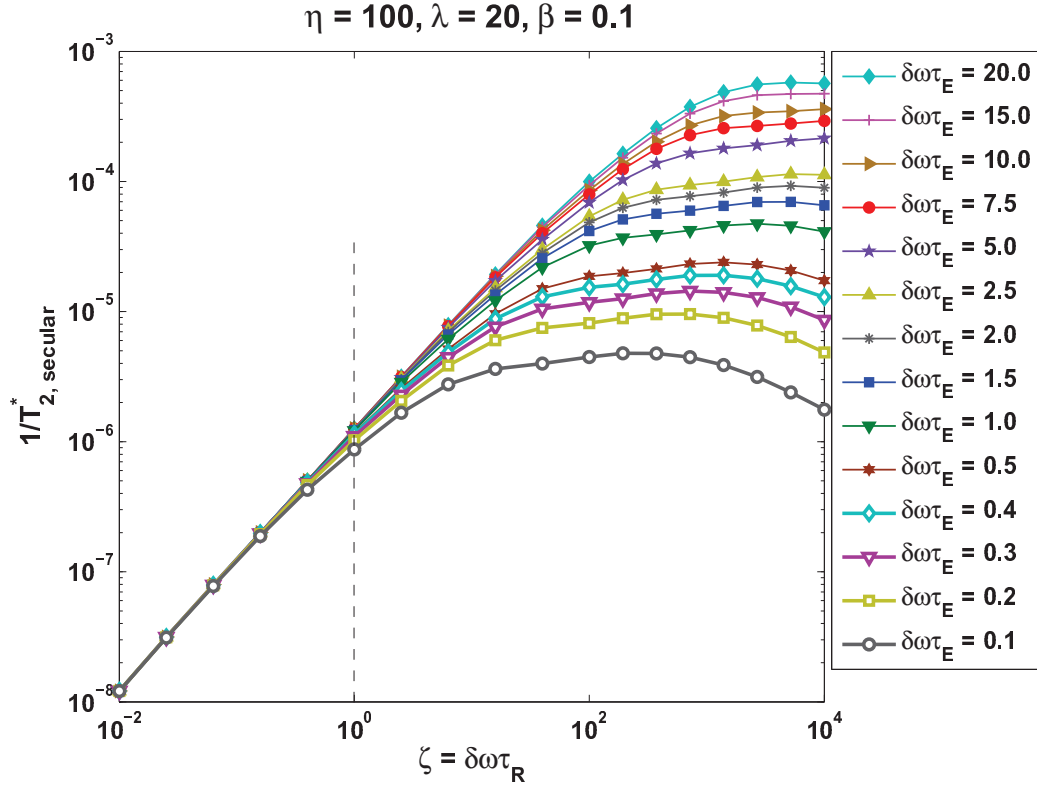


Figure 3.22: A plot of secular relaxation rate versus $\delta\omega\tau_R$ for different values of dimensionless half-echo spacing ($\delta\omega\tau_E$). Geometrical parameters used are: aspect ratio of macropore (η) = 100, aspect ratio of the clay flake (λ) = 20 and microporosity fraction (β) = 0.1

3.6 Conclusions

In this chapter we described a two dimensional model to study transverse relaxation in the presence of internal field gradients. Free induction decay (FID) in the presence of internal field gradients can exhibit non-monotonically decreasing behavior. This behavior was explained with the help of a test case involving no diffusion.

A simple two dimensional model is able to capture the spectrum of relaxation regimes for transverse relaxation. No echo spacing dependence of transverse relaxation rate is observed in motionally averaging regime. Localization and free diffusion regimes show strong dependence of transverse relaxation on echo spacing. Relaxation rates follow quadratic echo spacing dependence in free diffusion regime while less than quadratic dependence on echo spacing is observed for localization regime. A power-law dependence on echo-spacing is observed for crossover from one regime to another.

Chapter 4

Characterization of pore structure in vuggy carbonates

More than 50 % of the world's hydrocarbons are contained in carbonate reservoirs (Palaz and Marfurt 1997). Accurate characterization of pore structure of carbonate reservoirs is essential for design and implementation of enhanced oil recovery processes. However, characterizing pore structure in carbonates is a complex task due to the diverse variety of pore types seen in carbonates and extreme pore level heterogeneity.

Carbonate reservoirs have complex structures because of depositional and diagenetic features. Carbonates may contain not only matrix and fractures but also vugs. A vug can be defined as any pore that is significantly larger than a grain or inside of a grain. Vugs are commonly present as leached grains, fossil chambers, fractures, and large irregular cavities. Vugs are irregular in shape and vary in size from millimeters to centimeters. Vuggy pore space can be divided into separate-vugs and touching-vugs, depending on vug interconnection. Separate vugs are connected only through interparticle pore networks and do not contribute to permeability. Touching vugs are independent of rock-fabric



Figure 4.1: Core ID-1; Length = 9.0 inches, Diameter = 3.5 inches; Fractured, low porosity, No apparent vugs, uniform cylindrical shape

and form an interconnected pore system enhancing the permeability (Palaz and Marfurt 1997). Hence, the fluid flow properties like relative permeability depend on local vug-matrix heterogeneity and connectivity of vugs.

The carbonate samples which are focus of this study are very heterogeneous in pore structures. Some of the sample rocks are breccia and other samples are fractured. Some of the typical core samples are shown in the figures 4.1- 4.5. Core samples of length about 4-9 inches will be used for Tracer experiments. Smaller plugs of diameter 1.5 inch and length 1.5 inch were drilled from the core samples which were not well cored (non-uniform cross section) and were unsuitable for Tracer experiments.

In order to characterize the pore size in vuggy carbonates samples of interest, we use NMR along with tracer analysis. The distribution of porosity between micro and macro-porosity can be measured by NMR. However, NMR can not



Figure 4.2: Core ID-2; Length = 5.5 inches, Diameter = 3.5 inches; Vuggy, well cored, uniform cylindrical shape



Figure 4.3: Core ID-3; Length = 3.5, 6 inches, Diameter = 3.5 inches; Very vuggy, well cored, uniform cylindrical shape



Figure 4.4: Core ID-4; Length = 4 inches, Diameter = 4.0 inches; Some big vugs, well cored



Figure 4.5: Core ID-5; Length = 4.0 inches, Diameter = 4.0 inches; Breccia, very vuggy and heterogeneous

predict if different sized vugs are connected or isolated. Tracer analysis will be used to characterize the connectivity of the vug system and matrix. Tracer analysis will also give valuable insight on fraction of dead-end pores and dispersion effects.

4.1 NMR Experiments

Core-plugs of diameter 1.0 and 1.5 inches and lengths between 1.5 and 3.0 inches were drilled from the rock samples. The experimental protocol used is as follows:

1. **Cleaning:** Drilling mud and other solid particles from vugs were removed using a Water Pik. Core-plugs were first cleaned using a bath of Tetrahydrofuran (THF) followed by Chloroform and Methanol. Core-plugs were dried overnight in the oven at 80 °C. Figures 4.6 and 4.7 show the pictures of core-plugs before and after cleaning. Core-plugs were wrapped in heat shrink tubing to protect against wear and tear and chipping away of the sharp edges.
2. After cleaning, core-plugs were saturated with 1 % NaCl brine solution using vacuum saturation followed by pressure saturation at 1000 psi for 24 hours.
3. Core-plugs were weighed to calculate amount of brine taken during vacuum and pressure saturation steps.

4. Before performing experiment, core-plug was wrapped in paraffin film to avoid the gravity drainage of brine solution from big vugs.
5. Core-plugs were weighed after experiment to account for any evaporation of water during the experiment.

Figures 4.6 and 4.7 show the comparison between core-plugs before and after cleaning. We observe that after cleaning any residual oil is effectively removed from the core samples and vugs are free of any drilling solids.

4.2 NMR T_2 Relaxation and pore size distribution

In this section we describe the T_2 relaxation times obtained from NMR measurements on three different core-plugs. NMR experiments were performed on 100 % brine saturated core-plugs on 2 MHz Maran-SS. For experiments, half-echo spacing of 200 μ s was used and signal to noise ratio of 100 was used. Waiting time of 5 times the largest T_2 relaxation time component was used between successive scans.

Since the carbonate samples do not contain any paramagnetic clays, the shape of T_2 relaxation spectrum is representative of the pore size distribution of the sample. The largest T_2 relaxation component is typically around 2.7 seconds which corresponds to the T_2 relaxation time of the bulk water residing in large vugs. Smaller relaxation time components represent small sized pores.



Figure 4.6: A comparison of before (shown at left) and after (shown at right) cleaned pictures for a core-plug (Plug ID: 3V)

S. No.	Core ID	Diameter (cm)	Length (cm)	porosity (%)	Type
1	3V	3.7	3.2	11.9	vuggy
2	2V	3.7	3.6	14.3	vuggy
3	1H	3.8	5.7	13.5	vuggy
4	5H	3.8	3.3	4.8	no vugs

Table 4.1: Comparison of porosity for different core-plugs

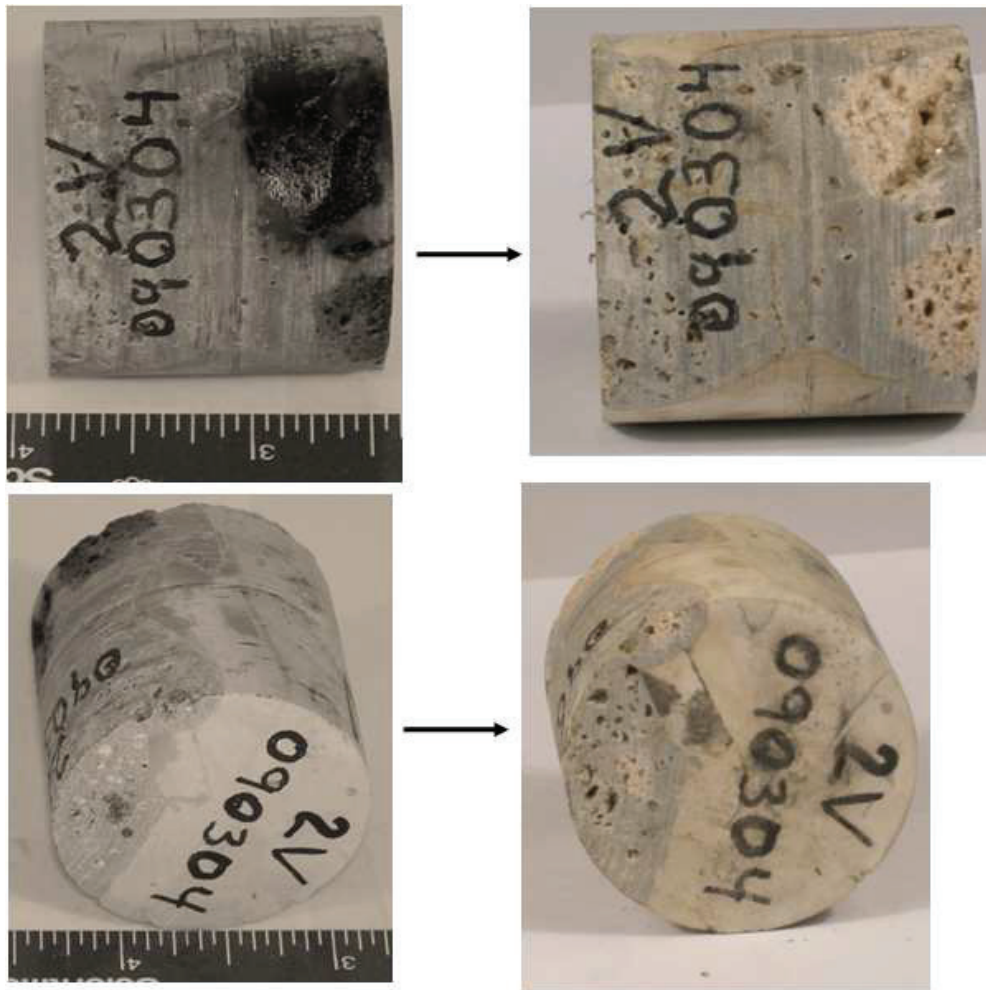


Figure 4.7: A comparison of before (shown at left) and after (shown at right) cleaned pictures for a core-plug (Plug ID: 2V)

Figures 4.8-4.12 show T_2 relaxation time spectrum for various core plugs taken from different source rocks. Black solid vertical line corresponds to the traditional cutoff value of 90 ms for carbonate rocks. The dashed vertical line separates the relaxation spectrum into non-vuggy and vuggy porosity by assuming that T_2 values of 750 ms and higher correspond to vugs ((Chang, Vinegar, Morriss and Straley 1997)). The permeability values for the majority of the core plugs are within the range of 0.5-6 mD. Figure 4.8 shows the T_2 relaxation time spectrum for a sample which had many visible large solution vugs on the surface. Figure 4.8 shows that for core plug 3V majority of the porosity resides in these large vugs and contribution of small pore sizes to porosity is very small. NMR response for core plug 2V (Figure 4.9) shows the peak at relaxation time of about 90 ms. Using the traditional cut off formula would classify 2V sample as non-pay. The low value of permeability suggests that the vugs do not form an interconnected pore network.

Figure 4.10 shows the T_2 relaxation time spectrum for a core plug 2VA. Although, this plug was drilled from the same source rock as the previous sample (Figure 4.9), NMR response shows a large contribution from vugs and relatively smaller contribution from small sized pores. Figure 4.11 and 4.12 show the T_2 relaxation time spectrum for core plugs 1H and 1HA. In both cases, we observe that relaxation time has contributions from small sized micro-pores, vugs and some intermediate size pores. The low value of permeability suggests that vugs

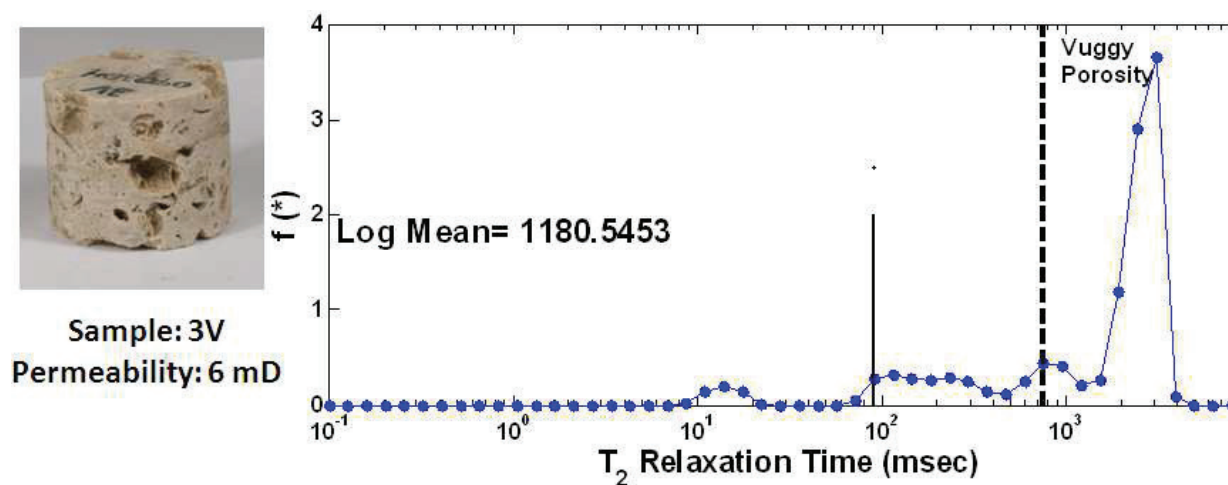


Figure 4.8: T_2 relaxation time spectrum for 100 % brine saturated core-plug (Plug ID: 3V)

are isolated vugs and do not create any interconnected flow channels.

NMR results suggest that these carbonate rocks are very heterogeneous. In some cases, vugs contribute most to the porosity while in other smaller pores are dominant. Samples taken within the proximity of 3 inches exhibit very different T_2 relaxation time spectrum. Figure 4.13 shows the lack of correlation between T_2 Log mean and the permeability for various core plugs. Chang et al. (1997) suggested a 750 msec cut off value to calculate the effective T_2 Log mean to correlate with the permeability value. Despite using the 750 msec cut off value to exclude the vug contribution to permeability, Figure 4.14 shows the lack of any significant correlation between permeability and T_2 Log mean.

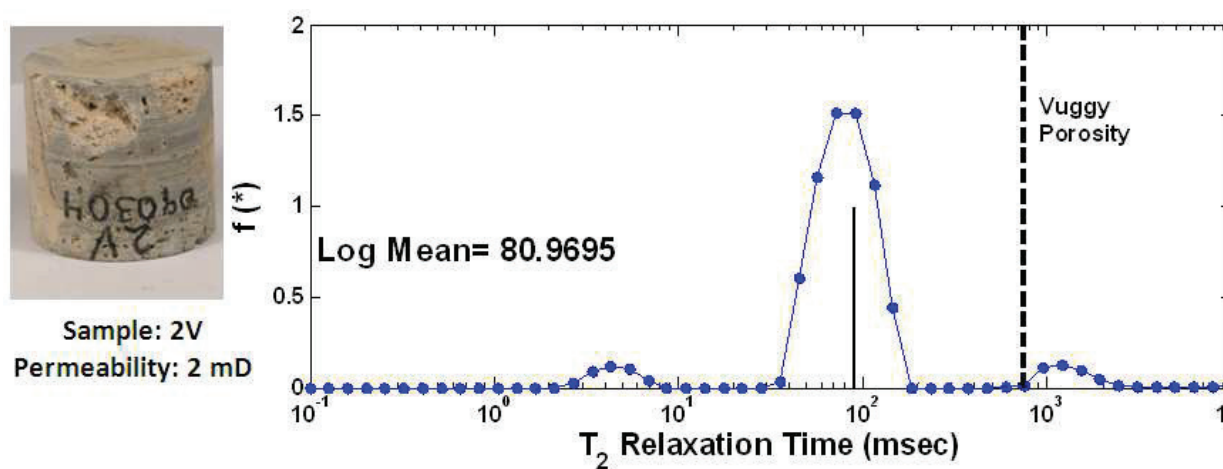


Figure 4.9: T_2 relaxation time spectrum for 100 % brine saturated core-plug (Plug ID: 2V)

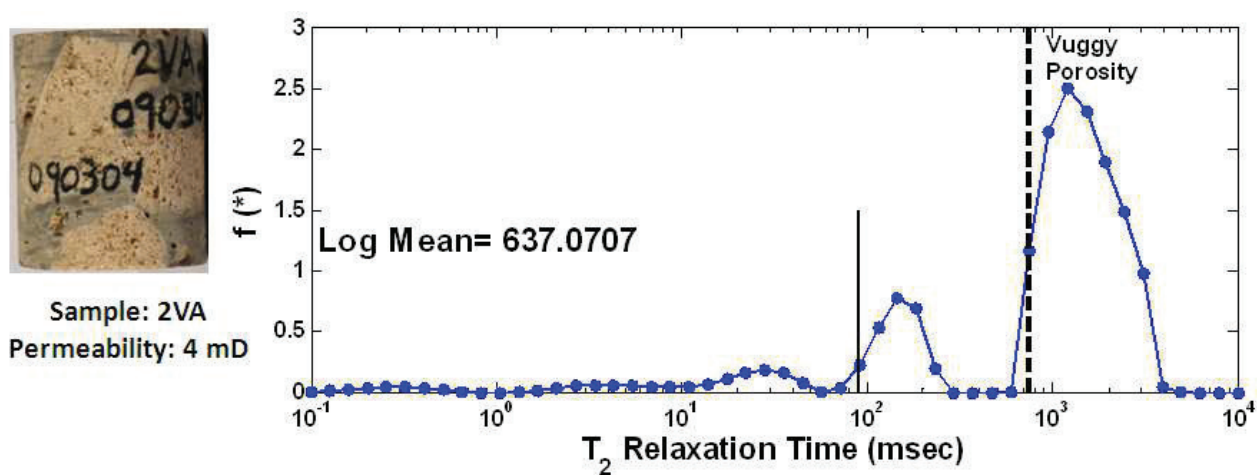


Figure 4.10: T_2 relaxation time spectrum for 100 % brine saturated core-plug (Plug ID: 2VA)

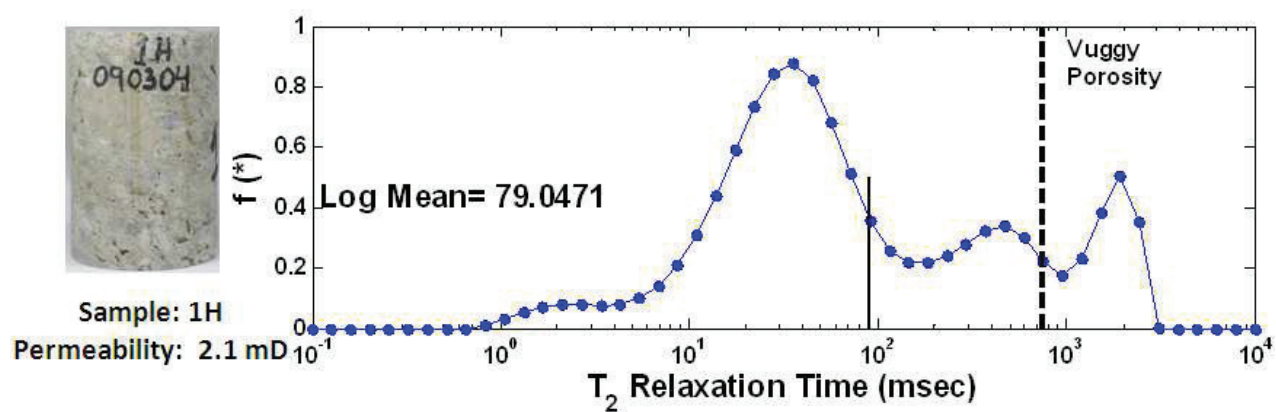


Figure 4.11: T_2 relaxation time spectrum for 100 % brine saturated core-plug (Plug ID: 1H)

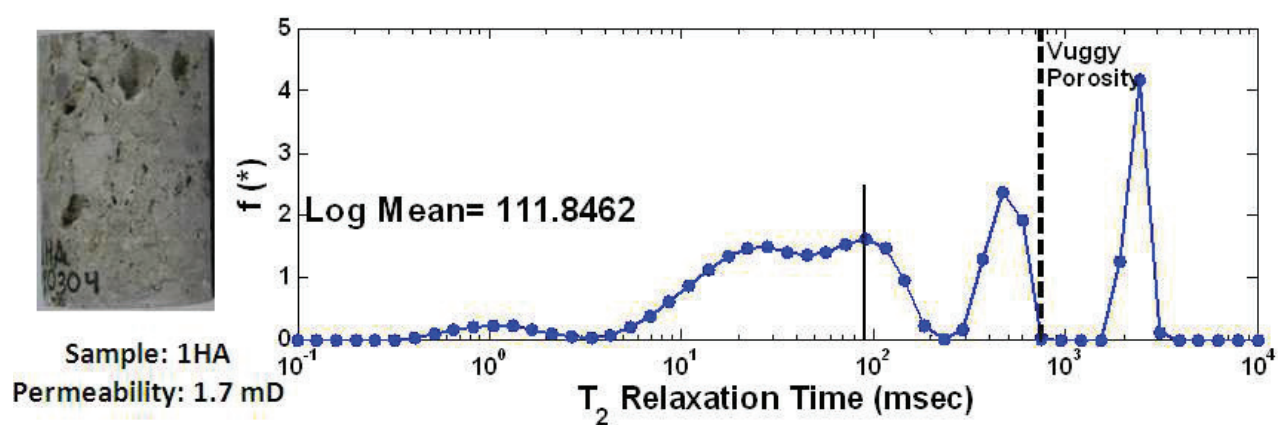


Figure 4.12: T_2 relaxation time spectrum for 100 % brine saturated core-plug (Plug ID: 1HA)

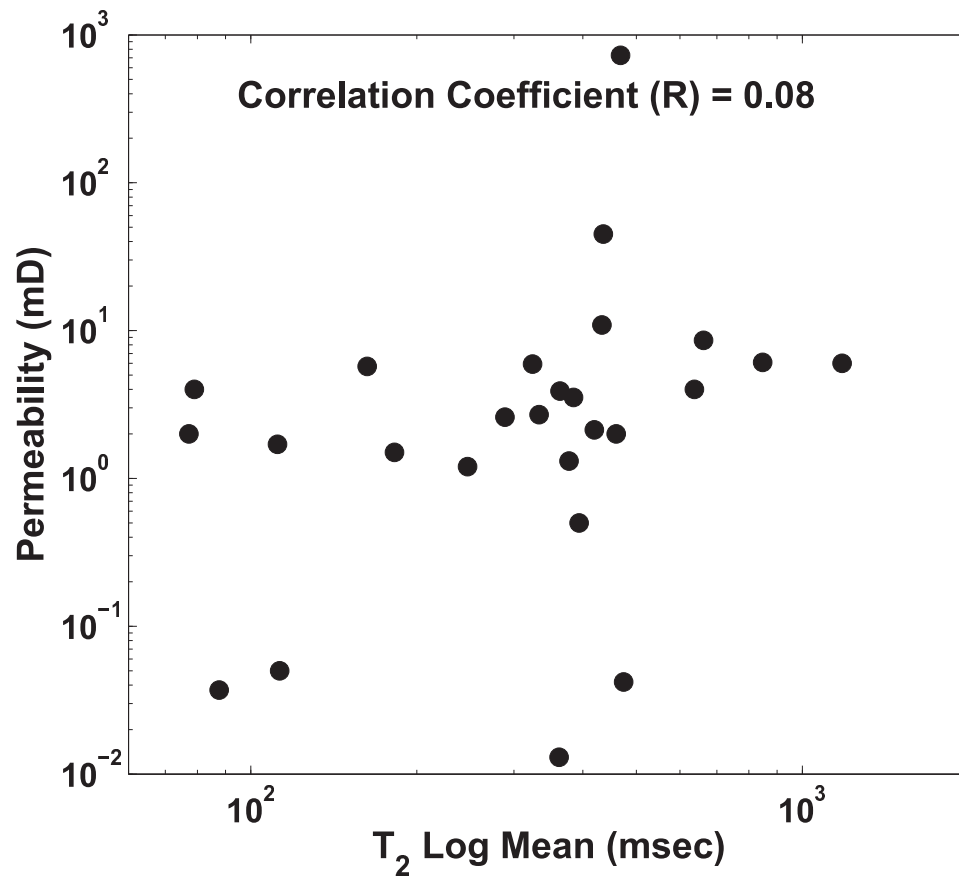


Figure 4.13: Permeability versus T_2 Log mean for various core samples

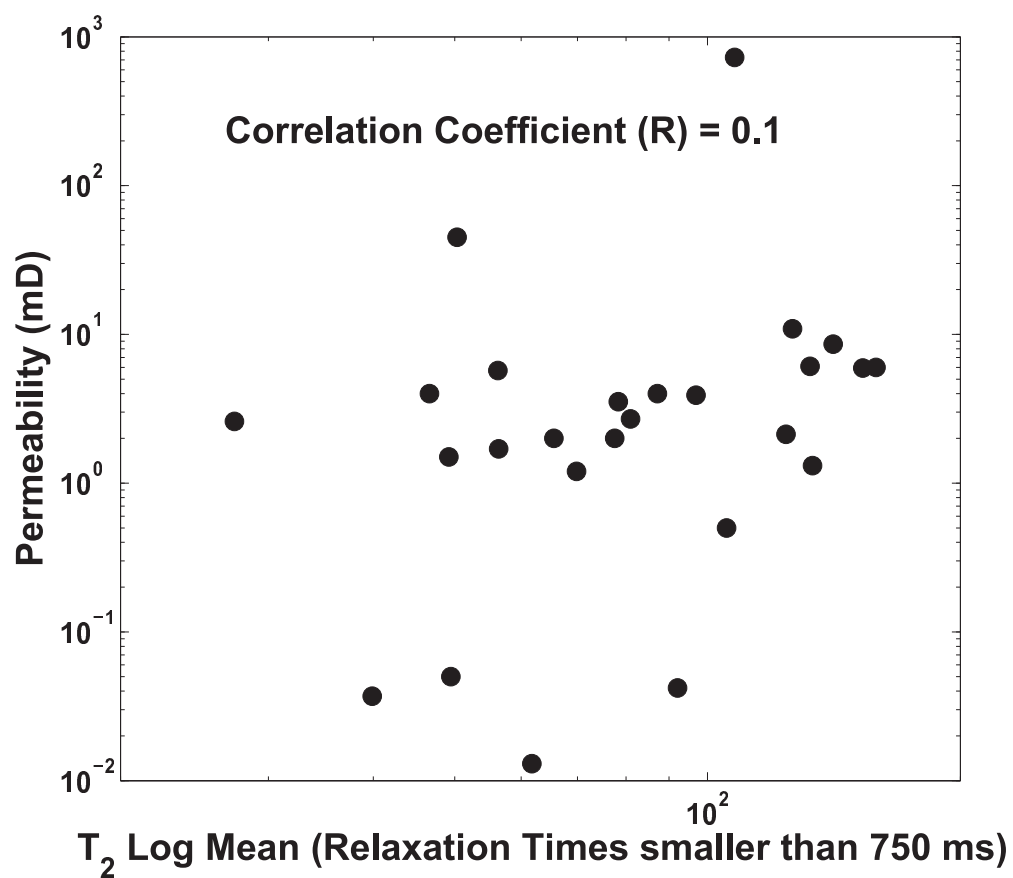


Figure 4.14: Permeability versus T_2 Log mean while using T_2 cut off of 750 msec for various core samples

4.3 Calculating specific surface area of the rock from NMR

T_2 distribution

The NMR T_2 distribution can be converted into pore size distribution using the surface relaxivity. The surface relaxivity can be computed by measuring the NMR T_2 relaxation time of 100% brine saturated crushed rock sample in powder form and the BET surface area of the crushed rock sample. The BET surface area of the sample was measured to be $1.5 \text{ m}^2/\text{gm}$.

$$\frac{1}{\rho T_2} = \frac{S}{V_{PV}} = \left(\frac{S}{W} \right)_{BET} \left(\frac{\phi}{1 - \phi} \right) \rho_g \quad (4.1)$$

$$\frac{S}{V_{PV}} = \frac{1}{\rho \sum_i f_i} \left(\sum_i \frac{f_i}{T_{2i}} \right) \quad (4.2)$$

The above equations can be used to calculate the surface relaxivity using the NMR T_2 distribution and the BET surface area. The value of surface relaxivity then can be used to calculate the specific surface area of the given sample using the following relationship:

$$\frac{S}{W} = \frac{\sum_i \frac{f_i}{T_{2i}}}{\rho \sum_i f_i} \left(\frac{1 - \phi}{\phi} \right) \frac{1}{\rho_g} \quad (4.3)$$

Where, ϕ is the porosity, $\left(\frac{S}{W} \right)_{BET}$ is the BET specific surface area, V_{PV} is the pore volume of the rock sample, ρ_g is the grain density and f_i is the amplitude

of the $T_2\rho$ component in NMR T_2 distribution. Figure 4.15 show the relationship between NMR T_2 distribution and the S/V distribution. The S/V distribution appears as mirror image of the NMR T_2 distribution. The figure 4.16 shows the NMR T_2 distribution of the 100% brine saturated crushed rock sample. The surface relaxivity of the crushed rock sample in powder form was calculated to be $7.4 \mu m/sec$. This value of surface relaxivity is used to compute the specific surface area of various rock samples using NMR T_2 distribution. Figure 4.17 shows the specific area (m^2/gm) of the some of the rock samples. We notice that the reservoir rock samples have as high as five times the specific surface area of the Silurian outcrop sample. This difference in specific surface area can result in higher value of surfactant adsorption for reservoir rock than that for the Silurian outcrop sample.

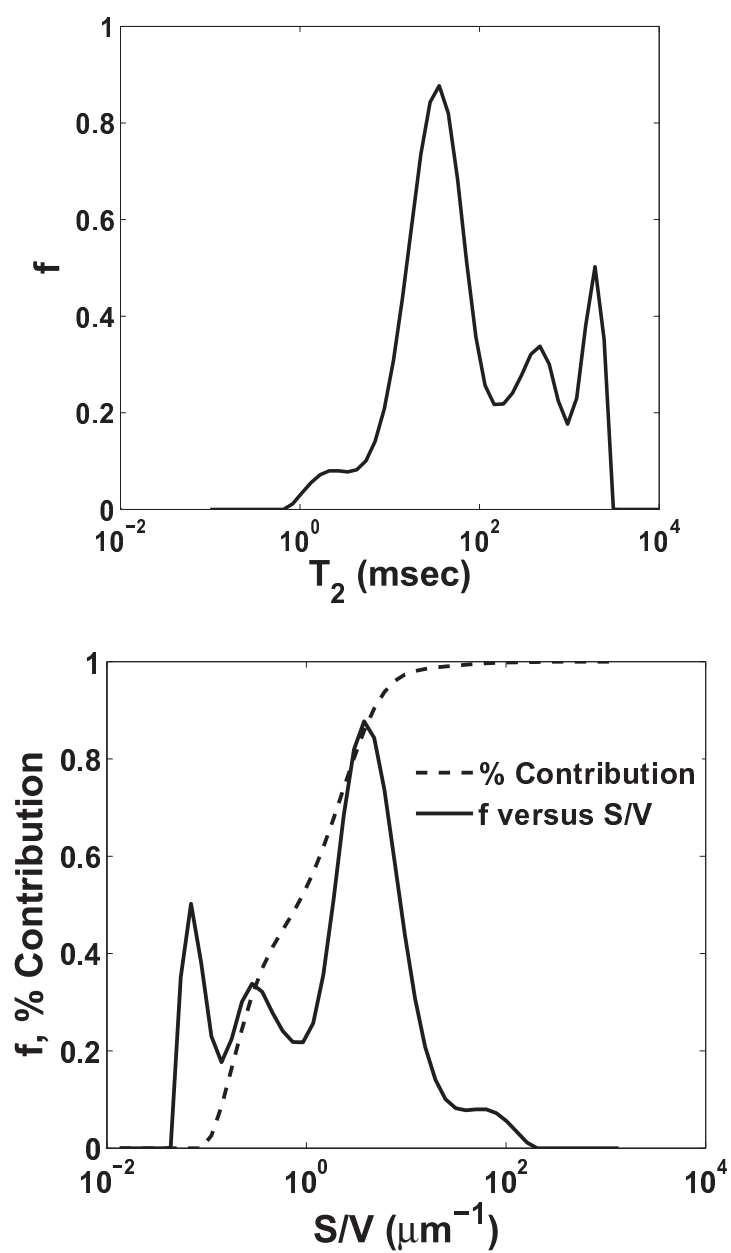


Figure 4.15: T_2 relaxation time and S/V spectrum for 100 % brine saturated core-plug (Plug ID: 1H)

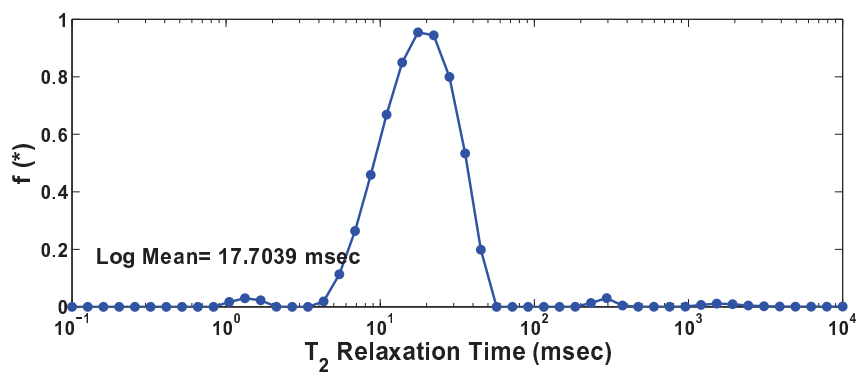


Figure 4.16: T_2 relaxation time spectrum for 100 % brine saturated crushed rock powder

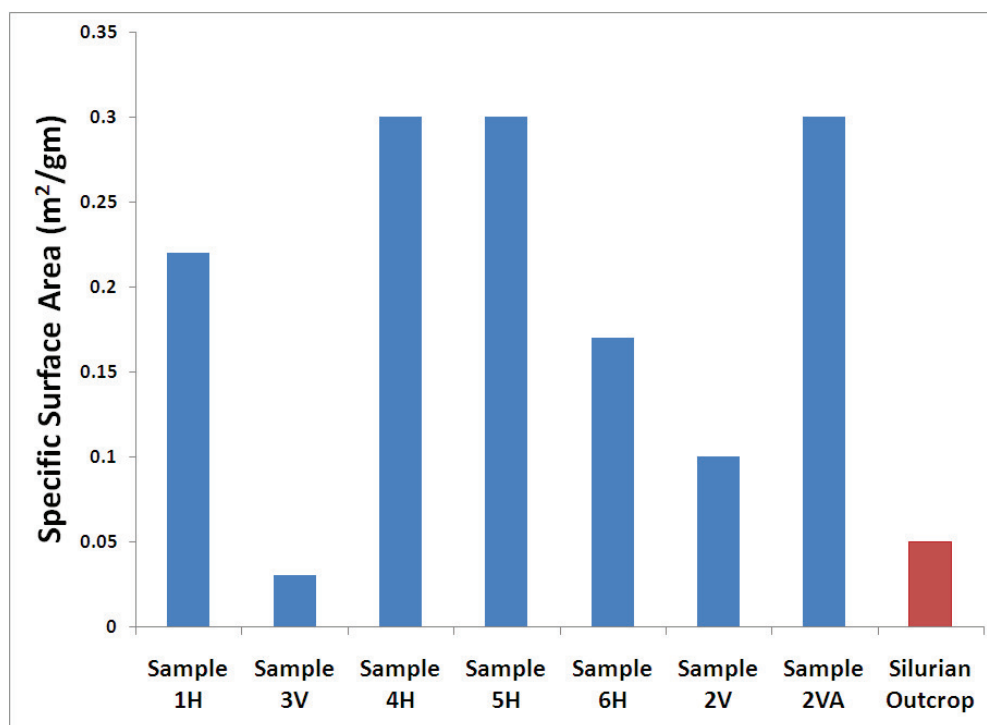


Figure 4.17: A bar chart for the specific surface area of several core plugs

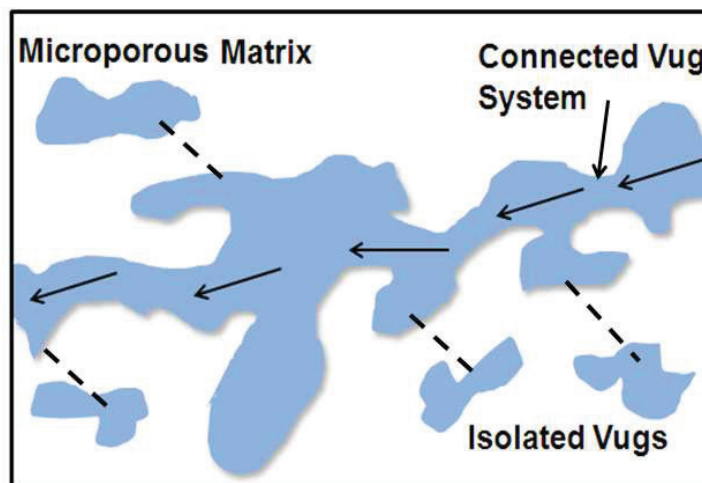


Figure 4.18: Schematic of the pore system containing interconnect flow channels, touching/isolated vugs and stagnant/dead end pores

4.4 Tracer Analysis

In this section, we describe methods to characterize the key features of pore structure such as fraction of dead-end pores and dispersion and capacitance effects. Figure 4.18 describes the schematics of the interactions between interconnected flow channels and stagnant or dead end pores. We use the modified version of differential capacitance model of Coats and Smith (1964) and a solution procedure developed by Baker (1975) to study dispersion and capacitance effects in cores. Brigham (1974) showed that differential capacitance model can be written for either flowing (effluent) concentration or in-situ concentration. The convection-dispersion equation (CDE) remains same for both concentrations. However, the

boundary conditions are different for flowing or in-situ concentrations. During tracer experiments, flowing concentrations are measured hence in the following formulation we work with flowing (effluent) concentrations. The differential capacitance model assumes:

1. The fluid flow is one dimensional
2. The fluid flow is single phase flow
3. The fluid and porous media are incompressible
4. The fluid density is constant
5. The porosity is constant through out the system

The model can be described by the following set of differential equations:

$$f \frac{\partial C}{\partial t} + (1 - f) \frac{\partial C^*}{\partial t} = K \frac{\partial^2 C}{\partial x^2} - \frac{u}{\phi} \frac{\partial C}{\partial x} \quad (4.4)$$

$$(1 - f) \frac{\partial C^*}{\partial t} = M(C - C^*) \quad (4.5)$$

The domain of interest is: $x > 0$ & $t > 0$

Where, K is dispersion coefficient, $(1 - f)$ is the fraction of dead end pores, ϕ is the porosity, M is the mass transfer coefficient, C is tracer concentration in flowing stream, C^* is the tracer concentration in stagnant volume and u is the superficial velocity. Interstitial velocity v can be defined as, $v = \frac{u}{\phi}$. The boundary

and initial conditions are:

$$C(0, t) = C_{\text{BC}}$$

$$C(\infty, t) = 0$$

$$C(x, 0) = C_{\text{IC}}$$

$$C^*(x, 0) = C_{\text{IC}}$$

C_{BC} is injected concentration at the inlet ($x=0$) and C_{IC} is the initial concentration in the system at the start of the experiment ($t=0$). The governing and boundary and initial conditions are made dimensionless as follows: $\hat{x} = \frac{x}{L}$, $\hat{t} = \frac{t}{t_0}$, $t_0 = \frac{L}{v}$; where v is the interstitial velocity $v = \frac{u}{\phi}$ and L is system length. Dimensionless concentrations are defined as:

$$\hat{C} = \left(\frac{C - C_{\text{IC}}}{C_{\text{BC}} - C_{\text{IC}}} \right) \quad \text{and} \quad \hat{C}^* = \left(\frac{C^* - C_{\text{IC}}}{C_{\text{BC}} - C_{\text{IC}}} \right)$$

Using the above mentioned dimensionless variables the governing equations become:

$$f \frac{\partial \hat{C}}{\partial \hat{t}} + (1 - f) \frac{\partial \hat{C}^*}{\partial \hat{t}} = N_K \frac{\partial^2 \hat{C}}{\partial \hat{x}^2} - \frac{\partial \hat{C}}{\partial \hat{x}} \quad (4.6)$$

$$(1 - f) \frac{\partial \hat{C}^*}{\partial \hat{t}} = N_M (\hat{C} - \hat{C}^*) \quad (4.7)$$

The dimensionless boundary and initial conditions become:

$$\hat{C}(0, \hat{t}) = 1$$

$$\hat{C}(\infty, \hat{t}) = 0$$

$$\hat{C}(\hat{x}, 0) = 0$$

$$\hat{C}^*(\hat{x}, 0) = 0$$

Where, the dimensionless groups N_M and N_K are defined as follows:

$$N_M = \frac{ML}{v} = \frac{L/v}{1/M} \quad \text{and} \quad N_K = \frac{K}{Lv} = \frac{\alpha}{v}$$

N_K is similar to the inverse of macroscopic Peclet number. N_M defines the ratio of the rate of mass transfer to the rate of convection. α is dispersivity which is the ratio of dispersion coefficient and interstitial velocity. The above set of differential equations with given boundary and initial conditions can be solved using Laplace transform. The solution depends only on three dimensionless parameters f , N_M and N_K . The solution can be expressed in terms of dimensionless Laplace variable as follows:

$$\mathcal{L}(\hat{C}) = \left(\frac{1}{\hat{s}}\right) \exp \left[\left(\frac{\hat{x}}{2N_K}\right) \left(1 - \sqrt{1 + 4N_K \hat{S} \left(f + \frac{N_M}{\hat{s} + \frac{N_M}{1-f}}\right)}\right) \right] \quad (4.8)$$

$$G(\hat{S}) = \frac{\mathcal{L}(\hat{C})}{\mathcal{L}(\hat{C}_{\text{BC}})} \quad (4.9)$$

$G(\hat{S})$ is the ratio of the Laplace transform of the effluent concentration to the Laplace transform of the boundary condition. This is referred as the Transfer function of the system. The resulting solution is numerically inverted into time domain using the computer program of Hollenbeck (1998) which is based on the algorithm of De Hoog, Knight and Stokes (1982). A plot of dimensionless effluent concentration as function of model parameters is shown below in Figure 4.19. Figure 4.19 shows the effluent concentration as a function of pore volume throughput for three distinct cases. When the flowing fraction is unity, effluent concentration curve is symmetric around one pore volume with the concentration of about 0.5 at one pore volume. This represents the case of the homogeneous system with dispersion. For the second case, the value of flowing fraction is 0.1 and the value of $N_M = 0.1$. In this scenario the effluent concentration rises rapidly due to small flowing fraction at early times followed by a long tail which represents small mass transfer between flowing and stagnant streams. For the third case, the flowing fraction is 0.1 but the value of N_M is three orders of magnitude higher than that for the second case. In third case, due to strong mass transfer between stagnant and flowing streams, the effluent concentration curve does not exhibit a sharp rise and a long tail at larger times. A large value of N_M causes the effluent concentration curve to appear similar to the case of a fictitious larger flowing fraction and small mass transfer. This is expected due

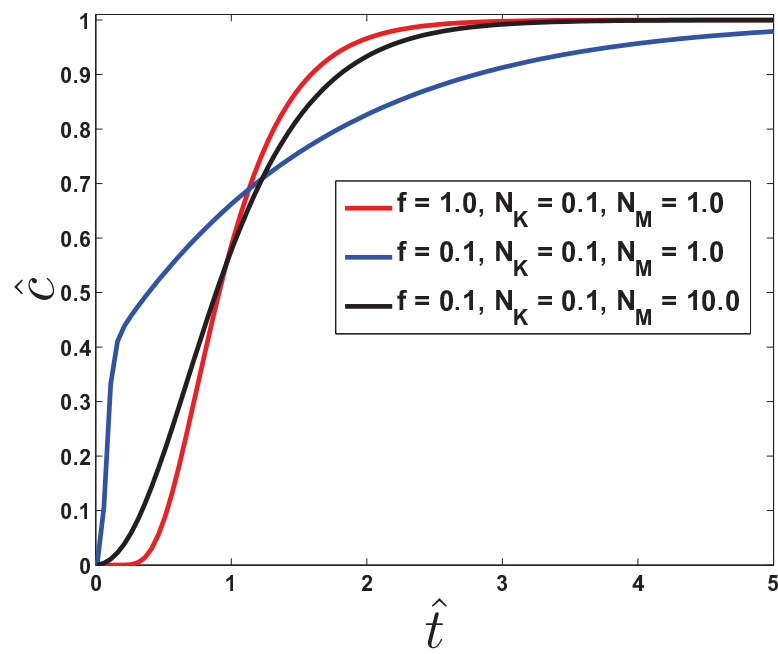


Figure 4.19: Effluent concentration versus pore volume throughput for a set of dimensionless parameters

to the fact that the solution to the Coat's and Smith model is not unique. The problem of the non-uniqueness of the solution will be discussed in more detail in the section describing the inversion process to obtain the fitted model parameters from tracer flow experiments.

4.5 Recovery Efficiency and Transfer Between Flowing And Stagnant Streams

Tracer flow analysis described in previous section can be complimented with the help of recovery efficiency calculations. Recovery efficiency is defined as the fraction of initial fluid in place displaced with injected tracer fluid.

$$\text{Recovery Efficiency} = \int_0^{\hat{t}_{max}} (1 - \hat{C}) d\hat{t}$$

Hence, recovery efficiency can be plotted as a function of pore volume throughput. When all of the initial fluid in place is displaced by injected tracer fluid, the recovery efficiency approaches unity. Two sets of synthetic datasets shown in figure 4.20 have the same value of flowing fraction and dispersivity (α) but different values of mass transfer group (N_M). In first case even though the effluent concentration approaches unity after 1.5 pore volumes, the recovery efficiency is only 0.4 and hence most of initial fluid in place has not been replaced by injected tracer fluid. Larger value of N_M in second case results in significant mass transfer between flowing and stagnant streams and recovery efficiency approaches unity

after about 2 pore volumes. Hence, recovery efficiency is an excellent measure of the fraction of dead end pores contacted by displacing tracer fluid.

4.6 Parameter estimation from experimental data of tracer concentration

Baker (1975) suggested that rather than transforming equation 4.8 into time domain for the purpose of parameter estimation, the experimental data could be transformed into the Laplace domain for obtaining fitted parameters using least square curve fitting. The sum of squared errors can be defined as:

$$E = \sum_{\hat{s}} \left| \left[\frac{\mathcal{L}(\hat{c})}{\mathcal{L}(\hat{c}_{BC})} \right]_{\text{calc}} - \left[\frac{\mathcal{L}(\hat{c})}{\mathcal{L}(\hat{c}_{BC})} \right]_{\text{exptl}} \right|^2 \quad (4.10)$$

The fitted parameters correspond to a set which minimizes the error defined by equation 4.10. For parameter estimation, a computer program is written which uses a built-in Matlab function for curve fitting based on Lavenberg-Marquardt algorithm (Marquardt 1963).

To check the accuracy of curve fitting routine, synthetic experimental data is generated for a known set of parameters. This synthetic data is treated as experimental data and fitted set of parameters are obtained. In another case, some random noise is added to the synthetic data as shown in figure 4.21 and the fitted set of parameters are obtained without any difficulty. When the value of

N_M is large, the fitted parameters may not be correct due to the non-uniqueness of the solution as shown in figure 4.23(A) where the inversion routine yields the incorrect value of the model parameters used to create synthetic data. This happens because a large value of the mass transfer coefficient allows the exchange between stagnant and flowing stream and resulting fitted parameters show apparent higher value of flowing fraction. To obtain unique set of parameters, we utilize the experimental data of effluent concentration at two different flow rates. We further assume that mass transfer between stagnant and flowing streams is dominated by diffusion process and the mass transfer coefficient does not depend on the flow rate. The dispersion coefficient (K) is assumed to vary linearly with the interstitial velocity (v). We use these additional constraints in the cost function of the parameter estimation algorithm and obtain the correct value of the fitted model parameters as shown in figure 4.23(B).

4.7 Setup for the Tracer flow experiments and the data acquisition protocol

The core holder for 1.5 inch diameter samples is Hassler type core holder. We have adopted similar design for fabricating the flow setup for 3.5 inch diameter core samples. Core holder for 3.5 inch diameter samples was custom fabricated in a machine shop. High impact PVC is used to fabricate the end pieces and spacers

of the core holder while readily available PVC pipes are used for the outside jacket of the core holder. A commercially available core holder is used for 4.0 inch diameter samples. Based on the NMR T_2 and permeability measurements, the larger diameter samples are better candidates to study the connectivity of vugs and to accurately characterize the pore structure. Sodium bromide is used as non-adsorbing tracer in the experiments. For experiments, the initial tracer concentration is 100 ppm and injected tracer boundary condition is 10,000 ppm. To measure the tracer concentration at outlet, a bromide ion sensitive electrode is used in combination with a flow cell. The total Halide concentration ($\text{Cl}^- + \text{Br}^-$) is kept at 0.15 M throughout the experiment to ensure the stable reading of the electrode. The Bromide ion sensitive electrode and the flow cell enable us to measure the tracer concentration with the help of a LabView data acquisition module without collecting multiple effluent samples in batch and analyzing them separately.

4.7.1 Reproducibility of tracer floods on core samples

Sodium Bromide is assumed to be a non adsorbing tracer in this study. Several experiments were conducted to check the validity of this assumption. One core plug (diameter of 1.5 inches) and one full core sample (diameter of 4.0 inches) were used to run a series of tracer flow experiments and subsequently restored to original initial condition by performing a restore flood of the initial condition.

Figure 4.24 shows the dimensionless effluent tracer concentration for the case of 10,000 ppm flood followed by a 100 ppm restore flood at roughly same interstitial velocity of 1.0 ft/day for a 1.5 inch diameter sample. We notice that the dimensionless effluent concentration curves agree very well with each other within the margin of experimental error. Figure 4.25 shows the effluent tracer concentration for several floods at relatively higher interstitial velocity of about 7.0 ft/day for a 4.0 inch diameter sample. The effluent concentration curves match very well with one another for three different cases of 100 ppm and 10,000 ppm floods. These experiments demonstrate that Sodium Bromide does not adsorb to the rock surface and no hysteresis is observed while restoring the core samples to their initial conditions.

4.8 Tracer Flow Experiments

4.8.1 Validation with sandpacks and homogeneous rock system

Two types of sandpack systems are used in tracer experiments. The length of each sandpack system is about one foot. The homogeneous sandpack is prepared by using a single sand layer which has fairly uniform particle size distribution. The heterogeneous sandpack consists of two layers of sand. The top layer sand is of low permeability and the bottom layer sand has a permeability value which is 19 times that of the top layer. Each sand layer occupies half of the volume in the

sand pack. This system represents a case where the flowing fraction would be less than one and there will be significant mass transfer between stagnant and flowing streams. Figure 4.26 shows the plot of effluent Tracer concentration versus pore volume throughput for both homogeneous and heterogeneous sandpacks. For the homogeneous sandpack, the plot of effluent tracer concentration is symmetric around one pore volume. However for the case of heterogeneous sandpack, Figure 4.26 shows early breakthrough of tracer which is a measure of smaller flowing fraction. We also notice that effluent concentration increases slowly after an early breakthrough. The flowing fraction for this case was interpreted to be about 0.65 from the effluent concentration data. Figure 4.27 shows the effluent concentration and the recovery efficiency for homogeneous Silurian outcrop sample. We notice that the effluent concentration curve is symmetric around one pore volume and the flowing fraction (f) was estimated to be unity from the inversion algorithm.

4.9 Characterization of heterogeneous samples

Flow experiments were conducted on vuggy and fractured core plugs of 1.0 and 1.5 inch diameter and full sized cores of diameter 3.5 and 4.0 inches. Darcy's law was used to calculate the brine permeability based on the pressure drops across the length of the core for the given set of flowrates. Despite being vuggy (as confirmed in NMR spectrum), the permeability value for the majority of the 1.0

and 1.5 inch diameter was in the range of 0.5-6 mD. Only few 1.5 inch diameter samples were found to have the permeability value of more than 10 mD. The range of permeability for full sized cores was found to be 65-310 mD with the exception of one 4.0 inch diameter sample whose permeability was calculated to be 5 mD. To ensure the reliability of the tracer data, it is necessary that the dead volume of the flow setup be much smaller than the pore volume of the sample. Hence, the tracer flow experiments were not conducted on 1.0 inch diameter samples because the pore volume of the plugs was smaller than the dead volume of the setup. The following sections will describe the tracer characterization of the different sized samples.

4.9.1 Tracer flow experiments on 1.5 inch diameter samples

In this section we discuss four of the tracer flow experiments conducted on different 1.5 inch diameter samples. One of the sample exhibits slow mass transfer between flowing and stagnant streams while the other three samples exhibit much higher mass transfer. Inverse of the mass transfer coefficient has units of time and represents the timescale required to achieve equilibrium transport between flowing and stagnant streams. Hence, an experiment conducted at a residence time which is much smaller than the $1/M$ would show non-equilibrium effects and strong dependence on the flow rate. The core samples exhibiting fast or slow mass transfer are characterized based on the value of the inverse of the

mass transfer coefficient expressed in “days”. NMR T_2 distribution which is a representative of the pore size distribution is also measured and presented along with tracer flow experiments for 1.5 inch diameter plugs. Sample 3V as shown in figure 4.28 represents a rock sample with the flowing fraction (f) of 0.5, dispersivity (α) of 1 cm and $1/M$ of 0.17 days. This experiment was performed at relatively faster flow rate of 15 ft/days. The corresponding residence time for this experiment is much smaller than $1/M$ and thus the displacement of the tracer from the flowing streams is not at equilibrium with the fluid in stagnant/dead end pores. This behavior is confirmed by the plot of the recovery efficiency in figure 4.28, where we see that after about 5 pore volumes only about 60% of the initial fluid in place is recovered. Figure 4.29 represents the rock sample 1H with the flowing fraction (f) of 0.2, dispersivity (α) of 0.8 cm and $1/M$ of 0.02 days or about 30 minutes. The experiment shown was conducted at the relatively slow flowrate of 1.4 ft/day. This corresponds to the residence time of about 3.2 hours which is much higher than the value of $1/M$. At such flowrate we should expect the equilibrium between flowing and stagnant/dead end pores. Figure 4.29 also shows the recovery efficiency for this flow experiment. We notice that after about 3 pore volumes the recovery efficiency reaches the value of unity and all of the initial fluid in place has been displaced by the injected tracer fluid.

Samples 3V and 1H also differ drastically in their respective T_2 relaxation time spectrums. The T_2 relaxation spectrum for sample 1H has a continuous

pore sizes distribution overlapping vugs, intermediate and small sized pores as shown in figures 4.29. Figure 4.29 shows that the sample 3V on the other hand does not have a significant overlap of relaxation times covering vugs, intermediate and small sized pores. This could be the reason that the sample 1H can have much higher value of the mass transfer coefficient in comparison to sample 3V.

The other two 1.5 inch diameter samples were drilled from the center of two different 3.5 inch diameter cores. These core have the flowing fractions of 0.7 and 0.32 respectively. The value of $1/M$ is calculated to be of 0.26 and 0.34 days respectively. The dispersivity (α) is calculated to be 1.2 and 1.7 cms respectively. The plots of effluent concentration and recovery efficiency are shown in figures 4.30 and 4.31. In both cases, the value of the recovery efficiency reaches close to unity after 5 pore volumes injected. Figures 4.30-4.31 also show the NMR T_2 relaxation spectrum for these core plugs. For the samples exhibiting strong mass transfer between flowing and stagnant streams, there is a significant overlap of relaxation times corresponding to small and intermediate sized pores with the relaxation times of the vugs.

Sample (ID)	Diameter (inch)	f	N_M	N_K	v ft/day)	$\alpha = \frac{K}{v}$ (cm)	1/M (days)
3V	1.5	0.5	0.01	0.31	15	1.0	0.17
1H	1.5	0.2	5.3	0.14	1.2	0.8	0.02
1.5C	1.5	0.71	0.81	0.16	0.62	1.2	0.26
1.5D	1.0	0.32	1.4	0.14	1.4	1.7	0.34

Table 4.2: Summary of estimated model parameters from various tracer flow experiments for 1.5 inch diameter core samples

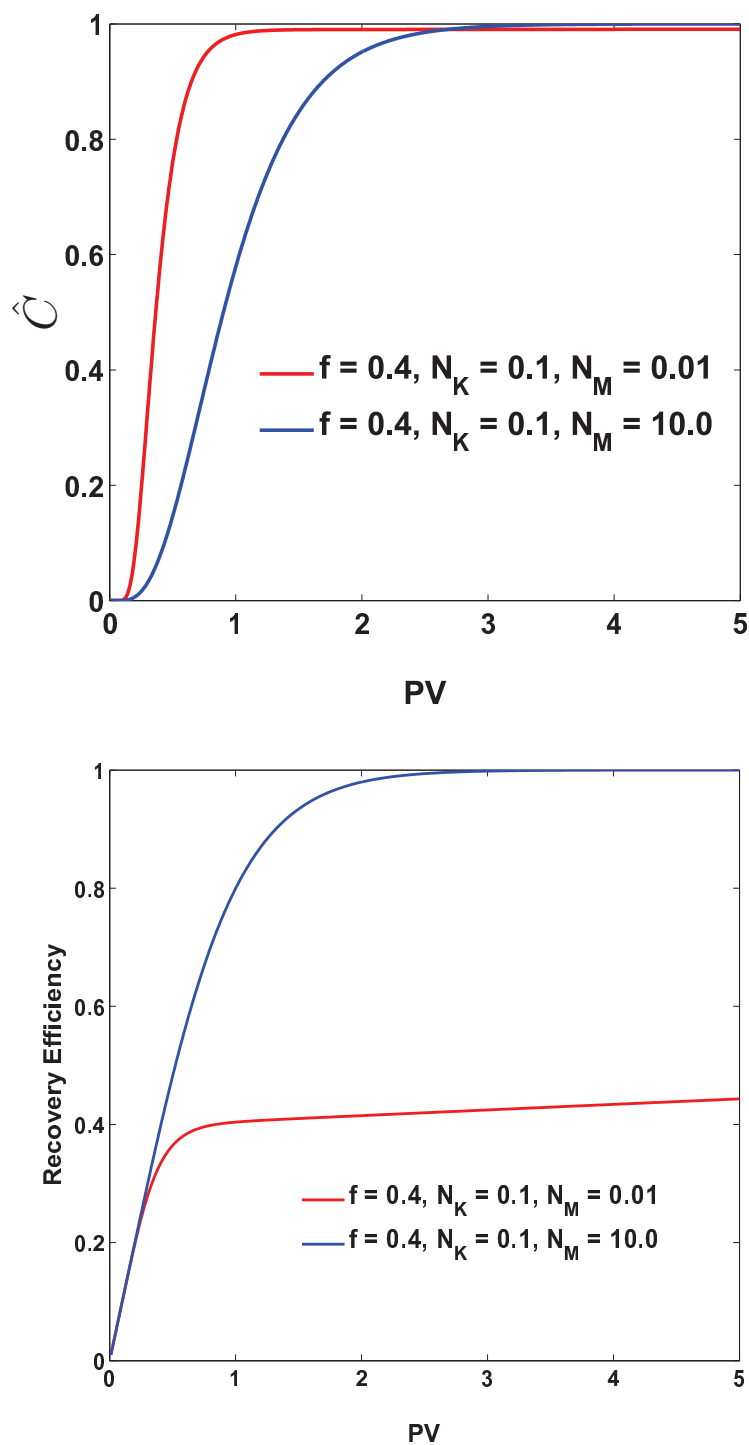


Figure 4.20: Plots of effluent concentration and recovery efficiency as a function of pore volume throughput illustrating importance of mass transfer between flowing and stagnant streams

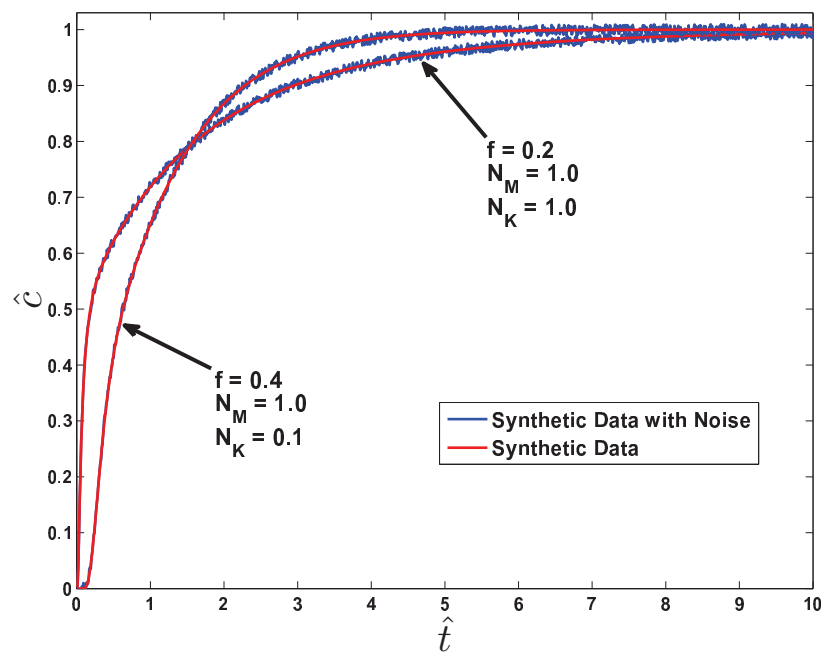


Figure 4.21: A comparison of synthetic data with and without noise used for benchmarking parameter estimation algorithm

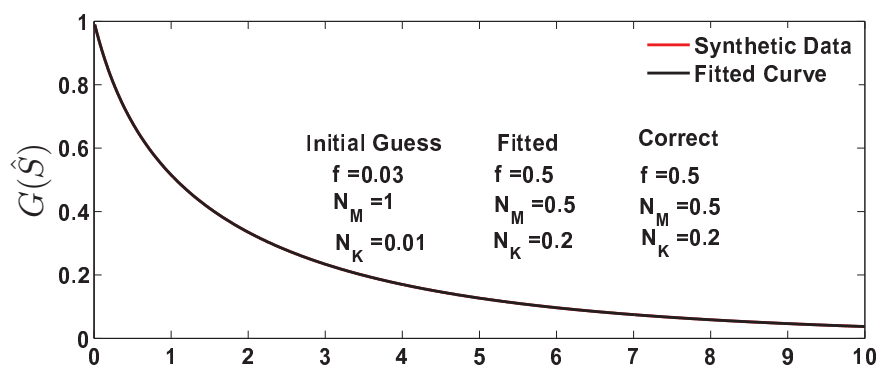


Figure 4.22: A comparison of transfer function for experimental data and fitted curve for parameter estimation

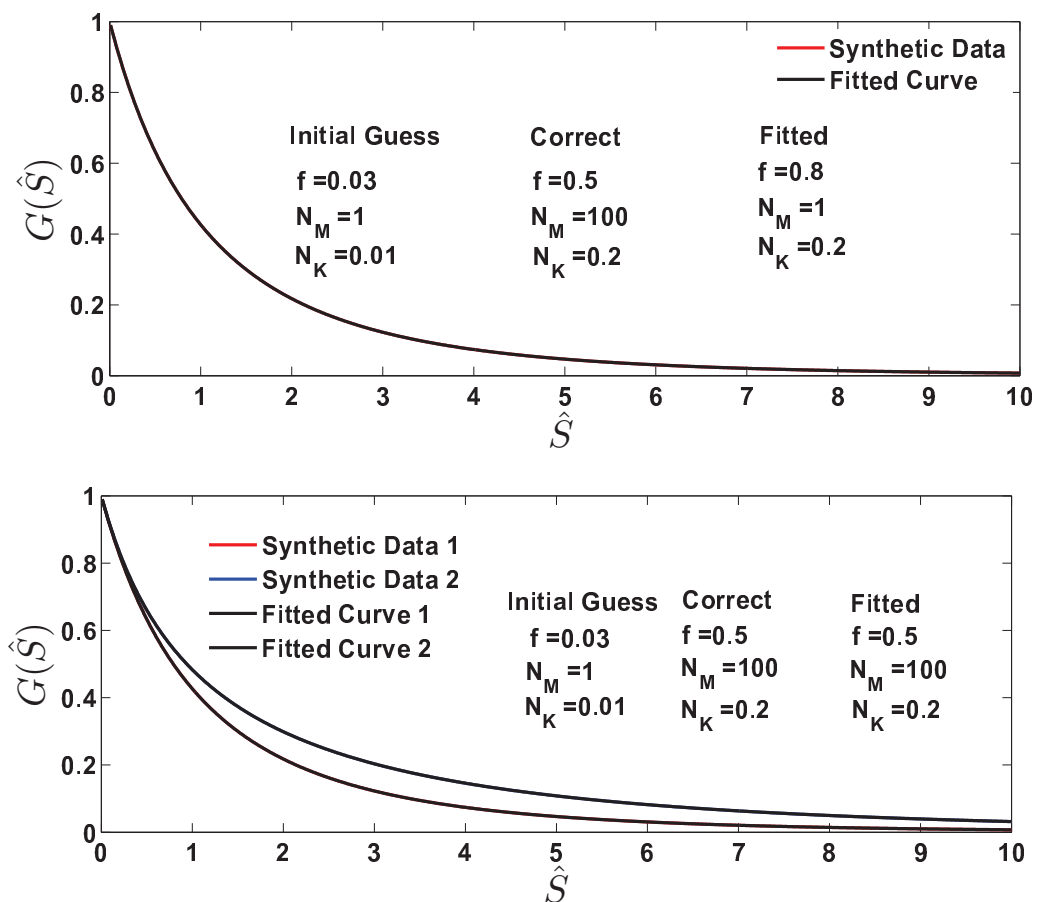


Figure 4.23: Comparison of fitted model parameters using the inversion routine when (A) Data at one flowrate is used and (B) When data at two flow rates is used

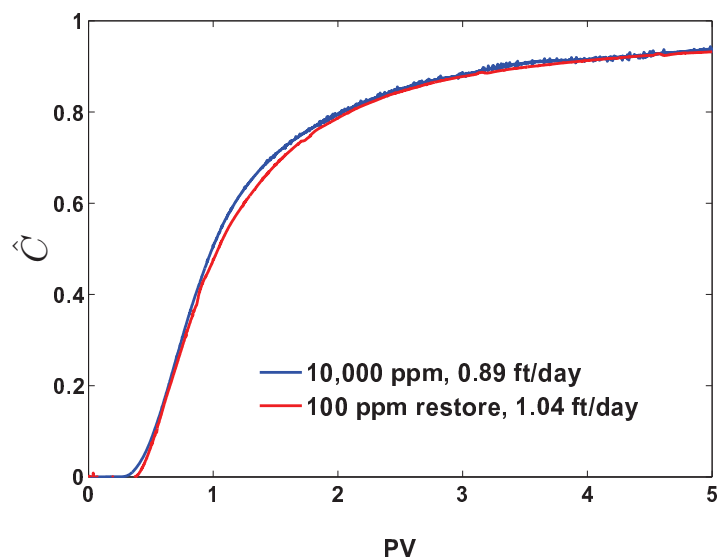


Figure 4.24: Effluent concentration versus pore volume throughput for 100 ppm and 10,000 ppm floods for similar values of the flowrates

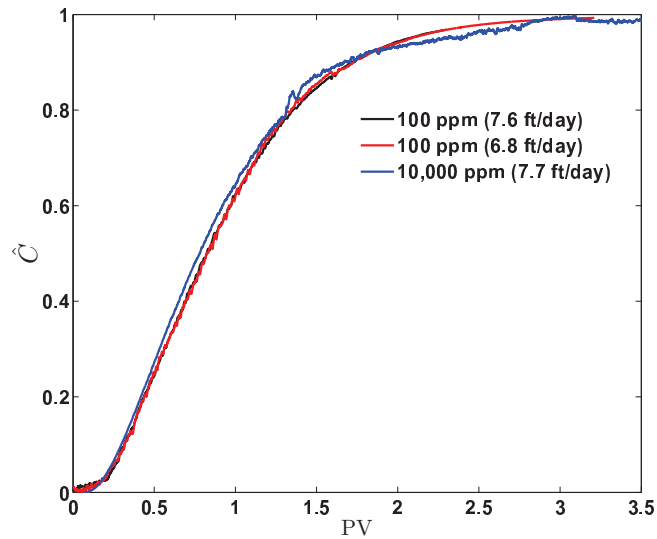


Figure 4.25: Effluent concentration versus pore volume throughput for 100 ppm and 10,000 ppm floods for several values of the flowrates

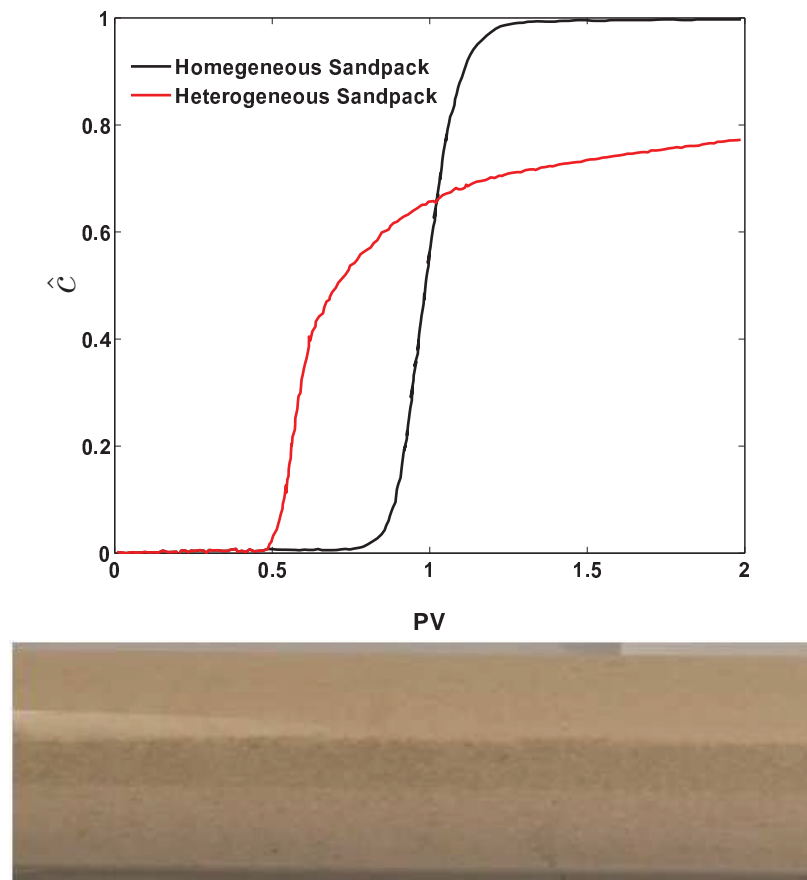


Figure 4.26: Effluent concentration versus pore volume throughput for homogeneous and heterogeneous sandpacks

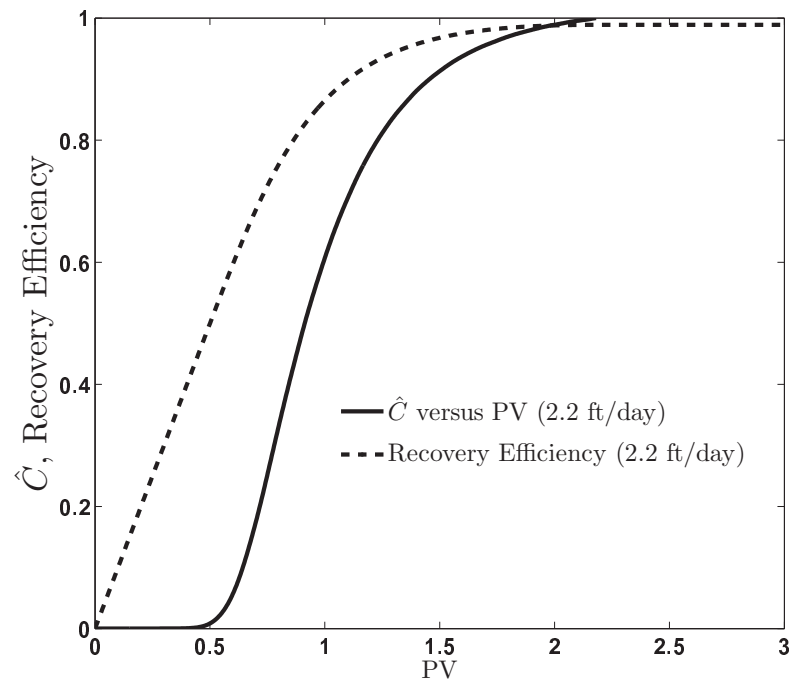


Figure 4.27: Effluent concentration and Recovery efficiency as a function of pore volume for homogeneous Silurian outcrop sample

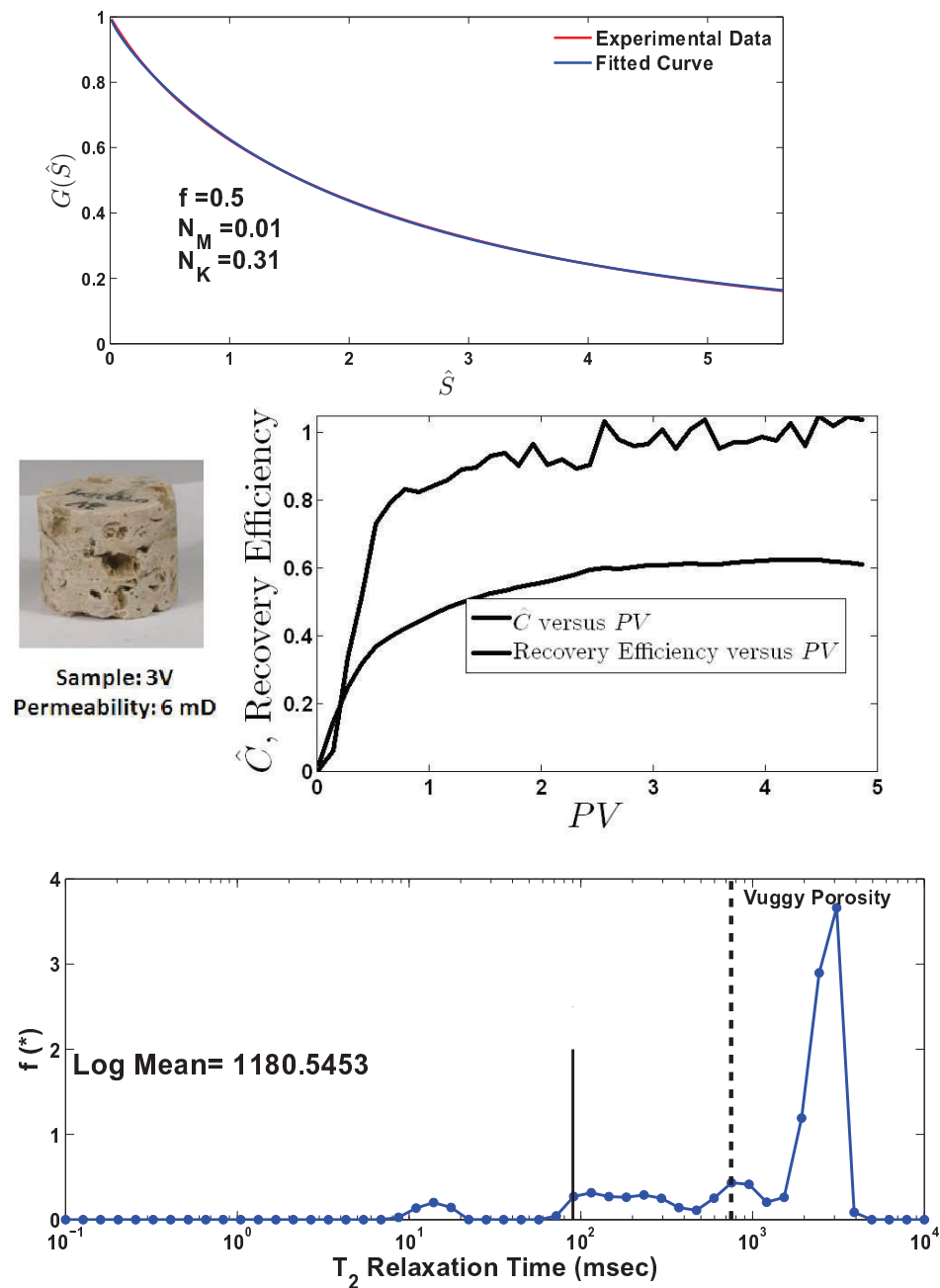


Figure 4.28: (A) Transfer function for the fitted parameters (B) Effluent concentration and recovery efficiency for core plug 3V (diameter = 1.5 inch, length = 1.25 inch) at the flow rate of 15 ft/day and (C) The corresponding NMR T_2 distribution for the core plug 3V

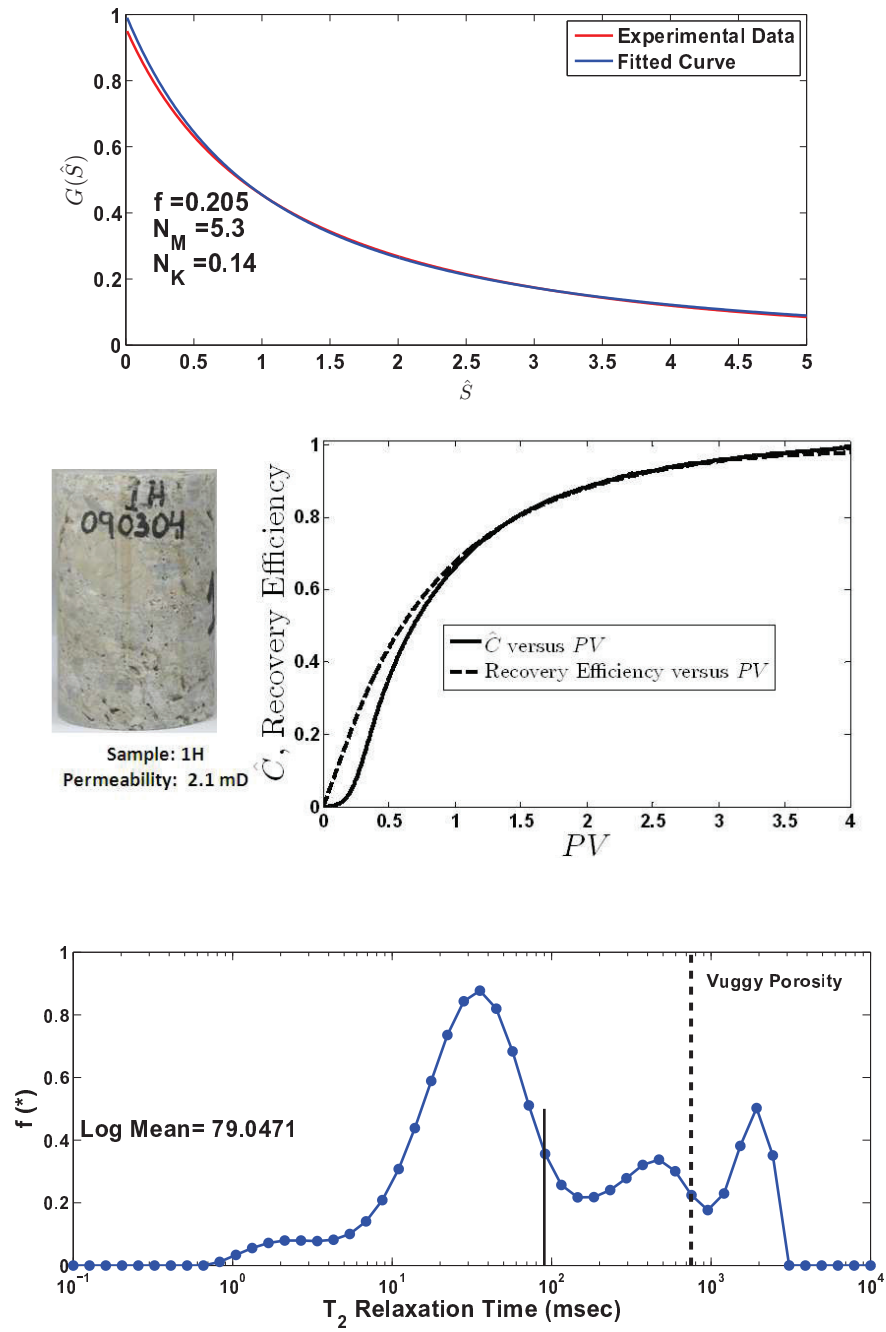


Figure 4.29: (A) Transfer function for fitted parameters (B) Effluent concentration and recovery efficiency for core plug 1H (diameter = 1.5 inch, length = 2.25 inch) at the flow rate of 1.4 ft/day and (C) The corresponding NMR T_2 distribution for the core plug 1H

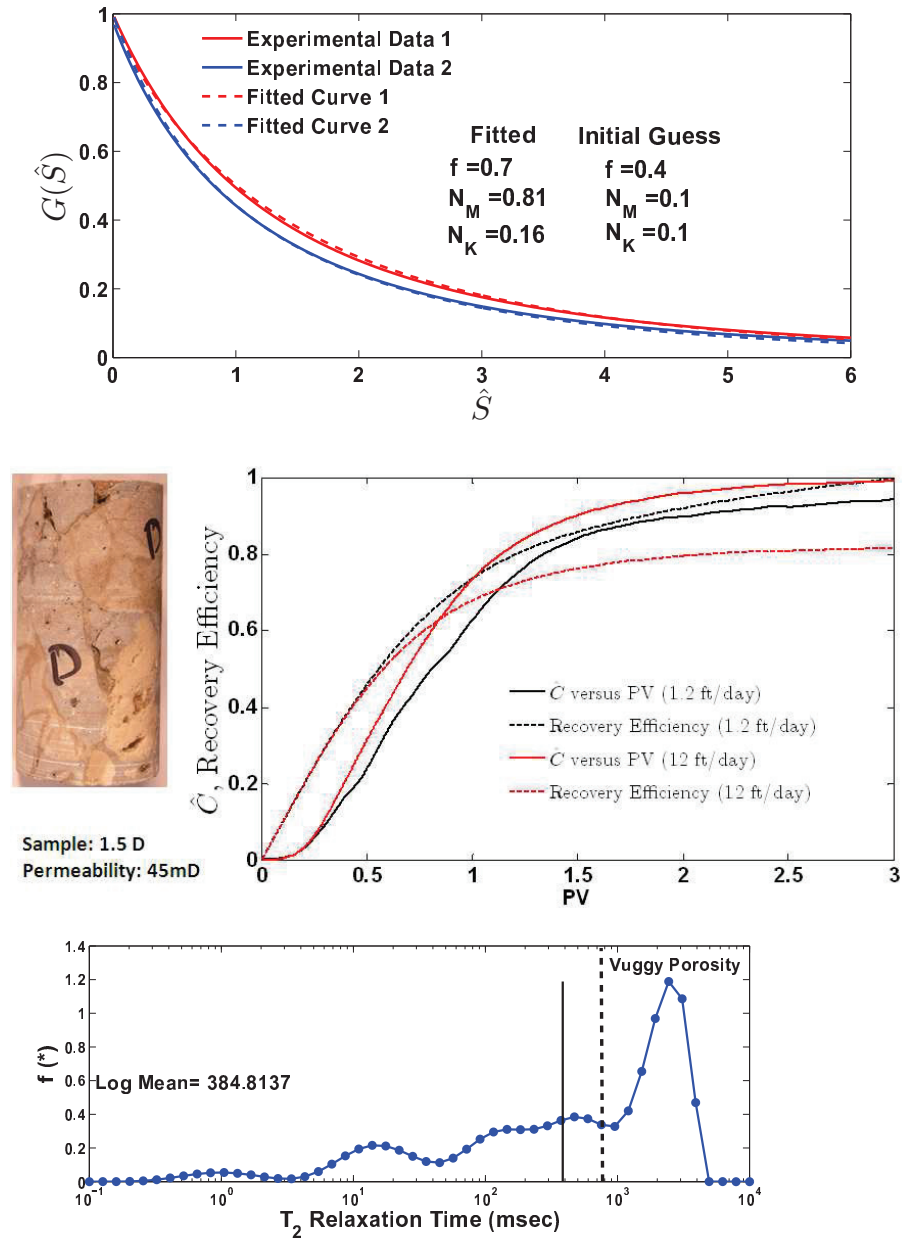


Figure 4.30: ((A) Transfer function for the fitted parameters (B) Effluent concentration and recovery efficiency for core plug 1.5D (diameter = 1.5 inch, length = 3 inch), (C) The corresponding NMR T_2 distribution for the core plug 1.5D

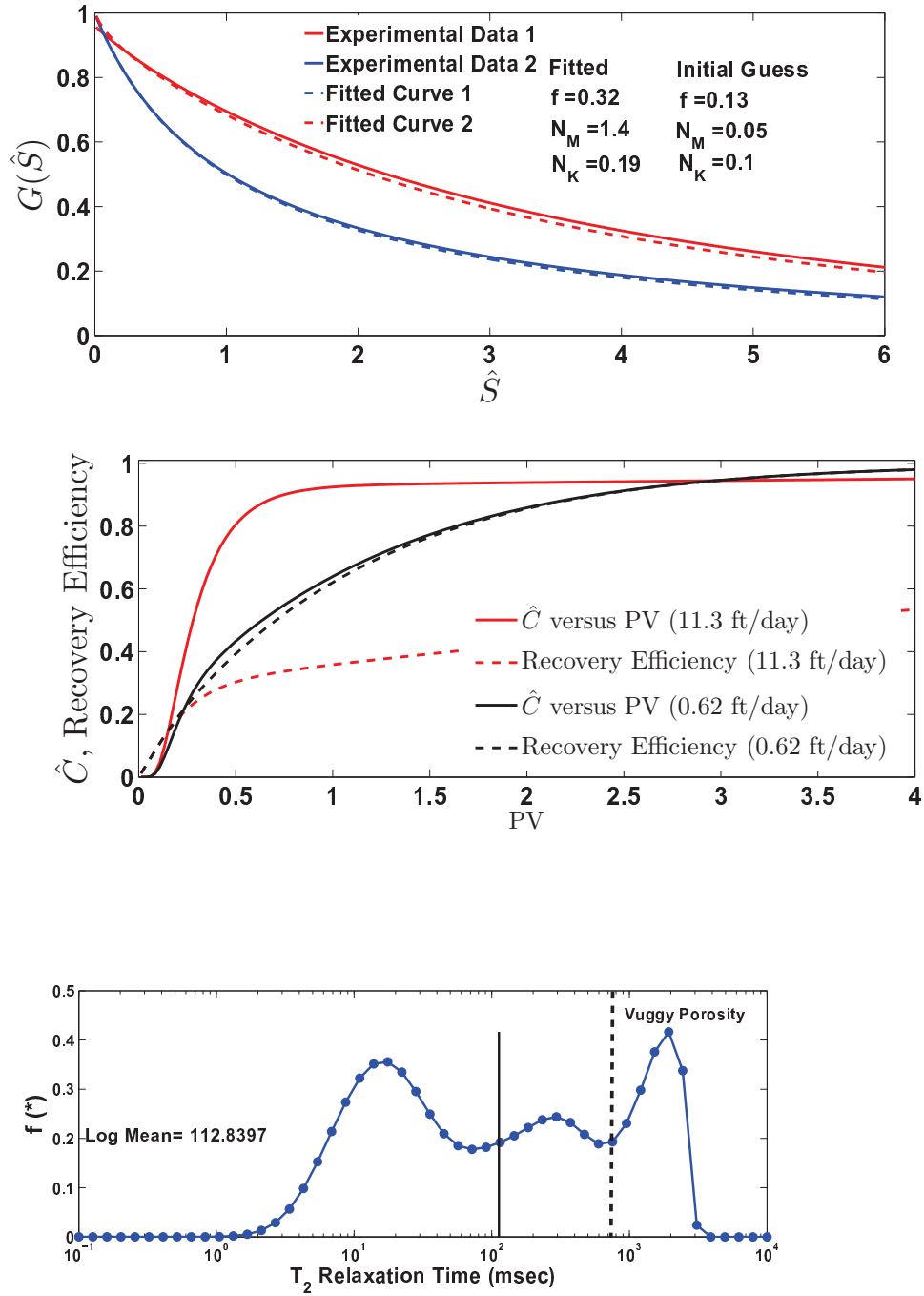


Figure 4.31: (A) Transfer function for the fitted parameters (B) Effluent concentration and recovery efficiency for core plug 1.5C (diameter = 1.5 inch, length = 3.5 inch), (C) The corresponding NMR T_2 distribution for the core plug 1.5B

4.10 Flow experiments on full sized cores

As discussed earlier, the permeability of the majority of the small sized core plugs (1.5 and 1.0 inch diameter) was in the range of 0.5-6 mD with the exception of few samples. The majority of these samples showed existence of vuggy porosity as shown in NMR T_2 relaxation. These small plugs were drilled from oil bearing rock of the reservoir whose effective permeability is of the order 5 darcy. This clearly shows that the vugs are non-touching thereby not enhancing the value of the permeability significantly. The size of the vugs in rock samples is of the order of few millimeters as the surface vugs are visible by the naked eye. Some of the vugs are larger than a centimeter. Hence, the diameter of the small plugs is not large enough to experience the enhancement of the permeability value due to the vugs/fractures networks.

Hence larger diameter samples (3.5 inches and 4.0 inches) may be a better candidate to conduct experiments to understand these complex heterogeneous systems. Larger diameter samples offer another advantage while conducting Tracer flow experiments. The pore volume of the larger diameter rocks is at least 10 times larger than the dead volume of the flow apparatus due to flow lines and the flow cell for the electrode. Smaller relative dead volume for larger diameter rock samples reduces artifacts like dispersion/mixing experienced during the flow lines and the flow cell. The ISCO pumps are used to displace the tracer fluid

through the rock sample. The fluctuations in the flow rates are more pronounced at relatively smaller flow rates (less than 1 ml/hr) needed for smaller sized core plugs. Hence, using larger diameter core plugs improves the quality of the data acquisition resulting in more accurate estimates of the fitted parameters during tracer flow experiments.

Figure 4.32 shows the transfer function for the fitted parameters for three different 3.5 inch diameter rock samples. The calculated values of the $1/M$ are 2.1 days, 4.3 days and 0.63 days for 3.5B, 3.5C and 3.5D respectively. The sample 3.5D exhibits strong mass transfer as is evidenced in the recovery efficiency shown in figure 4.33. A 4.0 inch diameter sample (4.0B) was found to have strong mass transfer even at the displacement rates of 12 ft/day. The value of $1/M$ for the sample 4.0B was calculated to be 0.1 days.

Figure 4.34 on the other hand shows the effluent concentration and recovery efficiency for the rocks samples exhibiting small mass transfer ($1/M = 2.1$ and 4.3 days). Figure 4.33 shows the effect of displacement rates (interstitial velocity) on mass transfer between flowing and stagnant streams. For sample 3.5B, the calculated value of the $1/M$ is 2.1 days. Experiments were conducted for three different interstitial velocities (21 ft/day, 1.8 ft/day and 0.36 ft/day). As the interstitial velocity is reduced to less than 1 ft/day, we notice a significant increase in the mass transfer between flowing and stagnant streams as evidenced by enhanced recovery efficiency shown in figure 4.34

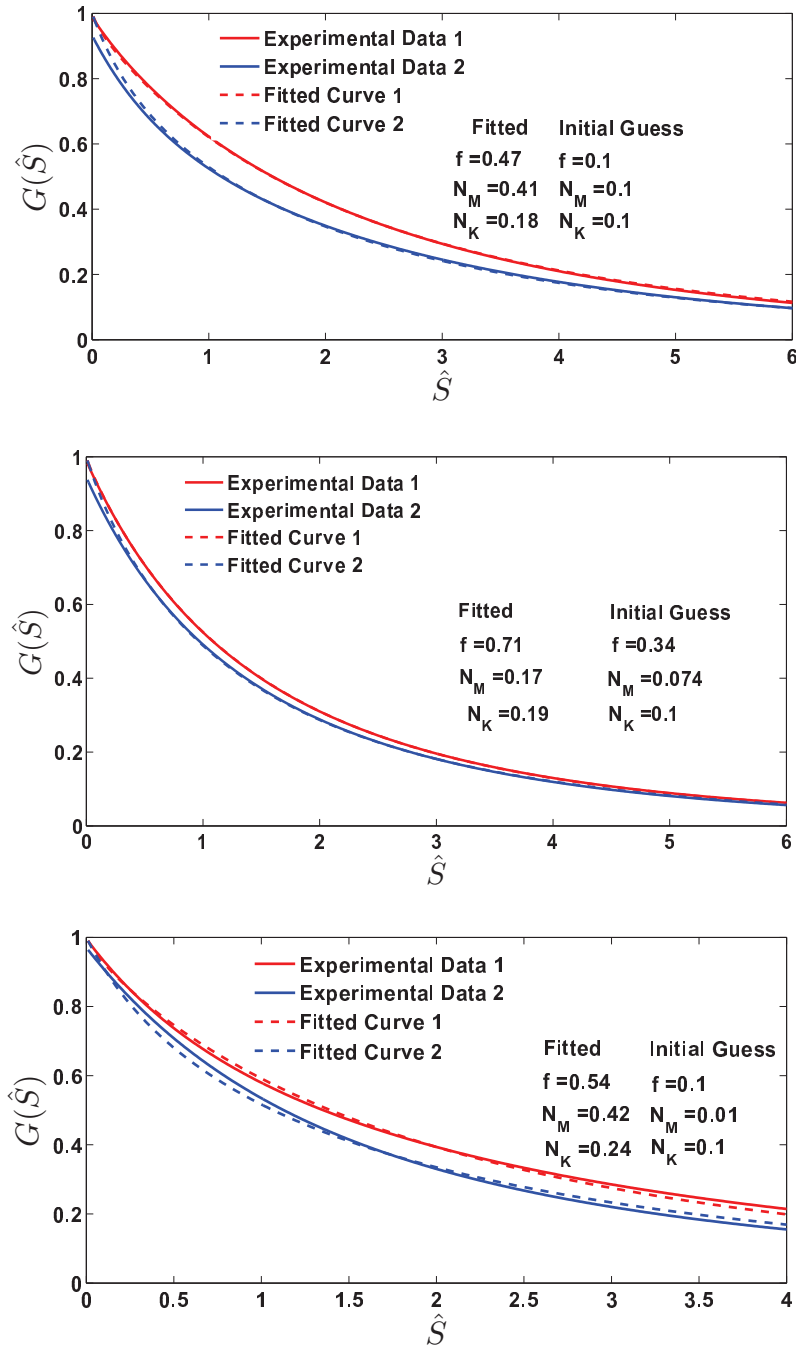


Figure 4.32: Transfer functions for the fitted parameters for 3.5B, 3.5C and 3.5D rock samples

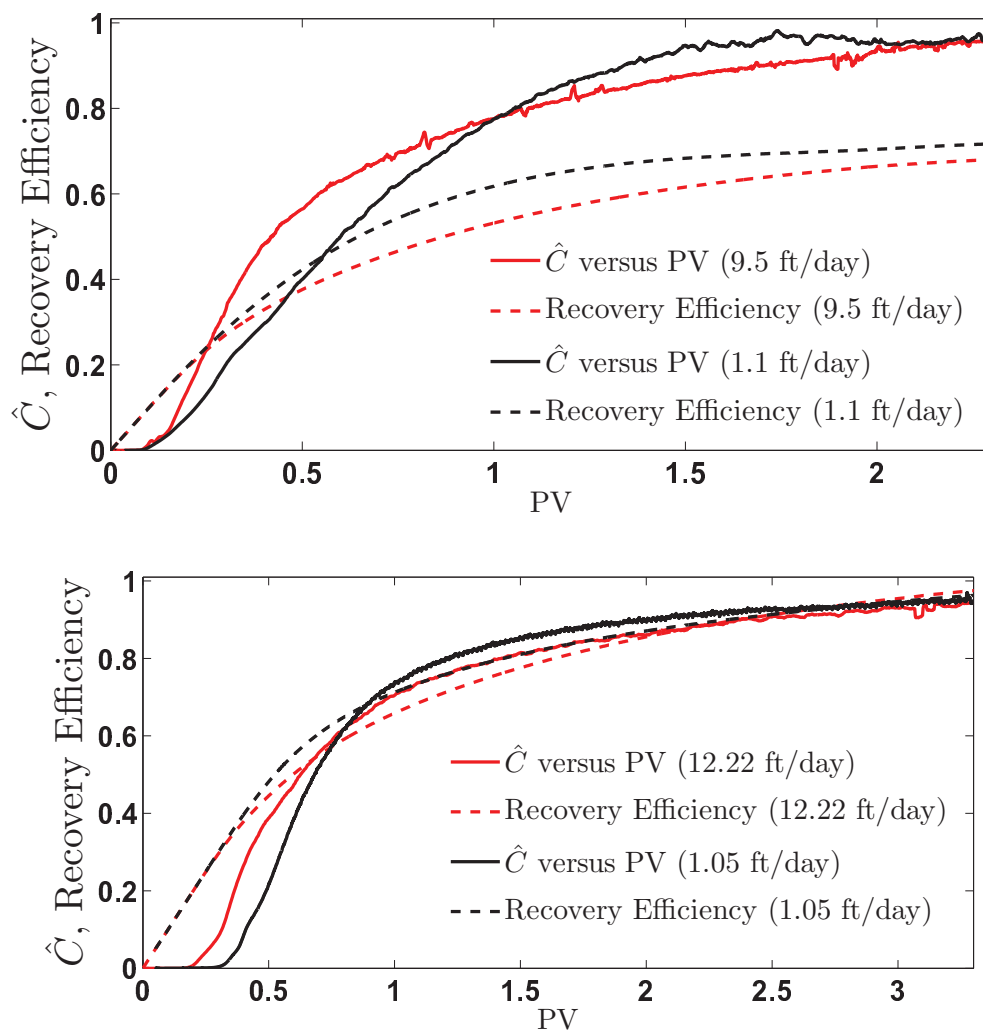


Figure 4.33: Effluent concentration and Recovery efficiency for the cases when strong mass transfer is observed. (A) Sample 3.5D with $1/M = 0.6$ days and (B) Sample 4.0B with $1/M = 0.1$ days

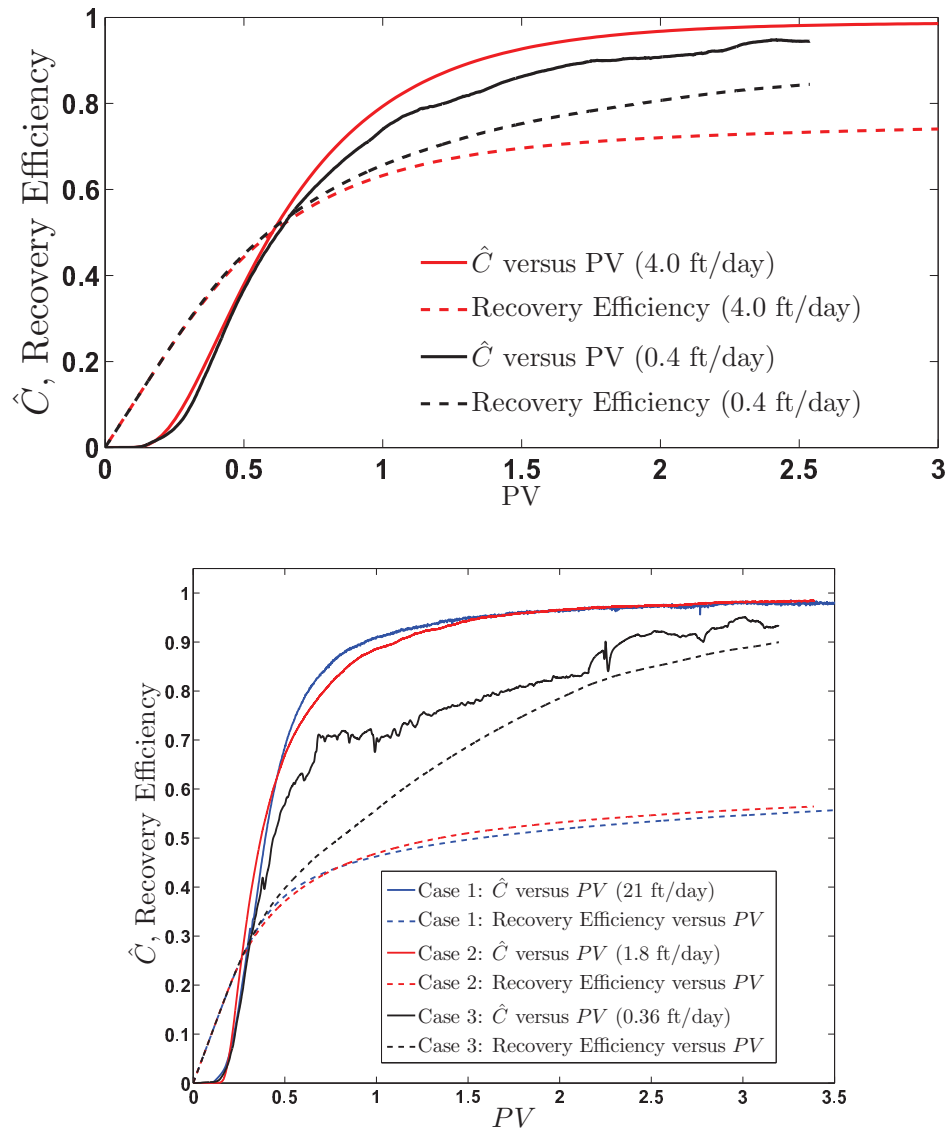


Figure 4.34: Effluent concentration and Recovery efficiency for the cases when mass transfer is small. (A) Sample 3.5C with $1/M = 2.1$ days and (B) Sample 3.5B with $1/M = 4.3$ days

After estimating unique model parameters from tracer flow experiments for a known sample, the effluent concentration and the recovery efficiency can be calculated as a function of pore volume throughput for various displacement rates as shown in figure 4.35. We find that at high displacements rates only fraction of dead end pores is contacted and the recovery is poor. As displacement rates are decreased we find an optimum rate at which recovery efficiency is significantly improved and reducing the displacement rates further are not useful. Experiments to characterize the pore structure in the laboratories should be conducted at flow rates which corresponds to N_M value of 1.0 or higher to ensure enough exchange between flowing and stagnant streams.

Estimated model parameters from tracer flow experiments are used to analyze different regimes of mass transfer. The regime of small mass transfer corresponds to the case when the value of dimensionless group for mass transfer is much smaller than unity ($N_M < 1$). In this regime effluent concentration/recovery efficiency versus pore volume throughput curves are strongly dependent on interstitial velocity. The regime of strong mass transfer corresponds to the case when the value of dimensionless group for mass transfer is much greater than unity ($N_M > 1$). In the regime of strong mass transfer there is no dependence of interstitial velocity on effluent concentration/recovery efficiency curve. Table 4.3 presents a summary of fitted values of the parameters characterizing several core samples. Some of these well characterized samples will be used to perform

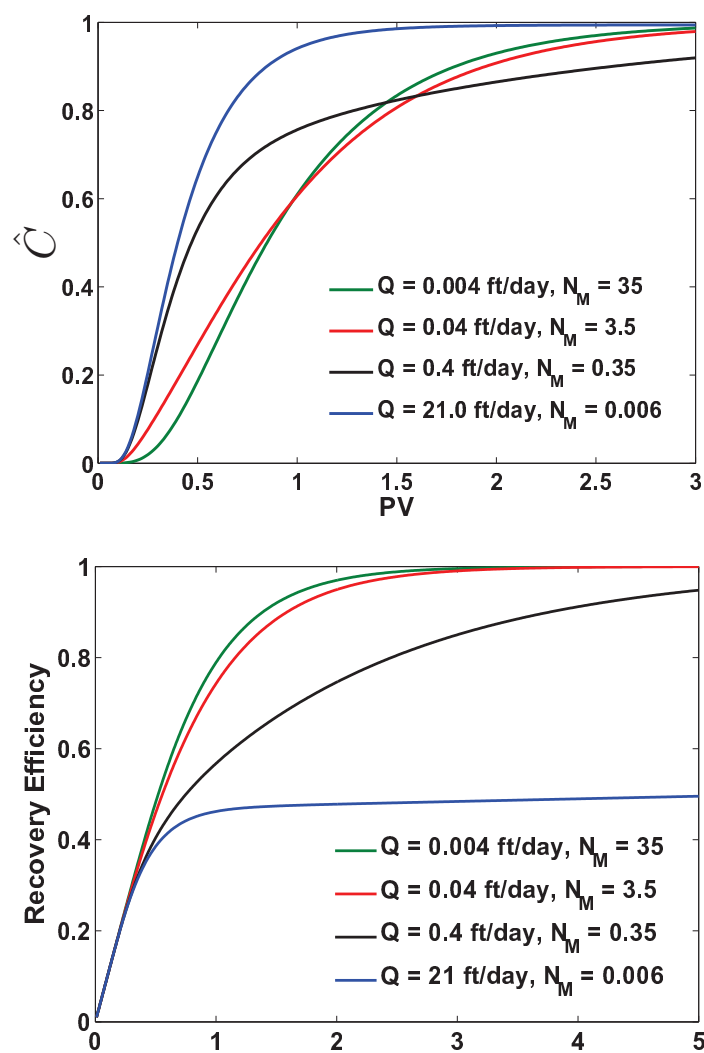


Figure 4.35: Calculated Effluent concentration and Recovery Efficiency for various interstitial velocities using parameters estimated from tracer flow experiments

Sample (ID)	Diameter (inch)	f	N_M	N_K	v (ft/day)	$\alpha = \frac{K}{v}$ (cm)	$1/M$ (days)
3.5B	3.5	0.47	0.41	0.15	0.36	1.6	2.12
3.5C	3.5	0.71	0.17	0.19	0.4	1.7	4.3
3.5D	3.5	0.54	0.42	0.24	1.1	2.1	0.63
4.0A	4.0	0.64	0.61	0.14	1.1	2.7	0.93
4.0B	4.0	0.73	3.1	0.23	1.05	1.7	0.1

Table 4.3: Summary of estimated model parameters from various tracer flow experiments for full core samples

the dynamic adsorption experiments to quantify the loss of surfactant to the rock surface during the displacement process.

4.11 Static and Dynamic adsorption of surfactant

To evaluate the loss of the surfactant on rock, both static and dynamic experiments are performed. The static test is done with centrifuge tubes using the crushed powder of the rock sample. The dynamic experiments will be performed in the presence of Sodium Bromide tracer to compare the breakthrough of the surfactants that of the non-adsorbing tracer. The tracer concentration will be recorded using an ion sensitive electrode and batch samples of the effluent will be collected at regular intervals to be analyzed separately.

A blend of 4:1 weight ratio (active material) of Neodol 67-7PO sulfate (N67) and C15-18 internal olefin sulfonate (IOS) from Stepan is used to study both

static and dynamic adsorption behavior on the rocks samples of interest. The NI blend is selected because it has already been tested on Yates and Midland farm fields. Both static as well as dynamic adsorption tests will be carried out at room temperature and with the background salinity 1 wt% NaCl. Both of the Neodol 67-7PO sulfate (N67) and C15-18 internal olefin sulfonate (IOS) are anionic surfactants and hence the total surfactant concentration of the NI blend can be accurately determined by Potentiometric titration with a cationic surfactant such as Benzethonium Chloride (Hyamine) or Tego.

4.11.1 Static adsorption of surfactant on the crushed rock powder

The static adsorption experiments were performed as follows. A rock sample was crushed into a homogeneous powder form and the BET surface area of the powder was found to be $1.5 \text{ m}^2/\text{gm}$. The known quantity (2 gms) of this rock powder was mixed with 10 ml of the NI blend surfactant solution of various concentrations in centrifuge tubes. The resulting mixture was shaken vigorously using a rotating shaker system for 24 hours. The following day, the samples were centrifuged at 4000 rpm for at least 25 minutes. The supernatant solution from the centrifuge tubes was carefully taken out and analyzed for the change in concentration of the total surfactant.

The equilibrium surfactant concentrations, that is the concentration of the supernatant solution were determined by potentiometric titration. Since the surface

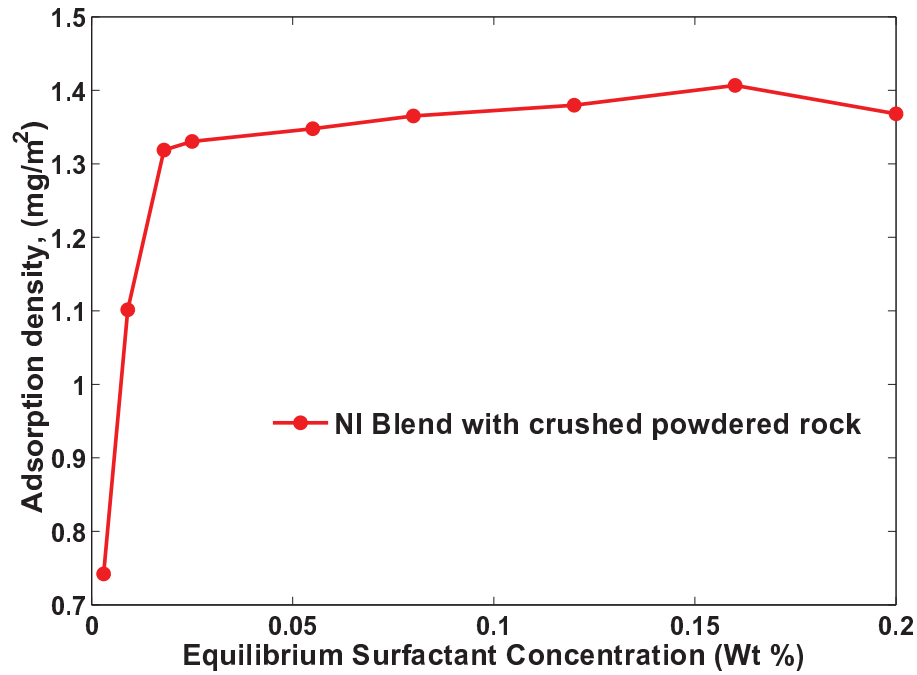


Figure 4.36: Adsorption on NI blend on crushed powder rock with BET area of $1.5 \text{ m}^2/\text{gm}$

area of the crushed rock powder is determined by BET adsorption, by comparing the initial and equilibrium surfactant concentration, the amount of surfactant adsorbed on the surface can be obtained as shown in figure 4.36. The total absorbant capacity of the powder can be calculated from the pleatau region and is evaluated to be $1.12 \frac{\text{mg}}{\text{m}^2}$. In next section, the dynamic adsorption experiments will be described and the loss of surfactant will be calculated.

4.11.2 Dynamic adsorption of the surfactant on the rock surface

The tracer flow experiments on vuggy and heterogeneous rock suggest that in order to remove the residual fluid in the dead ends or from the matrix of low porosity/permeability a suitable value of the displacement rate must be selected based on the interaction between flowing and stagnant streams characterized by the flowing fraction and the mass transfer coefficient. The flow of the surfactant solution through a heterogeneous rock is no different. Hence, for a heterogeneous rock sample the loss of surfactant due to the dynamic adsorption will be highly dependent on the residence time of the displacement process.

To better understand the dependence of the dynamic adsorption with displacement rate, we perform two controlled experiments. A rock sample (ID: 4.0A) of 4.0 inch diameter and 7.5 inch length which was visually similar along the length was selected and sliced into two equal pieces. The 4.0A rock sample has already been characterized by Tracer flow experiments and had the flowing fraction (f) of 0.64, dispersivity of 2.5 cm and the inverse of mass transfer coefficient ($1/M$) of 0.93 days. A different displacement rate will be used for the dynamic adsorption of 1.0 wt% of NI blend on each pieces. The surfactant solution also contains Sodium Bromide as a non-absorbing tracer. The concentration of the tracer will be measured online with an electrode. The effluent samples will be collected at different times and the concentration of the surfactant will be

measured by potentiometric titrations to obtain the breakthrough curves of the NI blend.

Figure 4.37 shows the comparison of the effluent surfactant concentration with that of the tracer for two displacement rates of 11.12 ft/day and 0.125 ft/day respectively. The first displacement rate was chosen such that the residence time is very fast in comparison to the $1/M$ value of 0.93 days. We notice that there is very little lag for the breakthrough of the surfactant. The slow flow of surfactant corresponds to the residence time of 2.5 days for one pore volume. This should allow enough time for the surfactant solution to come in equilibrium with the fluid in stagnant volume. Finally the two surfactant floods are compared with each other to show the lag of surfactant breakthrough for the slower flood.

The loss of the surfactant can be calculated using two methods. In first method we take the difference in pore volumes for the 0.5 dimensionless value of the tracer and surfactant concentrations. The second method is based on the mass balance and we integrate the area of the curve for both of the surfactant solutions and calculate the loss of surfactant. The specific surface area of the rock used in the dynamic adsorption experiment is calculated to be $0.18 \text{ m}^2/\text{gm}$ from NMR measurements. The specific surface area of the crushed powder used in static adsorption experiments was found to be $1.5 \text{ m}^2/\text{gm}$ from BET measurements. In order to compare the loss of the surfactant in the dynamic adsorption experiment with that during static adsorption tests, the loss of surfactant is scaled with the

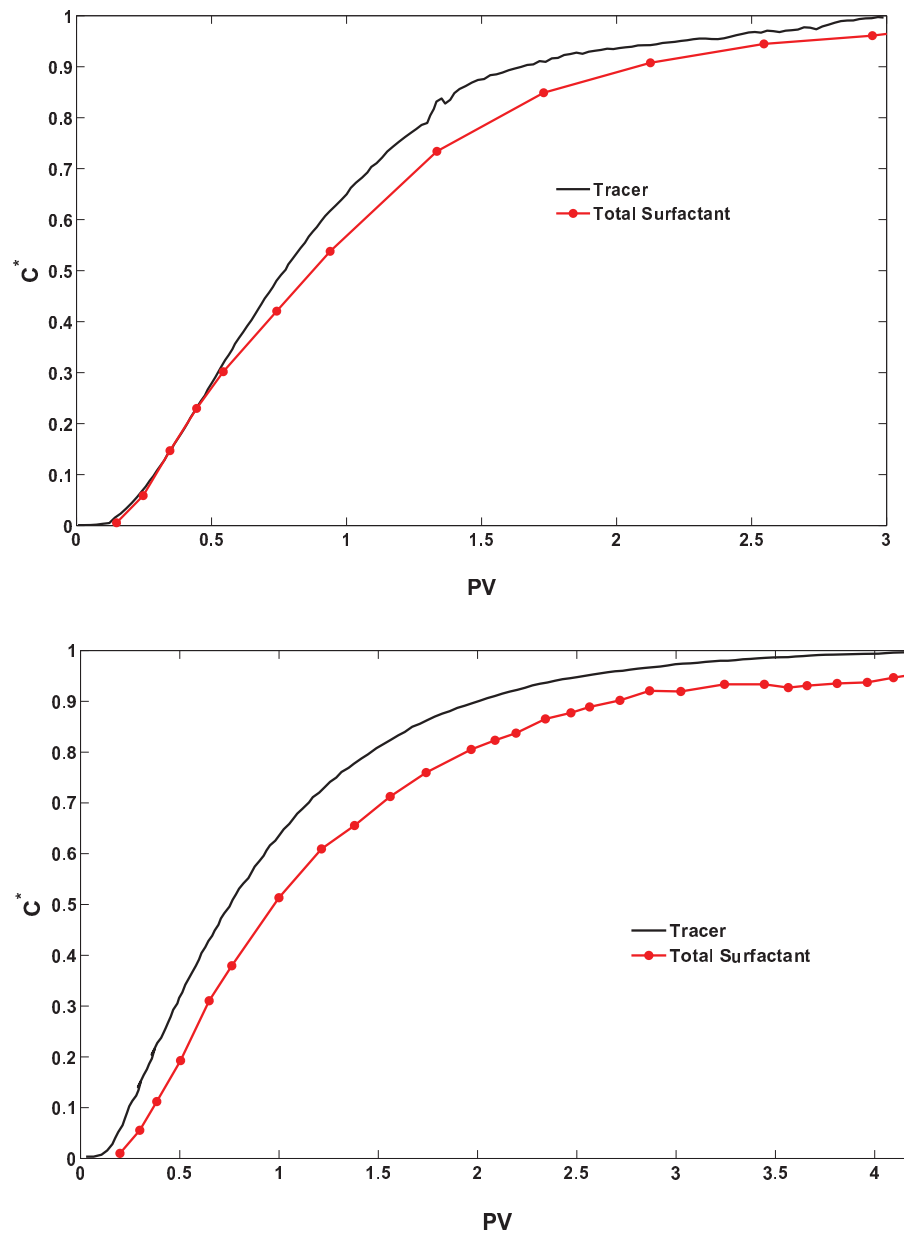


Figure 4.37: Adsorption of NI blend on a heterogeneous rock sample (A) Comparison of the surfactant fast flood with tracer (B) Comparison of the slow surfactant flood with tracer

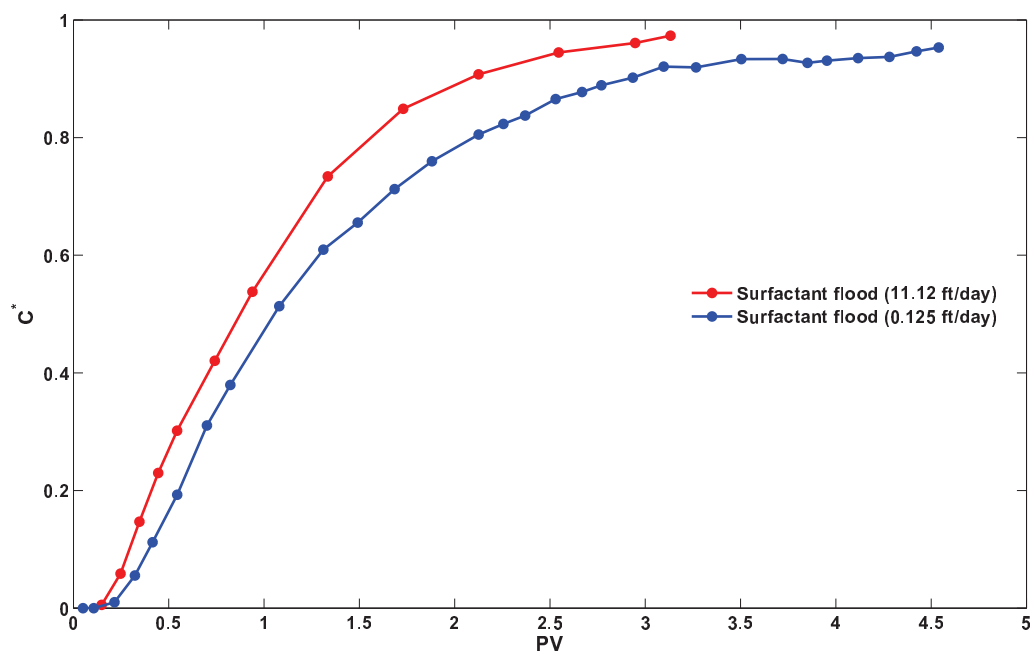


Figure 4.38: A comparison of fast and slow surfactant floods showing adsorption of NI blend on a heterogeneous rock sample

Sample (ID)	PV (ml)	v (ft/day)	Surfactant lag (PV)	Loss of Surfactant based on lag (mg/gm)	Loss of Surfactant mass balance (mg/gm)
1	112	11.12	0.1	0.06	0.03
2	105	0.125	0.23	0.13	0.23

Table 4.4: Summary of both surfactant flood and loss of surfactant due to dynamic adsorption

specific surface area of the rock. The rescaled value for the loss of surfactant in dynamic adsorption experiments becomes 1.95 mg surfactant per gm of the rock.

This value is about same as that found for the static adsorption experiments.

Chapter 5

Conclusions and Future Work

5.1 Conclusions

5.1.1 Modeling internal field gradients for claylined pores

Chapter 3 described a modeling based approach to study the effect of internal field gradients on the transverse relaxation. A two dimensional clay-flake model was used to simulate transverse relaxation for claylined pore space. We found that the Free induction decay (FID) in the presence of complex internal fields can exhibit non-monotonically decreasing behavior. This behavior was explained with the help of a test case involving no diffusion.

A simple two dimensional model is able to capture the spectrum of relaxation regimes for transverse relaxation. The relaxation regimes can be classified on the basis of the relative magnitudes of the different timescales for physical processes such as τ , τ and τ_{ω}^* . No echo spacing dependence of transverse relaxation rate is observed in motionally averaging regime. Localization and free diffusion regimes show strong dependence of transverse relaxation on echo spacing. Relaxation rates follow quadratic echo spacing dependence in free diffusion regime while less

than quadratic dependence on echo spacing is observed for localization regime. A power-law dependence on echo-spacing is observed for crossover from one regime to another.

5.2 Pore structure of vuggy carbonates

5.2.1 NMR Chracterization

The photographs of the core samples as well as NMR results suggest that these carbonate rocks are very heterogeneous. In some cases, vugs contribute the most to the porosity while in other smaller pores are dominant. Samples taken within the proximity of 3 inches exhibit very different T_2 relaxation time spectrum. The majority of the samples show small value of permeability and the correlation is very poor with the value of T_2 Log Mean with the permeability by using the current existing correlations. Brecciated samples having large solution vugs yields relatively higher value of permeabilities in the laboratory experiments. NMR T_2 relaxation spectrum can be used to calculate the distribution of porosity between vugs and other smaller sized pores. The distribution of the surface area of the pore space can also be calculated by with the help of the surface relaxivity. It is found that the samples representing the reservoir rock have much higher surface area in comparison to outcrop samples.

5.2.2 Characterization of the pore space by Tracer Analysis

Flow experiments suggested that the permeability of the rock samples is size dependent. Smaller size samples (1.0 inch and 1.5 inches diameter) have the permeability in the range of 0.5 – 6 mD. The range of permeability is 65 – 330 for large diameter samples (3.5 inch and 4.0 inch diameter) samples. Both 3.5 inch and 4.0 inch diameter samples have similar values of the permeabilities which are about two orders of magnitude higher than that for smaller core plugs.

Tracer flow experiments were conducted to understand the effect of the heterogeneities due to the presence of vugs and fractures. It was found that only a fraction of pore space form interconnected pathways for the passage of the displacing fluid. The rest of the pore space is part of dead end pores and/or stagnant volume. Mass transfer is governing mechanism for transport across flowing and stagnant streams. The timescale of mass transfer for some heterogeneous samples was found to be in several days. The assumption of the equilibrium between flowing and stagnant streams will be broken during fast displacement rate experiments resulting in poor recovery efficiency.

A control experiment for the dynamic adsorption was designed and conducted for two order of magnitude different displacement rates. It was found that for very small displacement rates 0.125 ft/day, the loss of the surfactant due to dynamic adsorption is similar to that found in the static adsorption experiments.

5.3 Future Work

5.3.1 Dynamic adsorption model for heterogeneous systems

The simplest realistic model to describe the surfactant adsorption in porous media is the so-called convection-dispersion model with linear adsorption with local concentration (Gabbanelli, Grattoni and Bidner 1987). This type of approach assumes that the adsorption isotherm can be approximated with a constant slope over the range of concentration. This model can be solved analytically however the assumptions of no dead volumes and linear adsorption isotherm are not valid for heterogeneous systems. We have shown that the differential capacitance model of Coats and Smith (1964) is able to describe the pore structure of the vuggy carbonates. We also know that the actual adsorption of the NI blend follows a Langmuir type isotherm as shown in the previous chapter. Thus, we use a model developed by (Bidner and Vampa 1989) which combines the Langmuir type isotherm with the differential capacitance model of Coats and Smith (1964). This model is defined by the following set of differential equations:

$$f \frac{\partial \hat{C}}{\partial \hat{t}} = -\frac{\partial \hat{C}}{\partial \hat{x}} + N_K \frac{\partial^2 \hat{C}}{\partial \hat{x}^2} - N_M (\hat{C} - \hat{C}^*) - \frac{La f}{J} [\hat{C} (1 - \Gamma) - E\Gamma] \quad (5.1)$$

$$\frac{\partial \hat{C}^*}{\partial \hat{t}} = \frac{N_M}{1-f} (\hat{C} - \hat{C}^*) - \frac{La}{J} [\hat{C}^* (1 - \Gamma^*) - E\Gamma^*] \quad (5.2)$$

$$\frac{\partial \hat{\Gamma}}{\partial \hat{t}} = \frac{1}{J} [\hat{C} (1 - \Gamma) - E\Gamma] \quad (5.3)$$

$$\frac{\partial \hat{\Gamma}^*}{\partial \hat{t}} = \frac{1}{J} [\hat{C}^* (1 - \Gamma^*) - E\Gamma^*] \quad (5.4)$$

Where, $\hat{C}$ and $\hat{C}^*$ are the normalized solute concentrations in the flowing phase and in the stagnant volume. Γ and Γ^* are the normalized chemical adsorption in flowing phase and in the stagnant volume. This set of dimensionless equations is characterized by six dimensionless groups.

1. f is the flowing fraction.
2. $N_K = \frac{K}{Lv}$ is the dimensionless group for dispersion which is the inverse of the Peclet Number (Pe).
3. $N_M = \frac{ML}{v}$ is the dimensionless group for mass transfer.
4. $La = \frac{A_{wr}Q_a}{\Phi C_0}$ is the Langmuir number, which measures the adsorptive capacity of the system.
5. $E = \frac{k_2}{k_1 C_0}$ is the Kinetic adsorption number, which relates desorption and adsorption rates
6. $J = \frac{v}{Lk_1 C_0}$ is the Flow rate number, which relates convection and adsorption.

Where, k_1 and k_2 are kinetic rate constants of adsorption and desorption, Q_a is the total adsorbent capacity and A_{wr} is the surface area of the rock per unit volume of the rock.

The tracer flow experiments can provide the first three dimensionless group characterizing the porous media. Total adsorbent capacity can be calculated from

the static adsorption experiments. If the kinetic rate constants for the adsorption and desorption are known, this model can be numerical solved to determine the loss of surfactant during dynamic flow experiments.

Appendix A

Manual on using bromide ion sensitive electrode in laboratory experiments

Introduction: This is a manual to use a combination type bromide ion sensitive electrode (ISE). The electrode is manufactured by Analytical Sensors and Instruments, Ltd. which is located in Sugarland, Texas. The electrode belongs to the “43 series” of their ion sensitive electrode catalog. The electrode measures total free bromide ion concentration in aqueous solution. The electrode is of combination type hence a reference electrode is not needed. This particular electrode is chosen because the electrode junction is located very close to the sensing element and hence the electrode requires a small sample volume (about 0.5 ml) for measurements. According to the manufacturer, the electrode has a shelf life of about 6 months to one year after which it should be replaced. The typical response time for the electrode is between 10-30 seconds.

Analytical Sensors & Instruments also have a bromide ion sensitive electrode from “12 series” which has 1) a faster response time 2) comes with an additional sensing module and 3) the electrolyte solution can be refilled. However, electrode junction is located farther from the sensing element and this electrode requires larger amount of sample volume (about 2-3 ml) for measurement.

Operation: When the electrode is immersed in a given aqueous solution containing free bromide ions, a DC voltage is generated which can be measured with the help of a multi-meter or other data acquisition interfaces such as LabView® data acquisition module. The range of the concentration of bromide

ion which can be measured is 0.4 ppm to 79,999 ppm. The electrode can be used at temperatures from 0 to 80 °C. It is important to keep total ion concentration same in all samples for consistent results. We achieve this by adding sodium chloride in the solution while keeping total halide ion concentration same for all of the samples. Presence of other ions in the solution affects the accuracy of electrode. Table 1 gives the maximum allowable ratio of other ions to bromide ions in the solution when concentrations are measured in either moles/L or ppm.

S. No.	Interfering ion	Maximum Ratio (when units are expressed as moles/L)	Maximum Ratio (when units are expressed as ppm)
1	OH ⁻	3×10^4	6.4×10^3
2	Cl ⁻	400	180
3	I ⁻	2×10^{-4}	3.2×10^{-4}
4	S ⁻²	10^{-6}	4.0×10^{-8}
5	CN ⁻	8×10^{-5}	2.6×10^{-6}
6	NH ₃	2	4.2×10^{-4}

Table 1: List of maximum allowable concentration of interfering ions for bromide electrode

Calibration of the electrode (Theory): The generated DC voltage from the electrode follows Nernst relationship as described in the equation below:

$$E = E_0 + \frac{2.303RT}{nF} \log_{10} a$$

Where: E_0 is a constant, T is the absolute temperature, F is Faraday constant, n is the valence of the ion and a is the activity of bromide ion in solution. At 25°C

for a tenfold change of concentration, the change in millivolt reading should be within 54 mV to 60 mV.

Calibration Procedure:

The calibrating samples are prepared using successive dilution method i.e. diluting from the sample of highest concentration of bromide ion to make smaller concentration solutions. The total molar concentration of Sodium Chloride and Sodium Bromide is kept constant at 0.125 M for all samples. For samples of increasing Br^{-1} concentration, the moles of Sodium Chloride are replaced by those of Sodium Bromide such that total molar halide concentration remains constant. The electrode response is faster if the total molar concentration of halides in the samples is kept constant. During measurements, it should be ensured that there are no air bubbles trapped between solution and the surface of sensing element. It takes about 30-60 seconds to reach 90% of the electrode response. The electrode reading reaches steady state in about 3-5 minutes. Change of 0.05 mV per minute or less should be used as an empirical rule of thumb to check steady state.

Figure 1 shows the plot of mV versus Br^{-1} concentration in parts per million. We observe that for low concentration the plot deviates from Nernst relationship. This happens because at low concentration of Br^{-1} , the ratio of concentration of Cl^{-1} to that of Br^{-1} is larger than maximum allowable ratio given in table 1. We found that for 100-10,000 ppm concentration range (0.125 molar total salinity), electrode follows Nernst relationship as described in figures 2 and 3. We

also notice that the slope of mV versus concentration plot is within 54 to 60 mV per decade of concentration change.

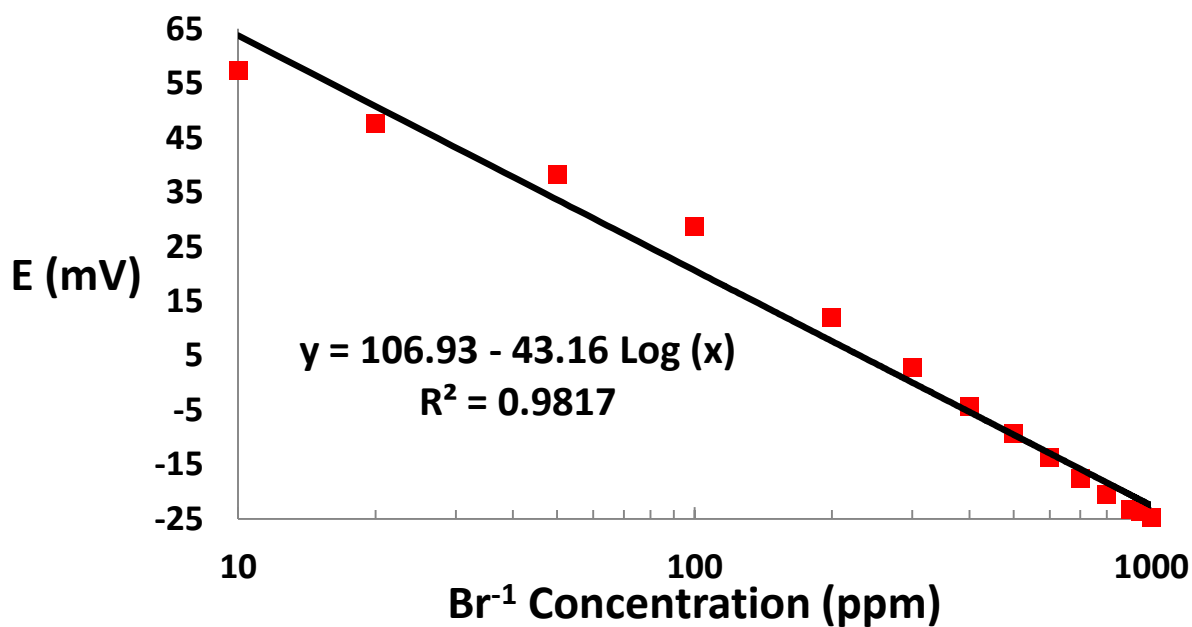


Figure 1: Calibration curve for the electrode in bulk solution for the Br⁻ concentration range of 10 to 1000 ppm (total halide concentration = 0.125 M)

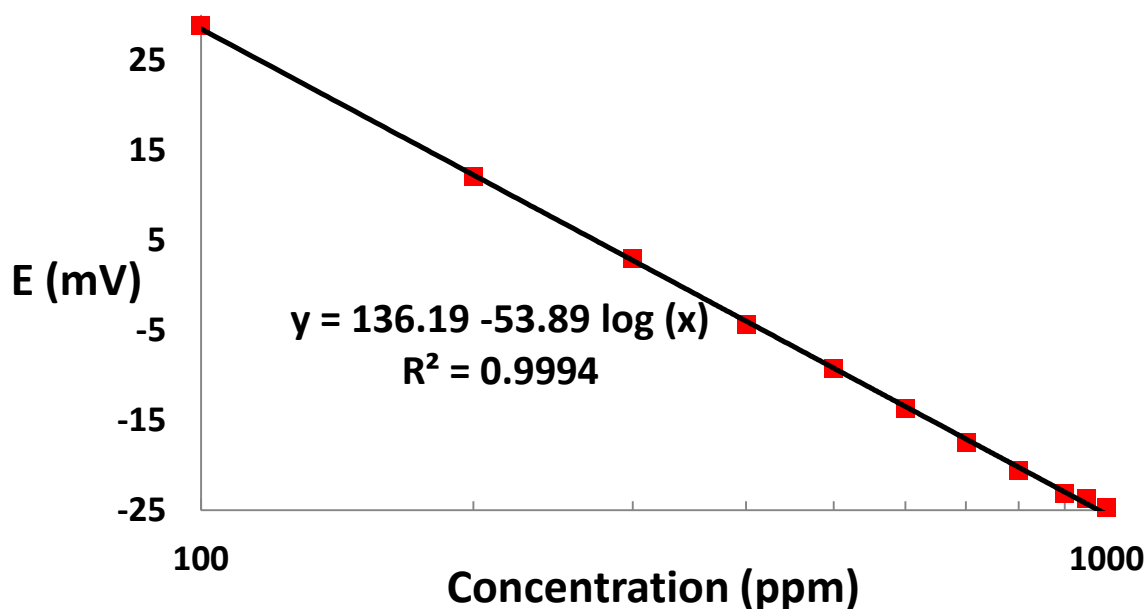


Figure 2: Calibration curve for the electrode in bulk solution for the Br^- concentration range of 100 to 1000 ppm (total halide concentration = 0.125 M)

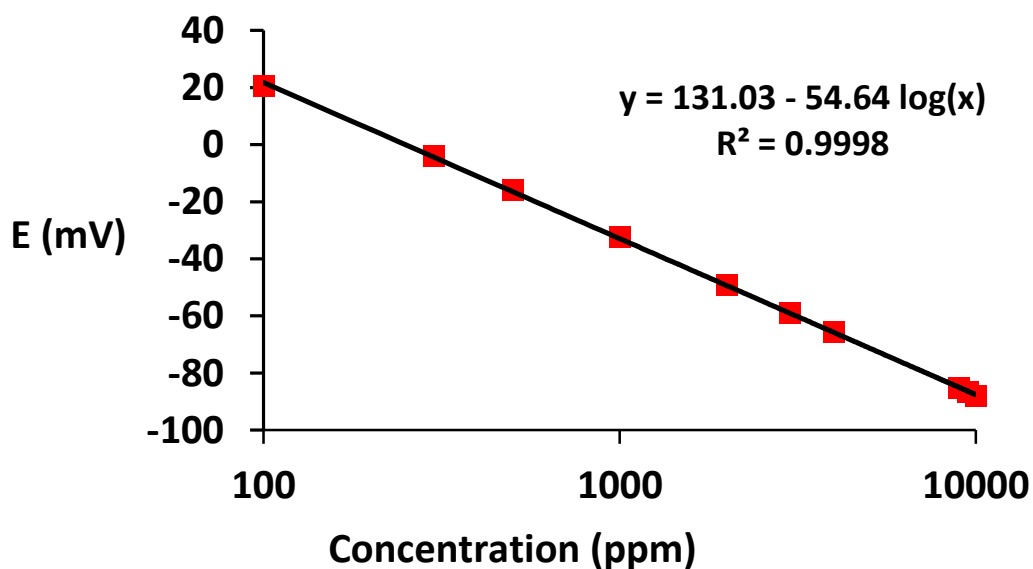


Figure 3: Calibration curve for the electrode in bulk solution for the Br^- concentration range of 100 to 10,000 ppm (total halide concentration = 0.125 M)

Conditioning of electrode prior to measurements and response time of the electrode:

The operating manual suggests that electrode be first immersed in ionic strength adjuster (ISA) for about 20-30 minutes before making measurements. Ionic strength adjuster is 0.5 M Sodium Nitrate (NaNO_3) solution. Figure 4 shows transient response of the electrode when it was preconditioned using ISA versus the case when it was not preconditioned prior to the measurement. Figure 4 shows that preconditioning electrode with ISA solution improves the response time of the electrode.

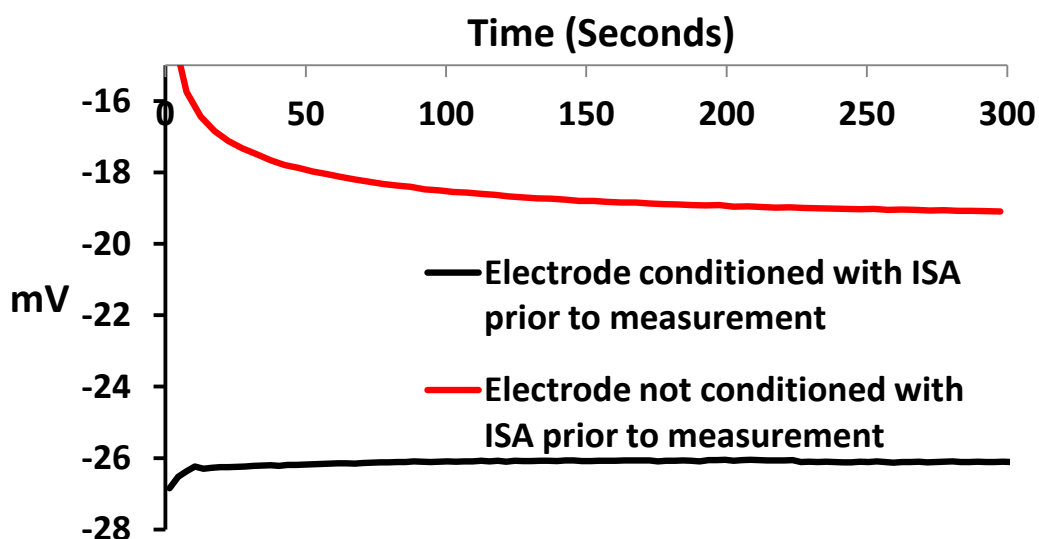


Figure 4: Comparison of the transient response of the electrode when it was preconditioned with ISA solution versus the case when it was not preconditioned with ISA solution

Recommendations for the use of electrode:

To get consistent results when using the bromide electrode, one must follow proper procedure. Start by placing the bromide in the ionic strength adjuster (ISA) solution for 20-30 minutes followed by the lowest concentration for around 10 minutes. For accurate results, recalibrate bromide electrode after an experiment on solutions where concentration is known. When placing the electrode into a solution, ensure that there are no bubbles on the surface of the sensing element.

The electrode should be rinsed with DI water in between static measurements. While the measurement for the voltage of a static reading is never completely stable, take your final measurement when the change in electrode reading is less than 0.05 mV per minute. Electrode should never be left immersed in de-ionized water. The electrode should be stored dry after experiment and must be preconditioned before any use.

Data acquisition and alising: We use a LabView® data acquisition module to read voltage from the electrode and write the data to a Microsoft excel file. The typical range of sampling rate for LabView® module is 500-2000 Hz. LabView® module uses an A/C power source at 60 Hz. Due to this, the electronic noise at 60 Hz is always added to the raw data read from the electrode. If proper care is not taken during sampling and averaging of the raw data, signal aliasing can occur which is shown in Figure 5. In this case we get an undulating noisy signal in place of a steady value.

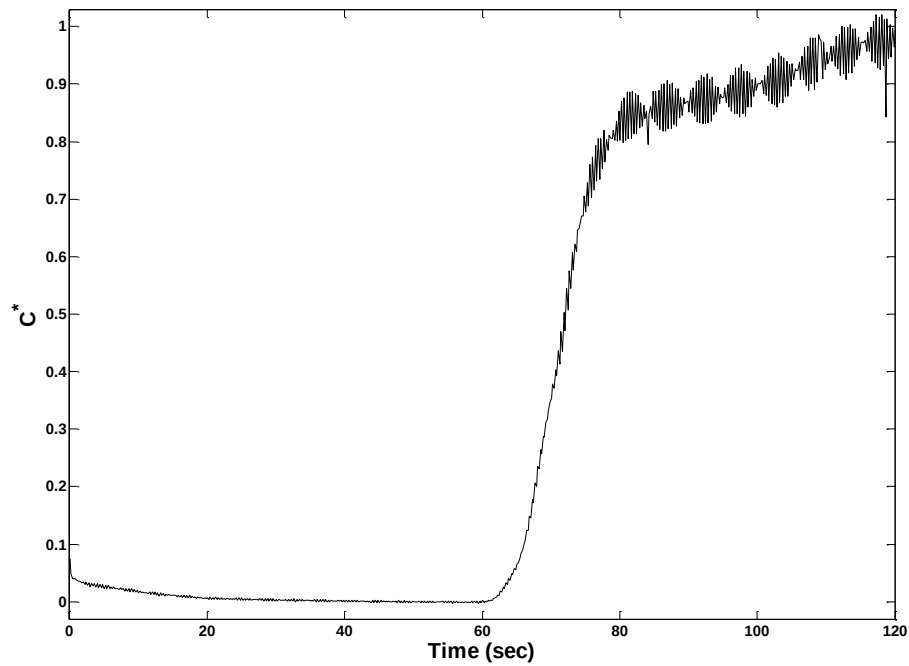


Figure 5: A plot showing strong signal aliasing

To further prove the existence of aliasing with 60 Hz A/C signal, we carry out power spectrum analysis of the raw data at various sampling frequencies which is shown in figure 6-9. We observe that a frequency of 60 Hz is always present in the raw data collected from the electrode.

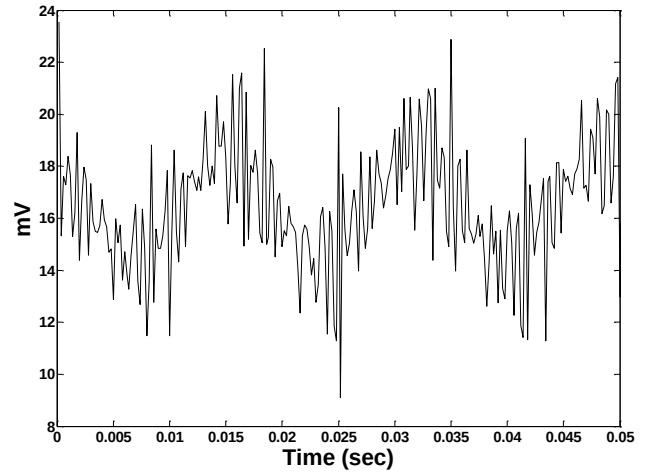
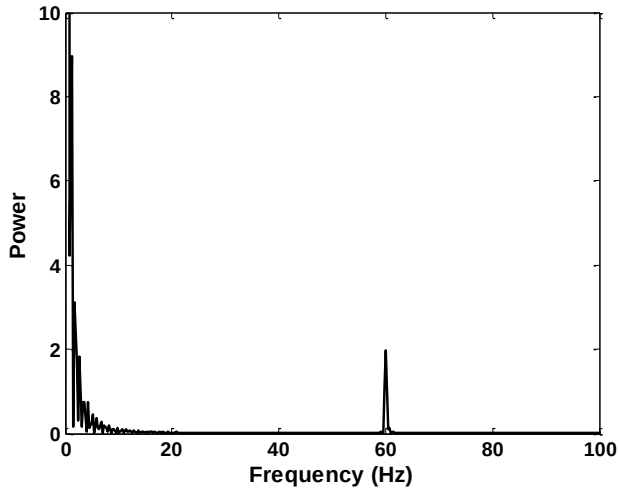


Figure 6: Power spectrum analysis of raw data collected at sampling rate of 5000 Hz

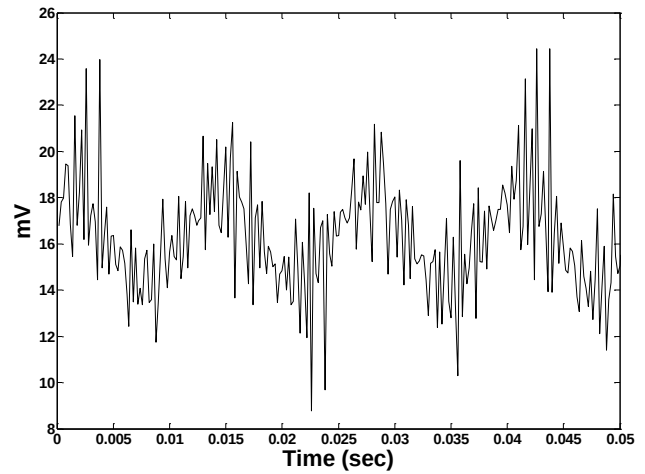
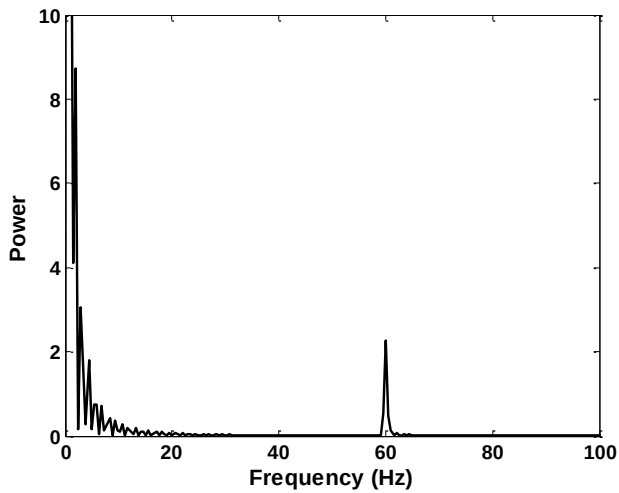


Figure 7: Power spectrum analysis of raw data collected at sampling rate of 4000 Hz

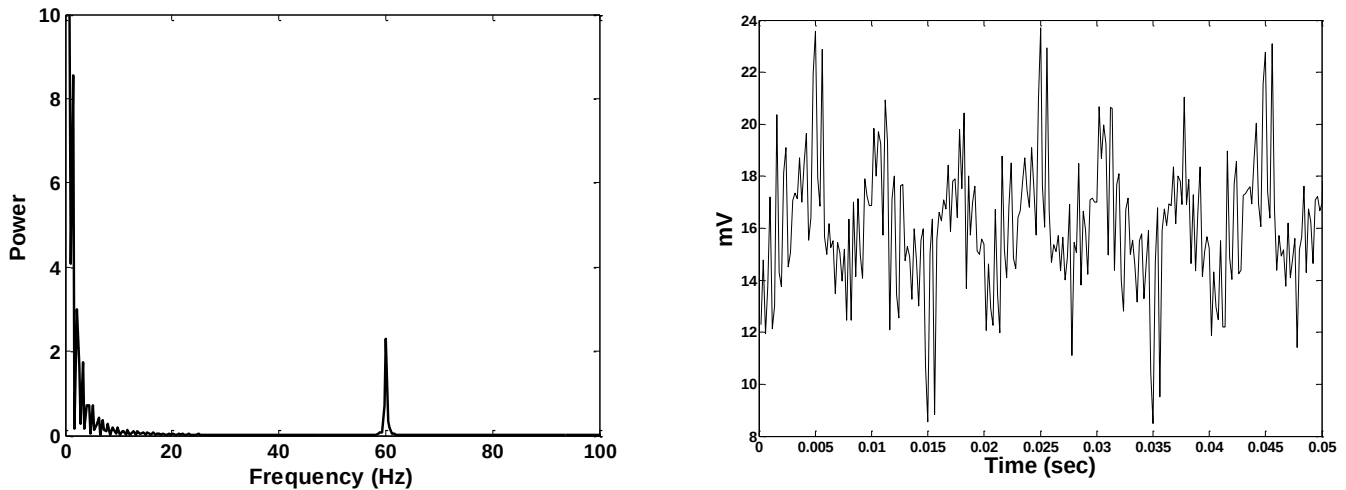


Figure 8: Power spectrum analysis of raw data collected at sampling rate of 2000 Hz

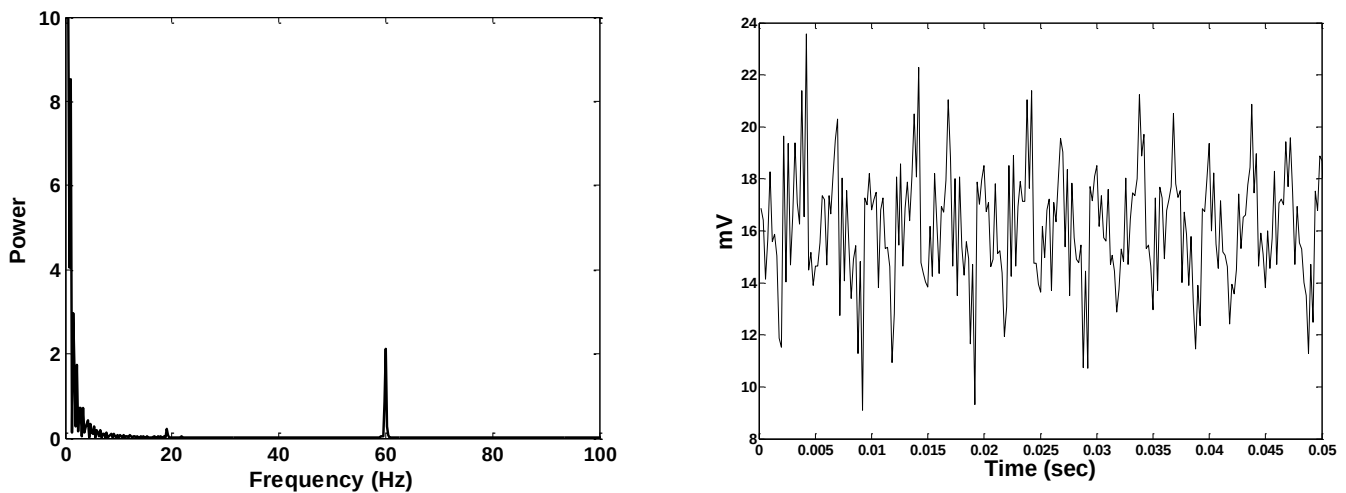


Figure 9: Power spectrum analysis of raw data collected at sampling rate of 1000 Hz

Figures 6-9 show the power spectrum analysis for the raw data as well as raw data acquired within first 50 milliseconds. Presence of 60 Hz interfering frequency is clearly illustrated in figure 6. The raw data plot shows three cycles of a sinusoidal wave whose frequency corresponds to 60 Hz (period = 16.7 ms).

Removing interference of 60 Hz wave:

If data is acquired over a small sampling window, this may result in aliasing of 60 Hz signal. This approach may also result in greater noise in sampled and averaged data. Figure 11 shows the right methodology to gather sampled and averaged data. In order to remove the effect of interfering frequency at 60 Hz, the raw data must be sampled and averaged over a window of acquisition time much larger than the period of 60 Hz wave as shown in figure 11.

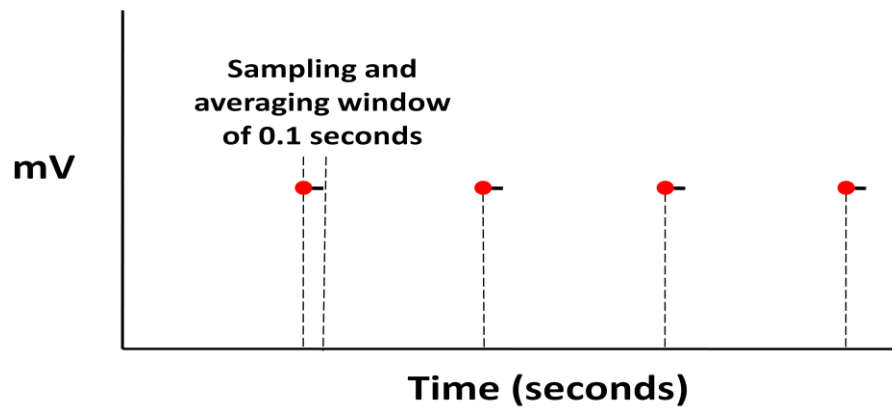


Figure 10: Data acquired over a small sampling interval may result in aliasing in data signal in certain situations

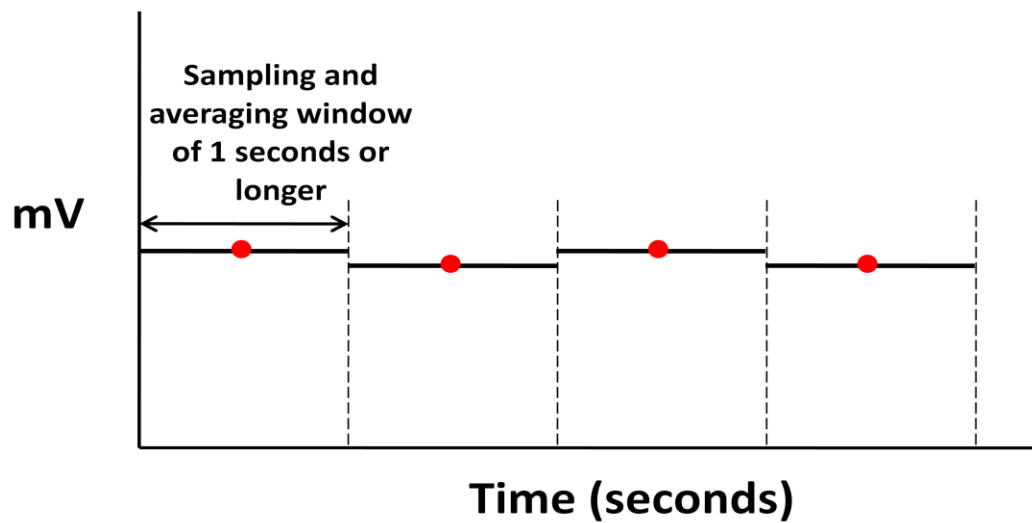


Figure 11: Data should be acquired over the whole range of sampling interval and should be averaged to represent the sampling interval at mid point

There are two parameters which directly affect the sampled and averaged data.

- A) **Sampling rate (Hz):** Sampling rate is the frequency at which LabView® module communicates with the electrode. In our experiments, sampling rates of 1000 Hz -2000 Hz were found to be adequate. Higher sampling rates results in large

amount of raw data and enough computer memory should be available to process the data.

B) Data acquisition window for sampling and averaging (sec): All data points collected in this time interval are stacked together and are averaged to reduce the noise and remove the interference of 60 Hz wave. As a rule of thumb, the data acquisition window should be at least 20-40 times the period of 60 Hz wave. The standard deviation of the sampled and averaged data is inversely proportional to the square root of the number of data points used in averaging. Hence, using a larger window of acquisition time for sampling and averaging not only removes the interferences of the 60 Hz wave but also improves signal to noise ratio as shown in figure 12.

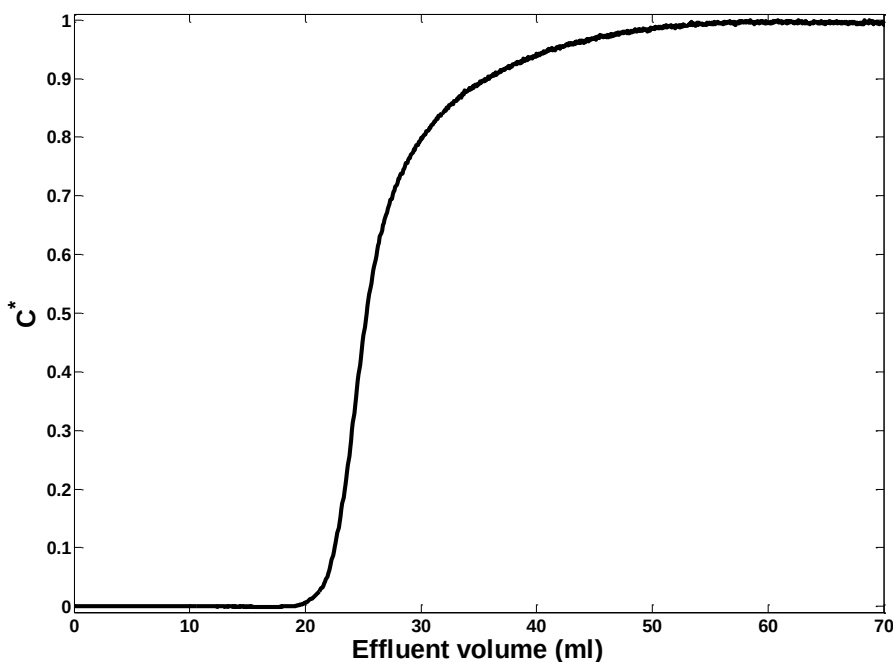


Figure 12: Using the correct sampling and averaging approach results in a smooth plot of effluent concentration versus effluent volumes

List of vendor websites:

- 1) Website of Analytical Sensors and Instruments:

<http://www.asi-sensors.com>

Contact person:

Alice Wong: awong@asi-sensors.com

- 2) Digital multi-meter can be purchased from any RadioShack store or from following website:

<http://www.multimeterwarehouse.com/digitalmultimeter.htm>

- 3) The catalog of different types of sensors available at Analytical Sensor and Instruments can be found at:

<http://www.asi-sensors.com/ASI/docs/asicatalog.pdf>

Bibliography

- ANAND, V. AND HIRASAKI, G. J. 2007a Diffusional coupling between micro and macroporosity for NMR relaxation in sandstones and grainstones. *Petrophysics* **48** [No. 4] 289–307.
- ANAND, V. AND HIRASAKI, G. J. 2007b Paramagnetic relaxation in sandstones: Distinguishing T1 and T2 dependence on surface relaxation, internal gradients and dependence on echo spacing. *Journal of Magnetic Resonance* **190** 68–85.
- ANJOS, S. M. C., DE ROS, L. F. AND SILVA, C. M. A. 2003 Chlorite authigenesis and porosity preservation in the upper cretaceous marine sandstones of the santos basin, offshore eastern Brazil, In: International Association of Sedimentologists Special Publication. *Clay Mineral Cements in Sandstones* **34** 291–316.
- APPEL, M., FREEMAN, J. J., PERKINS, R. B. AND HOFMAN, J. P. 1999 Restricted Diffusion and Internal Field Gradients. in *40th Annual Logging Symposium of the Society of Professional Well Log Analysts* .
- BAKER, L. 1975 Effects of dispersion and dead-end pore volume in miscible flooding. *Soc. Pet. Eng. AIME, Pap* **5632** 50.
- BERGMAN, D. J. AND DUNN, K.-J. 1995a NMR of diffusing atoms in a periodic porous medium in the presence of a nonuniform magnetic field. *Phys. Rev. E* **52** [No. 6] 6516–6535.
- BERGMAN, D. J. AND DUNN, K. J. 1995b Self-diffusion in a Periodic Porous-medium With Interface Absorption. *Physical Review E* **51** [No. 4] 3401–3416.
- BIDNER, M. AND VAMPA, V. 1989 A general model for convection-dispersion-dynamic adsorption in porous media with stagnant volume. *Journal of Petroleum Science and Engineering* **3** [No. 3] 267–281.

- BLOCH, S., LANDER, R. AND BONNELL, L. 2002 Anomalous High Porosity and Permeability in Deeply Buried Sandstone Reservoirs: Origin and Predictability. *AAPG Bulletin* **86** [No. 2] 301–328.
- BORGIA, G. C., BROWN, R. J. S. AND FANTAZZINI, P. 1995 Scaling of spin-echo amplitudes with frequency, diffusion coefficient, pore size, and susceptibility difference for the NMR of fluids in porous media and biological tissues. *Phys. Rev. E* **51** [No. 3] 2104–2114.
- BRIGHAM, W. 1974 Mixing equations in short laboratory cores. *Soc. Pet. Eng. J* **14** 91–99.
- BROOKS, R. A., MOINY, F. AND GILLIS, P. 2001 On T-2-shortening by weakly magnetized particles: The chemical exchange model. *Magnetic Resonance in Medicine* **45** [No. 6] 1014–1020.
- BROWN, R. J. S. AND FANTAZZINI, P. 1993 Conditions for initial quasilinear T_2^{-1} versus τ for Carr-Purcell-Meiboom-Gill NMR with diffusion and susceptibility differences in porous media and tissues. *Phys. Rev. B* **47** [No. 22] 14823–14834.
- BROWNSTEIN, K. R. AND TARR, C. E. 1979 Importance of classical diffusion in NMR studies of water in biological cells. *Phys. Rev. A* **19** [No. 6] 2446–2453.
- CARR, H. Y. AND PURCELL, E. M. 1954 Effects of Diffusion on Free Precession in Nuclear Magnetic Resonance Experiments. *Phys. Rev.* **94** [No. 3] 630–638.
- CEREPI, A., DURAND, C. AND BROSSE, E. 2002 Pore microgeometry analysis in low-resistivity sandstone reservoirs. *Journal of Petroleum Science and Engineering* **35** [No. 3-4] 205–232.
- CHANG, D., VINEGAR, H., MORRIS, C. E. AND STRALEY, C. 1997 Effective porosity, producible fluid and permeability in carbonates from NMR logging. *Log Analyst* **38** [No. 2].
- CHEN, Q. AND SONG, Y. Q. 2002 What is the shape of pores in natural rocks? *Journal of Chemical Physics* **116** [No. 19] 8247–8250.
- CLAUDINE, D., ETIENNE, B. AND ADRIAN, C. 2001 Effect of pore-lining chlorite on petrophysical properties of low-resistivity sandstone reservoirs. *SPE Reservoir Evaluation & Engineering, June* 231–239.
- COATS, K. AND SMITH, B. 1964 Dead-end pore volume and dispersion in porous media. *Soc. Pet. Eng. J* **4** [No. 1] 73–84.

- DE HOOG, F., KNIGHT, J. AND STOKES, A. 1982 An improved method for numerical inversion of Laplace transforms. *SIAM Journal on Scientific and Statistical Computing* **3** 357.
- DE SWIET, T. M. D. S. AND SEN, P. N. 1994 Decay of nuclear magnetization by bounded diffusion in a constant field gradient. *The Journal of Chemical Physics* **100** [No. 8] 5597–5604.
- DUNN, K. J., APPEL, M., FREEMAN, J. J., GARDNER, J. S., HIRASAKI, G. J., SHAFER, J. L. AND ZHANG, G. 2001 Interpretation of Restricted Diffusion and Internal Field Gradients in Rock Data. *Published in the Proceedings of 42nd Annual Symposium of Society of Professional Well Log Analysts, Houston, TX*.
- FANTAZZINI, P. AND BROWN, R. J. S. 2005 Initially linear echo-spacing dependence of I/T-2 measurements in many porous media with pore-scale inhomogeneous fields. *Journal of Magnetic Resonance* **177** [No. 2] 228–235.
- FOLEY, I., FAROOQUI, S. A. AND KLEINBERG, R. L. 1996 Effect of paramagnetic ions on NMR relaxation of fluids at solid surfaces. *Journal of Magnetic Resonance Series a* **123** [No. 1] 95–104.
- GABBANELLI, S., GRATTONI, C. AND BIDNER, M. 1987 Miscible flow through porous media with dispersion and adsorption. *Advances in water resources* **10** [No. 3] 149–158.
- GILLIS, P. AND KOENIG, S. H. 1987 Transverse Relaxation of Solvent Protons Induced by Magnetized Spheres - Application to Ferritin, Erythrocytes, and Magnetite. *Magnetic Resonance in Medicine* **5** [No. 4] 323–345.
- GILLIS, P., MOINY, F. AND BROOKS, R. A. 2002 On T-2-shortening by strongly magnetized spheres: A partial refocusing model. *Magnetic Resonance in Medicine* **47** [No. 2] 257–263.
- GLASEL, J. A. AND LEE, K. H. 1974 Interpretation of Water Nuclear Magnetic-resonance Relaxation-times in Heterogeneous Systems. *Journal of the American Chemical Society* **96** [No. 4] 970–978.
- GREBENKOV, D. S. 2007 Nuclear magnetic resonance restricted diffusion between parallel planes in a cosine magnetic field: An exactly solvable model. *Journal of Chemical Physics* **126** [No. 10].
- GUDBJARTSSON, H. AND PATZ, S. 1995 NMR diffusion simulation based on conditional random walk. *Medical Imaging, IEEE Transactions on* **14** [No. 4] 636–642.

- HAYES, J. B. 1970 Polytypism of chlorite in sedimentary rocks. *Clays and Clay Minerals* **18** [No. 5] 285–291.
- HIDAJAT, I., MOHANTY, K., FLAUM, M. AND HIRASAKI, G. 2004 Study of vuggy carbonates using NMR and X-Ray CT scanning. *SPE Reservoir Evaluation & Engineering* **7** [No. 5] 365–377.
- HOLLENBECK, K. 1998 INVLAP. M: A matlab function for numerical inversion of Laplace transforms by the de Hoog algorithm. [Online; accessed 05-July-2009].
URL: <http://www.isva.dtu.dk/staff/karl/invlap.htm>
- HURLIMANN, M. D. 1998 Effective gradients in porous media due to susceptibility differences. *Journal of Magnetic Resonance* **131** [No. 2] 232–240.
- HURLIMANN, M. D., HELMER, K. G., DESWIET, T. M. AND SEN, P. N. 1995 Spin Echoes in a Constant Gradient and in the Presence of Simple Restriction. *Journal of Magnetic Resonance, Series A* **113** [No. 2] 260–264.
- KENYON, W. E. 1997 Petrophysical principles of applications of NMR logging. *The Log Analyst* **38** [No. 2] 21–43.
- KLEINBERG, R. L. AND HORSFIELD, M. A. 1990 Transverse relaxation processes in porous sedimentary rock. *J. Magn. Reson* **88** [No. 9] 9–19.
- KLEINBERG, R. L., KENYON, W. E. AND MITRA, P. P. 1994 Mechanism of NMR Relaxation of Fluids in Rock. *Journal of Magnetic Resonance Series A* **108** [No. 2] 206–214.
- LA TORRACA, G. A., DUNN, K. J. AND BERGMAN, D. J. 1995 Magnetic susceptibility contrast effects on NMR T2 logging. *SPWLA 36th Annual Logging Symposium* 26–29.
- LE DOUSSAL, P. AND SEN, P. N. 1992a Decay of nuclear magnetization by diffusion in a parabolic magnetic field: An exactly solvable model. *Phys. Rev. B* **46** [No. 6] 3465–3485.
- LE DOUSSAL, P. AND SEN, P. N. 1992b Decay of nuclear magnetization by diffusion in a parabolic magnetic field: An exactly solvable model. *Phys. Rev. B* **46** [No. 6] 3465–3485.
- LOREN, J. D. AND ROBINSON, J. D. 1970 Relationship between pore size and fluid matrix properties and NMR measurements. *Transaction, AIME* **249** 268–278.

- LUCIA, F. 1999 *Carbonate reservoir characterization*. Springer Verlag,.
- MARQUARDT, D. W. 1963 An Algorithm for Least-Squares Estimation of Non-linear Parameters. *Journal of the Society for Industrial and Applied Mathematics* **11** [No. 2] 431–441.
- MITRA, P. P. AND SEN, P. N. 1992 Effects of microgeometry and surface relaxation on NMR pulsed-field-gradient experiments: Simple pore geometries. *Physical Review B* **45** [No. 1] 143–156.
- NEUMAN, C. H. 1974 Spin echo of spins diffusing in a bounded medium. *The Journal of Chemical Physics* **60** [No. 11] 4508–4511.
- PALAZ, I. AND MARFURT, K. 1997 *Carbonate seismology*. Society of Exploration Geophysicists,.
- PEACEMAN, D. AND RACHFORD JR, H. 1955 The numerical solution of parabolic and elliptic differential equations. *Journal of the Society for Industrial and Applied Mathematics* 28–41.
- RAMAKRISHNAN, T. S., FORDHAM, E. J., VENKATARAMANAN, L., FLAUM, M. AND SCHWARTZ, L. M. 1999 New interpretation methodology based on forward models for magnetic resonance in carbonates [C], Paper MMM. *Annual Logging Symposium Transactions, Society of Petrophysicists Well Log Analysts* .
- ROBERTSON, B. 1966 Spin-Echo Decay of Spins Diffusing in a Bounded Region. *Physical Review* **151** [No. 1] 273–277.
- RUESLÅTTEN, H., EIDESMO, T., LEHNE, K. AND RELLING, O. 1998 The use of NMR spectroscopy to validate NMR logs from deeply buried reservoir sandstones. *Journal of Petroleum Science and Engineering* **19** [No. 1] 33–43.
- SEN, P. N. 2004 Time-dependent diffusion coefficient as a probe of geometry. *Concepts in Magnetic Resonance* **23** [No. 1] 1–21.
- SONG, Y., LISITZA, N. V., ALLEN, D. F. AND KENYON, W. E. 2002 Pore geometry and its geological evolution in carbonate rocks. *Petrophysics* **43** [No. 5] 420–424.
- SONG, Y. Q. 2000 Determining pore sizes using an internal magnetic field. *Journal of Magnetic Resonance* **143** [No. 2] 397–401.
- SONG, Y. Q. 2001 Pore sizes and pore connectivity in rocks using the effect of internal field. *Magnetic Resonance Imaging* **19** [No. 3–4] 417–421.

- SONG, Y. Q., RYU, S. G. AND SEN, P. N. 2000 Determining multiple length scales in rocks. *Nature* **406** [No. 6792] 178–181.
- STORVOLL, V., BJØRLYKKE, K., KARLSEN, D. AND SAIGAL, G. 2002 Porosity preservation in reservoir sandstones due to grain-coating illite: a study of the Jurassic Garn Formation from the Kristin and Lavrans fields, offshore Mid-Norway. *Marine and Petroleum Geology* **19** [No. 6] 767–781.
- STRALEY, C., MORRISS, C. E., KENYON, W. E. AND HOWARD, J. J. 1991 NMR in Partially Saturated Rocks: Laboratory Insights on Free Fluid Index and Comparison with Borehole Logs. *SPWLA, 32nd Annual Logging Symposium* 1–25.
- STRALEY, C., MORRISS, C., KENYON, W. AND HOWARD, J. 1995 NMR in partially saturated rocks: laboratory insights on free fluid index and comparison with borehole logs. *Log Analyst* **36** 40–56.
- SUKSTANSKII, A. L. AND YABLONSKIY, D. A. 2002 Effects of Restricted Diffusion on MR Signal Formation. *Journal of Magnetic Resonance* **157** [No. 1] 92–105.
- TARCZON, J. C. AND HALPERIN, W. P. 1985 Interpretation of NMR diffusion measurements in uniform- and nonuniform-field profiles. *Phys. Rev. B* **32** [No. 5] 2798–2807.
- TORREY, H. C. 1956 Bloch Equations with Diffusion Terms. *Phys. Rev.* **104** [No. 3] 563–565.
- TOUMELIN, E., TORRES-VERDÍN, C., CHEN, S. AND FISCHER, D. 2003 Reconciling NMR measurements and numerical simulations: assessment of temperature and diffusive coupling effects on two-phase carbonate samples. *Petrophysics* **44** [No. 2] 91–107.
- TRANHAM, J. C. AND CLAMPITT, R. L. 1977 Determination of oil saturation after waterflooding in an oilwet reservoir-The North Burbank Unit, Tract 97 Project. *J. Pet. Technol* 491–500.
- VALCKENBORG, R. M. E., HUININK, H. P., V. D. SANDE, J. J. AND KOPINGA, K. 2002 Random-walk simulations of NMR dephasing effects due to uniform magnetic-field gradients in a pore. *Phys. Rev. E* **65** [No. 2] 021306.
- VELDE, B. 1995 *Origin and Mineralogy of Clays: Clays and the Environment*. Springer,.

- WAYNE, R. C. AND COTTS, R. M. 1966 Nuclear-Magnetic-Resonance Study of Self-Diffusion in a Bounded Medium. *Phys. Rev.* **151** [No. 1] 264–272.
- WEISSKOFF, R. M., ZUO, C. S., BOXERMAN, J. L. AND ROSEN, B. R. 1994 Microscopic Susceptibility Variation and Transverse Relaxation - Theory and Experiment. *Magnetic Resonance in Medicine* **31** [No. 6] 601–610.
- WILSON, M. AND PITTMAN, E. 1977 Authigenic clays in sandstones; recognition and influence on reservoir properties and paleoenvironmental analysis. *Journal of Sedimentary Research* **47** [No. 1] 3–31.
- WOESSNER, D. E. 1960 Self-diffusion measurements in liquids by the spin-echo technique. *Sci. Instrum* **31**.
- WOESSNER, D. E. 1961 Effects of diffusion in nuclear magnetic resonance spin-echo experiments. *J. Chem. Phys* **34**.
- WOESSNER, D. E. 1963 NMR spin-echo self-diffusion measurements on fluids undergoing restricted diffusion. *The Journal of Physical Chemistry* **67** [No. 6] 1365–1367.
- WORDEN, R. H. AND MORAD, S. 2003 Clay minerals in sandstones: controls on formation, distribution and evolution, In: International Association of Sedimentologists Special Publication. *Clay Mineral Cements in Sandstones* **34** 3–41.
- ZHANG, G. Q. AND HIRASAKI, G. J. 2003 CPMG relaxation by diffusion with constant magnetic field gradient in a restricted geometry: numerical simulation and application. *Journal of Magnetic Resonance* **163** [No. 1] 81–91.
- ZHANG, G. Q., HIRASAKI, G. J. AND HOUSE, W. V. 2001 Effect of Internal Field Gradients on NMR Measurements. *Petrophysics* **42** [No. 1] 37–47.
- ZHANG, G. Q., HIRASAKI, G. J. AND HOUSE, W. V. 2003 Internal field gradients in porous media. *Petrophysics* **44** [No. 6] 422–434.
- ZHANG, Q. 2001 NMR Formation Evaluation: Hydrogen Index, Wettability and Internal Field Gradients. *PhD Thesis* .
- ZIELINSKI, L. J. AND HÜRLIMANN, M. D. 2005 Probing short length scales with restricted diffusion in a static gradient using the CPMG sequence. *Journal of Magnetic Resonance* **172** [No. 1] 161–167.