RICE UNIVERSITY

NMR Surface Relaxation, Wettability and OBM Drilling Fluids

By

Jiansheng Chen

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 Engineering

Clarence A. Miller, Louis Calder Professor Chemical Engineering

Walter G. Chapman, Professor Chemical Engineering

Stanley A. Dodds, Professor Physics and Astronomy

Waylon V. House, Professor Texas Tech University

John L. Shafer Reservoir Management Group Inc.

HOUSTON, TEXAS

MAY, 2005
INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

UMI Microform 3168069
Copyright 2005 by ProQuest Information and Learning Company.
All rights reserved. This microform edition is protected against unauthorized copying under Title 17, United States Code.

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346
ABSTRACT

NMR Surface Relaxation, Wettability and

OBM drilling Fluids

by

Jiansheng Chen

NMR surface relaxation mechanisms and their dependence on temperature were investigated. Paramagnetic ions are a very important factor of surface relaxation. The mechanism of the surface enhanced dipole-dipole interaction is negligible when the paramagnetic ion mechanism is strong. In such case, surface relaxivity of both water and oil depends only weakly on temperature. However, in cases when paramagnetic ion mechanism is weak, the contribution from surface enhanced dipole-dipole interaction could dominate the total surface relaxation rate. In such case, surface relaxivity of both water and oil decreases with temperature.

Effects of synthetic oil base mud (OBM) surfactants on wettability alteration, NMR response and irreducible water saturation ($S_{wir}$) were systematically examined. The originally strongly water-wet Berea and limestone cores are altered to be intermediate-wet or oil-wet by OBM surfactants. As a result, $S_{wir}$ from NMR $T_2$, cutoff model with the default assumption of water-wetness generally underestimates the measured value. The magnitude of underestimation depends on the type of OBM surfactants, their concentration in the flushing fluid, and the flushing volume. The magnitude of underestimation correlates with the Amott-Harvey wettability index. These results
suggest that the effects of OBM invasion on estimation of $S_{wir}$ can be minimized by controlling the volume of OBM invasion and the concentration of OBM surfactants.

Mechanisms of $S_{wir}$ underestimation and modifications of NMR interpretation when wettability alteration occurs were investigated. In the case of an oil-bearing rock at $S_{wir}$, OBM invasion does not significantly decrease the actual $S_{wir}$, but changes the water and oil relaxation time distributions due to wettability alteration. This is visualized by the $D$-$T_2$ map. When wettability alteration occurs (water-wet to intermediate-wet or oil-wet), a $T_{2,cutoff}$ value larger than the one based on water-wetness is needed because the irreducible water relaxes at a longer relaxation time. Correlation between this modified $T_{2,cutoff}$ value and the Amott-Harvey wettability index was found.

Three unusual NMR properties were observed for the filtered OBM filtrates due to the unexpected presence of trace amount of paramagnetic particulates. Interactions between the filtered OBMF and rock samples can cause wettability alteration, enhanced surface relaxation and increased internal gradient strength.
ACKNOWLEDGEMENTS

First of all, I am very grateful to my thesis advisor Dr. George J. Hirasaki for both his spiritual and academic guidance and advices. He sets a great example for the rest of my life. I also greatly appreciate Dr. Clarence A. Miller, Dr. Walter G. Chapman, Dr. John L. Shafer, Dr. Stanley A. Dodds and Dr. Waylon V. House who serve in my thesis committee.

My special thanks go to Dr. John L. Shafer for his insightful suggestions about my research. I would also like to thank Dr. Songhua Chen, Dr. Daniel Georgi and Dr. Gigi Zhang at Baker Atlas for their invaluable guidance during my summer internship. They help me a lot to grow professionally.

Many thanks go to Chuck Devier at PTS Labs International for his great help of my experiments. Thank Paul Martin and Robert Lee at Core Laboratories for the sample coring, porosity, permeability and mercury injection capillary pressure measurements. Thank Mario Winkler and Rod Perkins at Shell for the Karl-Fisher analysis. Thank Tim Borbas at ConocoPhillips for the OBM samples. Thank Freddi Curby at Numar Lab Services Group for the filtrate pressing experiment. Thank Bill Reese and Glenn Van Gaalen at ExxonMobil for the magnetic susceptibility measurements. Thank Gong Min Fu at Rice University for the ICP measurements. Thank Mark Flaum for his help in the $D-T_2$ measurements and discussions of my research.

Finally, I wish to acknowledge Department of Energy (grand number DE-RA26-98BC15200) and Rice Consortium of Processes in Porous Media for the financial support.

Mostly importantly, thank my wife Chunyu Wang and my families for their love and sacrifices. Thank God for his wonderful grace and love.
TABLE OF CONTENTS

TITLE PAGE .................................................................................................................i

ABSTRACT ...................................................................................................................ii

ACKNOWLEDGEMENTS ...............................................................................................iv

TABLE OF CONTENTS .................................................................................................v

LIST OF TABLES ...........................................................................................................viii

LIST OF FIGURES .........................................................................................................x

NOMENCLATURE ..........................................................................................................xvii

Chapter 1  Introduction .............................................................................................1

Chapter 2  NMR in Porous Media and NMR Well Logging .................................3
  2.1 Analytical Solution of Relaxation Time of Fluids in a Single Pore ...............3
  2.2 Three Types of Relaxation Mechanisms .......................................................5
     2.2.1 Bulk Relaxation .........................................................................................6
     2.2.2 Surface Relaxation ....................................................................................7
     2.2.3 Relaxation due to Diffusion .....................................................................7
  2.3 Formation Evaluation from NMR .................................................................8
     2.3.1 Porosity .....................................................................................................8
     2.3.2 Permeability .............................................................................................9
     2.3.3 Bulk Volume Irreducible .........................................................................11

Chapter 3  NMR Surface Relaxation ..................................................................12
  3.1 Literature Review ..............................................................................................12
     3.1.1 KST model ..............................................................................................12
     3.1.2 Kleinberg model ....................................................................................14
     3.1.3 Surface diffusion model .........................................................................16
     3.1.4 Experimental Investigations on NMR Surface Relaxation ..................17
  3.2 Materials and Experimental Procedures .......................................................23
     3.2.1 Unconsolidated Silica Particles .................................................................23
     3.2.2 Acid Washing Procedures ................................................................ ......23
     3.2.3 Ion Coating Procedures .........................................................................25
     3.2.4 NMR $T_1$, $T_2$ Relaxation Time Measurements ..................................26
3.3 Experimental Results and Discussions ................................................. 27
  3.3.1 Comparison of Surface Relaxivity between Berea Sandstones and Texas Cream Limestones ................................................. 27
  3.3.2 Surface Relaxivity $\rho_1$, $\rho_2$ and $\rho_2/\rho_1$ Ratio for Silica Samples with respect to Acid Washing and Ion Coating .................. 30
  3.3.3 Effects of Surface Enhanced Dipole-dipole Interaction on Surface Relaxation .................................................. 33
  3.3.4 Surface Relaxation at Elevated Temperatures ............................ 39
  3.3.5 Combined Effect of Surface Relaxation and Diffusion Coupling ........ 45
3.4 Conclusions .................................................................................. 48

Chapter 4  Effect of OBM surfactants on Wettability Alteration and NMR Responses ......................................................... 50
  4.1 Literature Review ......................................................................... 50
    4.1.1 OBM Surfactants, Their Potential on Wettability Alteration and the Effect on NMR Responses ............................................ 50
    4.1.2 Models of estimating $S_{wir}$ (BVI) from NMR ......................... 52
  4.2 Materials and Experimental Procedures ......................................... 57
    4.2.1 Berea and Texas Cream Limestone Cores ................................. 58
    4.2.2 Base Oil, Crude Oil, OBM Surfactants and Flushing Fluids .......... 58
    4.2.3 Rock Saturation Preparation ................................................... 59
    4.2.4 Flushing Set-up and Process with OBM surfactants .................. 60
    4.2.5 Amott-Harvey Wettability Index Measurements ....................... 61
    4.2.6 NMR $D-T_2$ measurements ................................................... 62
  4.3 Experimental Results and Discussions .......................................... 63
    4.3.1 NMR Bulk Properties of the OBM Surfactants ......................... 63
    4.3.2 Wettability Alteration of Berea and Limestone Cores by OBM Surfactants ................................................................. 65
    4.3.3 Effects of Wettability Alteration by OBM Surfactants on NMR Estimated $S_{wir}$ .......................................................... 73
    4.3.4 Mechanism of $S_{wir}$ Underestimation and Modifications of NMR Interpretation When Wettability Alteration Occurs ............ 90
  4.4 Conclusions ................................................................................. 94

Chapter 5  Study of Wettability from NMR Method ................................ 96
  5.1 Literature Review ......................................................................... 96
  5.2 Materials and Experimental Procedures ....................................... 98
    5.2.1 Unconsolidated Silica Flour and Calcite ................................ 99
    5.2.2 Base Oils and Model Surfactants ............................................ 99
    5.2.3 Saturation Preparation for the Unconsolidated Silica Flour and Calcite ................................................................. 100
    5.2.4 Contact Angle Measurements ................................................. 100
Chapter 6  Effects of Paramagnetic Particulate in the OBM Filtrates on NMR Responses .......................................................... 125

6.1 Materials ............................................................................. 125
   6.1.1 Synthetic Oil Base Mud Samples .................................. 125
   6.1.2 Reservoir Cores .......................................................... 126

6.2 Experimental Results and Discussions .............................. 126
   6.2.1 Unusual NMR Bulk Properties of OBMF .................. 127
   6.2.2 Interactions of OBMF with Reservoir Cores and Outcrop Berea Cores ......................................................... 143

6.3 Conclusions ...................................................................... 154

Chapter 7  Conclusions ............................................................. 155

Chapter 8  Future Work ............................................................ 160

REFERENCES ........................................................................ 161

APPENDIX ............................................................................. 168

Part A Determination of Surface Relaxivity and Pore Size Distribution by Comparison between Mercury Capillary Pressure Curve and NMR Relaxation Time Distribution ................................................................. 168
   A.1 Descriptions of Capillary Pressure Models .................. 168
   A.2 Model Fitting of the Mercury Capillary Pressure Curves .... 170
   A.3 Comparison between Mercury Capillary Pressure Curve and Relaxation Time Distribution: Surface Relaxivity ........ 173
   A.4 Pore Size Distributions of Berea and Texas Cream limestone Cores from NMR and Hg Capillary Pressure Curves....... 175

Part B $T_1$, $T_2$ Relaxation time distributions of OBM surfactants ... 180

Part C Data Summary .............................................................. 182
LIST OF TABLES

TABLE 3.1.4.1 Catalog of surface relaxivity $\rho_1$ for water saturated unconsolidated materials with well-defined surface area from BET or grain size...19

TABLE 3.2.1.1 Mean diameter and BET surface area of the silica particles.........23

TABLE 3.3.3.1 Numerical values of surface relaxivity $\rho_{2,ps}$ and $\rho_{2,d}$ of water........36

TABLE 4.2.2.1 Components and main functions of the four OBM surfactant systems...59

TABLE 4.3.1.1 $T_1$, $T_2$ log mean values of all the OBM surfactants studied..........64

TABLE 4.3.2.1 Amott-Harvey wettability indices of Berea and Texas Cream limestone cores after flushing with (SB + OBM surfactants)...68

TABLE 4.3.3.1 Interfacial tension and contact angle for air/brine and SB/brine systems76

TABLE 5.2.1.1 Mean diameter and BET surface area of the silica flour and calcite......99

TABLE 6.1.2.1 Porosity and air permeability of the reservoir cores...................126

TABLE 6.1.2.2 Typical composition of the reservoir cores by XRD analysis. .........126

TABLE 6.2.1.1 $T_1$, $T_2$ and diffusivity for the base oils and filtered OBMF ............129

TABLE 6.2.1.2 $T_1$, $T_2$ and $T_1/T_2$ ratio at different concentration of magnetite ferrofluid particles..............................................................................................................141

TABLE A.2.1 Porosity and permeability of Berea and Texas Cream limestone cores...171

TABLE A.2.2 Parameters of model fitting (Bimodal Log Normal) for Berea cores......173

TABLE A.2.3 Parameters of model fitting (Log Normal) for Texas Cream limestone cores.........................................................................................................................173

TABLE C. 1 $T_{2,cutoff}$ of the Berea cores at the original water-wet condition.........182

TABLE C.2 Contact angles of water/glass slide/oil and water/marble/oil systems with model surfactants DDA and SA..............................................................183

TABLE C.3 Contact angles of water/glass slide/oil and water/marble/oil systems with OBM surfactants LLD, BOO, VERSA and NOVA.................................183
TABLE C.4 Summary of surface relaxivity of water and oil in 100% $S_w$, 100% $S_o$ and water/oil partially saturated silica flour and calcite........................................................................184

TABLE C.5 NMR water wettability index, $T_2$ log mean values are used in the calculation........................................................................................................185

TABLE C.6 NMR water wettability index, $T_2$ mode values are used in the calculation........................................................................................................185

TABLE C.7 NMR oil wettability index, $T_2$ mode values are used in the calculation........................................................................................................186

TABLE C.8 $T_2$ mode values of Berea cores at 100% $S_o$........................................................................186

TABLE C.9 Combined NMR wettability indices, $T_2$ mode values are used in the calculation........................................................................................................187
LIST OF FIGURES

FIGURE 2.3.1.1 Schematic plot of porosity model for an invaded zone from NMR well logging.................................................................9

FIGURE 3.1.4.1 Catalog of surface relaxivity $\rho_1$ for sandstones.................................................................19

FIGURE 3.2.2.1 $T_2$ relaxation time of washing supernatant with respect to acid washing of fine silica sand.........................................................24

FIGURE 3.2.3.1 $T_2$ relaxation time distributions of coated fine silica sand saturated with 100% $S_w$. Concentrations of FeCl$_3$ in the 1.0 mol/l HCl solution were 0.0025, 0.1, 0.5 or 1.0 mol/l in the procedures of preparing for the silica samples......................................................26

FIGURE 3.3.1.1 Histogram of surface relaxivities of water in 100% $S_w$ Berea cores.................................................................29

FIGURE 3.3.1.2 Histogram of surface relaxivities of water in 100% $S_w$ Texas Cream limestone cores.................................................................29

FIGURE 3.3.2.1 Comparison of surface relaxivity $\rho_1$ and $\rho_2$ of water in 100% $S_w$ coated, original and washed fine silica sand.................................................................31

FIGURE 3.3.2.2 Surface relaxivity $\rho_1$ and $\rho_2$ of water in 100% $S_w$ silica sand (left) and silica flour (right).................................................................32

FIGURE 3.3.2.3 $\rho_2/\rho_1$ ratios of water in 100% $S_w$ silica sand (left) and silica flour (right) with respect to acid washing.................................................................32

FIGURE 3.3.3.1 $T_2$ relaxation time distributions of coated, original and washed silica sand. In each plot, sample A stands for 100% H$_2$O saturation and sample B stands for 10% H$_2$O-90% D$_2$O (in molar fraction) saturation.................................................................37

FIGURE 3.3.3.2 $T_2$ relaxation time distributions of original and washed silica flour. In each plot, sample A stands for 100% H$_2$O saturation and sample B stands for 10% H$_2$O-90% D$_2$O (in molar fraction) saturation.................................................................38

FIGURE 3.3.3.3 $T_2$ relaxation time distributions of coated and original silica gel. In each plot, sample A stands for 100% H$_2$O saturation and sample B stands for 10% H$_2$O-90% D$_2$O (in molar fraction) saturation.................................................................38

FIGURE 3.3.4.1 Change of bulk relaxation rate $1/T_2$ of decane and water with respect to temperature.................................................................40

FIGURE 3.3.4.2 $T_2$ relaxation time distributions of original silica sand saturated with 100% water (top plot), 100% decane (middle plot) and the corresponding surface relaxivities (bottom plot) at 24.4 °C, 45 °C, 60 °C, 75 °C and 90 °C.................................................................42
FIGURE 3.3.4.3 $T_2$ relaxation time distributions of coated silica sand saturated with 100% water (top plot), 100% decane (middle plot) and the corresponding surface relaxivities (bottom plot) at 24.4 °C, 45 °C, 60 °C, 75 °C and 90 °C........................................43

FIGURE 3.3.4.4 $T_2$ relaxation time distributions of 100% water saturated original silica gel (top plot) and the corresponding surface relaxivities (bottom plot) at 24.4 °C, 45 °C, 60 °C, 75 °C and 90 °C........................................44

FIGURE 3.3.5.1 $T_1$, $T_2$ relaxation time distributions of the original silica gel at 24.4 °C and 90 °C.........................................................46

FIGURE 3.3.5.2 $T_2$ relaxation time distributions of 100% water saturated coated silica gel and the corresponding surface relaxivities at 24.4 °C, 45 °C, 60 °C, 75 °C and 90 °C...47

FIGURE 3.3.5.3 $T_1$ relaxation time distributions of 100% water saturated North Burbank at 28 °C and 90 °C........................................48

FIGURE 4.1.2.1 Schematic description of cutoff BVI model. A fixed $T_{2,\text{cutoff}}$ partitions the spectrum of $T_2$ relaxation time distribution into BVI and FFI........................................53

FIGURE 4.1.2.2 Schematic description of the determination of $T_{2,\text{cutoff}}$ from NMR measurements of core sample at 100% $S_w$ and $S_{\text{wir}}$ (air/brine) conditions. $T_{2,\text{cutoff}}$ is the $T_2$ value at which the cumulative intensity of the relaxation time distribution at 100% $S_w$ condition is equal to the asymptotical cumulative intensity at $S_{\text{wir}}$ (air/brine) condition...54

FIGURE 4.2.4.1 Schematic plot of the flushing set-up........................................61

FIGURE 4.3.1.1 $T_1$ and $T_2$ distributions of OBM surfactant LE MUL.................................64

FIGURE 4.3.2.1 Amott-Harvey wettability indices of Berea cores after flushing........65

FIGURE 4.3.2.2 Amott-Harvey wettability indices of Texas Cream limestone cores after flushing.........................................................66

Figure 4.3.2.3 $D-T_2$ maps of 100% $S_w$, after forced brine imbibition and bulk SB for Berea B72 (left, water-wet after flushing) and B77 (right, oil-wet after flushing)..............71

Figure 4.3.2.4 $D-T_2$ maps of 100% $S_w$, after forced brine imbibition and bulk SB for Texas Cream limestone L15 (left, water-wet after flushing) and L2 (right, oil-wet after flushing)........................................72

FIGURE 4.3.3.1 Cross-plot of $S_{\text{wir}}$ by weighing and from $T_{2,\text{cutoff}}$ of 33 ms for Berea cores at the original water-wet condition........................................74

FIGURE 4.3.3.2 Comparison of measured $S_{\text{wir}}$ between air/brine, crude/brine and SB/brine for Berea and limestone cores........................................75
FIGURE 4.3.3.3 Calculated capillary pressure curves of Berea and Texas Cream limestone showing much more different wetting phase saturation between air/brine and SB/brine for Texas Cream limestone than for Berea at the same capillary pressure of 100 psi

FIGURE 4.3.3.4 Incremental and cumulative $T_2$ distributions for Berea B4 and B13 at 100% $S_w$, $S_{wir}$ with air, $S_{wir}$ with SB + NOVA and after flushing (only for B13)

FIGURE 4.3.3.5 Incremental and cumulative $T_2$ distributions for Berea B30 and B66 at 100% $S_w$, $S_{wir}$ with air, $S_{wir}$ with crude oil and after flushing

FIGURE 4.3.3.6 Interference of $T_2$ relaxation time of bulk crude oil with that of irreducible water (Berea core B30)

FIGURE 4.3.3.7 Incremental and cumulative $T_2$ distributions for limestone L15 and L59 at 100% $S_w$, $S_{wir}$ with SB, and after flushing

FIGURE 4.3.3.8 $S_{wir}$ measured by weighing and estimated from $T_2$, cutoff of 33 ms for air/brine and (SB + surf.)/brine at different concentrations of NOVA. 0%: B4, 0.5%: B3, 1%: B19, 2%: B20, 3%: B13

FIGURE 4.3.3.9 Magnitude of $S_{wir}$ underestimation with respect to the OBM surfactants concentration in the centrifuging fluid (Berea cores)

FIGURE 4.3.3.10 $S_{wir}$ measured by weighing (air/brine and crude/brine) and estimated from $T_2$, cutoff of 33 ms (crude/brine and after flushing) at different concentrations of BOO. 0%: B30, 0.5%: B16, 1%: B45, 2%: B58, 3%: B66

FIGURE 4.3.3.11 Magnitude of $S_{wir}$ underestimation with respect to the OBM surfactants concentration in the flushing fluid (Berea cores)

FIGURE 4.3.3.12 Magnitude of $S_{wir}$ underestimation with respect to the OBM surfactant concentration in the flushing fluid (Texas Cream limestone cores)

FIGURE 4.3.3.13 Effects of flushing volume on $S_{wir}$ underestimation for Berea B40 (top) and Texas Cream limestone L8 (bottom)

FIGURE 4.3.3.14 Magnitude of $S_{wir}$ underestimation versus Amott-Harvey index for Berea and Texas Cream limestone cores

Figure 4.3.4.1 Karl-Fisher analysis of water amount in the flushing effluents, B31: flushed with 10 PV SB, B66: flushed with 10 PV SB + 3% BOO, B26: flushed with 10 PV SB + 3% NOVA

FIGURE 4.3.4.2 $D-T_2$ maps of 100% $S_w$ and after flushing for Berea B77. The vertical dashed line corresponds to $T_2$, cutoff of 33 ms

xii
FIGURE 4.3.4.3 Modified values of $T_2$, cutoff versus magnitude of $S_{w, r}$ underestimation for both Berea cores and Texas Cream limestone cores. ......................................................... 93

FIGURE 4.3.4.4 Modified values of $T_2$, cutoff versus Amott-Harvey wettability index for both Berea cores and Texas Cream limestone cores. ......................................................... 94

FIGURE 5.3.1.1 Contact angles of brine/glass slide/oil systems. Oil phase: escaid, escaid plus 0.74% DDA and escaid plus 0.5% SA ................................................................. 103

FIGURE 5.3.1.2 Contact angles of brine/marble/oil systems. Oil phase: SB, SB plus 0.74% DDA and SB plus 0.5% SA ................................................................. 103

FIGURE 5.3.1.3 Contact angles of brine/glass slide/oil systems. Oil phase: SB, SB plus 0.5% OBM surfactants LLD, BOO, VERSA and NOVA ........................................ 104

FIGURE 5.3.1.4 Contact angles of brine/marble/oil systems. Oil phase: SB, SB plus 0.5% OBM surfactants LLD, BOO, VERSA and NOVA ........................................ 104

FIGURE 5.3.2.1 $T_2$ relaxation time distribution (a) and the effective surface relaxivity of water and/or oil (b) at 100% $S_w$, 100% $S_o$, 30% $S_w$ with pure oil (Escaid) and 30% $S_w$ with oil plus DDA (0.74% wt), silica flour ................................................................. 108

FIGURE 5.3.2.2 $T_2$ relaxation time distributions (a) and the effective surface relaxivity of water and/or oil (b) at 100% $S_w$, 100% $S_o$, 40% $S_w$ with pure oil (SB) and 43% $S_w$ with oil plus SA (0.5% wt), calcite ................................................................. 109

FIGURE 5.3.2.3 $T_2$ relaxation time distributions and the effective surface relaxivity of water and oil at 21% $S_w$ with pure oil (Escaid) and 21% $S_w$ with oil plus SA (0.5% wt), silica flour ................................................................. 110

FIGURE 5.3.2.4 $T_2$ relaxation time distributions and the effective surface relaxivity of water and oil at 38% $S_w$ with pure oil (SB) and 43% $S_w$ with oil plus DDA (0.74% wt), calcite ................................................................. 110

FIGURE 5.3.2.5 Comparison of $T_2$ relaxation time distributions (a) and the effective surface relaxivity (b) of water and oil for 18% $S_w$ saturated silica flour (# 2) among cases with different concentration of LLD in the oil phase of SB ................................................................. 113

FIGURE 5.3.2.6 $T_2$ relaxation time distribution (a) and surface relaxivity (b) of water or oil for silica flour (# 2) saturated with 40% $S_w$ with SB, 40% $S_w$ with SB + 1% BOO, 40% $S_w$ with SB + 1% VERSA, 36% $S_w$ with SB + 1% NOVA and 40% $S_w$ with SB + 1% LLD ................................................................. 115

FIGURE 5.3.2.7 $T_2$ relaxation time distribution (a) and surface relaxivity (b) of water and oil for calcite (# 2) saturated with 49% $S_w$ with SB, 50% $S_w$ with SB + 1% LLD, 55% $S_w$
with SB + 1% BOO, 52% $S_w$ with SB + 1% VERSA and 61% $S_w$ with SB + 1% NOVA........................................................................................................115

FIGURE 5.3.2.8 Surface area per molecule of the OBM surfactants versus the ratio of the molecular weight of the OBM surfactants to that of SA. Assumption: all of the OBM surfactants adsorb on the mineral surface........................................116

FIGURE 5.3.3.1 Correlation between NMR water wettability index and Amott-Harvey index, log mean values of the $T_2$ relaxation time distributions of water are used........119

FIGURE 5.3.3.2 Correlation between NMR water wettability index and Amott-Harvey index, mode values of the $T_2$ relaxation time distributions of water are used........120

FIGURE 5.3.3.3 Correlation between NMR oil wettability index and Amott-Harvey index, mode values of the $T_2$ relaxation time distributions of oil are used...........122

FIGURE 5.3.3.4 $D-T_2$ maps of Berea B37 at 100% $S_o$ saturation...............................122

FIGURE 5.3.3.5 Cross plot of combined NMR wettability index versus Amott-Harvey wettability index..................................................................................123

FIGURE 6.2.1.1 Impact of the filtration methods on NMR relaxation time of the OBMF........................................................................................................128

FIGURE 6.2.1.2 Comparison of $T_2$ between base oils and filtered OBMF.................130

FIGURE 6.2.1.3 Comparison between $T_1$ and $T_2$ for the filtered OBMF...................130

FIGURE 6.2.1.4 $D-T_2$ maps of base oil and filtered OBMF...........................................131

FIGURE 6.2.1.5 Diffusivity versus $T_2$ for base oils, filtered OBMF and correlation between $D$ and $T_2$ for hydrocarbon..............................................................131

FIGURE 6.2.1.6 Comparison of $T_2$ between SB, SB + 3% BOO and SB + 3% NOVA. .........................................................................................................................132

FIGURE 6.2.1.7 $D-T_2$ maps of SB (left plot) and SB + 3% BOO (right plot)..................133

FIGURE 6.2.1.8 Particle size distribution of filtered OBMF #2 from DLS measurement.........................................................................................................................134

FIGURE 6.2.1.9 HCl leaching of paramagnetic particulates from the OBMF..............135

FIGURE 6.2.1.10 Concentration of paramagnetic elements in the filtered OBMF by ICP measurement..............................................................................................136
FIGURE 6.2.1.11 $T_1$, $T_2$ relaxation times of SB and SB + 3% NOVA + ferrofluid...138

FIGURE 6.2.1.12 $T_1/T_2$ ratio and echo spacing dependence of $T_2$ for three systems: Fe$^{3+}$ in HCl, filtered OBMF and fresh-state reservoir core #199 at $S_{wir}$ with base oil...139

FIGURE 6.2.1.13 Effective $T_1$, $T_2$ relaxation rate versus iron concentration in water solution of magnetite ferrofluid particles...141

FIGURE 6.2.1.14 Effective $T_2$ relaxation rate versus concentration of Fe$^{3+}$ in HCl, pH = 2...142

FIGURE 6.2.1.15 $T_1/T_2$ ratio versus iron concentration in water solution of magnetite ferrofluid particles...142

FIGURE 6.2.2.1 Comparison of $T_1$ of centrifuged oil as bulk versus inside the fresh-state core #196...144

FIGURE 6.2.2.2 $T_1$ and $T_2$ (at multiple echo spacing) of core #200 (water-wet) and core #477 (intermediate-wet) at $S_{wir}$ with decane...145

FIGURE 6.2.2.3 $T_2$ relaxation time distributions of core #206 before and post OBMF flushing...147

FIGURE 6.2.2.4 (a) $D$-$T_2$ map of core #206 at $S_{wir}$ with base oil post OBMF flushing...148

FIGURE 6.2.2.4 (b) Distributions of diffusivity (left) and local gradient strength (right) experienced by oil...148

FIGURE 6.2.2.5 Monitor of oil $T_2$ peak with respect to aging time after flushing with filtered OBMF (core #140) and pressed OBMF (core #165)...149

FIGURE 6.2.2.6 $D$-$T_2$ maps of sample #140 and #165 at $S_{wir}$ with base oil before and after OBMF flushing...150

FIGURE 6.2.2.7 Internal gradient strength distributions of sample #140 (left) and #165 (right) at $S_{wir}$ with base oil before and after OBMF flushing...151

FIGURE 6.2.2.8 $D$-$T_2$ maps of Berea B83 at $S_{wir}$ with SB (left), after flushing (middle) and after aging (right)...152

FIGURE 6.2.2.9 Internal gradient strength of Berea B83 at $S_{wir}$ with SB, after flushing and after aging...152

FIGURE 6.2.2.10 $D$-$T_2$ maps of Berea B71 at $S_{wir}$ with SB (left), after flushing (middle) and after aging (right)...153
FIGURE 6.2.2.11 Internal gradient strength of Berea B71 at $S_{wir}$ with SB, after flushing and after aging.................................................................153

FIGURE A.2.1 Hg capillary pressure curves for Berea B18, B53 and B69.............171

FIGURE A.2.2 Hg capillary pressure curves for limestone L84, L61 and L24.........171

FIGURE A.2.3 Model fittings of Leverett J function for Berea B18.....................172

FIGURE A.2.4 Model fittings of Leverett J function for limestone L24...............172

FIGURE A.4.1 Incremental and cumulative pore size distributions for Berea B18, (a) and (b): from $T_2$ and Hg capillary pressure curve calculated by Bimodal Log Normal model, (c): from $T_2$ and measured Hg capillary pressure curve........................................177

FIGURE A.4.2 Bimodal Log Normal fitting of the measured data for Berea core B18.178

FIGURE A.4.3 Incremental and cumulative pore size distributions for Texas Cream limestone L2 from $T_2$ and Hg capillary pressure calculated by Log Normal model......179

FIGURE B.1 $T_1$, $T_2$ distributions of LE SUPERMUL, BIO COAT, OMNI MUL, OMNI TEC, NOVA MUL, NOVA WET, VERSA MUL and VERSA COAT.......................180
### NOMENCLATURE

- $a$: Pore size
- $A$: Cross section area
- $A_d$: Dipolar coupling constant
- $A_o$: Surface area covered by oil in the pore space
- $A_s$: Scalar hyperfine constant
- $A_T$: Total surface area in the pore space
- $A_w$: Surface area covered by water in the pore space
- $BVI$: Bulk volume irreducible
- $D_0$: Self-diffusivity of fluid
- $D_{app}$: Apparent diffusivity of fluid
- $E_m$: Activation energy associated with the surface chemical bond
- $E_s$: Activation energy associated with the molecular diffusion jump
- $f_0$: Intensities of bins in the relaxation time distribution
- $FFI$: Free fluid index
- $G$: Strength of the magnetic field gradient
- $g_{ext}$: Strength of the applied gradient in the $D-T_2$ measurements
- $g_{loc}$: Local gradient strength
- $\langle H_{loc}^2 \rangle$: Mean square of the local magnetic field strength
- $I_{AH}$: Amott-Harvey wettability index
- $I_{C}^{NMR}$: Combined NMR wettability index
- $I_{O}^{NMR}$: NMR oil wettability index
- $I_{W}^{NMR}$: NMR water wettability index
- $J$: Leverett $J$ function
- $m(X, t)$: Magnetization density at time $t$ and position $X$
- $M(t)$: Total magnetization at time $t$
- $M_0$: Magnetization at time zero
- $N$: Number of nuclear spins in the bulk
- $N_p$: Number of nuclear spins associated with the surface paramagnetic centers
- $N_s$: Number of nuclear spins in other parts of the surface layer
- $P_c$: Capillary pressure
- $q$: Volumetric flow rate
- $<r>$: Average electron-nuclear distance
$r_b$  Pore body size
$r_B$  Bulk relaxation rate
$r_t$  Pore throat size
$R$  Gas constant
$R^2$  Coefficient of linear correlation
$R_w$  Thickness of water film on the surface
$S$  Pore surface area
$S$  Reduced wetting phase saturation
$S_o$  Oil saturation
$S_w$  Water saturation
$S_{wi}$  Initial saturation in capillary pressure measurement
$S_{wir}$  Irreducible water saturation
$S_{wr}$  Residual water saturation from capillary pressure measurement
SNR  Signal to noise ratio in NMR $T_1$, $T_2$ measurements
$T$  Temperature
$T_1$  Longitudinal relaxation time
$T_{1,e}$  Electron spin-lattice relaxation time
$T_{1,B}$  $T_1$ bulk relaxation time
$T_{1,p}$  $T_1$ relaxation time involving the dilute paramagnetic centers on the surface
$T_{1,s}$  $T_1$ relaxation time outside the surface paramagnetic centers
$T_2$  Transverse relaxation time
$T_{2B-LM}$  Log mean value of the $T_2$ relaxation time distribution
$T_{2,cutoff}$  Cutoff value of $T_2$ to estimate $S_{wir}$ from NMR
$T_{2D}$  $T_2$ relaxation time due to diffusion
$T_{2,e}$  Electron spin-spin relaxation time
$T_{2,max}$  Maximum value of the $T_2$ bins in the relaxation time distribution
$T_{2,min}$  Minimum value of the $T_2$ bins in the relaxation time distribution
TE  Echo spacing in NMR $T_2$ measurements
$T_n$  Relaxation times
$V_{FD}$  Volume of water displaced by forced oil drainage
$V_{FI}$  Volume of oil displaced by forced brine imbibition
$V_o$  Pore volume covered by oil
$V_P$  Pore volume
$V_{SD}$  Volume of water displaced by spontaneous oil drainage
$V_{SI}$  Volume of oil displaced by spontaneous brine imbibition
$V_w$  Pore volume covered by water
\( W_i \) Weighing function
\( \alpha \) Geometry constant
\( \chi^2 \) Merit function
\( \delta \) Minimal distance between proton spin and electron spin
\( \delta_0 \) Amott oil wettability index
\( \delta_w \) Amott water wettability index
\( \Delta p/\Delta x \) Pressure difference over a distance of \( \Delta x \)
\( \Delta E \) Effective activation energy
\( \phi \) Porosity
\( \phi_e \) Effective porosity
\( \phi_t \) Total porosity
\( \gamma \) Proton geomagnetic ratio
\( \gamma_s \) Electron geomagnetic ratio
\( \eta \) Fluid viscosity
\( k \) Permeability
\( \lambda_n \) Eigenvalues
\( \mu \) Fluid viscosity
\( \theta \) Contact angle
\( \rho \) Surface relaxivity
\( \rho_1 \) Spin-spin surface relaxivity
\( \rho_2 \) Spin-lattice surface relaxivity
\( \rho_{2,d} \) Surface relaxivity due to surface-enhanced dipole-dipole interaction
\( \rho_{2,ps} \) Surface relaxivity due to paramagnetic centers on the surface
\( \rho_{2,o} \) Surface relaxivity of oil
\( \rho_{2,w} \) Surface relaxivity of water
\( \rho_{\text{eff}} \) Effective surface relaxivity
\( \rho_g \) Grain density
\( \sigma \) Interfacial tension
\( \sigma_s \) Surface density of paramagnetic center
\( \tau \) Correlation time
\( \tau_c \) Correlation time
\( \tau_s \) Residence time
\( \tau_m \) Correlation time for the surface translational diffusion
\( \omega_h \) Angular resonance frequency of proton
$\omega_3$  Angular resonance frequency of electron
Chapter 1 Introduction

Low field NMR well logging is a powerful and noninvasive technique in determining reservoir properties such as porosity, permeability, irreducible water saturation, residual oil saturation and pore size distribution. The relaxation rate of fluids contained in porous media is much greater than that of bulk values primarily due to the surface relaxation at the pore-grain interface. Therefore, it is important to understand the mechanisms of NMR surface relaxation and its dependence on temperature.

Wettability is another important parameter affecting NMR surface relaxation and for the interpretation of NMR well logging. It is usually assumed that the formation is water-wet and oil relaxes at its bulk relaxation time. However, in cases when oil base mud drilling fluids are used, the original water-wetness of the formation could be altered to be intermediate-wet or oil-wet due to invasion of OBM drilling fluids containing surfactants. As a result of the wettability alteration from water-wet to intermediate-wet or oil-wet, the primary formation properties from NMR interpretation such as irreducible water saturation and permeability may be incorrect. This is a long-standing industry concern.

Therefore, the objectives of this study are as follows,

1. NMR surface relaxation mechanisms and their dependence on temperature,

2. Quantitative wettability alteration by OBM surfactants and its effects on NMR estimated irreducible water saturation,

3. Modification of NMR interpretation of irreducible water saturation when wettability alteration occurs,
4. Model development of characterizing rock wettability from NMR relaxation time,

5. NMR properties of OBM filtrates.

A brief introduction of the Chapters in this thesis is as follows,

Chapter 2 reviews the general background about the applications of NMR in porous media and well logging.

Chapter 3 illustrates the dependence of surface relaxivity on mineralogy, surface paramagnetic ions and temperature.

Chapter 4 identifies the wettability alteration of both Berea and Texas Cream limestone cores by OBM surfactants and its effect on NMR estimated irreducible water saturation. It also develops the modification of NMR interpretation of $S_{wir}$ when wettability alteration occurs.

Chapter 5 first illustrates the quantitative connection between wettability and NMR relaxation time, and then proposes and tests a novel NMR model to quantify rock wettability by two NMR indices from either water or oil relaxation time.

Chapter 6 investigates NMR bulk properties of OBM filtrates and their interaction with the core samples.

Finally, Chapter 7 concludes this study and Chapter 8 suggests the future work.
Chapter 2  NMR in Porous Media and NMR Well Logging

This chapter reviews the general background about the applications of NMR in porous media and well logging. It includes analytical solution of relaxation time of fluids in a single pore with simple geometry, three types of relaxation mechanisms (bulk relaxation, surface relaxation and relaxation due to diffusion), and formation evaluation from NMR such as porosity, permeability, bulk volume irreducible and so on.

2.1  Analytical Solution of Relaxation Time of Fluids in a Single Pore

Brownstein and Tarr (1979) were pioneers who presented an analytical solution of relaxation time of fluids in a single pore with simple geometry. They described the magnetization decay of fluids in a single pore as a diffusion process characterized by three parameters: the pore size \( a \), surface relativity \( \rho \), and self-diffusivity of the fluid \( D \). Based on this, they expressed the total magnetization \( M(t) \) for a fluid sample of volume \( V \) confined by a surface \( S \) as follows,

\[
M(t) = \iiint_V m(X,t) dV = M(0) \sum_{n=1}^{n} f_n \cdot \exp\left(-\frac{t}{T_n}\right)
\]  

(2.1.1)

\[
T_n = \frac{a^2}{D\lambda_n^2}
\]

(2.1.2)

Where \( m(X,t) \) is the magnetization density at time \( t \) and position \( X \), \( f_n \) and \( T_n \) are relative intensities and relaxation times, respectively. When bulk relaxation rate \( r_b \) was considered, \( T_n \) becomes (Wilkinson, 1991),
\[ T_n = \left( r_n + \frac{D\lambda_n^2}{a^2} \right)^{-1} \]  \hspace{1cm} (2.1.3)

Brownstein and Tarr gave analytical solutions to Equation 2.1.1 for three simple pore geometries: slab, cylinder and sphere.

For slab geometry,

\[ m(z,t) = m_0 \cdot \sum_{n=1}^{\infty} \frac{4 \sin \lambda_n}{2 \lambda_n + \sin 2\lambda_n} \cos \left( \frac{\lambda_n z}{a} \right) \exp \left( -\frac{D\lambda_n^2}{a^2} t \right) \]  \hspace{1cm} (2.1.4)

\[ f_n = \frac{4 \sin^2 \lambda_n}{\lambda_n (2\lambda_n + \sin 2\lambda_n)} \]  \hspace{1cm} (2.1.5)

For cylindrical geometry,

\[ m(r,t) = m_0 \cdot \sum_{n=1}^{\infty} \frac{2J_1(\lambda_n) \cdot J_0(\lambda_n r/a)}{\lambda_n (J_0^2(\lambda_n) + J_1^2(\lambda_n))} \exp \left( -\frac{\lambda_n^2 D}{a^2} t \right) \]  \hspace{1cm} (2.1.6)

\[ f_n = \frac{4J_1^2(\lambda_n)}{\lambda_n^2 (J_0^2(\lambda_n) + J_1^2(\lambda_n))} \]  \hspace{1cm} (2.1.7)

For spherical geometry,

\[ m(r,t) = m_0 \cdot \sum_{n=1}^{\infty} \frac{4(\sin \lambda_n - \lambda_n \cos \lambda_n) a \sin(\lambda_n r/a)}{\lambda_n (2\lambda_n - \sin 2\lambda_n)} \cdot \frac{r}{\exp\left(-\frac{\lambda_n D}{a^2} t\right)} \]  \hspace{1cm} (2.1.8)

\[ f_n = \frac{12(\sin \lambda_n - \lambda_n \cos \lambda_n)^2}{\lambda_n^3 (2\lambda_n - \sin 2\lambda_n)} \]  \hspace{1cm} (2.1.9)

In the above Equations, \( \lambda_n \) are the eigenvalues such that,

slab geometry \hspace{1cm} \( \lambda_n \cdot \tan \lambda_n = \frac{\rho a}{D} \) \hspace{1cm} (2.1.10)

cylindrical geometry \hspace{1cm} \( \frac{\lambda_n \cdot J_1(\lambda_n)}{J_0(\lambda_n)} = \frac{\rho a}{D} \) \hspace{1cm} (2.1.11)
spherical geometry \[1 - \lambda_n \cdot \cot(\lambda_n) = \frac{\rho \alpha}{D}\] (2.1.12)

Brownstein and Tarr showed that there were three relaxation regions depending on the value of the dimensionless group \(\rho \alpha / D\) as follows,

1. Fast-diffusion region \(\rho \alpha / D \ll 1\)
2. Intermediate-diffusion region \(1 < \rho \alpha / D < 10\)
3. Slow-diffusion region \(\rho \alpha / D \gg 10\)

In the fast-diffusion region, Brownstein and Tarr proved that only the first relative intensity contributed significantly to the total magnetization (Equation 2.1.1), that is, \(n = 1\). The eigenvalue \(\lambda_1\) was then analytically solved by them and substituted into Equation (2.1.2) to have,

\[
\left(\frac{1}{T_n}\right)_{n=1} = r_B + \alpha \frac{\rho}{\alpha} = r_B + \rho \frac{S}{V}
\] (2.1.13)

Where \(\alpha\) equals to 1, 2 or 3 for slab, cylindrical and spherical geometry, respectively.

The analytical solution of relaxation time as illustrated above theoretically confirms that NMR can give valuable information about the porous media.

### 2.2 Three Types of Relaxation Mechanisms

There are three types of relaxation mechanisms underlying the applications of NMR well logging. They are bulk relaxation, surface relaxation and relaxation due to diffusion. These three types of relaxation mechanisms contribute in parallel to the total relaxation rate. For spin-lattice or \(T_1\) relaxation,

\[
\frac{1}{T_1} = \frac{1}{T_{1B}} + \frac{1}{T_{1S}}
\] (2.2.1)
For spin-spin or $T_2$ relaxation,

$$\frac{1}{T_2} = \frac{1}{T_{2B}} + \frac{1}{T_{2S}} + \frac{1}{T_{2D}}$$  \hspace{1cm} (2.2.2)$$

Where $T_{1,2B}$, $T_{1,2S}$ and $T_{2D}$ are bulk relaxation, surface relaxation and relaxation due to diffusion, respectively.

The following subsections review the general principles and applications of reservoir fluid typing and formation evaluation in NMR well logging by each type of relaxation mechanisms.

### 2.2.1 Bulk Relaxation

Each pure bulk fluid has a characteristic relaxation time depending on its physical properties such as viscosity, and environmental parameters such as temperature and pressure. Based on this, in the literature there are correlations developed to connect the physical properties of a reservoir fluid with NMR relaxation time. For example, bulk relaxation time of dead crude oils was correlated as a function of either viscosity (Equation 2.2.1.1, Morris, et al. 1997) or viscosity over temperature (Equation 2.2.1.2, Vinegar, 1995; Equation 2.2.1.3, Zhang, et al. 1998),

$$T_{2B,LM} = \frac{1.2}{\eta^{0.9}} \text{ at ambient temperature}$$  \hspace{1cm} (2.2.1.1)$$

$$T_{2B,LM} = \frac{1.2T}{298\eta}$$  \hspace{1cm} (2.2.1.2)$$

$$T_{2B,LM} = \frac{1.2}{(298)^{0.9}}\left(\frac{T}{\eta}\right)^{0.9} = 0.0071\left(\frac{T}{\eta}\right)^{0.9}$$  \hspace{1cm} (2.2.1.3)$$

Where $T_{2B,LM}$ is the log mean value of the $T_2$ relaxation time distribution (sec), $\eta$ is the fluid viscosity (cp) and $T$ is temperature (K).
2.2.2 Surface Relaxation

Fluids relax faster at the grain surface than in the bulk phase by the additional surface relaxation mechanism. This provides the sensitivity of NMR to pore size, permeability and irreducible water saturation (Coates et al. 1999). Moreover, surface relaxation provides the sensitivity of NMR to wettability, because whichever fluid (water or oil) is in direct contact with the grain surface has a relaxation time shorter than the bulk value, while fluids not in contact with the mineral surface relax as bulk fluid. The mechanisms of surface relaxation and studies on wettability by NMR technique are reviewed in the sections of literature review of chapter 3 and chapter 5, respectively.

2.2.3 Relaxation due to Diffusion

$T_2$ relaxation is enhanced by molecular diffusion in a magnetic field gradient. For example, in the case of unrestricted diffusion,

$$\frac{1}{T_{2D}} = \frac{\gamma^2 (G \cdot TE)^2 D}{12} \quad (2.2.3.1)$$

Where $D$ is the self-diffusivity of the fluid, $G$ is the strength of the magnetic field gradient, $\gamma$ is the geomagnetic ratio of proton, $TE$ is the echo spacing in NMR $T_2$ measurements. Practically, it is sufficient to provide more than an order of magnitude contrast in $T_2$ relaxation time of live oils by this diffusion mechanism with different values of echo spacing and gradient strength (Chen, et al., 2003). Moreover, this diffusion relaxation mechanism can be applied to differentiate water from oil, gas from oil, or between oils with different viscosity.
2.3 Formation Evaluation from NMR

The primary formation evaluation from NMR well logging are porosity, permeability and bulk volume irreducible, as reviewed below.

2.3.1 Porosity

Porosity is defined as the fraction of the rock bulk volume occupied by pore fluid,

$$\phi \equiv \frac{\text{pore volume}}{\text{bulk volume}}$$  \hspace{1cm} (2.3.1.1)

NMR provides a good way of measuring porosity, because the NMR response only comes from the fluids in the pore space but not from the rock matrix. In a laboratory core analysis, NMR porosity matches well with that by Boyle's law. For rock sample saturated with low salinity brine,

$$\phi_{\text{NMR}} = \frac{M_{0,\text{sample}} / V_{\text{sample}}}{M_{0,\text{pure H}_2\text{O}} / V_{\text{pure H}_2\text{O}}}$$  \hspace{1cm} (2.3.1.2)

Where $V_{\text{sample}}$ is the bulk volume of the rock sample, $M_0$ is the total magnetization at time zero. $M_0$ can be determined by extrapolation to time zero of the measured time domain signal $M(t)$ or by summation of all the intensities of the bins of the relaxation time distribution. That is,

$$M_0 = \lim_{t \to 0} M(t) \quad \text{or} \quad M_0 = \sum_i f_i$$  \hspace{1cm} (2.3.1.3)

In laboratory measurements, a calibration sample such as 0.05% wt CuSO$_4$ solution can be used instead of pure water due to its faster relaxation time.

In NMR well logging, several types of porosities are generally referred to, such as total porosity $\phi$, effective porosity $\phi_e$, free fluid index FFI, bulk volume irreducible BVI
and so on (Coates et al. 1999). Figure 2.3.1.1 shows such porosities for an invaded zone from NMR well logging.

<table>
<thead>
<tr>
<th>Matrix and dry clay</th>
<th>Clay-bound water</th>
<th>Capillary-bound water</th>
<th>Moveable water</th>
<th>Mud filtrate</th>
<th>Oil</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMR porosity model</td>
<td>MCBW</td>
<td>BVI</td>
<td>Effective porosity $\phi_e$</td>
<td>FFI</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Total porosity $\phi_t$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

FIGURE 2.3.1.1 Schematic plot of porosity model for an invaded zone from NMR well logging (from Coates et al. 1999).

In this study, BVI includes both capillary bound water and clay bound water.

2.3.2 Permeability

Permeability is defined as the “ability” of the rock for fluid to flow through. Permeability is an important reservoir parameter because it determines how fast the oil, gas and water can be produced from the formation. The absolute permeability is derived by Darcy’s law,

$$k = \frac{\mu q}{A \Delta p / \Delta x} \tag{2.3.2.1}$$

Where $\mu$ is viscosity of the fluid, $A$ is the area of a cross section, $q$ is the volumetric flow rate, and $\Delta p / \Delta x$ is the pressure difference over a distance of $\Delta x$. From this definition, permeability has the dimension of length squared.
NMR provides a good way of measuring rock permeability. Because both permeability and NMR relaxation time is related with the rock pore sizes. Although the pertinent length scale of rock permeability is pore “throat” size while NMR relaxation time is a mapping of pore “body” size (Equation 2.1.13), the good correlation between pore throat size and pore body size for sandstones resolves this difference.

In NMR well logging data interpretation, there are two commonly used permeability models from NMR relaxation time: Coates model (Coates et al. 1991, 1993) and Mean $T_2$ model (Straley et al. 1997).

The input parameters of Coates model are porosity, BVI and FFI,

$$k = 10^4 \cdot \phi^4 \cdot \left( \frac{\text{FFI}}{\text{BVI}} \right)^2$$  \hspace{1cm} (2.3.2.2)

The input parameters of mean $T_2$ model are porosity and $T_{2,1M}$,

$$k = 4.6 \cdot \phi^4 \cdot T_{2,1M}^2$$  \hspace{1cm} (2.3.2.3)

Practically, mean $T_2$ model works well for water-bearing zone, because it was derived from brine saturated rock samples. Coates model is preferred for hydrocarbon-bearing zone. In terms of mineralogy, both models work better for sandstones than for carbonates. This is because carbonates not only occur in a wider variety of pore sizes and shapes, but also exhibit more heterogeneous distribution of pore sizes (Dunn et al. 2002).

For carbonate reservoirs, studies of Chang et al. (1997) suggested that Mean $T_2$ model still worked well if all the relaxation time components above 750 ms were excluded from the total relaxation time distribution in calculating porosity and $T_{2,1M}$. Alternatively, Hidajat et al. (2004) developed correlations of permeability estimation for vuggy carbonates from NMR and x-ray CT scanner.
2.3.3 Bulk Volume Irreducible

Bulk volume irreducible BVI is the product of porosity and irreducible water saturation,

\[ \text{BVI} = \phi \cdot S_{irr} \]  \hspace{1cm} (2.3.3.1)

Where irreducible water saturation \( S_{irr} \) is the portion of pore space in which the water is not producible under a certain capillary pressure or a certain height above free water. It includes both the capillary bound water and clay bound water (Figure 2.3.1.1).

BVI is a very important parameter about the reservoir formation. Because on one hand, it can be used to predict the water cut by comparing with the total water volume from resistivity log data. On the other hand, it is one of the input parameters of permeability estimation from Coates model.

In the literature, there are three models to estimate BVI from NMR, i.e., cutoff BVI model, spectral BVI model and Bi-exponential model. These three models will be reviewed in detail in Chapter 4.
Chapter 3  NMR Surface Relaxation

This chapter illustrates the dependence of surface relaxivity on mineralogy, surface paramagnetic ions and temperature. Surface relaxivities of silicate and carbonate materials are compared. The contributions due to the surface enhanced dipole-dipole interactions and paramagnetic ions are quantified. The objective of this chapter is to better understand NMR surface relaxation mechanisms and to explain the different behaviors of temperature dependence of surface relaxation as observed in the literature and this study as well.

3.1  Literature Review

Among the three types of relaxation mechanism (bulk relaxation, surface relaxation and relaxation due to diffusion), surface relaxation is the most important petrophysical principle underlying the applications of NMR well logging. This section reviews the proposed mechanisms of surface relaxation in the literature, including KST model, Kleinberg model, and surface translational diffusion model. This section also reviews the experimental investigations on NMR surface relaxation in the literature.

3.1.1  KST model

The enhancement of spin-lattice relaxation rate of fluid in porous media by the so called “wall effects” was first proposed by Korringa, Seavers and Torrey (1962). KST model is the basic principle of surface relaxation in porous media. In this concept, two kinds of surface relaxation processes were posed. The first kind involves the dilute
paramagnetic centers on the surface layer and is characterized by a relaxation time $T_{1,p}$. The second kind occurs outside the surface paramagnetic centers and is characterized by a relaxation time $T_{1,s}$. These two surface relaxation processes contribute in parallel to the total relaxation rate together with bulk relaxation $T_{1,B}$. It follows that,

$$\frac{1}{T_1} = \frac{1}{T_{1,B}} \cdot \frac{N_s}{N} \cdot \frac{1}{T_{1,s} + \tau} + \frac{N_p}{N} \cdot \frac{1}{T_{1,p} + \tau}$$

(3.1.1.1)

Where $N_p$, $N_s$ and $N$ are the numbers of nuclear spins associated with the paramagnetic centers on the surface layer, in other parts of the surface layer, and in the bulk, respectively. $\tau$ is the correlation time characterizing the exchange process between the spins on the surface layer and the spins in the bulk.

A simplified formula of $T_{1,p}$ for proton-electron dipolar interaction was given in KST model as follows,

$$\frac{1}{T_{1,p}} = \frac{1}{10} \frac{\gamma_s^2 \gamma_i^2 \hbar^2}{\langle r \rangle^6} \left[ \frac{3 \tau_{c,1}}{1 + \omega_i^2 \tau_{c,1}^2} + \frac{7 \tau_{c,2}}{1 + \omega_s^2 \tau_{c,2}^2} \right]$$

(3.1.1.2)

$$\frac{1}{\tau_{c,1}} = \frac{1}{\tau_{c,0}} + \frac{1}{T_{1,e}}$$

(3.1.1.3)

$$\frac{1}{\tau_{c,2}} = \frac{1}{\tau_{c,0}} + \frac{1}{T_{2,e}}$$

(3.1.1.4)

Where $\gamma_s$ and $\gamma_i$ are the gyromagnetic ratio of electron and proton, respectively, $\omega_s$ and $\omega_i$ are the angular resonance frequency of electron and proton, respectively, $\hbar$ is the plank’s constant divided by $2\pi$, $\langle r \rangle$ is the average electron-nuclear distance, $\tau_{c,0}$ is the correlation time characterizing the molecular motion of liquid on the surface, $T_{1,e}$ and $T_{2,e}$ are the electron spin-lattice and spin-spin relaxation time, respectively.
KST model expressed $T_{1,s}$ as follows,

$$\frac{1}{T_{1,s}} = \gamma_i^2 \left\langle H_{loc}^2 \right\rangle \frac{\tau_{c,0}}{1 + \omega_i^2 \tau_{c,0}^2}$$

(3.1.1.5)

Where $\left\langle H_{loc}^2 \right\rangle$ is the mean square of the local magnetic field strength.

The general expression of KST model (Equation 3.1.1.1) implies that surface relaxation rate of fluid in porous media depends on temperature, because the correlation times are generally temperature dependent.

### 3.1.2 Kleinberg model

Kleinberg et al. (1994) applied KST model to natural rocks which contain relatively large amount of paramagnetic impurities (approximately 1%). They assumed that paramagnetic relaxation mechanism dominates the total surface relaxation rate, and that any other relaxation mechanisms which depend on diffusion, molecular motion, or the residence time of the fluid molecules on the surface can be neglected. The key basis of these assumptions was the observation in the literature until then that relaxation times of water saturated sandstones were largely independent of temperature from 25 to 175 °C (Latour et al. 1992). With these assumptions, Kleinberg model simplified Equation (3.1.1.1) to be as follows,

$$\frac{1}{T_1} = \frac{1}{T_{1,B}} + \frac{N_p}{N} \cdot \frac{1}{T_{1,p}}$$

(3.1.2.1)

With the same assumptions, Kleinberg model extended KST model to the case of spin-spin surface relaxation,
\[
\frac{1}{T_2} = \frac{1}{T_{2,0}} + \frac{N_p}{N} \cdot \frac{1}{T_{2,p}}
\]  
(3.1.2.2)

Where \(T_{2,p}\) is the spin-spin relaxation time associated with the surface paramagnetic centers.

\(T_{1,p}\) and \(T_{2,p}\) in Kleinberg model were modified from Solomon-Bloembergen Equations (Solomon, 1955; Bloembergen, 1957) of paramagnetic relaxation mechanism in solution. \(T_{1,p}\) and \(T_{2,p}\) are as follows,

\[
\frac{1}{T_{1,p}} = \frac{s(s+1)}{15} \left( \frac{\alpha A_d}{h} \right)^2 \left[ \frac{6 \tau_{c,1}}{1 + \omega_s^2 \tau_{c,1}^2} + \frac{14 \tau_{c,2}}{1 + \omega_s^2 \tau_{c,2}^2} \right] + \frac{s(s+1)}{3} \left( \frac{A_s}{h} \right)^2 \left[ \frac{2 \tau_{c,2}}{1 + \omega_s^2 \tau_{c,2}^2} \right]
\]  
(3.1.2.3)

\[
\frac{1}{T_{2,p}} = \frac{s(s+1)}{15} \left( \frac{\alpha A_d}{h} \right)^2 \left[ 4 \tau_{c,1} + \frac{3 \tau_{c,1}}{1 + \omega_s^2 \tau_{c,1}^2} + \frac{13 \tau_{c,2}}{1 + \omega_s^2 \tau_{c,2}^2} \right] + \frac{s(s+1)}{3} \left( \frac{A_s}{h} \right)^2 \left[ \tau_{c,1} + \frac{\tau_{c,2}}{1 + \omega_s^2 \tau_{c,2}^2} \right]
\]  
(3.1.2.4)

\[
A_d = \frac{\gamma_1 \gamma_s h^2}{\langle r^3 \rangle}
\]  
(3.1.2.5)

Where \(A_d\) and \(A_s\) are dipolar coupling constant and scalar hyperfine constant, respectively. \(\alpha\) is a constant factor. Other nomenclatures are the same as before.

Kleinberg model further simplified \(T_{1,p}\) and \(T_{2,p}\) with the assumption of \(\omega_s \tau_{c,2} \gg 1\) and \(\omega_s \tau_{c,1} \ll 1\) (extreme narrowing approximation),

\[
\frac{1}{T_{1,p}} = \frac{s(s+1)}{15} \left( \frac{\alpha A_d}{h} \right)^2 6 \tau_{c,1}
\]  
(3.1.2.6)

\[
\frac{1}{T_{2,p}} = \frac{s(s+1)}{15} \left( \frac{\alpha A_d}{h} \right)^2 7 \tau_{c,1} + \frac{s(s+1)}{3} \left( \frac{A_s}{h} \right)^2 \tau_{c,1}
\]  
(3.1.2.7)
Where correlation time $\tau_{c,1}$ has the same expression as Equation (3.1.1.3). $\tau_{c,1}$ was assumed in Kleinberg model to be dominated by electron spin-lattice relaxation time, that is,

$$\tau_{c,1} = T_{1,e}$$ (3.1.2.8)

The key assumptions of the simplifications in Kleinberg model were the temperature independence of surface relaxation, which was supported by the studies of Latour et al. (1992). However, several recent studies in the literature showed that surface relaxation rate changed with temperature for the systems they investigated (Godefroy, 2001a, 2001b, Straley, 2002). These different behaviors of temperature dependence of surface relaxation will be illustrated in more detail later in this chapter.

### 3.1.3 Surface diffusion model

A surface diffusion model was presented by Korb et al. (1997) and Godefroy et al. (2001a, 2001b). Unlike the KST model, which differentiated the fluid molecules on the surface layer to be those whose relaxation involves the surface paramagnetic centers and those whose relaxation does not, the surface diffusion model considered an ensemble of the fluid molecules on the surface layer. The molecules in the surface-affected liquid phase exchange fast with the bulk liquid phase. In this model, the dipole-dipole interactions were modulated by a two-dimensional translational diffusion of the mobile proton spin in the dipolar field of the electron spin fixed at the pore surface. Their calculations show that,

$$\frac{1}{T_1} = \frac{1}{T_{1,B}} + \frac{N_s}{N} \frac{\pi \sigma_s}{20 \delta^4} (\gamma_r \gamma_h h)^2 s(s+1)\tau_m \ln \left[ \frac{1 + \omega_1^2 \tau_m^2}{(\tau_m / \tau_s)^2 + \omega_1^2 \tau_m^2} \right]$$ (3.1.3.1)
\[
\frac{1}{T_2} = \frac{1}{T_{2,B}} + \frac{N_s}{N} \frac{\pi \sigma_s (\gamma_1 \gamma_s \hbar)^2 s(s+1)}{20 \delta^4} \cdot \tau_m
\]  

(3.1.3.2)

Where \(N_s/N\) is the ratio of the amount of fluid molecules on the surface layer to the total amount of fluid molecules, \(\sigma_s\) is the surface density of paramagnetic centers, \(\delta\) is the minimal distance between proton spin \(I\) and electron spin \(s\) on the surface layer, \(\tau_s\) is the residence time of proton spins moving on the surface layer, \(\tau_m\) is the correlation time for the surface translational diffusion,

\[
\tau_m = \tau_{m,0} \exp\left(\frac{\Delta E}{RT}\right)
\]  

(3.1.3.3)

\[
\Delta E = E_m - E_s
\]  

(3.1.3.4)

Where \(\tau_{m,0}\) is a constant, \(R\) is the gas constant, \(\Delta E\) is the effective activation energy describing the surface translational motion, \(E_m\) is the activation energy associated with the individual molecular diffusing jumps, \(E_s\) is the activation energy associated with the surface chemical bonding. One such chemical bonding is the hydrogen bonding between the water molecule and the hydroxyl group on the silicate surface (Zhuravlev, 2000).

Surface diffusion model as expressed in Equations 3.1.3.1 to 3.1.3.4 implies that surface relaxation rate depends on temperature depending on the sign (plus or minus) of the effective activation energy \(\Delta E\).

### 3.1.4 Experimental Investigations on NMR Surface Relaxation

The models of NMR surface relaxation mechanisms as reviewed above are generally qualitative. It is difficult to apply them to concisely calculate the surface relaxation time of a fluid in porous media, because the model parameters such as
correlation times usually can not be concisely determined. Therefore, besides model studies of surface relaxation, numerous experimental investigations on NMR surface relaxation of both model systems and natural rock samples were performed in the literature.

One of the focuses of the experimental investigations of surface relaxation was on the phenomenological parameters of surface relaxivities $\rho_1$ and $\rho_2$. The numerical values of $\rho_1$ and $\rho_2$ were calculated from the relaxation times and surface area to volume ratio as follows,

$$\rho_{1,2} = \frac{1/T_{1,2} - 1/T_{1,2,n}}{S/V_p}$$  \hspace{1cm} (3.1.4.1)

Where $S$ and $V_p$ are the surface area and the corresponding pore volume confined by this surface, respectively.

Numerical values of surface relaxivity greatly depend on the methods of surface area to volume ratio measurements. Figure 3.1.4.1 shows that surface relaxivity $\rho_1$ varies over two to three orders of magnitude among different methods of surface area to volume ratio determination, such as BET gas adsorption, mercury injection capillary pressure, thin section optical microscopy, PFG spin echo technique and so on (Kleinberg, 1999). This is because different methods measure different internal surface area depending on the length resolution of the measurement. For example, BET gas adsorption depends on an angstrom length scale but optical microscopy depends on a micron length scale.

Surface relaxivities $\rho_1$ of water saturated unconsolidated silicate materials with well-defined surface area reported in the literature were summarized in Table 3.1.4.1. The surface area was either from BET measurement or calculated from grain size. Notice that
much smaller $\rho_1$ value of quartz sand was reported by Bryar (2000) than that by Brown (1958), Borgia (1996) or Hinedi (1997). Moreover, consistently smaller values of $\rho_1$ were reported for silica gel than other silicate materials.

![Pore Image Analysis Chart]

FIGURE 3.1.4.1 Catalog of surface relaxivity $\rho_1$ for sandstones (Kleinberg, 1999).

TABLE 3.1.4.1 Catalog of surface relaxivity $\rho_1$ for water saturated unconsolidated materials with well-defined surface area from BET or grain size.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$\rho_1$ ((\mu\text{m/s}))</th>
<th>Reference source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz sand</td>
<td>1.5</td>
<td>Brown (1958)</td>
</tr>
<tr>
<td>Quartz sand</td>
<td>1.6</td>
<td>Borgia (1996)</td>
</tr>
<tr>
<td>Quartz sand</td>
<td>2.9 - 3.1</td>
<td>Hinedi (1997)</td>
</tr>
<tr>
<td>Quartz sand</td>
<td>(1.3 \pm 1.5) \times 10^{-2}\</td>
<td>Bryar (2000)</td>
</tr>
<tr>
<td>Porcelain</td>
<td>4</td>
<td>Loren (1970)</td>
</tr>
<tr>
<td>Alumina</td>
<td>3</td>
<td>Brown (1982)</td>
</tr>
<tr>
<td>Glass beads</td>
<td>5</td>
<td>Brown (1982)</td>
</tr>
<tr>
<td>Glass beads</td>
<td>11</td>
<td>Straley (1987)</td>
</tr>
<tr>
<td>Synthetic Ca silicate</td>
<td>0.4 - 4.0</td>
<td>Foley (1996)</td>
</tr>
<tr>
<td>Silica gel</td>
<td>((3.1 - 7.7) \times 10^{-3})</td>
<td>Hinedi (1997)</td>
</tr>
<tr>
<td>Silica gel</td>
<td>(1.2 \times 10^{-3})</td>
<td>Bryar (2000)</td>
</tr>
</tbody>
</table>
There are less data of surface relaxivity of carbonates in the literature, so they are not systematically summarized here but are mentioned in the following sections of this chapter.

Effect of paramagnetic ions on surface relaxivity was quantitatively investigated by Kenyon et al. (1995), Foley et al. (1996), Bryar et al. (2000) and Valckenberg et al. (2001). BET method was used for determination of surface area for all these studies. Kenyon et al. (1995) measured surface relaxivity \( \rho_1 \) of water in calcite with adsorbed Mn\( ^{2+} \) ions. They found that there is a “flattening behavior” of the relationship between surface relaxivity and the “indicated surface concentration” of adsorbed Mn\( ^{2+} \) ions, which means that surface relaxivity \( \rho_1 \) increases to a plateau value as the surface concentration of adsorbed Mn\( ^{2+} \) ions increases. This plateau value of \( \rho_1 \) is roughly 50 times that of the pure calcite.

Foley et al. (1996) measured surface relaxivity \( \rho_1 \) and \( \rho_2 \) of water in a series of synthetic calcium silicates (CaSiO\(_3\)) with known surface concentrations of iron or manganese paramagnetic ions. They found that \( \rho_1 \) and \( \rho_2 \) of water increased linearly with the concentration of paramagnetic ions on the surface as follows,

\[
\rho_1 = (4.05 + 0.000819 \cdot C_{\text{Fe,ppm}}) \mu\text{m/sec}
\]

\[
\rho_2 = (3.96 + 0.00227 \cdot C_{\text{Fe,ppm}}) \mu\text{m/sec}
\]

\[
\rho_1 = (0.406 + 0.000919 \cdot C_{\text{Mn,ppm}}) \mu\text{m/sec}
\]

\[
\rho_2 = (2.01 + 0.00106 \cdot C_{\text{Mn,ppm}}) \mu\text{m/sec}
\] (3.1.4.2)

Similarly, Bryar et al. (2000) studied the paramagnetic effects of iron species on NMR relaxation of fluid protons in water saturated quartz sand and silica gel. They found
that surface relaxivity $\rho_1$ of water in silica gel increased by an order of magnitude when only 0.01% of the silica gel surface sites were occupied by adsorbed Fe$^{3+}$ ions. They also found that surface relaxivity $\rho_1$ of water in silica gel increased linearly with the surface concentration of precipitated Fe(III) oxyhydroxide. For the mixture of silica gel and pseudobrookite (Fe$_2$TiO$_5$) grain saturated with water, they found that surface relaxivity $\rho_1$ of water increases linearly with the percentage of Fe$_2$TiO$_5$ in the solid mixture up to about 25% wt. Similar results were obtained by Valckenborg et al. (2001) with the mixture of kaolin clay powder and Fe$_2$O$_3$ powder saturated with water in the range of Fe$_2$O$_3$ concentration up to about 10% wt.

Effect of paramagnetic ions on surface relaxivity as reviewed above implies that paramagnetic ion is a very important factor affecting surface relaxation. Another factor investigated in the literature affecting surface relaxivity is temperature. This is of practical importance because laboratory experiments are generally performed at room temperature but the real well logging operation may be at elevated temperatures.

Effect of temperature on surface relaxivities was investigated by Latour et al. (1992), Foley et al. (1996), Ramakrishnan et al. (1999), Korb (2001), Godefroy et al. (2001a, 2001b) and Straley (2002). Latour et al. (1992) measured $T_1$ relaxation times of water saturated six sandstones and five carbonates over the temperature range of 25 °C to 175 °C. They found that surface relaxivity $\rho_1$ of all the water saturated sandstones and most of the carbonates depended only weakly on temperature. Foley et al. (1996) studied $T_2$ relaxation times of two calcium silicate samples saturated with water over the temperature range of 25 °C to 175 °C. the two calcium silicate samples contain iron with concentration of 200 ppm and 1%, respectively. They found that there was little or no
effect of temperature on $T_2$ relaxation time for both samples. Ramakrishnan et al. (1999) reported temperature dependence of $T_2$ relaxation times of two water saturated carbonate rocks from Middle East. They found that there was a clear and systematic shift to longer relaxation times when the temperature increased from 30 °C to 130 °C, resulting in smaller surface relaxivity when temperature increases. A further study of this work by Straley (2002) showed that there were two groups of contrasting carbonate samples. While one group of carbonate samples showed a substantial shift to longer relaxation time when temperature increased, as reported by Ramakrishnan et al. (1999), the other group of carbonate samples had little or no temperature dependence.

The saturation fluid in most of the above studies was water. Temperature dependence of surface relaxivity with both water and oil as the saturation fluids was investigated by Korb (2001) and Godefroy et al. (2001a, 2001b) over the temperature range of 30 °C to 100 °C. They studied synthetic silica carbide (SiC), calcite (CaCO$_3$), two sandstones (outcrop and reservoir) and two carbonates (outcrop and reservoir). They found that surface relaxivities of water in the silica carbide packing and sandstones increased with temperature, while surface relaxivity of water in the calcite and carbonates decreased with temperature. As to oil, they found that surface relaxivity of dodecane in the silica carbide and both reservoir sandstone and carbonate decreases with temperature.

The experimental investigations on NMR surface relaxation as reviewed above suggest that the key parameter determining the different behaviors of surface relaxivity (for example, the temperature dependence) may be the amount of paramagnetic ions on the surface. The objective of our study is to test this hypothesis and to better understand the surface relaxation mechanisms.
3.2 Materials and Experimental Procedures

Material used in this chapter together with their physical properties and the experimental procedures are listed in this section. The material includes unconsolidated silica particles. The experimental procedures introduce the acid washing and paramagnetic ion coating of the silica samples, and NMR $T_1$, $T_2$ relaxation time measurements at room and elevated temperatures.

3.2.1 Unconsolidated Silica Particles

The mean diameter and BET surface area of the silica sand, silica flour, silica gel are listed in Table 3.2.1.1. The silica sand and silica flour are 99% SiO$_2$ (U. S. Silica Company). The silica gel was from Aldrich Chemical Company.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Mean diameter</th>
<th>BET surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica sand</td>
<td>120-140 mesh</td>
<td>0.08</td>
</tr>
<tr>
<td>Silica flour</td>
<td>1.7 $\mu$m</td>
<td>2.0</td>
</tr>
<tr>
<td>Silica gel</td>
<td>70-230 mesh</td>
<td>472.8</td>
</tr>
</tbody>
</table>

3.2.2 Acid Washing Procedures

The acid washing procedures were as follows. First, about 20 grams of fine silica sand or silica flour was mixed with 1 liter washing solution in a beaker. The washing solution is 1.0 mol/l hydrochloric acid and 0.1% wt sodium EDTA solution with volume ratio of 10:1. Then the mixture of fine silica sand or silica flour and the washing solution
were stirred by a magnet bar for about 14 hours. After the particles settle down on the bottom of the beaker, about 10 ml of the clear supernatant was taken for NMR $T_2$ relaxation time measurement. Then the supernatant was poured out and the silica particles were rinsed several times by DI water till neutral pH value. The above washing procedures were repeated for several times. After each time, the $T_2$ relaxation time of the washing supernatant was measured (Figure 3.2.2.1). When it reached asymptotically to the characteristic bulk $T_2$ value of the pure washing solution, indicating that there were no more irons on the mineral surface which could be washed off, the washing procedures were ended.

![Graph](image)

**FIGURE 3.2.2.1** $T_2$ relaxation time of washing supernatant with respect to acid washing of fine silica sand.
3.2.3 Ion Coating Procedures

The procedures of coating the silica sand or silica gel with Fe$^{3+}$ were as follows. First, the mixture of about 18 grams of dried silica sand or silica gel and 10 ml FeCl$_3$ (in 1.0 mol/l HCl solution) were stirred by a magnet bar in a 100 ml glass beaker. The concentrations of FeCl$_3$ in 1.0 mol/l HCl solution were 0.0025, 0.1, 0.5 or 1.0 mol/l to accomplish different amount of coating. Then 45 ml of 1.0 mol/l NH$_4$OH solution was slowly added into the beaker during a period of 10 minutes while stirring. During this process, the pH value of the solution mixture increased, leading to slow precipitation of Fe(OH)$_3$ onto the surface of the silica particles. The pH value of the solution mixture reached about 10 after adding 45 ml of 1.0 mol/l NH$_4$OH solution. Finally, the silica particles were completely rinsed with DI water (generally about 30 times of rinsing).

Figure 3.2.3.1 shows the $T_2$ relaxation time distributions of coated fine silica sand saturated with 100% $S_w$. In the coating procedures of preparing for these samples, the concentrations of FeCl$_3$ in 1.0 mol/l HCl solution were 0.0025, 0.1, 0.5 or 1.0 mol/l, respectively. As expected, when the concentration of FeCl$_3$ in 1.0 mol/l HCl solution increased, more precipitation of Fe(OH)$_3$ occurs on the silica sand surface, leading to shorter relaxation time of water in the sand pack. In the experimental results shown later, we refer the “coated” sample to the case of 1.0 mol/l FeCl$_3$ in the coating procedures.
FIGURE 3.2.3.1 $T_2$ relaxation time distributions of coated fine silica sand saturated with 100% $S_w$. Concentrations of FeCl$_3$ in the 1.0 mol/l HCl solution were 0.0025, 0.1, 0.5 or 1.0 mol/l in the procedures of preparing for the silica samples.

3.2.4 NMR $T_1$, $T_2$ Relaxation Time Measurements

NMR $T_1$, $T_2$ relaxation time measurements were performed at both room and elevated temperatures. The room temperature measurements were done with a MARAN 2 spectrometer and the elevated temperature measurements were done with a MARAN Ultra spectrometer at PTS Labs (PTS Labs International, Houston, TX). Both spectrometers operate at approximately 2 MHz. Consistent results were obtained with identical samples by these two instruments at room temperature. $T_1$ and $T_2$ measurements were made by the standard Inversion Recovery (IR) and CPMG pulse sequences, respectively. The signal to noise ratio (SNR) of the $T_1$, $T_2$ measurements is about 100:1. A non-linear least square inversion method previously developed in our laboratory
(Chuah, 1996, Huang, 1997) was used to estimate the multi-exponential relaxation time distributions.

A recirculating heating system is applied for the $T_1$, $T_2$ measurements at elevated temperatures. The recirculating system is filled with proton-free fluorinert which does not generate NMR signal. A water cooling system is used to prevent overheating of the magnet. Test with known amount of fluid sample was performed, the magnetization at elevated temperatures agrees with the theoretical prediction by curie’s law. This ensures that there is no fluid loss at elevated temperatures. The temperature points of this study are 24.4 °C, 45 °C, 60 °C, 75 °C and 90 °C.

3.3 Experimental Results and Discussions

This section presents first the experimental results of comparison of surface relaxivity between Berea sandstone and Texas Cream limestone, then the surface relaxivity $\rho_1$, $\rho_2$ and $\rho_2/\rho_1$ ratio for water saturated particles with respect to acid washing and ion coating, then the contribution of surface enhanced dipole-dipole interaction to surface relaxation, and finally the temperature dependence of surface relaxivity of water saturated silica particles.

3.3.1 Comparison of Surface Relaxivity between Berea Sandstones and Texas Cream Limestones

Surface relaxivities of water in 100% $S_w$ Berea and Texas Cream limestone are compared. The Berea and Texas Cream limestone cores are from the wettability study
with OBM surfactants (section 4.2.1). Since the numerical value of surface relaxivity greatly depends on the methods of surface area measurements (as reviewed in section 3.1.4), in this section the surface relaxivities of water in 100% S_w Berea and Texas Cream limestone are both determined by comparing Hg capillary pressure curves (measured or model calculated) and NMR relaxation time distributions. The details of the determination of surface relaxivity and the resulting pore size distributions from NMR and Hg capillary pressure curves are in part A of the Appendix.

Figure 3.3.1.1 shows the histogram of the surface relaxivities of water in 100% S_w Berea cores. For all the samples studied, $\rho_{2,\text{eff}} = (13.2 \pm 0.7) \mu$m/s. Similarly, Figure 3.3.1.2 shows the histogram of the surface relaxivities of water in 100% S_w Texas Cream limestone cores. For all the samples studied, $\rho_{2,\text{eff}} = (5.7 \pm 0.7) \mu$m/s. In comparison, surface relaxivity of water in the 100% S_w Berea sandstones is about 2.3 times larger than that in the 100% S_w Texas Cream limestones. This is consistent to the literature observation. The ratio of surface relaxivity of water in 100% S_w reservoir sandstones to that of reservoir carbonates was determined to be 2.1 and 3.6 by Hürlimann et al. (1994) and Huang (1997), respectively.
FIGURE 3.3.1.1 Histogram of surface relaxivities of water in 100% $S_w$ Berea cores, $\rho_{2\text{eff}} = (13.2 \pm 0.7) \mu\text{m/s}$.

FIGURE 3.3.1.2 Histogram of surface relaxivities of water in 100% $S_w$ Texas Cream limestone cores, $\rho_{2\text{eff}} = (5.7 \pm 0.7) \mu\text{m/s}$. 
3.3.2 Surface Relaxivity $\rho_1, \rho_2$ and $\rho_2/\rho_1$ Ratio for Silica Samples with respect to Acid Washing and Ion Coating

The role of paramagnetic centers on surface relaxation mechanisms was investigated by acid washing and iron coating of the silica samples. Refer to section 3.2.2 and 3.2.3 for the procedures of acid washing and paramagnetic ion coating, respectively. Surface relaxivity $\rho_1, \rho_2$ of these fluid saturated silica samples were calculated as follows,

$$\rho_{1,2} = \frac{\phi}{1 - \phi} \cdot \frac{1/T_{1,2} - 1/T_{1,2,B}}{S_g \cdot \rho_g}$$

(3.3.2.1)

Where $\phi$ is porosity, $S_g$ and $\rho_g$ is the BET surface area and grain density, respectively. $T_{1,2}$ is the Log Mean value of the relaxation time distribution,

$$T_{1,2,LM} = \exp\left(\frac{\sum f_i \cdot \ln(T_{1,2,i})}{\sum f_i}\right)$$

(3.3.2.2)

Where $T_{1,2,i}$ and $f_i$ are the bins of relaxation times and intensities in the multi-exponential relaxation time distribution, respectively.

Consistent to the literature results, our experimental results show that paramagnetic center on the mineral surface is a very important factor affecting NMR surface relaxation. Figure 3.3.2.1 shows that for 100% $S_w$ fine silica sand, surface relaxivity $\rho_1$ and $\rho_2$ of water in the coated : original : washed sample is about 57:8:1 and 31:5:1, respectively. Additionally, for 100% $S_w$ silica gel, surface relaxivity $\rho_1$ and $\rho_2$ of water in the coated : original sample is about 50:1 and 7:1, respectively.
FIGURE 3.3.2.1 Comparison of surface relaxivity $\rho_1$ and $\rho_2$ of water in 100% $S_w$ coated, original and washed fine silica sand.

The acid washing results provide some other interesting observations. Figure 3.3.2.2 shows that for both 100% $S_w$ fine silica sand and silica flour, surface relaxivity $\rho_1$ and $\rho_2$ of water decrease with respect to acid washing. This is expected because more and more paramagnetic ions are washed off the mineral surface by the acid solution. However, surface relaxivity $\rho_1$ and $\rho_2$ go to a finite plateau value at the end of washing, which account for 10% and 17% of the original value for $\rho_1$ and $\rho_2$, respectively. It suggests that there may be other mechanisms for surface relaxation besides paramagnetic centers, which will be illustrated in more detail in section 3.3.3 of this chapter. Moreover, in term of $\rho_2/\rho_1$ ratio, Figure 3.3.2.3 shows that $\rho_2/\rho_1$ ratio generally increases and deviates further from the mean value for natural rocks (Kleinberg et al., 1993) with respect to acid
washing. In comparison, $\rho_2/\rho_1$ ratio is closer to this mean value for the original silica sand (2.0) and silica flour (1.9), or the coated silica sand (1.6) and silica gel (1.3).

FIGURE 3.3.2.2 Surface relaxivity $\rho_1$ and $\rho_2$ of water in 100% $S_w$ silica sand (left) and silica flour (right).

FIGURE 3.3.2.3 $\rho_2/\rho_1$ ratios of water in 100% $S_w$ silica sand (left) and silica flour (right) with respect to acid washing (*: base on sample sets in Kleinberg et al., 1993).
3.3.3 Effects of Surface Enhanced Dipole-Dipole Interaction on Surface Relaxation

Section 3.3.2 showed that surface relaxivity $\rho_1$ and $\rho_2$ of water in 100% $S_w$ silica sand and silica flour go to an asymptotic value at the end of acid washing. It was then hypothesized that there may be other mechanisms of surface relaxation besides paramagnetic ions. One such mechanism could be the surface enhanced dipole-dipole interaction (Straley, 2002). This is because theoretically, proton dipole-dipole interaction is enhanced near the surface due to hindered translational and rotational motion of fluid molecule near the surface. This section quantifies the contribution from surface enhanced dipole-dipole interaction to surface relaxation for the various systems investigated in this study.

The contribution from surface enhanced dipole-dipole interaction to surface relaxation was quantified by Straley’s method (2002). Two identical samples were saturated with either 100% H$_2$O (labeled as sample A) or 10% H$_2$O-90% D$_2$O in molar fraction (labeled as sample B). In comparison of the relaxation time of water in sample A and B, because the fraction of protons which are in contact with surface paramagnetic centers is the same, the contribution from surface paramagnetic centers to surface relaxation is the same in sample A and B. However, the numbers of neighboring protons which are in contact with one specified proton in sample B is only one fifth of that in sample A due to dilution. This is true whether the specified proton is in the bulk space of the pore or near the pore surface. Therefore, the contribution from surface enhanced dipole-dipole interaction to surface relaxation, as well as the bulk relaxation due to dipole-dipole interaction, is reduced in sample B compared with sample A. It is therefore the magnitude of change of the total surface relaxation rate of water from sample A to
sample B that determines the significance of the contribution from surface enhanced dipole-dipole interaction to surface relaxation.

Numerically, for surface relaxivity of water in sample A,

\[
(\rho_{2,ps} + \rho_{2,d}) = \frac{\phi}{1 - \phi} \cdot \frac{1/T_2 - 1/T_{2,B}}{S_g \cdot \rho_g}
\]  \hspace{1cm} (3.3.3.1)

Where the total surface relaxivity \( \rho_2 \) (as in Equation 3.3.2.1) is divided into two parts, \( \rho_{2,ps} \) is the surface relaxivity due to interactions of protons with surface paramagnetic centers, and \( \rho_{2,d} \) is the surface relaxivity due to surface enhanced dipole-dipole interactions.

For surface relaxivity of water in sample B, \( \rho_{2,ps} \) remains the same as that in sample A but \( \rho_{2,d} \) reduces from that in sample A. With the argument illustrated earlier in this section, the degree of reduction of \( \rho_{2,d} \) is the same as that of the bulk relaxation rate. It then follows that for surface relaxivity of water in sample B,

\[
(\rho_{2,ps} + 0.33\rho_{2,d}) = \frac{\phi}{1 - \phi} \cdot \frac{1/T_2 - 1/T_{2,B}}{S_g \cdot \rho_g}
\]  \hspace{1cm} (3.3.3.2)

The coefficient of 0.33 in Equation (3.3.3.2) was determined by the degree of reduction from sample A to sample B of the bulk relaxation rate due to proton dipole-dipole interaction. That is,

\[
\frac{(1/T_{2,B})_{\text{oxygen free, sample A}}}{(1/T_{2,B})_{\text{air saturated, sample B}} - (1/T_{2,B})_{\text{oxygen, sample B}}}
\]  \hspace{1cm} (3.3.3.3)

Bulk \( T_2 \) values in Equation 3.3.3.3 were either measured or from the literature.

Finally, \( \rho_{2,ps} \) and \( \rho_{2,d} \) were obtained by simultaneously solving Equations 3.3.3.1 and 3.3.3.2.
Before looking at the numerical values of $\rho_{2,ps}$ and $\rho_{2,d}$ for the various systems investigated in this study, let's first look at the difference of $T_2$ distributions of water in Sample A and B. Figure 3.3.3.1 shows the $T_2$ distributions of coated, original and washed silica sand saturated with either 100% H$_2$O (sample A) or 10% H$_2$O-90% D$_2$O (sample B). Because of its high total surface relaxivity, (Figure 3.3.2.1), the coated silica sand has a similar $T_2$ distribution of water in sample B to that in sample A. As a comparison, the total surface relaxivity of water in the original silica sand of 100% H$_2$O saturation is smaller than that in the coated silica sand (Figure 3.3.2.1). Therefore, the $T_2$ distribution of water in sample B is noticeably separate from that in sample A and has a longer $T_2$ relaxation time (smaller surface relaxation rate). Finally, the $T_2$ distribution of water in sample B of the washed silica sand moves further away to longer relaxation time from that in sample A. Similar results were obtained with the original versus washed silica flour (Figure 3.3.3.2), and the coated versus original silica gel (Figure 3.3.3.3).

The implication of Figure 3.3.3.1, Figure 3.3.3.2 and Figure 3.3.3.3 is that when the surface relaxation due to paramagnetic centers is strong (such as the case of water in the coated silica sand), the contribution of the surface enhanced dipole-dipole interaction is negligible. By contrast, when the surface relaxation due to paramagnetic centers is weak (such as the case of water in the washed silica sand), the contribution of the surface enhanced dipole-dipole interaction becomes more significant.

The numerical values of $\rho_{2,ps}$ and $\rho_{2,d}$ of water in the various systems investigated in this study are listed in Table 3.3.3.1. In comparison among the coated, original and washed fine silica sand, $\rho_{2,d}$ of water are relatively close to each other but $\rho_{2,ps}$ are much more different. It means that coating (washing) process only increases
(decreases) the contribution from paramagnetic mechanism. Moreover, $\rho_{2,d}$ accounts for only 1% for the coated silica sand but increases to 18% and 62% for the original and washed silica sand, respectively. This trend is the same for the silica flour and silica gel samples. The reason is unclear yet that $\rho_{2,d}$ of the silica gel is much smaller than that of the fine silica sand or silica flour samples, but it could be due to the fact that the total surface relaxivity for the original silica gel is also much smaller.

**TABLE 3.3.3.1 Numerical values of surface relaxivity $\rho_{2,ps}$ and $\rho_{2,d}$ of water**

<table>
<thead>
<tr>
<th>Surface relaxivity</th>
<th>Fine silica sand</th>
<th>Silica flour</th>
<th>Silica gel</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_{2,ps}$ $\mu$m/s</td>
<td>coated 32.51</td>
<td>original 4.90 ± 0.17</td>
<td>washed 0.71</td>
</tr>
<tr>
<td>$\rho_{2,d}$ $\mu$m/s</td>
<td>0.34</td>
<td>0.88 ± 0.36</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Table 3.3.3.1 also shows that $\rho_{2,d}$ of water in the fine silica sand and silica flour samples is close to the plateau value of the surface relaxivity of water in the washed fine sand and silica flour (Figure 3.3.2.2), respectively. This agreement further suggests that surface enhanced dipole-dipole interaction is an intrinsic contribution to surface relaxation besides paramagnetic centers.
FIGURE 3.3.3.1 $T_2$ relaxation time distributions of coated, original and washed silica sand. In each plot, sample A stands for 100% H$_2$O saturation and sample B stands for 10% H$_2$O-90% D$_2$O (in molar fraction) saturation.
FIGURE 3.3.3.2 $T_2$ relaxation time distributions of original and washed silica flour. In each plot, sample A stands for 100% H$_2$O saturation and sample B stands for 10% H$_2$O-90% D$_2$O (in molar fraction) saturation.

FIGURE 3.3.3.3 $T_2$ relaxation time distributions of coated and original silica gel. In each plot, sample A stands for 100% H$_2$O saturation and sample B stands for 10% H$_2$O-90% D$_2$O (in molar fraction) saturation.
3.3.4 Surface Relaxation at Elevated Temperatures

It was reviewed in section 3.1.4 that there are different behaviors of temperature dependence of surface relaxation from the studies in the literature. It was then hypothesized that the amount of paramagnetic ions on the surface is the key parameter determining those different behaviors. In more detail of this hypothesis, surface relaxation depends only weakly on temperature when the paramagnetic ions dominate the total surface relaxation rate. However, when paramagnetic ion mechanism is weak, surface relaxation depends more strongly on temperature. This section tests this hypothesis using the coated, original and washed silica samples which have different amount of paramagnetic ions. $T_1$, $T_2$ relaxation time distributions and the corresponding surface relaxivities are presented for each sample at different temperatures.

As a comparison basis, Figure 3.3.4.1 shows the change of bulk relaxation rate ($1/T_2$) of water and decane versus temperature. As expected, their bulk relaxation rate decreases with temperature. This is because at higher temperature the rate of molecular translational and rotational motion increases, resulting in reduced spectral density of magnetic fluctuations at the proton Larmor frequency and thus reduced relaxation rate due to intra-molecular and inter-molecular dipole-dipole interactions (Abragam, 1961).
FIGURE 3.3.4.1 Change of bulk relaxation rate $1/T_2$ of decane and water with respect to temperature

The first sample studied was the original silica sand saturated with either 100% water or 100% decane. To compare the temperature dependence of surface relaxation with that of bulk relaxation, we left on purpose a thin layer of bulk water on the top of the 100% water saturated sand pack. Figure 3.3.4.2 shows that while $T_2$ relaxation time of this thin layer of bulk water increases with temperature, $T_2$ of water in the sand pack slightly decreases with temperature. In terms of surface relaxivity, the surface relaxivities of both water and decane slightly increase with temperature.

Logically, the next samples to be studied are the ones with a much higher or much lower surface relaxivity than that of the original silica sand, which are the two extreme cases when paramagnetic ion dominates the surface relaxation or the contribution from paramagnetic ion is weak. Coated silica sand and the original silica gel were selected for
this purpose based on the surface relaxivity values in Table 3.3.3.1. The washed silica sand was not selected because there is no substantial separation between $T_2$ of water or decane in the sand pack and that of bulk water or decane.

Figure 3.3.4.3 shows the $T_2$ relaxation time distributions and the corresponding surface relaxivities of 100% water and 100% decane saturated coated silica sand at different temperatures. In comparison with the results for the original silica sand (Figure 3.3.4.2), $T_2$ relaxation time and the corresponding surface relaxivities of both water and decane keep constant when temperature increases. It proves our hypothesis that when the paramagnetic ion dominates the surface relaxation, surface relaxivity is independent of temperature.

Figure 3.3.4.4 shows the $T_2$ relaxation time distributions and the corresponding surface relaxivities of 100% water saturated original silica gel at different temperatures. This is for the other extreme case when the contribution from paramagnetic ion to surface relaxation is weak (Table 3.3.3.1). In this case, surface relaxivity of water decreases with temperature. The degree of decrease is similar to that of bulk water relaxation rate $1/T_2$ with respect to temperature (Figure 3.3.4.1). This similarity suggests that surface enhanced dipole-dipole interaction as illustrated in section 3.3.3 is the mechanism accounting for the temperature dependence of surface relaxation in this sample.
FIGURE 3.3.4.2 $T_2$ relaxation time distributions of original silica sand saturated with 100% water (top plot), 100% decane (middle plot) and the corresponding surface relaxivities (bottom plot) at 24.4 °C, 45 °C, 60 °C, 75 °C and 90 °C.
FIGURE 3.3.4.3 $T_2$ relaxation time distributions of coated silica sand saturated with 100% water (top plot), 100% decane (middle plot) and the corresponding surface relaxivities (bottom plot) at 24.4 °C, 45 °C, 60 °C, 75 °C and 90 °C.
FIGURE 3.3.4.4 $T_2$ relaxation time distributions of 100% water saturated original silica gel (top plot) and the corresponding surface relaxivities (bottom plot) at 24.4 ºC, 45 ºC, 60 ºC, 75 ºC and 90 ºC.

Diffusion coupling is also observed from Figure 3.3.4.4. First, the relaxation time distribution is generally bimodal because the silica gel particle is porous in itself. Secondly, more efficient diffusion coupling takes place at higher temperature between water molecules in the intra-particle micro-pores and the inter-particle macro-pores of the
silica gel particles. For example, at the lowest temperature of 24.4 °C, there are substantial intensities around both peaks of the bimodal $T_2$ relaxation time distributions. However, at the highest temperature of 90 °C, the intensities around the peak at shorter $T_2$ relaxation times decrease substantially and the whole $T_2$ relaxation time distribution is more like unimodal. Diffusion coupling and its combination with surface relaxation will be addressed in more detail in section 3.3.5.

3.3.5 Combined Effects of Surface Relaxation and Diffusion Coupling

The combined effect of surface relaxation and diffusion coupling on the relaxation time distribution was further studied with more observation results. All the following observations apply to samples with a physical bi-modal structure of pore sizes. First, Figure 3.3.5.1 shows that for 100% water saturated original silica gel, $T_1$ relaxation time distributions are more unimodal while $T_2$ relaxation time distributions are more bimodal at both temperatures of 24.4 °C and 90 °C. Secondly, Figure 3.3.5.2 shows that for 100% water saturated coated silica gel, both $T_1$ and $T_2$ relaxation time distributions are bimodal at each temperature, reflecting the actual micro-pore and macro-pore structure. However, when temperature increases, both the shorter and longer relaxation times of the $T_1$ and $T_2$ distributions move closer to the middle values. Finally, Figure 3.3.5.3 shows that for the 100% water saturated nature reservoir rock North Burbank, $T_1$ relaxation time distribution at 28 °C shows shoulders indicating the actual micro-porosity of the clay flakes (Zhang, et al, 2001), while $T_1$ relaxation time distribution at 90 °C is more unimodal.
Observations shown in Figure 3.3.4.4 and Figures 3.3.5.1 to 3.3.5.3 suggest that the combined effect of surface relaxation and diffusion coupling on the relaxation time distributions depends on surface relaxivity, fluid diffusivity and pore structure. At a given pore structure and fluid diffusivity, water molecules diffuse over longer length before they relax on the surface when the surface relaxivity is smaller, resulting in more unimodal relaxation time distribution. This is the case for Figure 3.3.5.1, because surface relaxivity $\rho_1$ is much smaller than $\rho_2$ ($\rho_2/\rho_1$ ratio is 9.4 and 6.8 at 24.4 °C and 90 °C, respectively). Alternatively, at a given pore structure and approximately constant surface relaxivity, water molecules also diffuse over longer length before they relax on the surface when the diffusivity (temperature) is higher, leading to more unimodal relaxation time distribution. This is the case for Figure 3.3.5.2 and Figure 3.3.5.3.

**FIGURE 3.3.5.1** $T_1$, $T_2$ relaxation time distributions of the original silica gel at 24.4 °C and 90 °C.
FIGURE 3.3.5.2 $T_2$ relaxation time distributions of 100% water saturated coated silica gel and the corresponding surface relaxivities at 24.4 °C, 45 °C, 60 °C, 75 °C and 90 °C.
FIGURE 3.3.5.3 $T_1$ relaxation time distributions of 100% water saturated North Burbank at 28 °C and 90 °C.

3.4 Conclusions

Surface relaxivity of 100% water saturated core samples are obtained by comparison between Hg capillary pressure curve (measured or model calculated) and NMR relaxation time distributions. Results show that surface relaxivity of water in the 100% $S_w$ Berea cores is about 2.3 times that of the Texas Cream limestone cores used in this study.

Results of acid washing and paramagnetic ion coating show that paramagnetic ion is a very important factor affecting surface relaxation. For example, $\rho_1$ and $\rho_2$ decreases with respect to acid washing as more and more ions are washed off the surface. However, $\rho_1$ and $\rho_2$ goes to a finite plateau value at the end of washing, accounting for 10% and 17% of the original value, respectively. It suggests that other mechanism exists besides paramagnetic ions for NMR surface relaxation. In addition, $\rho_2/\rho_1$ ratio generally
increases and deviates further from the mean value of “natural rocks” (Kleinberg et al., 1993) with respect to acid washing, while $\rho_2/\rho_1$ ratio is close to that mean value for both original and coated samples.

Mechanism of the surface enhanced dipole-dipole interaction is quantified by comparison between relaxation rates of identical samples saturated with either 100% H$_2$O or 10% H$_2$O-90% D$_2$O. Results show that contribution from surface enhanced dipole-dipole interaction is negligible when paramagnetic ion mechanism is strong. However, in cases when paramagnetic ion mechanism is weak, the contribution from surface enhanced dipole-dipole interaction could dominate the total surface relaxation rate.

In agreement to the mechanism of surface enhanced dipole-dipole interaction, results of temperature dependence of surface relaxation show that surface relaxivity decreases with temperature when the contribution of paramagnetic ion to surface relaxation is weak, while surface relaxivity depends only weakly on temperature when paramagnetic ion mechanism dominates the total surface relaxation rate.

Diffusion coupling between the micro-pores and macro-pores is observed. Results suggest that the combined effect of surface relaxation and diffusion coupling on the relaxation time distribution depends on surface relaxivity, fluid diffusivity and the pore structure.
Chapter 4  Effect of OBM surfactants on Wettability Alteration and NMR Responses

This chapter identifies the wettability alteration of both Berea and limestone cores by synthetic oil base mud (OBM) surfactants and its effect on NMR estimated irreducible water saturation ($S_{wir}$). It also develops the modification of NMR interpretation of $S_{wir}$ when wettability alteration occurs.

4.1  Literature Review

This section reviews first the various components of synthetic OBM, and then the potential of wettability alteration by OBM surfactants and its effect on NMR responses, and finally the models of estimating $S_{wir}$ from NMR interpretation in the literature.

4.1.1 OBM Surfactants, Their Potential on Wettability Alteration and the Effect on NMR Responses

Oil base drilling muds have several advantages. First, they bring higher drilling rate and better well bore stability (Darley, 1988). Secondly, they can be used in zones such as problem shale or deep, hot hole, which could not be drilled safely or efficiently with a water base mud (McKinney, 1988). Finally, synthetic oil base muds meet more strict environmental requirements.

OBM has various components such as water, base oil, density control particles, emulsifiers, oil-wetting agents and so on. The base oil could be diesel, refined mineral oil distillation cut ranging from carbon numbers $C_{12}$ to $C_{18}$, and synthetic internal olefins (for
synthetic OBM), depending on the environmental requirements. Mineral particles such as barite are added to increase the density of the drilling mud. Primary and secondary emulsifiers are added to make the internal water phase emulsified in the external oil phase (W/O emulsion). Oil wetting agents are added to make the drilled cuttings and density control particles oil-wet, so that they can stably suspend in the oil phase. Excess amount of emulsifiers and oil wetting agents is often added to maintain the stability and rheological properties of the mud system (McKinney, 1988, Ballard, 1988). The excess amount of addition also helps to make up for their loss to the drilled cuttings.

Among the various OBM components, the wettability alteration materials are mainly the emulsifiers and oil-wetting agents (Yan, 1993). Potentially, these OBM surfactants may invade into the near well bore formation with the base oil and change the originally preferential water-wet mineral surface to mix-wet or preferentially oil-wet (McCaffery, 2002). This happens especially during the spurt-loss period before the mud cake fully builds up.

It was reported that OBM invasion altered the reservoir rock and affected formation evaluation from NMR well logging and special core analysis (Marschall, 1997, Zwaag, 2001). Marschall et al. (1997) investigated the effects of invert OBM on primary MRI Log determinations. They found that the emulsifiers and oil-wetting agents in the filtrate could change the wetting preference (water-wet to oil-wet) of the rock surfaces, thus altering primary NMR parameters such as permeability and BVI. Moreover, the wetting change was found to be dependent on the rock quality (permeability and porosity) and the concentration of emulsifiers and oil-wetting agent in the filtrate. Zwaag et al. (2001) investigated the effects of drilling fluid filtrate invasion on NMR $T_2$ relaxation
time distribution. They found that for both sandstone and chalk samples studied, the
invasion of drilling fluid filtrate introduced significant changes in mean $T_2$ and NMR-
derived permeability.

Literature studies as reviewed above showed that OBM surfactants affected
wettability and NMR response. However, quantitative connection between the effects of
OBM invasion on NMR derived parameters (such as irreducible water saturation and
permeability) and some independent quantitative wettability measurements has not been
investigated. This is the focus of our study.

4.1.2 Models of Estimating $S_{\text{wir}}$ (BVI) from NMR

There are three models in the literature to estimate BVI from NMR relaxation
time. They are cutoff BVI model, spectral BVI model and Bi-exponential model. They
are reviewed in detail in the following subsections.

4.1.2.1 Cutoff BVI Model

The cutoff BVI model is based on a fixed value of $T_{2, \text{cutoff}}$, which partitions the
spectrum of a $T_2$ relaxation time distribution of 100% brine saturated rock into two parts
(Figure 4.1.2.1). The small pores with $T_2$ relaxation times below $T_{2, \text{cutoff}}$ correspond to
irreducible water (BVI), while the larger pores with $T_2$ relaxation times above $T_{2, \text{cutoff}}$
correspond to movable water (FFI). In this cutoff BVI concept,

$$BVI = \phi \cdot \frac{\int_{T_{2, \text{min}}}^{T_{2, \text{cutoff}}} f_{i, S_w=100\%} (T_2) \cdot dT_2}{\int_{T_{2, \text{min}}}^{T_{2, \text{max}}} f_{i, S_w=100\%} (T_2) \cdot dT_2}$$

(4.1.2.1)
Where $\phi$ is porosity, $T_{2,\text{min}}$, $T_{2,\text{max}}$ are the minimum and maximum values of the $T_2$ bins in the relaxation time distribution, respectively. $f_i$ are the intensities corresponding to $T_{2,i}$.

![Graph](image)

**FIGURE 4.1.2.1** Schematic description of cutoff BVI model. A fixed $T_{2,\text{cutoff}}$ partitions the spectrum of $T_2$ relaxation time distribution into BVI and FFI.

In core analysis, $T_{2,\text{cutoff}}$ is determined by NMR measurements of core sample at 100% $S_w$ and $S_{\text{wir}}$ (air/brine) conditions (Figure 4.1.2.2). $T_{2,\text{cutoff}}$ is the $T_2$ value at which the cumulative intensity of the relaxation time distribution at 100% $S_w$ condition is equal to the asymptotical cumulative intensity at $S_{\text{wir}}$ (air/brine) condition. That is,

$$
\int_{T_{2,\text{min}}^{T_{2,\text{cutoff}}}} f_{i,S_w=100\%} (T_{2,i}) \cdot dT_{2,i} = \int_{T_{2,\text{min}}^{T_{2,\text{cutoff}}}} f_{i,S_{\text{wir}}} (T_{2,i}) \cdot dT_{2,i}
$$

(4.1.2.2)
Numerically, a $T_{2, \text{cutoff}}$ value of 33 ms was obtained for sandstone and 92 ms for carbonate based on a statistical average from a set of experimental measurements (Morris et al. 1993, Straley et al. 1997).

![Graph showing $T_2$ values](image)

**FIGURE 4.1.2.2** Schematic description of the determination of $T_{2, \text{cutoff}}$ from NMR measurements of core sample at 100% $S_w$ and $S_{\text{wir}}$ (air/brine) conditions. $T_{2, \text{cutoff}}$ is the $T_2$ value at which the cumulative intensity of the relaxation time distribution at 100% $S_w$ condition is equal to the asymptotical cumulative intensity at $S_{\text{wir}}$ (air/brine) condition.

### 4.1.2.2 Spectral BVI Model

The cutoff BVI model works well for rocks with a broad pore size distribution. However, there are cases where its application leads to incorrect results (Coates et al. 1998, Chen et al. 1998). For example, Coates et al. (1998) studied some coarse-grained
sandstones saturated with 100% $S_w$, they found that the relaxation times were well above the fixed $T_{2,\text{cutoff}}$ of 33 ms for sandstone, which leaded to zero $S_{\text{wir}}$ by the fixed $T_{2,\text{cutoff}}$ model. However, they found that after oil displacement or air/water de-saturation of the 100% $S_w$ sample, a small peak appears below 33 ms corresponding to the water remaining on the pore surface. From this they concluded that not only the water in the small pores but also the thin film of water on the surface of the bigger pores contributes to $S_{\text{wir}}$. Their observations were confirmed by Chen et al. (1998).

A spectral BVI concept was introduced by Coates et al. (1998) and Chen et al. (1998). In this concept, each pore size was assumed to contain a certain amount of irreducible water. Therefore, each $T_2$ bin component ($T_{2,i}$) of the relaxation time distribution of the 100% $S_w$ rock was associated with a weighing function $W_i(T_{2,i})$ of the irreducible water. BVI was then calculated as follows,

$$\text{BVI} = \phi \cdot \sum_{i=1}^{n} W_i(T_{2,i}) \cdot f_i(T_{2,i}) \quad (4.1.2.3)$$

Where $n$ is the number of $T_2$ bin components in the relaxation time distribution.

One way to calculate the weighing function was based on simple geometry model of slab, cylinder or sphere (Coates et al. 1998, Chen et al. 1998),

$$W_i(T_{2,i}) = \frac{(\alpha \cdot \rho_2 T_{2,i})^\alpha - (\alpha \cdot \rho_2 T_{2,i} - R_w)^\alpha}{(\alpha \cdot \rho_2 T_{2,i})^\alpha} \quad \text{when} \quad T_{2,i} > \frac{R_w}{\alpha \cdot \rho_2} \quad (4.1.2.4)$$

$$W_i(T_{2,i}) = 1 \quad \text{when} \quad T_{2,i} \leq \frac{R_w}{\alpha \cdot \rho_2} \quad (4.1.2.5)$$

Where $\alpha$ is a constant which equals to 1, 2 or 3 for slab, cylindrical and spherical geometry, respectively. $R_w$ is the water film thickness in the larger pores.
\[ R_w = \frac{2\sigma \cos \theta}{P_c} \]  \hspace{1cm} (4.1.2.6)

Where \( \sigma \) is the interfacial tension between the wetting and non-wetting phase, \( \theta \) is the contact angle, \( P_c \) is the capillary pressure corresponding to irreducible water condition.

Another way to calculate the weighing function was based on empirical correlations (Coates et al. 1998, Chen et al. 1998). Coates et al. (1998) studied 340 sandstones and 71 carbonates and came up with the following empirical correlations,

For sandstone,
\[
W_i(T_{2,i}) = \frac{1}{1 + 0.0618T_{2,i}} \]  \hspace{1cm} (4.1.2.7)

For carbonate,
\[
W_i(T_{2,i}) = \frac{1}{1 + 0.0113T_{2,i}} \]  \hspace{1cm} (4.1.2.8)

Another empirical correlation was presented by Chen, et al. (1998) as follows,

\[
W_i(T_{2,i}) = \frac{f_{i, s_{\text{w}}}(T_{2,i})}{f_{i, s_{\text{w}}=100\%}(T_{2,i})} \]  \hspace{1cm} (4.1.2.9)

### 4.1.2.3 Bi-exponential BVI Model

In addition to the cutoff and spectral BVI models, a bi-exponential BVI model was developed by Dunn et al. (2002). In this model, BVI was determined from the \( T_{2,1\text{M}} \) of the relaxation time distribution as follows,

\[
BVI = \phi \cdot [0.6101\exp\left(\frac{-T_{2,1\text{M}}}{15.9}\right) + 0.3688\exp\left(-\frac{T_{2,1\text{M}}}{276.8}\right)] \]  \hspace{1cm} (4.1.2.10)

This empirical correlation was based on the experimental data in the NMR rock catalog of samples from England and Norway (Dunn et al. 2002).
4.1.2.4 Applications of BVI Models

The BVI models reviewed above are empirical because the numerical constants were obtained from the best fit of experimental data for the specific group of samples studied. In practice, it was suggested that the larger value should be taken of that from cutoff and spectral BVI models (Coates et al. 1998).

Several situations complicate the determination of BVI. First, it was shown that for rock samples with significant amounts of paramagnetic or clay compounds, there is a large shift of the $T_2$ relaxation time distribution to short times, resulting in a smaller $T_2$, cutoff than the default value of 33 ms (Zhang et al. 1998). Secondly, for the heavy oil formation, the relaxation time of the heavy oil may overlap with that of the irreducible water, causing overestimated BVI if the default $T_2$, cutoff is used. Finally, wettability alteration of the formation from water-wet to more oil-wet may cause the relaxation time of irreducible water to increase and/or the relaxation time of the oil to decrease, both complicating the determination of BVI. Quantitative investigation of the last case is the focus of this chapter.

4.2 Materials and Experimental Procedures

This section first lists the main materials used in this chapter with their physical properties, and then illustrates the experimental procedures. The materials include Berea and Texas Cream limestone cores, base oil, crude oil and synthetic OBM surfactants. The experimental procedures introduce the preparation of rock saturations, flushing process with OBM surfactants, Amott-Harvey wettability index measurements and the NMR $D$-$T_2$ measurements.
4.2.1  Berea and Texas Cream Limestone Cores

In this study, Berea and Texas Cream limestone are used to stand for sandstone and carbonate, which are the two common mineral materials in the reservoir formation. They were cored from large outcrop slabs. Each core is 1' in diameter by 1' in length. The Berea cores are very similar to each other with porosity range of 0.17 to 0.19 and air permeability range of 81 to 147 md. The limestones are also very similar to each other with porosity range of 0.23 to 0.25 and air permeability range of 6 to 10 md. The advantage of using similar Berea cores and similar limestone cores is to exclude the effects due to variability of sample property (such as porosity, permeability, and mineralogy) and thus to focus on the effects due to OBM surfactants on wettability alteration and NMR responses.

4.2.2  Base Oil, Crude Oil, OBM Surfactants and Flushing Fluids

The base oil used is Sf Base (SB) from the industry. It is mainly a mixture of internal olefins with C\textsubscript{16} to C\textsubscript{18}. The density and viscosity of SB are 0.78 g/ml and 2.7 cp, respectively. The crude oil used is a North-Sea crude oil. The API gravity and viscosity of this crude oil is 29.2 API and 15 cp, respectively. We selected this crude oil because it is a water-wet crude oil on Berea cores, as shown later in this chapter.

Four systems of OBM surfactants from the industry were used in this study. Their code names are LLD, BOO, NOVA and VERSA. Each surfactant system is a mixture of two or three types of OBM surfactants, consisting of emulsifiers and oil-wetting agents. Table 4.2.2.1 lists the components and main functions of these four OBM surfactant systems.
TABLE 4.2.2.1 Components and main functions of the four OBM surfactant systems

<table>
<thead>
<tr>
<th>Name</th>
<th>Components</th>
<th>Main functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLD</td>
<td>LE MUL</td>
<td>Stabilizer, aid suspension property, reduce filtration</td>
</tr>
<tr>
<td></td>
<td>LE SUPERMUL</td>
<td>Emulsifier, oil wetting agent</td>
</tr>
<tr>
<td></td>
<td>DEEP TREAT</td>
<td>Oil wetting agent</td>
</tr>
<tr>
<td>BOO</td>
<td>BIO COTE</td>
<td>Oil wetting agent</td>
</tr>
<tr>
<td></td>
<td>OMNI TEC</td>
<td>Emulsifier</td>
</tr>
<tr>
<td></td>
<td>OMNI MUL</td>
<td>Emulsifier, secondary wetting agent</td>
</tr>
<tr>
<td>NOVA</td>
<td>NOVA WET</td>
<td>Wetting agent</td>
</tr>
<tr>
<td></td>
<td>NOVA MUL</td>
<td>Emulsifier</td>
</tr>
<tr>
<td>VERSA</td>
<td>VERSA COAT</td>
<td>Wetting agent</td>
</tr>
<tr>
<td></td>
<td>VERSA MUL</td>
<td>Emulsifier</td>
</tr>
</tbody>
</table>

The flushing fluids were simulated by mixing a specified amount of OBM surfactants with base oil. The ratio among the emulsifiers and oil-wetting agents was based on their amount used in the whole mud. The mixture of flushing fluids is then aged in an oven at 75 °C for 18 hours to simulate reservoir condition at elevated temperature. We believe that the flushing fluids thus prepared were a reasonable simplification to the real OBM filtrate invaded into the near wellbore formation, because it was shown that the wettability alteration materials among the various components of the whole mud are mainly the emulsifiers and oil-wetting agents (Yan, 1993), which are the focus of this study.

4.2.3 Rock Saturation Preparation

The Berea and limestone cores were 100% brine (5% wt sodium chlorite in DI water) saturated as follows. The dry core was evacuated for 8 hours by a vacuum pump. Brine was introduced into the vacuum vessel and the core remained immersed in brine for
8 hours under vacuum. Then the core was placed in a bottle of brine with a loosely fitting rubber stopper and pressurized at 1000 psi for 8 hours in a pressure cell.

The 100% brine saturation was reduced to irreducible water saturation by centrifugation with air, base oil or crude oil in an L5-50P model centrifuge. The centrifuge speed corresponded to a capillary pressure of 100 psi. The centrifugation duration was 16 hours plus an additional hour after the sample was turned upside down. Turning the sample upside down for the last additional hour helped to reach a more homogeneous fluid saturation along the axial direction of the core.

4.2.4 Flushing Set-up and Process with OBM surfactants

The cores at irreducible water saturation with crude oil or base oil were flushed with OBM flushing fluid in a Hassler core holder (Temco, Oklahoma). Figure 4.2.4.1 is the schematic plot of the flushing set-up. The confining pressure is about 1000 psi. The flushing rate is 9 ml/hour and 3 ml/hour by a syringe pump for Berea and limestone cores, respectively. Under these different flushing rates, a similar capillary pressure is obtained for Berea and limestone cores with different permeability. According to Darcy’s law, the capillary pressure of flushing is approximately several psi. The standard flushing volume is 10 PV. But several Berea and limestone cores were flushed with a series of volumes of 1, 3, 5, 7, 10 and 15 PV. The concentrations of the OBM surfactants in the flushing fluid are 0%, 0.1%, 0.3%, 0.5%, 1%, 2% and 3%, wt%.
FIGURE 4.2.4.1 Schematic plot of the flushing set-up

4.2.5 Amott-Harvey Wettability Index Measurements

Amott-Harvey wettability index measurements follow the flushing process and NMR measurements. In the following illustration of the procedure of Amott-Harvey measurements, “imbibition” means water displacing oil, “drainage” means oil displacing water, “spontaneous” means no centrifuge and “forced” means by centrifuge. For the Amott water index, the flushed core was first immersed in brine in a standard imbibition cell for at least 48 hours, and the volume of oil displaced by spontaneous imbibition of brine ($V_{SI}$) was recorded. Then the core was centrifuged under brine with a capillary pressure of -25 psi, and the volume of oil displaced by forced imbibition of brine ($V_{FI}$) was recorded. The Amott water index was calculated as follows,

$$
\delta_w = \frac{V_{SI}}{V_{SI} + V_{FI}}
$$

(4.2.5.1)

After the Amott water index measurement, the Amott oil index was similarly measured,
\[ \delta_o = \frac{V_{SD}}{V_{SD} + V_{FD}} \]  

(4.2.5.2)

Where \( V_{SD} \) is the volume of water displaced by spontaneous drainage of oil after at least 48 hours, \( V_{FD} \) is the volume of water displaced by forced drainage of oil by centrifuging with a capillary pressure of 100 psi. The Amott-Harvey index was then calculated as follows,

\[ I_{AH} = \delta_w - \delta_o \]  

(4.2.5.3)

4.2.6 NMR \( D-T_2 \) measurements

In addition to the standard NMR \( T_1, T_2 \) measurements (Chapter 3, section 3.2.4), NMR \( D-T_2 \) measurements were also performed. A 2-\( D \) map of \( T_2 \) relaxation time in the \( x \)-axis and the apparent fluid diffusivity in the \( y \)-axis was obtained from each \( D-T_2 \) measurements (the Matlab programs of generating the \( D-T_2 \) map were licensed to our research group from Schlumberger). The details of the pulse sequence and various applications of \( D-T_2 \) technique can be found in the following references (Hürlimann et al. 2002 and 2003, Freedman et al. 2003). In this chapter, \( D-T_2 \) technique was used for the visualization of wettability alteration by the OBM surfactants as later illustrated.

The parameters of the \( D-T_2 \) measurements are as follows. Each measurement was carried out at 9 diffusion times. At each diffusion time, 3000 echoes were collected with echo spacing of 400 \( \mu \)s. The number of scans was 200 and 400 for fluid and core samples, respectively.
4.3 Experimental Results and Discussions

This section presents first the experimental results of NMR bulk properties of the OBM surfactants, and then the wettability alteration of Berea and limestone cores by OBM surfactants, and then the effect of this wettability alteration on NMR estimated $S_{wir}$, and finally the modification of NMR interpretation of $S_{wir}$ when wettability alteration occurs.

4.3.1 NMR Bulk Properties of the OBM Surfactants

NMR $T_1$, $T_2$ measurements of the bulk OBM surfactants were performed. More information about the OBM surfactants can be obtained from the NMR relaxation time measurements because so far such data has not been published in the literature. Figure 4.3.1.1 shows an example of the $T_1$, $T_2$ (at two echo spacing of 0.32 and 1 ms) relaxation time distributions for one of the OBM surfactants called LE MUL (Table 4.2.2.1). Both $T_1$ and $T_2$ relaxation time distributions are broad with over three orders of magnitude in relaxation times, indicating that the OBM surfactant has multiple components. Moreover, $T_1$ and $T_2$ relaxation time are short with the log mean values of 31.7 ms and 16.2 ms for $T_1$ and $T_2$ (at echo spacing of 0.32 ms) of LE MUL, suggesting that the OBM surfactant is composed of big molecules. $T_1$, $T_2$ relaxation time distributions for other OBM surfactants studied are shown in Figure B.1 of Appendix part B.

Table 4.3.1.1 summarizes the log mean $T_1$, $T_2$ values of all the OBM surfactants measured in this study. Notice that both $T_1/T_2$ and the ratio of $T_2, \text{TE} = 1\text{ ms}$ to $T_2, \text{TE} = 0.32\text{ ms}$ are larger than unity. This also indicates that the OBM surfactants have some heavy components (Zhang, 2003).
FIGURE 4.3.1.1 $T_1$ and $T_2$ distributions of OBM surfactant LE MUL

TABLE 4.3.1.1 $T_1$, $T_2$ log mean values of all the OBM surfactants studied

<table>
<thead>
<tr>
<th>OBM surfactant</th>
<th>$T_1$ (ms)</th>
<th>$T_2$ (ms)</th>
<th>$T_2$ (ms)</th>
<th>$T_1/T_2$</th>
<th>$(T_2, TE = 1 ms) / (T_2, TE = 0.32 ms)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LE MUL</td>
<td>31.7</td>
<td>16.2</td>
<td>23.4</td>
<td>1.95</td>
<td>1.44</td>
</tr>
<tr>
<td>LE SUPERMUL</td>
<td>52.7</td>
<td>26.3</td>
<td>35.8</td>
<td>2.01</td>
<td>1.36</td>
</tr>
<tr>
<td>BIO COTE</td>
<td>19.0</td>
<td>15.5</td>
<td>17.5</td>
<td>1.23</td>
<td>1.13</td>
</tr>
<tr>
<td>OMNI TEC</td>
<td>21.1</td>
<td>10.4</td>
<td>16.6</td>
<td>2.03</td>
<td>1.60</td>
</tr>
<tr>
<td>OMNI MUL</td>
<td>63.3</td>
<td>28.6</td>
<td>42.8</td>
<td>2.22</td>
<td>1.50</td>
</tr>
<tr>
<td>NOVA WET</td>
<td>13.1</td>
<td>6.4</td>
<td>8.4</td>
<td>2.04</td>
<td>1.31</td>
</tr>
<tr>
<td>NOVA MUL</td>
<td>43.4</td>
<td>28.8</td>
<td>32.2</td>
<td>1.51</td>
<td>1.12</td>
</tr>
<tr>
<td>VERSA MUL</td>
<td>48.9</td>
<td>39.2</td>
<td>41.3</td>
<td>1.25</td>
<td>1.05</td>
</tr>
<tr>
<td>VERSA COAT</td>
<td>36.0</td>
<td>18.3</td>
<td>26.6</td>
<td>1.97</td>
<td>1.45</td>
</tr>
</tbody>
</table>
4.3.2 Wettability Alteration of Berea and Limestone Cores by OBM Surfactants

Figure 4.3.2.1 and Table 4.3.2.1 show the Amott-Harvey wettability indices of Berea cores after flushing. It includes a base case when Amott-Harvey measurement was performed after the crude oil/brine saturation stage without fluid flushing (B44, Table 4.3.2.1). The corresponding Amott-Harvey index is +0.93, which means that the crude oil used in this study does not alter the wettability of the Berea core. This confirms that the following wettability alteration of the Berea cores is totally due to the OBM surfactants but not due to the crude oil.

![Amott-Harvey wettability indices of Berea cores after flushing.](image)

FIGURE 4.3.2.1 Amott-Harvey wettability indices of Berea cores after flushing.

When there are no OBM surfactants in the flushing fluid, the Amott-Harvey indices are close to +1 (mean value: +0.93). It means that the Berea cores are originally
strongly water-wet. However, for all the four OBM surfactant systems, when their concentrations in the flushing fluid are as low as 0.5%, the strongly water-wet Berea cores are altered to be intermediate-wet. With the increase of concentration, the Berea cores are altered to be intermediate-wet for VERSA, slightly oil-wet for LLD, but more oil-wet for BOO and NOVA. Reasons of the different behaviors among these OBM surfactant systems are not clear due to lack of detailed information of their structures.

Similarly, Figure 4.3.2.2 and Table 4.3.2.1 shows the Amott-Harvey wettability indices of the Texas Cream limestone cores after flushing. OBM surfactant systems of BOO and NOVA were examined for the limestone cores, because they altered the wettability of Berea cores more seriously than the other two OBM surfactant systems as shown above.

FIGURE 4.3.2.2 Amott-Harvey wettability indices of Texas Cream limestone cores after flushing.
The results of wettability alteration of the Texas Cream limestones by the OBM surfactants are similar to that of the Berea cores. When there are no OBM surfactants in the flushing fluid, the Amott-Harvey indices are close to +1 (mean value: +0.78). It means that the Texas Cream limestone cores are originally water-wet. However, when the OBM surfactants concentration in the flushing fluid is as low as 0.5%, the limestone cores are altered to be slightly oil-wet (NOVA) and oil-wet (BOO). This is a stronger degree of wettability alteration than that of the Berea cores at the same concentration of 0.5% (Table 4.3.2.1). Based on this, we examined two more cases where the concentrations of BOO in the flushing fluid are 0.3% and 0.1%. It shows that the Texas Cream limestone cores are still altered to be oil-wet by 0.3% BOO and intermediate-wet by even 0.1% BOO.
TABLE 4.3.2.1 Amott-Harvey wettability indices of Berea and Texas Cream limestone cores after flushing with (SB + OBM surfactants)

<table>
<thead>
<tr>
<th>Core #</th>
<th>Surfactant system</th>
<th>Concentration</th>
<th>$\delta_w$</th>
<th>$\delta_o$</th>
<th>$I_{MH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B44</td>
<td>-</td>
<td>0%</td>
<td>0.93</td>
<td>0</td>
<td>0.93</td>
</tr>
<tr>
<td>B27</td>
<td>-</td>
<td>0%</td>
<td>0.95</td>
<td>0</td>
<td>0.95</td>
</tr>
<tr>
<td>B30</td>
<td>-</td>
<td>0%</td>
<td>0.92</td>
<td>0</td>
<td>0.92</td>
</tr>
<tr>
<td>B72</td>
<td>-</td>
<td>0%</td>
<td>0.93</td>
<td>0</td>
<td>0.93</td>
</tr>
<tr>
<td>B56</td>
<td>VERSA</td>
<td>0.5%</td>
<td>0.08</td>
<td>0</td>
<td>0.08</td>
</tr>
<tr>
<td>B57</td>
<td>VERSA</td>
<td>1%</td>
<td>0.05</td>
<td>0</td>
<td>0.05</td>
</tr>
<tr>
<td>B107</td>
<td>VERSA</td>
<td>2%</td>
<td>0.03</td>
<td>0</td>
<td>0.03</td>
</tr>
<tr>
<td>B32</td>
<td>LLD</td>
<td>0.5%</td>
<td>0.08</td>
<td>0.06</td>
<td>0.02</td>
</tr>
<tr>
<td>B28</td>
<td>LLD</td>
<td>1%</td>
<td>0.04</td>
<td>0.14</td>
<td>-0.10</td>
</tr>
<tr>
<td>B34</td>
<td>LLD</td>
<td>2%</td>
<td>0.03</td>
<td>0.38</td>
<td>-0.35</td>
</tr>
<tr>
<td>B16</td>
<td>BOO</td>
<td>0.5%</td>
<td>0.08</td>
<td>0.2</td>
<td>-0.12</td>
</tr>
<tr>
<td>B45</td>
<td>BOO</td>
<td>1%</td>
<td>0.06</td>
<td>0.44</td>
<td>-0.38</td>
</tr>
<tr>
<td>B58</td>
<td>BOO</td>
<td>2%</td>
<td>-0.04</td>
<td>0.48</td>
<td>-0.52</td>
</tr>
<tr>
<td>B66</td>
<td>BOO</td>
<td>3%</td>
<td>0.05</td>
<td>0.56</td>
<td>-0.51</td>
</tr>
<tr>
<td>B91</td>
<td>BOO</td>
<td>3%</td>
<td>0.01</td>
<td>0.51</td>
<td>-0.50</td>
</tr>
<tr>
<td>B26</td>
<td>NOVA</td>
<td>3%</td>
<td>0</td>
<td>0.60</td>
<td>-0.60</td>
</tr>
<tr>
<td>B77</td>
<td>NOVA</td>
<td>3%</td>
<td>0.01</td>
<td>0.57</td>
<td>-0.56</td>
</tr>
<tr>
<td>B80</td>
<td>NOVA</td>
<td>3%</td>
<td>0</td>
<td>0.68</td>
<td>-0.68</td>
</tr>
<tr>
<td>B40</td>
<td>NOVA</td>
<td>3%</td>
<td>0</td>
<td>0.66</td>
<td>-0.66</td>
</tr>
<tr>
<td>L15</td>
<td>-</td>
<td>0%</td>
<td>0.89</td>
<td>0</td>
<td>0.89</td>
</tr>
<tr>
<td>L45</td>
<td>-</td>
<td>0%</td>
<td>0.69</td>
<td>0</td>
<td>0.69</td>
</tr>
<tr>
<td>L53</td>
<td>-</td>
<td>0%</td>
<td>0.76</td>
<td>0</td>
<td>0.76</td>
</tr>
<tr>
<td>L70</td>
<td>NOVA</td>
<td>0.5%</td>
<td>0</td>
<td>0.39</td>
<td>-0.39</td>
</tr>
<tr>
<td>L7</td>
<td>NOVA</td>
<td>1%</td>
<td>0</td>
<td>0.38</td>
<td>-0.38</td>
</tr>
<tr>
<td>L2</td>
<td>NOVA</td>
<td>3%</td>
<td>0</td>
<td>0.53</td>
<td>-0.53</td>
</tr>
<tr>
<td>L72</td>
<td>BOO</td>
<td>0.1%</td>
<td>0</td>
<td>0.13</td>
<td>-0.13</td>
</tr>
<tr>
<td>L57</td>
<td>BOO</td>
<td>0.3%</td>
<td>0</td>
<td>0.61</td>
<td>-0.61</td>
</tr>
<tr>
<td>L16</td>
<td>BOO</td>
<td>0.5%</td>
<td>0</td>
<td>0.86</td>
<td>-0.86</td>
</tr>
<tr>
<td>L35</td>
<td>BOO</td>
<td>1%</td>
<td>0</td>
<td>0.88</td>
<td>-0.88</td>
</tr>
<tr>
<td>L36</td>
<td>BOO</td>
<td>2%</td>
<td>0</td>
<td>0.89</td>
<td>-0.89</td>
</tr>
<tr>
<td>L59</td>
<td>BOO</td>
<td>3%</td>
<td>0</td>
<td>0.90</td>
<td>-0.90</td>
</tr>
<tr>
<td>L8</td>
<td>BOO</td>
<td>3%</td>
<td>0</td>
<td>0.85</td>
<td>-0.85</td>
</tr>
</tbody>
</table>
Wettability alteration of Berea and Texas Cream limestone cores by the OBM surfactants, as shown above by Amott-Harvey wettability index measurements, is visualized by the $D-T_2$ maps (Figure 4.3.2.3 and 4.3.2.4). In a $D-T_2$ map, the result is displayed by a two dimensional plot of the $T_2$ relaxation time in the x-axis and the apparent fluid diffusivity in the y-axis. With the additional diffusivity axis, water and oil responses can be separated from each other by a diffusivity cutoff (the horizontal dash dotted thick line in the middle plots of Figure 4.3.2.3 and Figure 4.3.2.4). Components with diffusivity above this cutoff value correspond to water and components with diffusivity below this cutoff value correspond to oil. This separation of water and oil responses is very helpful to our studies of wettability, especially in cases when water and oil relaxation time distribution from a standard $T_2$ measurement overlap with each other.

The methodology of using $D-T_2$ maps to visualize wettability alteration is to compare $T_2$ relaxation time of water after forced brine imbibition with that of 100% $S_w$, and to compare $T_2$ relaxation time of oil after forced brine imbibition with that of bulk oil. The vertical dash dotted thick lines in Figure 4.3.2.3 and Figure 4.3.2.4 are added to help to visualize these comparisons. As an example, Figure 4.3.2.3 shows that for the water-wet sample after flushing (B72, Table 4.3.2.1), after forced brine imbibition water relaxes very close to that of 100% $S_w$ (at strongly water-wet condition), and most of the oil relaxes at its bulk relaxation time. It means that almost all the surface is still covered by water, shielding the oil from any surface relaxation contribution. As a comparison, for the oil-wet sample after flushing (B77, Table 4.3.2.1), after forced brine imbibition, water relaxes at relaxation times longer than that of 100% $S_w$ (at strongly water-wet condition), and almost all the oil relaxes at relaxation times shorter than its bulk value. It means that
now some of the mineral surface is contacted by oil. These fluid distributions derived from the $D-T_2$ maps are in good agreement with the wettability conditions.

Similarly, Figure 4.3.2.4 shows an example of the visualization of wettability alteration of the Texas Cream limestone cores. For the water-wet sample after flushing (L15, Table 4.3.2.1), water relaxes very close to that of 100% $S_w$ and oil relaxes as bulk oil after forced brine imbibition. As a comparison, for the oil-wet sample after flushing (L2, Table 4.3.2.1), water relaxes at relaxation times longer than that of 100% $S_w$ and oil relaxes at relaxation times shorter than the bulk oil.
Figure 4.3.2.3 $D-T_2$ maps of 100% $S_w$, after forced brine imbibition and bulk SB for Berea B72 (left, water-wet after flushing) and B77 (right, oil-wet after flushing)
Figure 4.3.2.4 $D-T_2$ maps of 100% $S_w$, after forced brine imbibition and bulk SB for Texas Cream limestone L15 (left, water-wet after flushing) and L2 (right, oil-wet after flushing).
4.3.3 Effects of Wettability Alteration by OBM Surfactants on NMR Estimated $S_{wir}$

Qualitatively speaking, wettability alteration changes the relaxation time distributions of water and oil in the pore space. Therefore, $S_{wir}$ from NMR interpretation may be affected by this wettability alteration. This section first addresses the methodology of estimating $S_{wir}$ from NMR interpretation, and then shows the quantitative effects of OBM surfactant concentration and flushing volume on $S_{wir}$, and finally correlates $S_{wir}$ estimated from NMR with Amott-Harvey wettability indices.

4.3.3.1 Estimation of $S_{wir}$ from NMR Interpretation

Among the three models of $S_{wir}$ estimation from NMR as reviewed in section 4.1.2 ($T_2, \text{cutoff}$ model, spectral BVI model, and bi-exponential model), the traditional $T_2, \text{cutoff}$ model is used. This is for simplicity and to focus our study on the effect of wettability alteration on $S_{wir}$ estimation. Moreover, the $T_2, \text{cutoff}$ model works well for the Berea and Texas Cream limestone cores when they are at the original water-wet condition as shown below.

The determination of the specific $T_2, \text{cutoff}$ of the Berea cores used in this study is as follows. Each core was saturated with 100% $S_w$ and then de-saturated under air by centrifuge at 100 psi. $S_{wir}$ was measured by weighing the core. The measured value of $S_{wir}$ was then used to calculate the $T_2, \text{cutoff}$ at which the cumulative intensity of the relaxation time distribution at 100% $S_w$ equals the measured value of $S_{wir}$. From the Berea cores which have the air/brine de-saturation stage (34 of them) at the original water-wet
condition, $T_2$, cutoff was determined to be $32.9 \pm 3.0$ ms (Arithmetic mean) or $32.7 \pm 3.0$ ms (geometric mean).

$T_2$, cutoff of the Berea cores is very close to the default value of 33 ms. Figure 4.3.3.1 shows the cross-plot of measured $S_{\text{wir}}$ by weighing and estimated $S_{\text{wir}}$ from $T_2$, cutoff of 33 ms (100% $S_w$). They correlate very well with each other. $T_2$, cutoff of 33 ms was then used to estimate $S_{\text{wir}}$ after flushing for the Berea cores. Refer to Table C.1 of Appendix C for the individual $T_2$, cutoff values for each Berea core.

![Cross-plot of $S_{\text{wir}}$ by weighing and from $T_2$, cutoff of 33 ms for Berea cores at the original water-wet condition.](image)

**FIGURE 4.3.3.1** cross-plot of $S_{\text{wir}}$ by weighing and from $T_2$, cutoff of 33 ms for Berea cores at the original water-wet condition.

Before going to the determination of the specific $T_2$, cutoff for the Texas Cream limestone cores used in this study, it is worthy to point out one difference between the Berea and Texas Cream limestone cores. Figure 4.3.3.2 shows that for the Texas Cream
limestone cores the measured value of $S_{wir}$ of air/brine is much different from that of SB/brine. While for the Berea cores the measured values of $S_{wir}$ of air/brine, crude/brine or SB/brine are closer to each other.

![Comparison of measured $S_{wir}$ between air/brine, crude/brine and SB/brine for Berea and limestone cores.](image)

**FIGURE 4.3.3.2** Comparison of measured $S_{wir}$ between air/brine, crude/brine and SB/brine for Berea and limestone cores.

The different behavior between Berea and Texas Cream limestone as shown above can be explained by their capillary pressure curves. Figure 4.3.3.3 shows the calculated capillary pressure curves for Berea and Texas Cream limestone (refer to Appendix part A for details of the model calculation of capillary pressure curves). At a given capillary pressure of 100 psi, for Berea the calculated irreducible water saturation of air/brine from the capillary pressure curve is close to that of the SB/brine. However, for Texas Cream limestone the calculated irreducible water saturation of air/brine and SB/brine are much different. For reference, Table 4.3.3.1 lists the values of interfacial
tension and contact angle for air/brine and SB/brine systems used in the calculation of irreducible water saturation at water-wet condition. The interfacial tension was measured by pendent drop method and the contact angles were from the measurements of brine/glass slide/oil and brine/marble/oil systems by captive drop method (section 5.2.4).

![Graphs showing capillary pressure curves for Berea and limestone](image)

**FIGURE 4.3.3.3** Calculated capillary pressure curves of Berea and Texas Cream limestone showing much different wetting phase saturation between air/brine and SB/brine for Texas Cream limestone than for Berea at the same capillary pressure of 100 psi.

**TABLE 4.3.3.1** Interfacial tension and contact angle for air/brine and SB/brine systems

<table>
<thead>
<tr>
<th></th>
<th>Interfacial tension $\sigma$ (dyne/cm)</th>
<th>Contact angle $\theta$ (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berea</td>
<td></td>
<td></td>
</tr>
<tr>
<td>air/brine</td>
<td>72</td>
<td>0</td>
</tr>
<tr>
<td>SB/brine</td>
<td>18.5</td>
<td>15</td>
</tr>
<tr>
<td>Limestone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>air/brine</td>
<td>72</td>
<td>0</td>
</tr>
<tr>
<td>SB/brine</td>
<td>18.5</td>
<td>19</td>
</tr>
</tbody>
</table>

*: The reason for such low tension of SB/brine is not clear, but the value is duplicable.
The determination of the specific $T_{2, \text{cutoff}}$ for the Texas Cream limestone cores is slightly different from that for the Berea cores due to the reasons illustrated above. Because the wettability alteration and in turn its effect on $S_{\text{wir}}$ estimation were examined by flushing the SB/brine saturated Texas Cream limestone cores, the specific $T_{2, \text{cutoff}}$ value for each limestone core was determined to be the $T_2$ value at which the cumulative intensity of the relaxation time distribution at SB/brine equals to the measured value of $S_{\text{wir}}$ at SB/brine. $T_{2, \text{cutoff}}$ is $(34.7 \pm 3.1)$ ms for all the limestone cores studied at water-wet condition (17 of them).

4.3.3.2 Effects of Wettability Alteration on NMR Estimated $S_{\text{wir}}$

**Berea cores:** The effects of wettability alteration by the OBM surfactants on the estimation of $S_{\text{wir}}$ of the Berea cores from $T_{2, \text{cutoff}}$ model was examined by either centrifuging the 100% $S_w$ cores under (SB + OBM surfactants) or flushing the crude/brine or SB/brine saturated core with (SB + OBM surfactants). This corresponds to the OBM invasion of water-bearing zone or more realistic oil-bearing zone.

Two OBM surfactant systems of NOVA and BOO were used to examine the effect of OBM invasion of 100% brine saturated Berea cores on $S_{\text{wir}}$. As an example, Figure 4.3.3.4 shows the normalized incremental and cumulative $T_2$ distributions of Berea cores at 100% $S_w, S_{\text{wir}}$ with air, and $S_{\text{wir}}$ after centrifuging under (SB + NOVA). Core B4 was centrifuged under SB, while core B13 was centrifuged under (SB + 3% NOVA) and further flushed with 10 PV (SB + 3% NOVA). It shows that $T_{2, \text{cutoff}}$ of 33 ms gives a good estimation of $S_{\text{wir}}$ for B4 at SB/brine. However, for B13 after centrifuging under SB
+ 3% NOVA, $S_{wir}$ from $T_2$, cutoff of 33 ms is smaller than that measured from air/brine.

This effect is more obvious after further flushing with 10 PV SB + 3% NOVA.

**Incremental**

**Cumulative**

**Berea B4 (centrifuged under SB)**

**Berea B13 (centrifuged under SB + 3% NOVA)**

**FIGURE 4.3.3.4** Incremental and cumulative $T_2$ distributions for Berea B4 and B13 at 100% $S_w$, $S_{wir}$ with air, $S_{wir}$ with SB + NOVA and after flushing (only for B13)
All the four OBM surfactant systems were examined for the effect of OBM invasion of crude/brine saturated Berea core on $S_{\text{wir}}$. Figure 4.3.3.5 shows an example of the normalized incremental and cumulative $T_2$ distributions of Berea cores at 100% $S_w$, $S_{\text{wir}}$ with air, $S_{\text{wir}}$ with crude oil and after flushing. Berea B30 was flushed with 10 PV SB; while Berea B66 was flushed with 10 PV (SB + 3% BOO). It shows that for Berea B30 which remains strongly water-wet after flushing (Table 4.3.2.1), $T_{2\text{, cutoff}}$ of 33 gives a good estimation of $S_{\text{wir}}$ after flushing. As a comparison, for core B66 which is altered to be oil-wet after flushing (Table 4.3.2.1), the same $T_{2\text{, cutoff}}$ of 33 ms underestimates the measured value of $S_{\text{wir}}$ after flushing.

Figure 4.3.3.5 also shows that for the Berea cores at $S_{\text{wir}}$ with crude oil, $T_{2\text{, cutoff}}$ of 33 ms overestimates the measured value of $S_{\text{wir}}$. This is because the relaxation time of bulk crude oil interferes with that of the irreducible water (Figure 4.3.3.6). The $T_2$ of bulk crude oil has a long tail of short relaxation times below the $T_{2\text{, cutoff}}$ of 33 ms. The magnitude of overestimation is $(0.076 \pm 0.018)$ PV for all the Berea cores studied which have the crude/brine saturation stage (31 of them).
FIGURE 4.3.3.5 Incremental and cumulative $T_2$ distributions for Berea B30 and B66 at 100% $S_w$, $S_{wr}$ with air, $S_{wr}$ with crude oil and after flushing
FIGURE 4.3.3.6 Interference of $T_2$ relaxation time of bulk crude oil with that of irreducible water (Berea core B30)

**Texas Cream limestone cores**: The effects of wettability alteration by the OBM surfactants on the estimation of $S_{wir}$ of the Texas Cream limestone cores from $T_{2,\text{cutoff}}$ model was examined by flushing the SB/brine saturated core with (SB + OBM surfactants). Two OBM surfactant systems of NOVA and BOO were examined. Figure 4.3.3.7 shows an example of the normalized incremental and cumulative $T_2$ distributions of limestone cores at 100% $S_w$, $S_{wir}$ with air, $S_{wir}$ with SB and after flushing. Limestone L15 was flushed with 10 PV SB; while limestone L59 was flushed with 10 PV (SB + 3% BOO). It shows that the $T_{2,\text{cutoff}}$ determined in section 4.3.3.1 gives a good estimation of $S_{wir}$ after flushing when the core is still water-wet (L15). However, the $T_{2,\text{cutoff}}$
underestimates the measured value of $S_{wir}$ when the core is altered from water-wet to oil-wet (L59).

Incremental  
Cumulative

Limestone L15 (water-wet after flushing)

Limestone L59 (oil-wet after flushing)

FIGURE 4.3.3.7 Incremental and cumulative $T_2$ distributions for limestone L15 and L59 at 100% $S_w$, $S_{wir}$ with SB, and after flushing
4.3.3.3 Effect of OBM Surfactants Concentration

Section 4.3.3.2 showed examples of the $T_2$ distributions corresponding to the two extreme concentrations of OBM surfactants in the flushing fluid. This section summarizes the effect of OBM surfactants concentration on $S_{wir}$ including all the concentrations. Once again, the effects of wettability alteration by the OBM surfactants on the estimation of $S_{wir}$ of the Berea cores was examined by either centrifuging the 100% $S_w$ cores under (SB + OBM surfactants) or flushing the crude/brine or SB/brine saturated core with (SB + OBM surfactants). While the effect on the Texas Cream limestone cores was examined by flushing the SB/brine saturated core with (SB + OBM surfactants).

Figure 4.3.3.8 shows an example of the measured and estimated $S_{wir}$ for the 100% $S_w$ Berea cores centrifuged under (SB + NOVA) at different concentrations. After centrifuging under (SB + NOVA)/brine, $S_{wir}$ measured by weighing and estimated from $T_2$, cutoff both decrease when the concentration of NOVA in SB increases. Using $S_{wir}$ measured by weighing for air/brine saturated core as a comparison basis, which corresponds to no OBM invasion of 100% $S_w$ saturated core, Figure 4.3.3.9 shows that the magnitude of underestimated $S_{wir}$ from $T_2$, cutoff increases with the concentration of OBM surfactants in SB. Moreover, the magnitude of underestimation further increases after flushing.
FIGURE 4.3.3.8 $S_wir$ measured by weighing and estimated from $T_c$ of 33 ms for air/brine and (SB + surf.)/brine at different concentrations of NOVA. 0%: B4, 0.5%: B3, 1%: B19, 2%: B20, 3%: B13.

FIGURE 4.3.3.9 Magnitude of $S_wir$ underestimation with respect to the OBM surfactants concentration in the centrifuging fluid and further flushing fluid (Berea cores).
Figure 4.3.3.10 shows an example of the measured and estimated values of $S_{wir}$ for Berea cores flushed with OBM surfactant system of BOO at different concentrations. Measured $S_{wir}$ for air/brine and crude/brine, as well as estimated $S_{wir}$ for crude/brine and after flushing are shown for each core. As the concentration of BOO in the flushing fluid increases, $S_{wir}$ was more severely underestimated after flushing. Once more, the estimated $S_{wir}$ for crude/brine is overestimated because of the tail of the crude oil relaxation time distribution (Figure 4.3.3.6).

![Graph showing $S_{wir}$ values](image)

**FIGURE 4.3.3.10** $S_{wir}$ measured by weighing (air/brine and crude/brine) and estimated from $T_{2,\text{cutoff}}$ of 33 ms (crude/brine and after flushing) at different concentrations of BOO. 0%: B30, 0.5%: B16, 1%: B45, 2%: B58, 3%: B66.

Figure 4.3.3.11 shows the effects of concentration on Berea cores for the four OBM surfactant systems studied. Delta $S_{wir}$ is the magnitude of $S_{wir}$ underestimation
defined as $S_{wir, \text{weighing}} - S_{wir, T2, \text{cutoff}}$. It generally increases with the concentration of OBM surfactant in the flushing fluid. Among the four OBM surfactant systems, NOVA and BOO underestimate the $S_{wir}$ more seriously than VERSA, with LLD in between. These differences are consistent with the Amott-Harvey wettability indices as discussed later in this chapter. Figure 4.3.3.12 shows the similar trend of the effects of concentration on the Texas Cream limestone cores for NOVA and BOO.
FIGURE 4.3.3.11 Magnitude of $S_{swr}$ underestimation with respect to the OBM surfactants concentration in the flushing fluid (Berea cores).

FIGURE 4.3.3.12 Magnitude of $S_{swr}$ underestimation with respect to the OBM surfactant concentration in the flushing fluid (Texas Cream limestone cores).
4.3.3.4 Effects of Flushing Volume

The effects of flushing volume on the estimation of $S_{wir}$ was investigated using (SB + 3% BOO) for both Berea and limestone cores. Figure 4.3.3.13 shows that the estimated $S_{wir}$ starts to obviously deviate from the measured value after about 3 PV flushing, and it reaches a plateau after about 7 PV flushing. It suggests that the fluid loss control in the drilling process may be a key factor in minimizing the NMR misinterpretation due to OBM invasion.

![Graph showing effects of flushing volume on $S_{wir}$ for Berea B40 and Texas Cream limestone L8](image)

FIGURE 4.3.3.13 Effects of flushing volume on $S_{wir}$ underestimation for Berea B40 (top) and Texas Cream limestone L8 (bottom)
4.3.3.5 Correlations of $S_{wir}$ Underestimation with Amott-Harvey Wettability Indices

Figure 4.3.3.14 shows the correlation between the magnitude of $S_{wir}$ underestimation and the corresponding Amott-Harvey index. Here the four OBM surfactant systems were not differentiated. In the intermediate-wet to oil-wet region, the magnitude of underestimation increases linearly with the decrease of the Amott-Harvey index ($R^2 = 0.81$ for the Berea cores and $R^2 = 0.67$ for the Texas Cream limestone cores).

![Graph showing the correlation between $S_{wir}$ underestimation and Amott-Harvey index for Berea and Texas Cream limestone cores.](image)

FIGURE 4.3.3.14 Magnitude of $S_{wir}$ underestimation versus Amott-Harvey index for Berea and Texas Cream limestone cores.

When extrapolated to Amott-Harvey index of -1, which corresponds to strongly oil-wet condition, the magnitude of underestimation is about 0.126 for the Berea cores and 0.078 for the limestone cores. These values are reasonable in the sense that they are
smaller than $S_{wir}$ measured from weighing (0.224 ± 0.011 PV for all the Berea cores studied and 0.173 ± 0.006 PV for all the Texas Cream limestone cores studied). It suggests that even when the core has been altered to be strongly oil-wet, there is still some water remaining in the small pores. As expected, in the water-wet region, Delta $S_{wir}$ is around zero, which means that there is no underestimation.

The implication of Figure 4.3.3.14 is that if in reality, the wettability alteration is controlled to be only intermediate-wet, then $S_{wir}$ will not be severely underestimated by the default $T_2$ cutoff for water-wet condition.

4.3.4 Mechanism of $S_{wir}$ Underestimation and Modifications of NMR Interpretation When Wettability Alteration Occurs

The above sections show that after OBM flushing of crude/brine or SB/brine saturated Berea or Texas Cream limestone cores, $S_{wir}$ is underestimated when wettability alteration occurs. But how much of the underestimation is due to the actual change of $S_{wir}$ (physically flushed out of the pore space or due to emulsification of water by OBM surfactants)? This question was examined by the quantitative Karl-Fisher analysis of the water amount in the flushing effluents.

Figure 4.3.4.1 shows the amount of water in the flushing effluent, as well as the measured and estimated $S_{wir}$ after flushing for Berea B31 (flushed with 10 PV SB), B26 (flushed with 10 PV (SB+3% NOVA)) and B66 (flushed with 10 PV (SB+3% BOO)). It shows that the amount of water in the flushing effluent is relatively small compared with the total amount of $S_{wir}$ underestimation. It means that the actual $S_{wir}$ does not change much due to wettability alteration.
Figure 4.3.4.1 Karl-Fisher analysis of water amount in the flushing effluents, B31: flushed with 10 PV SB, B66: flushed with 10 PV (SB + 3% BOO), B26: flushed with 10 PV (SB + 3% NOVA).

The mechanism of $S_{\text{wir}}$ underestimation due to wettability alteration is also visualized by the $D-T_2$ maps. Figure 4.3.4.2 shows the $D-T_2$ maps of Berea B77 at 100% $S_w$ and after flushing with 10 PV (SB + 3% NOVA). The vertical dash line corresponds to $T_{2, \text{cutoff}}$ of 33 ms. By definition, for 100% $S_w$ at strongly water-wet condition (top plot of Figure 4.3.4.2), water with $T_2$ relaxation time below the $T_{2, \text{cutoff}}$ corresponds to irreducible water. However, due to the wettability alteration of B77 from water-wet to oil-wet after flushing (Table 4.3.2.1), some of the irreducible water relaxes above the $T_2$, $\text{cutoff}$ value after flushing (bottom plot of Figure 4.3.4.2), and the amount of water relaxing below the $T_{2, \text{cutoff}}$ decreases significantly. If the wettability alteration is not noticed and the same $T_{2, \text{cutoff}}$ of 33 ms as for water-wet condition is used, $S_{\text{wir}}$ will be underestimated.
100% $S_w$

![Graph of $D-T_2$ maps of 100% $S_w$ and after flushing with 10 PV (SB + 3% NOVA) for Berea B77. The vertical dashed line corresponds to $T_{2, \text{cutoff}}$ of 33 ms.](image)

FIGURE 4.3.4.2 $D-T_2$ maps of 100% $S_w$ and after flushing with 10 PV (SB + 3% NOVA) for Berea B77. The vertical dashed line corresponds to $T_{2, \text{cutoff}}$ of 33 ms.)
The mechanism of $S_{\text{swir}}$ underestimation as illustrated above confirms that a larger value of $T_{2, \text{cutoff}}$ should be used when wettability alteration occurs. Figure 4.3.4.3 quantitatively shows that for both Berea and limestone, the larger the magnitude of $S_{\text{swir}}$ underestimation, the larger the modified $T_{2, \text{cutoff}}$ value should be. The coefficients of the linear correlation are $R^2 = 0.90$ for the Berea cores and $R^2 = 0.78$ for the Texas Cream limestone cores.

\begin{center}
\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure}
\caption{FIGURE 4.3.4.3 Modified values of $T_{2, \text{cutoff}}$ versus magnitude of $S_{\text{swir}}$ underestimation for both Berea cores and Texas Cream limestone cores.}
\end{figure}
\end{center}

Finally, Figure 4.3.4.4 shows the correlation between the modified values of $T_2$, $\text{cutoff}$ versus the Amott-Harvey index. In the region of intermediate-wet to oil-wet, they
generally correlate with each other. The coefficients of linear correlation are $R^2 = 0.72$ for the Berea cores and $R^2 = 0.40$ for the Texas Cream limestone cores. The worse linear correlation for the Texas Cream limestone cores could be due to less data points of the limestones than that of the Berea. As expected, at the water-wet region, there is no need for modification.

![Graph showing modified values of $T_2$, cutoff versus Amott-Harvey wettability index for both Berea cores and Texas Cream limestone cores.](image)

**FIGURE 4.3.4.4** Modified values of $T_2$, cutoff versus Amott-Harvey wettability index for both Berea cores and Texas Cream limestone cores.

### 4.4 Conclusions

$T_1$, $T_2$ bulk relaxation time distributions of the OBM surfactants generally range over two or three orders of magnitude, indicating that the OBM surfactants are mixture of
many components. Their short $T_1$, $T_2$ relaxation time and $T_1/T_2$ ratio being larger than unity suggest that the OBM surfactants are composed of heavy components.

Wettability alteration of Berea and Texas Cream limestone by the OBM surfactants are examined. The originally water-wet Berea and Texas Cream limestone are altered to be at least intermediate-wet or even oil-wet by the OBM surfactants, depending on the type, the flushing volume and their concentration in the flushing fluid. These wettability alteration determined by Amott-Harvey wettability index measurements is also visualized by the NMR $D$-$T_2$ measurements.

Effect of wettability alteration on $S_{wr}$ estimated from NMR $T_{2,\text{cutoff}}$ model is investigated. $T_{2,\text{cutoff}}$ model works well for the Berea and Texas Cream limestone when they are at their original water-wet condition. However, for an oil-bearing rock, $S_{wr}$ from $T_{2,\text{cutoff}}$ model after flushing generally underestimates the measured value of $S_{wr}$ due to wettability alteration from water-wet to intermediate-wet or oil-wet. The magnitude of underestimation correlates with the Amott-Harvey index.

Modification of the $T_{2,\text{cutoff}}$ model when wettability alteration occurs is proposed. Since the actual $S_{wr}$ after OBM flushing for an oil-bearing rock does not change much but is underestimated by the default $T_{2,\text{cutoff}}$ at water-wet condition, a larger value of $T_{2,\text{cutoff}}$ can be used to estimate $S_{wr}$ when wettability alteration occurs. The modified value of $T_{2,\text{cutoff}}$ correlates with the Amott-Harvey index.

This study also shows that for the crude/brine saturated Berea, $T_{2,\text{cutoff}}$ model overestimates the measured value of $S_{wr}$. This is due to the interference of bulk relaxation time of the crude oil used in this study with that of the irreducible water. It suggested that in crude oil bearing zone/formation, $T_{2,\text{cutoff}}$ for $S_{wr}$ estimation needs to be modified.
Chapter 5  Study of Wettability from NMR Method

This chapter illustrates the quantitative connection between wettability and NMR relaxation time. First, it demonstrates the nature of wettability effects on NMR relaxation time by $\rho_{2,\text{eff}}$, the effective surface relaxivity. Then it shows that the quantitative change of $\rho_{2,\text{eff}}$ of either water or oil is directly related with wettability alteration. Finally, it proposes and tests a novel NMR model to quantify rock wettability by two NMR indices from either water or oil relaxation time.

5.1 Literature Review

Wettability is defined as “the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids” (Craig, 1971). Wettability is very important in porous media because it controls the location, flow and fluid distributions. It also affects capillary pressure, relative permeability, waterflood behavior, irreducible water saturation, residual oil saturation and so on (Anderson, 1986). Therefore, it is desirable to know the in-situ wettability condition of the formation. The traditional methods of quantifying wettability include contact angle, Amott-Harvey wettability index and combined Amott USBM methods.

Fatt (1956) started the pioneering work using uncoated sand as water-wet porous media and Dri-film treated sand as oil-wet porous media. They found that water relaxed faster in the water-wet system than in the oil-wet system. Moreover, they also found that the relaxation time of water in the mixture of oil-wet and water-wet sand varied linearly with the percentage of the oil-wet sand. These observations were confirmed by later work by Saraf et al. (1970) with water-wet glass bead and oil-wet polymer bead.

The link between wettability and NMR relaxation was also explored when both water and oil were present, which is more representative of oil reservoirs. Øren et al. (1994) studied $T_1$ relaxation time of water-wet Berea sandstones at various saturations during low rate water imbibition displacements. They found that oil relaxed at its bulk value when a continuous water film spread over the pore surfaces. Straley et al. (1995) obtained similar results for kerosene/water partially saturated sandstone, in which kerosene relaxed at its bulk value, rather than the shorter $T_1$ when kerosene fully saturated the dry sandstone. Studies for intermediate-wet sandstone (Borgia, et al., 1991, Rueslåtten, et al., 1994) also showed that information about wettability and oil-water configurations could be determined from NMR relaxation time.

Similar studies were done for carbonate samples. Hsu et al. (1992) measured $T_1$ of water in carbonate cores with different wetting characteristics. They found that $T_1$ relaxation rate of water in oil-wet cores was about 50% less than that in water-wet cores. Howard (1994, 1998) studied NMR $T_1$ and $T_2$ relaxation time of water-wet and oil-wet fine-grained chalks at different water saturations. He founded that wettability and water saturation could be determined from the relaxation time distributions, and that the estimated water saturation correlated well with the core analysis value.
NMR technique was also used to detect the wettability condition of rock or soil samples with different fluid combinations (Devereux, et al., 1967, Zhang, et al., 2000, Manalo, et al., 2003). Devereux et al. (1967) founded that the adsorption of surface-active components such as asphaltene from the crude oil could change the surface relaxation rate of water, indicating that the wettability of the rock surface was changed. Zhang et al. (2000) founded that Bentheim and Berea sandstones were water-wet with refined oil, but became mixed-wet with crude oil after aging. Manalo et al. (2003) reported that the wettability of their soil samples can be determined by using low field NMR, which was shown to provide more consistent results than the traditional ethanol droplet and water drop penetration time methods.

In summary, numerous studies as reviewed above showed that NMR could determine the wettability condition of rock samples. However, the quantitative connection between wettability and NMR characteristic parameter has been investigated by only a few studies (Howard, 1998, Guan, et al., 2002, Fleury, et al., 2003). The objective of this study is to quantitatively examine the connection between wettability and NMR surface relaxivity, and to propose a NMR model to characterize rock wettability.

5.2 Materials and Experimental Procedures

This section first lists the main materials used in this chapter with their physical properties, and then illustrates the experimental procedures. The materials include unconsolidated silica flour and calcite, Berea cores, base oils, model surfactants and OBM surfactants. Among them, the Berea cores and OBM surfactants have been
introduced in Chapter 4 and will not be introduced again here. The experimental procedures introduce preparation of saturations for the unconsolidated silica flour and calcite, and the contact angle measurements.

5.2.1 Unconsolidated Silica Flour and Calcite

Unconsolidated silica flour (U.S. Silica Company) and calcite (Solvay Minerals Company) were used in this study. Silica flour and calcite were selected to stand for the silicate and carbonate material, which are the two common mineral materials in the reservoir formation. Table 5.2.1.1 lists the mean diameter and BET surface area for the silica flour and calcite particles. The two samples in the group of silica flour and calcite are very similar to each other, respectively. But we label them separately due to slight difference in the BET surface area.

| TABLE 5.2.1.1 Mean diameter and BET surface area of the silica flour and calcite |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Sample          | Silica flour    | Calcite         |
|                 | # 1 | # 2 | # 1 | # 2 |
| Mean diameter (µm) | 1.7 | 1.3 | 0.07 | 0.07 |
| BET surface area (m²/g) | 2.0 | 2.2 | 21.8 | 17.9 |
| Grain density (g/cm³) | 2.65 |    | 2.71 |    |

5.2.2 Base Oils and Model Surfactants

Base oils of Escaid and SB (refer to chapter 4 for properties of SB) were used in this study as the hydrocarbon phase. Escaid is a light hydro-treated petroleum distillate with a density of 0.80g/ml and viscosity of 1.78 cp.

Besides the OBM surfactants (refer to chapter 4 for more information), two model surfactants of dodecylamine (DDA) and stearic acid (SA) were used in this study. DDA
is a cationic surfactant and SA is an anionic surfactant. We picked DDA and SA because they stand for the two typical groups of surfactants and are similar in structure to the OBM surfactants.

5.2.3 Saturation Preparation for the Unconsolidated Silica Flour and Calcite

The procedure of the 100% water or 100% oil saturation of the silica flour or calcite is as follows. The oven dried silica flour or calcite particles were slowly added into water or oil in a beaker and stirred with a magnet bar. The slurry was then centrifuged at 2800 rpm for 15 minutes. The supernatant liquid layer was removed after centrifuge.

The procedure of water/oil partial saturation of the silica flour or calcite is as follows. First the slurry of 100% water saturation was removed into a large, flat Petri dish to be heated in an oven at 80 °C. The particles were stirred during heating to make the sample homogeneous. Since they stuck together due to water evaporation, the particles were then ground by a pestle in a mortar before they were added to an excess amount of oil in a centrifuge tube. Ultra-sonication was then performed to further separate the stuck particles. Finally, the sample was centrifuged at 2800 rpm for 15 minutes and the supernatant liquid layer removed. The sample was weighed in each step to determine the porosity and water saturation.

5.2.4 Contact Angle Measurements

The captive drop method (Yang, 2000) was used in this study to measure the contact angles of brine/glass slide/oil or brine/marble/oil systems. The glass slide or
marble plate was cleaned using methanol and acetone. The marble plate was further polished under DI water. Both receding and advancing contact angles were measured. A microburet was filled with oil and placed about 2 mm above the substrate surface of glass slide or marble plate, which was equilibrated with brine in a glass cell. For the receding contact angle, an oil drop was slowly formed and pressed against the substrate surface, and then the receding contact angle was measured with the goniometer after 30 minutes. For the advancing contact angle, the oil drop was then slowly withdrawn from the substrate surface until the contact line moved. The advancing contact angle was measured after another 30 minutes.

5.3 Experimental Results and Discussions

Qualitatively speaking, wettability and NMR surface relaxation are related. Since wettability controls the fluid distribution and the affinity of fluid with the surface. While NMR surface relaxation determines that whichever fluid contacting the surface has a relaxation time much shorter than that of the bulk fluid.

This section first presents the experimental results of wettability alteration of silicate (glass slide) and carbonate (marble) surfaces by DDA, SA and OBM surfactants, then uses these cases of wettability alteration to quantitatively demonstrate that wettability affects NMR surface relaxation through the change of the effective surface relaxivity, and finally proposes and tests NMR wettability indices to characterize rock wettability.
5.3.1 Wettability Alteration of Silicate and Calcite Surface

Cases of wettability alteration of silicate and calcite surfaces by DDA and SA were detected by the contact angle measurements. Figure 5.3.1.1 shows that the glass surface is preferentially water-wet when the oil phase is pure escaid or escaid plus 0.5% SA, but the glass surface becomes oil-wet when the oil phase is escaid plus 0.74% DDA. For the marble surface, Figure 5.3.1.2 shows that it is preferentially water-wet in both receding and advancing directions when the oil phase is pure SB or SB plus 0.74% DDA, but the marble surface becomes oil-wet in advancing direction when the oil phase is SB plus 0.5% SA. All these wettability alterations refer to the surface which is in contact with the oil.

The wettability alteration shown above is due to the surfactant adsorption. Because cationic surfactant DDA has a positively charged head group, it can adsorb onto the negatively charged silicate surface but not onto the positively charged calcite surface. By contrast, SA is an anionic surfactant with a negatively charged head group, which adsorbs onto the calcite surface but not onto the silicate surface.

Cases of wettability alteration of silicate and calcite surfaces by the OBM surfactants were also detected by the contact angle measurements. Figure 5.3.1.3 shows that 0.5% wt OBM surfactants present in the oil phase change the originally water-wet glass surface to oil-wet in advancing direction. Similarly, Figure 5.3.1.4 shows that marble surface changes to oil-wet in both receding and advancing directions by 0.5% wt OBM surfactants in the oil phase.

Data of the contact angles as illustrated above are summarized in Table C.2 and C.3 in Appendix C.
FIGURE 5.3.1.1 Contact angles of brine/glass slide/oil systems. Oil phase: escaid, escaid plus 0.74% DDA and escaid plus 0.5% SA.

FIGURE 5.3.1.2 Contact angles of brine/marble/oil systems. Oil phase: SB, SB plus 0.74% DDA and SB plus 0.5% SA.
FIGURE 5.3.1.3 Contact angles of brine/glass slide/oil systems. Oil phase: SB, SB plus 0.5% OBM surfactants LLD, BOO, VERSA and NOVA.

FIGURE 5.3.1.4 Contact angles of brine/marble/oil systems. Oil phase: SB, SB plus 0.5% OBM surfactants LLD, BOO, VERSA and NOVA.
5.3.2 Effect of Wettability Alteration on Surface Relaxivity for Water/oil Partially Saturated Silica Flour and Calcite

For 100% $S_w$ or 100% $S_o$, surface relaxivity $\rho_2$ is calculated by Equation (5.3.2.1), assuming that relaxation due to diffusion is negligible,

$$\rho_2 = \frac{V_p}{A_T} \frac{1}{T_2} - \frac{1}{T_{2,b}}$$  \hspace{1cm} (5.3.2.1)

Where $V_p$ and $A_T$ are the total pore volume and surface area, respectively.

Similarly, for water/oil partial saturation, surface relaxivity of water and oil are calculated as follows,

$$\rho_{2,w} = \frac{V_w}{A_w} \frac{1}{T_{2,w}} - \frac{1}{T_{2,w,b}}$$  \hspace{1cm} (5.3.2.2)

$$\rho_{2,o} = \frac{V_o}{A_o} \frac{1}{T_{2,o}} - \frac{1}{T_{2,o,b}}$$  \hspace{1cm} (5.3.2.3)

Where $\rho_{2,w}$ and $\rho_{2,o}$ are based on the actual surface area ($A_w$, $A_o$) and pore volume ($V_w$ and $V_o$) covered by water and oil phase, respectively.

To demonstrate the effect of wettability on NMR response, Equations (5.3.2.2) and (5.3.2.3) are rearranged as follows,

$$\rho_{2,w, eff} = \rho_{2,w} \frac{A_w}{A_T} = \frac{V_p}{A_T} S_w \left( \frac{1}{T_{2,w}} - \frac{1}{T_{2,w,b}} \right)$$  \hspace{1cm} (5.3.2.4)

$$\rho_{2,o, eff} = \rho_{2,o} \frac{A_o}{A_T} = \frac{V_p}{A_T} S_o \left( \frac{1}{T_{2,o}} - \frac{1}{T_{2,o,b}} \right)$$  \hspace{1cm} (5.3.2.5)

Where $S_w$ and $S_o$ are water and oil saturation, respectively. Qualitatively speaking, since wettability determines both the surface coverage of the pore fluid and its affinity...
with the mineral surface (Hirasaki, 1991), it affects $\frac{A_w}{A_T} \left( \frac{A_0}{A_T} \right)$ and $\rho_{2,w} \left( \rho_{2,o} \right)$. Therefore, the product of surface relaxivity and surface coverage of the corresponding phase is combined as an effective surface relaxivity.

The quantitative effect of wettability on surface relaxivity is investigated with water/oil partially saturated silica flour and calcite using the cases of wettability alteration as detected in section 5.3.1. Two cases were compared. In one case the oil phase is pure base oil. In the other case, the oil phase is base oil plus a specified amount of surfactant. The surfactant could be the model surfactant of DDA and SA, or the OBM surfactant systems of LLD, VERSA, NOVA, and BOO.

Figure 5.3.2.1 shows that for silica flour partially saturated with water and pure escaid, $\rho_{2,w,eff}$ is about the same as that of 100% $S_w$, and $\rho_{2,o,eff}$ is much less than that of 100% $S_o$. This is because the silica flour is still preferentially water-wet when the oil phase is pure escaid (Figure 5.3.1.1). Therefore, the affinity of the water phase with the surface is about the same as that of 100% $S_w$, and almost all the surface area of the silica flour particles is covered by water, which means that $A_w \approx A_T$ and $A_0 < A_T$ (Equation (5.3.2.4) and (5.3.2.5)). In comparison, for silica flour partially saturated with water and Escaid plus 0.74% DDA, $\rho_{2,w,eff}$ decreases and $\rho_{2,o,eff}$ increases. This is because now the silica flour surface changes to be partially oil-wet or locally oil-wet (Figure 5.3.1.1) due to DDA adsorption. Therefore, both the surface coverage by water and its affinity with the surface decrease, resulting in decreased $\rho_{2,w,eff}$ according to Equation (5.3.2.4). For
the oil phase, both the surface coverage and affinity increase, leading to increased $\rho_{2,0,\text{eff}}$ according to Equation (5.3.2.5).

For the same reason, Figure 5.3.2.2 shows that for calcite partially saturated with water and pure SB, in which the calcite is still preferentially water-wet (Figure 5.3.1.2), $\rho_{2,\text{w,eff}}$ is about the same as that of 100% $S_w$, and $\rho_{2,0,\text{eff}}$ is much less than that of 100% $S_o$. However, for calcite partially saturated with water and SB plus 0.5% SA, in which the calcite surface becomes partially or locally oil-wet (Figure 5.3.1.2) due to SA adsorption, $\rho_{2,\text{w,eff}}$ decreases and $\rho_{2,0,\text{eff}}$ increases.

Without wettability alteration, surface relaxivity of either water or oil is unchanged, as shown by two cases. One case is for water/oil partially saturated silica flour with the oil phase being pure escaid versus escaid plus 0.5% SA (Figure 5.3.2.3). The other case is for water/oil partially saturated calcite with the oil phase being pure SB versus SB plus 0.74% DDA (Figure 5.3.2.4). In both cases, no wettability alteration occurs due to any surfactant adsorption (Figure 5.3.1.1 and 5.3.1.2). As a result, $\rho_{2,\text{w,eff}}$ and $\rho_{2,0,\text{eff}}$ is unchanged.
FIGURE 5.3.2.1 $T_2$ relaxation time distribution (a) and the effective surface relaxivity of water and/or oil (b) at 100% $S_w$, 100% $S_o$, 30% $S_w$ with pure oil (Escaid) and 30% $S_w$ with oil plus DDA (0.74% wt), silica flour.
(a) $T_2$ distribution

$$f$$

$T_2$ (ms)

- 40% Sw, SB
- 100% Sw
- Bulk SB
- 43% Sw, SB + SA
- 100% So
- Bulk water

(b) Surface relaxivity

FIGURE 5.3.2.2 $T_2$ relaxation time distributions (a) and the effective surface relaxivity of water and/or oil (b) at 100% $S_w$, 100% $S_o$, 40% $S_w$ with pure oil (SB) and 43% $S_w$ with oil plus SA (0.5% wt), calcite.
FIGURE 5.3.2.3 $T_2$ relaxation time distributions and the effective surface relaxivity of water and oil at 21% $S_w$ with pure oil (escaid) and 21% $S_w$ with oil plus SA (0.5% wt), silica flour.

FIGURE 5.3.2.4 $T_2$ relaxation time distributions and the effective surface relaxivity of water and oil at 38% $S_w$ with pure oil (SB) and 43% $S_w$ with oil plus DDA (0.74% wt), calcite.
Results shown above are for the model surfactants of DDA and SA. They provide some comparison basis for the results with the OBM surfactants of LLD, VERSA, NOVA, and BOO as shown below.

The effect of wettability alteration by the OBM surfactants on NMR surface relaxation of water/oil partially saturated silica flour behaves similarly to that by model surfactant DDA. Figure 5.3.2.5 shows that $\rho_{2,w,\text{eff}}$ decreases and $\rho_{2,o,\text{eff}}$ increases when there is 0.12% LLD in the oil phase. This effect of surface relaxivity shift is stronger when the concentration of LLD in the oil phase is larger. Similarly, the addition of OBM surfactants VERSA, NOVA and BOO in the oil phase also bring a shift of surface relaxivity of both water and oil (Figure 5.3.2.6). That is, $\rho_{2,w,\text{eff}}$ decreases and $\rho_{2,o,\text{eff}}$ increases.

The effect of wettability alteration by the OBM surfactants on NMR surface relaxation of water/oil partially saturated calcite is somewhat unexpected. Because contact angle measurements as in Figure 5.3.1.3 and Figure 5.3.1.4 show that the OBM surfactants alter both the preferential water-wet glass slide and calcite, it was expected that the OBM surfactants present in the oil phase would bring similar surface relaxivity shift on silica flour to that on calcite. However, when the concentration of OBM surfactants in the oil phase is 1%, Figure 5.3.2.7 shows that $T_2$ relaxation time and surface relaxivity do not change much for either water or oil for water/oil partially saturated calcite. Our speculation was that the local concentration of OBM surfactants on the calcite surface may be too small to bring any $T_2$ shift for either water or oil. This could be due to the high molecular weight of the OBM surfactants, as suggested by their
short $T_1$, $T_2$ relaxation times (Chapter 4, section 4.3.1), and the high surface area of the calcite particles (Table 5.2.1.1).

This speculation was examined by the calculation of local concentration of OBM surfactants on silica flour or calcite surfaces for several cases mentioned above. It was assumed that all of the surfactants in the oil phase adsorb onto the surface, which gives a maximum local concentration of surfactants for comparison. Since the molecular weight of the emulsifiers and oil-wetting agents is unknown, the x-axis in Figure 5.3.2.8 was plotted as the ratio of molecular weight of OBM surfactants to that of SA, the model surfactant used before. Figure 5.3.2.8 shows that the surface area covered by one molecule of OBM surfactants on the calcite surface (case 3) is about 10 times larger than that on silica flour surface (case 2), and is about 50 times larger than that of SA on the calcite surface (case 1) when the molecular weight of emulsifier or oil-wetting agent is 100 times larger than that of SA. This means that the local concentration of emulsifiers or oil-wetting agents on the calcite surface may be too small to bring any $T_2$ shift for either water or oil.

Surface relaxivity values of water and oil in 100% $S_w$, 100% $S_o$ and water/oil partially saturated silica flour and calcite are summarized in Table C.4 in Appendix C.
FIGURE 5.3.2.5 Comparison of $T_2$ relaxation time distributions (a) and the effective surface relaxivity (b) of water and oil for 18% $S_w$ saturated silica flour (#2) among cases with different concentration of LLD in the oil phase of SB.
FIGURE 5.3.2.6 $T_2$ relaxation time distribution (a) and surface relaxivity (b) of water or oil for silica flour (# 2) saturated with 40% $S_w$ with SB, 40% $S_w$ with SB + 1% BOO, 40% $S_w$ with SB + 1% VERSA, 36% $S_w$ with SB + 1% NOVA and 40% $S_w$ with SB + 1% LLD.
FIGURE 5.3.2.7 $T_2$ relaxation time distribution (a) and surface relaxivity (b) of water and oil for calcite (# 2) saturated with 49% $S_w$ with SB, 50% $S_w$ with SB + 1% LLD, 55% $S_w$ with SB + 1% BOO, 52% $S_w$ with SB + 1% VERSA and 61% $S_w$ with SB + 1% NOVA.
FIGURE 5.3.2.8 Surface area per molecule of the OBM surfactants versus the ratio of the molecular weight of the OBM surfactants to that of SA. Assumption: all of the OBM surfactants adsorb on the mineral surface.
5.3.3 NMR Wettability Index and Correlations with Amott-Harvey Index

The previous sections demonstrated that the effective surface relaxivity of water and oil is related with the wettability condition. Based on the concept of the effective surface relaxivity, this section proposes two wettability indices from NMR relaxation times to characterize rock wettability.

The NMR wettability indices are defined as the normalization of the effective surface relaxivity with respect to the maximum surface relaxivity. By this definition, their values are between 0 and 1.

\[ I_{W}^{\text{NMR}} = \frac{\rho_{2,\text{w,eff}}}{\rho_{2,\text{w,max}}} \]  \hspace{1cm} (5.3.3.1)

\[ I_{o}^{\text{NMR}} = \frac{\rho_{2,\text{o,eff}}}{\rho_{2,\text{o,max}}} \]  \hspace{1cm} (5.3.3.2)

Where \( I_{W}^{\text{NMR}} \) is NMR water wettability index and \( I_{o}^{\text{NMR}} \) is NMR oil wettability index.

Similar to the definition of the Amott-Harvey index, the difference between the NMR water wettability index and the NMR oil wettability index defines a combined NMR wettability index,

\[ I_{C}^{\text{NMR}} = I_{W}^{\text{NMR}} - I_{o}^{\text{NMR}} \]  \hspace{1cm} (5.3.3.3)

For water, \( \rho_{2,\text{w,max}} \) corresponds to 100% \( S_{w} \) at strongly water-wet condition.

Substitute Equations (5.3.2.1) and (5.3.2.4) into (5.3.3.1), we have,

\[ I_{W}^{\text{NMR}} = \left( \frac{1}{T_{2,\text{w}}} - \frac{1}{T_{2,\text{w,B}}} \right) \cdot S_{w} \cdot I\left( \frac{1}{(T_{2,\text{w},S_{w}=1})_{\text{water wet}}} - \frac{1}{T_{2,\text{w,B}}} \right) \]  \hspace{1cm} (5.3.3.4)
Similarly, for oil, $\rho_{2,O,max}$ corresponds to 100% $S_o$ at strongly oil-wet condition.

Substitute Equations (5.3.2.1) and (5.3.2.5) into (5.3.3.2), we have,

$$I_0^{\text{NMR}} = \left( \frac{1}{T_{2,0}} - \frac{1}{T_{2,0,B}} \right) \cdot S_o \bigg/ \left( \frac{1}{(T_{2,O,S_o=1})_{\text{oil wet}}} - \frac{1}{T_{2,O,B}} \right)$$  (5.3.3.5)

The definition of NMR water and oil wettability indices as shown above cancels out other factors affecting the effective surface relaxivity such as mineralogy, pore structure, concentration of paramagnetic impurities on the surface. Thus only the factor of wettability is examined.

The model of NMR wettability indices was tested by comparing with the independent Amott-Harvey wettability index. The test samples are the Berea cores used in Chapter 4 (Table 4.3.2.1). Correlations between NMR water and oil wettability indices and Amott-Harvey wettability indices are shown by water relaxation time after forced brine imbibition and oil relaxation time after forced oil drainage, which were obtained from NMR $D-T_2$ measurements (Chapter 4, section 4.2.6). The reasons for selecting these two cases are that the saturation for brine after forced imbibition and for oil after forced drainage is relatively higher, so that better signal to noise ratio of the NMR $D-T_2$ measurements is gained for the corresponding water and oil phase.

For the NMR water wettability index (Equation 5.3.3.4), $(T_{2,w,S_w=1})_{\text{water wet}}$ and $T_{2,w}$ correspond to the log mean (data point in Figure 5.3.3.1 used log mean) or mode (data point in Figure 5.3.3.2 used mode) value of the $T_2$ relaxation time distributions of water at 100% $S_w$ and after forced brine imbibition, respectively. Once again, the $T_2$
relaxation time distributions of water after forced brine imbibition are from the $D-T_2$ measurements. In both cases when $T_2$ log mean or mode is used in the calculation, the NMR water wettability index correlates well with the Amott-Harvey wettability index. The coefficient of linear correlation is $R^2 = 0.87$ when $T_2$ log mean is used (Figure 5.3.3.1) and $R^2 = 0.93$ when $T_2$ mode is used (Figure 5.3.3.2).

![Graph showing the correlation between NMR water wettability index and Amott-Harvey index. The equation of the linear regression line is $y = 0.41x + 0.52$ with $R^2 = 0.87$.](image)

**FIGURE 5.3.3.1** Correlation between NMR water wettability index and Amott-Harvey index, log mean values of the $T_2$ relaxation time distributions of water are used.
FIGURE 5.3.3.2 Correlation between NMR water wettability index and Amott-Harvey index, mode values of the $T_2$ relaxation time distributions of water are used.

For the NMR oil wettability index (Equation 5.3.3.4), $(T_{2,o,S_o=1})_{oil\: wett}$ and $T_{2,o}$ correspond to the mode value of the $T_2$ relaxation time distributions of oil at 100% $S_o$ saturation (SB + OBM surfactants) and after forced oil drainage, respectively. Once again, The $T_2$ relaxation time distributions of oil after forced oil drainage are from the $D$-$T_2$ measurements. The $T_2$ log mean value was not used for the NMR oil wettability index. This is because at 100% $S_o$ saturation the smallest pores are filled with oil, but after forced oil drainage the smallest pores are filled with irreducible water.

Figure 5.3.3.3 shows that in the intermediate-wet to oil-wet region, NMR oil wettability index correlates well with the Amott-Harvey wettability index. The coefficient of linear correlation is $R^2 = 0.79$. The water-wet points do not follow the correlation well, but this limitation is probably due to the internal gradient effect of the
Berea cores used in this study. It means that $T_2$ of oil inside the rock is shorter than the bulk value even at water-wet condition due to internal gradient effect, resulting in non-zero NMR oil wettability index (Equation 5.3.3.5).

The internal gradient effect of Berea cores was seen clearly from the $D-T_2$ map at 100% $S_o$. Figure 5.3.3.4 shows that the apparent diffusivity of oil inside the smallest pore is much higher than that of the bulk oil. Alternatively, the internal gradient strength of 100% $S_w$ Berea (3 cores) determined by $T_2$ at multiple echo spacing is $(28.6 \pm 2.8) \text{ G/cm}$, higher than that of the standard Berea cores.
FIGURE 5.3.3.3 Correlation between NMR oil wettability index and Amott-Harvey index, mode values of the $T_2$ relaxation time distributions of oil are used.

FIGURE 5.3.3.4 $D-T_2$ map of Berea B37 at 100% $S_o$ saturation.
Finally, for the combined NMR wettability index (mode values of $T_2$ are used for both water and oil for consistency), the cross plot (Figure 5.3.3.5) shows that it also correlates well with the Amott-Harvey index ($R^2 = 0.80$). In summary, the good correlation between NMR wettability indices (either NMR water index, NMR oil index or combined NMR index) and the Amott-Harvey indices suggests that quantitative information about the rock wettability can be obtained from NMR measurements.

Values of NMR wettability indices as shown in this section are summarized in Table C.5 to C.9 of Appendix C.

![Graph showing the correlation between Amott-Harvey index and combined NMR index.](image)

**FIGURE 5.3.3.5** Cross plot of combined NMR wettability index versus Amott-Harvey wettability index
5.4 Conclusions

Wettability alteration of silicate and calcite surface by the model surfactant DDA and SA or the OBM surfactants is detected by the contact angle measurements of water/glass slide/oil and water/marble/oil systems. 0.74% wt DDA in the oil phase alters the preferential water-wet glass slide surface but not the marble surface; while 0.50% wt SA in the oil phase alters the preferential water-wet marble surface but not the glass slide surface. The addition of 0.50% wt LLD, BOO, VERSA and NOVA alters both the preferential water-wet glass slide and marble surface. All these wettability alterations refer to the surface which is in contact with the oil.

Wettability effect on NMR relaxation time was demonstrated by $\rho_2$, eff, the effective surface relaxivity. The quantitative change of $\rho_2$, eff of either water or oil was shown to be directly related with wettability alteration. For water/oil partially saturated silica flour, the effective surface relaxivity of water decreases and the effective surface relaxivity of oil increases with the addition of 0.74% wt DDA or 1% wt OBM surfactants in the oil phase. Similarly, for water/oil partially saturated calcite, the effective surface relaxivity of water decreases and the effective surface relaxivity of oil increases with the addition of 0.50% SA in the oil phase. These changes are directly related with the wettability alteration. By contrast, the effective surface relaxivity of either water or oil remains unchanged when there is no wettability alteration.

Based on the concept of effective surface relaxivity, a novel model of NMR wettability index was proposed and tested. NMR water, oil and combined wettability indices correlate with the independent Amott-Harvey wettability index, suggesting that quantitative information about rock wettability can be obtained from NMR measurements.
Chapter 6  Effects of Paramagnetic Particulate in the OBM Filtrates on NMR Responses

This chapter presents our studies in a cooperative research program between Reservoir Management Group, Schlumberger Doll Research, PTS Labs International, ConocoPhillips, and Rice University. It was observed that hydrocarbon $T_2$ peak shifted to shorter relaxation time in CMR (trademark of Schlumberger) logs one week after the drilling than the LWD logs two days after the drilling (Shafer et al., 2004). The obvious question about this observation is: what happened during the time period between CMR and LWD logs? The objective of our work is to identify the main mechanisms which cause the apparent shortening of hydrocarbon $T_2$ peak. The following sections first introduce the fluid and rock samples from the field, and then present the experimental results and discussions.

6.1  Materials

6.1.1  Synthetic Oil Base Mud Samples

Five synthetic oil base mud samples were studied. They were from the nearby wells to those with CMR and LWD logs. It is possible that their components may be more complicated than that of freshly-made mud samples due to circulation and re-use. The bottle of mud sample as received from the field has a clear supernatant oil phase on the top and solid particles settled down on the bottom. For each mud sample, the corresponding base oil used for that mud was received as well.
6.1.2 Reservoir Cores

The reservoir cores from the cored well were studied. They are 1.5' in diameter and 1.5' in length. Table 6.1.2.1 lists the porosity and air permeability of these reservoir cores. In this study, we refer to two states of the reservoir cores as fresh-state and extracted-state. The fresh-state stands for as received from the field; while the extracted-state stands for miscibly extracted with a series of solvents including toluene, methanol, and tetrahydrofuran. Table 6.1.2.2 lists a typical composition of the reservoir core by XRD analysis. It indicates the presence of magnetite. The porosity, permeability and XRD analysis of the reservoir cores as in Table 6.1.2.1 and 6.1.2.2 were obtained by PTS Labs International Inc.

<table>
<thead>
<tr>
<th>Core #</th>
<th>140</th>
<th>165</th>
<th>200</th>
<th>206</th>
<th>477</th>
<th>199</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity (%)</td>
<td>33.5</td>
<td>26.5</td>
<td>32.0</td>
<td>31.1</td>
<td>30.8</td>
<td>-</td>
</tr>
<tr>
<td>Air permeability (md)</td>
<td>345</td>
<td>70</td>
<td>684</td>
<td>48</td>
<td>92</td>
<td>-</td>
</tr>
</tbody>
</table>

**TABLE 6.1.2.1 Porosity and air permeability of the reservoir cores**

**TABLE 6.1.2.2 Typical composition of the reservoir core by XRD analysis, core 206**

<table>
<thead>
<tr>
<th>Core 206</th>
<th>Quartz &amp; Feldspar</th>
<th>Calcite &amp; Dolomite</th>
<th>Siderite</th>
<th>Magnetite</th>
<th>Pyrite</th>
<th>Clays</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whole core (%)</td>
<td>42</td>
<td>21</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>14</td>
</tr>
<tr>
<td>Heavy components (%)</td>
<td>1</td>
<td>26</td>
<td>7</td>
<td>63</td>
<td>3</td>
<td>0</td>
</tr>
</tbody>
</table>

6.2 Experimental Results and Discussions

To answer the question of what happened during the time period between CMR and LWD logs causing the apparent hydrocarbon $T_2$ peak shift to shorter relaxation time, it is important to first understand the NMR bulk properties of the oil base mud filtrate
(OBMF), as well as its interaction with the core when it invades into the formation. This is because the hydrocarbon centrifuged out of the fresh-state core typically contains about 20% to 25% OBMF and 75% to 80% dead reservoir crude oil as determined by gas chromatography analysis (Shafter et al., 2004).

The following sections first present the observation of unusual NMR properties of the OBMF, then propose and test the hypothesis of the unexpected presence of paramagnetic particulates in the OBMF causing the unusual NMR properties, and finally illustrate the interaction of the OBMF with both reservoir and outcrop Berea cores, which results in wettability alteration from water-wet to intermediate-wet or oil-wet, enhanced surface relaxation, and higher internal gradient strength.

6.2.1 Unusual NMR Bulk Properties of OBMF

6.2.1.1 Impact of the Filtration Methods on the NMR Bulk Properties of OBMF

The filtration methods to get the OBMF out of the whole mud have a big effect on the NMR bulk properties of OBMF. Two kinds of filtration methods were examined in this study. One method was to take the clear supernatant oil phase on the top of the mud sample and filter it with syringe and 0.22 μm filter paper (MILLEX®GP Filter Unit). The OBMF thus acquired is referred to as filtered supernatant OBMF. The other method was to take the mixture of the whole mud and press it with 5 μm filter paper. The OBMF thus acquired is referred to as pressed OBMF. In this pressing process, there were several first drops coming through the filter paper before the mud cake fully built up, these first drops were kept separately for NMR measurements. Figure 6.2.1.1 shows that $T_2$ relaxation time of the filtered OBMF is much shorter than that of the corresponding base oil. For the
pressed OBMF, the $T_2$ relaxation time is close to that of the corresponding base oil. However, for those first several drops in the pressing process, the $T_2$ relaxation time is still shorter than that of the corresponding base oil and closer to that of the filtered OBMF.

In an actual drilling process in the field, there is some spurt loss before the mud cake fully builds up. So the filtrate invaded into the formation can be regarded as a mixture of the filtered OBMF and pressed OBMF. However, the ratio of the filtered OBMF to the pressed OBMF is unknown and may vary from case to case. Therefore, the extreme case of the filtered OBMF is investigated in the following sections. This gives a maximum effect.

![Graph showing impact of filtration methods on NMR relaxation time]

**FIGURE 6.2.1.1** Impact of the filtration methods on NMR relaxation time of the OBMF
6.2.1.2 Unusual NMR Properties of the Filtered OBMF

Three unusual NMR properties were observed for the filtered OBMF. First, they have a relaxation time much shorter than that of the corresponding base oil (16% to 38% for $T_2$ and 50% to 70% for $T_1$). This was shown in Figure 6.2.1.1 for one of the sample. It is similar for all the samples studied (Figure 6.2.1.2).

Secondly, $T_1$ relaxation times of the OBMF are about twice that of the $T_2$ relaxation times (Figure 6.2.1.3); while the corresponding base oil has a $T_1/T_2$ ratio of about 1. The $T_1/T_2$ ratio of the filtered OBMF will be further investigated in section 6.2.1.5.

Finally, the filtered OBMF deviates from the correlation between diffusivity and $T_2$ relaxation time for hydrocarbons (Lo, 1999, 2002; Freedman et al. 2001). This is because the diffusivities of the filtered OBMF and the corresponding base oil are similar but the filtered OBMF has a shorter $T_2$ (Table 6.2.1.1). This deviation was visualized by the $D$-$T_2$ map (Figure 6.2.1.4). Figure 6.2.1.5 summarizes the results for all the samples studied. Base oils follow the correlation but filtered OBMF deviate from this correlation. In the literature, Chen et al. (2004) also found that the base oils and filtrates studied do not follow the same correlation between $T_2$ and viscosity/temperature developed for hydrocarbons.

### TABLE 6.2.1.1 $T_1$, $T_2$ and diffusivity for the base oils and filtered OBMF

<table>
<thead>
<tr>
<th>sample #</th>
<th>T2 (ms)</th>
<th>T1 (ms)</th>
<th>T1/T2</th>
<th>D (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>base oil filtrate</td>
<td>base oil filtrate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>668.4 251.9</td>
<td>689.9 477.5</td>
<td>1.03 1.90</td>
<td>4.40E-06 4.82E-06</td>
</tr>
<tr>
<td>2</td>
<td>635.1 220.0</td>
<td>409.7 -</td>
<td>1.86 2.22</td>
<td>3.34E-06 2.90E-06</td>
</tr>
<tr>
<td>3</td>
<td>1010.2 163.4</td>
<td>362.6 -</td>
<td>2.06 3.72E-06</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>681.1 225.4</td>
<td>744.0 464.6</td>
<td>1.09 2.06</td>
<td>3.06E-06 3.94E-06</td>
</tr>
<tr>
<td>5</td>
<td>714.9 186.9</td>
<td>762.0 380.2</td>
<td>1.07 2.03</td>
<td>3.25E-06 2.93E-06</td>
</tr>
<tr>
<td>SB</td>
<td>701.5 -</td>
<td>704.6 -</td>
<td>1.00 -</td>
<td>4.29E-06 -</td>
</tr>
</tbody>
</table>

129
FIGURE 6.2.1.2 Comparison of $T_2$ between base oils and filtered OBMF

FIGURE 6.2.1.3 Comparison between $T_1$ and $T_2$ for the filtered OBMF
FIGURE 6.2.1.4 $D$-$T_2$ maps of base oil and filtered OBMF

FIGURE 6.2.1.5 Diffusivity versus $T_2$ for base oils, filtered OBMF and correlation between $D$ and $T_2$ for hydrocarbon
6.2.1.3 Hypothesis and Proof of the Reasons of the Unusual NMR Properties of the Filtered OBMF

The previous sections presented that the filtered OBMF had three unusual NMR properties. To detect the reasons of these unusual NMR properties, we started from the main components of the filtered OBMF: base oil, OBM surfactants, and submicron solid particles.

The mixture of base oil plus a small amount of OBM surfactants was first excluded to be the reason of the unusual NMR properties. Because the following three normal NMR properties were observed for base oil SB plus 3% OBM surfactant system of NOVA or BOO,

1. $T_2$ relaxation time is close to that of the base oil SB (5% and 8% smaller for SB + 3% BOO and SB + 3% NOVA, respectively, Figure 6.2.1.6),

2. $T_1/T_2$ ratio is about 1,

3. No deviation from the correlation between diffusivity and $T_2$ (Figure 6.2.1.7).

![Graph showing T2 values for SB, SB + 3% BOO, and SB + 3% NOVA](image)

FIGURE 6.2.1.6 Comparison of $T_2$ between SB, SB + 3% BOO and SB + 3% NOVA.
FIGURE 6.2.1.7 $D_T$ maps of SB (left plot) and SB + 3% BOO (right plot)

It is known that a trace amount of paramagnetic material in the fluid greatly shortens the fluid relaxation time. Based on this fact, we hypothesized that the unusual NMR properties are due to the presence of some paramagnetic particulates in the filtered OBMF. To test this hypothesis, Dynamic Light Scattering (DLS) measurement (ZetaPALS, Brookhaven Instruments) was first performed on the OBMF. Figure 6.2.1.8 shows that there are indeed some submicron particles in the filtered OBMF. The mean diameter of the particles is 83.4 nm. The paramagnetic characteristics of these particulates was further investigated by the HCl leaching, Ion Coupled Plasma (ICP), magnetic susceptibility and XRD measurements as follows.
FIGURE 6.2.1.8 Particle size distribution of filtered OBMF #2 from DLS measurement

The selection of HCl leaching to prove the paramagnetic characteristics of the particulates was based on the experience that some paramagnetic ions were washed off the surface of the silica flour or silica sand particles by HCl solution (Chapter 3, section 3.2.2). The procedure of the HCl leaching of the filtered OBMF is as follows. First, OBMF and HCl (1.0 Mol/l, Fisher scientific) were mixed (volume ratio of OBMF to HCl is 6:4) and stirred by a shaker (Labquake™, Barnstead Thermolyne) for 24 hours. Two separate phases exist after stirring. NMR $T_2$ measurement was then performed on this mixture of water and oil phases.

Figure 6.2.1.9 shows that $T_2$ relaxation time of the filtered OBMF increases after contacting with HCl, while the $T_2$ relaxation time of the HCl decreases significantly. This suggests that some of the fast relaxing materials in the OBMF phase have transferred to the HCl phase after contact.
FIGURE 6.2.1.9 HCl leaching of paramagnetic particulates from the OBMF

ICP technique applies very well to prove the paramagnetic characteristics of the particulates because it can detect trace amount of element. Therefore, ICP measurements (Optima 4300 DV, PerinElmer Instruments) were performed on the diluted HCl (10 times dilution, for the protection of ICP equipment) before and after contacting with the filtered OBMF. Since the types of element of the fast relaxing materials were unknown before measurements, five common paramagnetic elements were pre-selected for analysis. They are Fe, Mn, Cu, Co, Ni. Measurements show that the HCl phase after contacting with the filtered OBMF do have substantial amount of paramagnetic materials. It means that the
particulates in the original filtered OBMF are paramagnetic. The dominant paramagnetic elements are Fe (65 ppm) and Mn (8.6 ppm) as shown in Figure 6.2.1.10.

![Bar chart showing concentration of paramagnetic elements (Fe, Mn, Co, Cu, Ni) in the filtered OBMF by ICP measurement.](image)

**FIGURE 6.2.1.10** Concentration of paramagnetic elements in the filtered OBMF by ICP measurement.

The paramagnetic characteristics of the particulates in the filtered OBMF were further proved by the magnetic susceptibility and XRD measurements. Magnetic susceptibility and XRD measurements were performed on the dried mud cake which was obtained from the pressing process of the whole mud. Because the filtered OBMF has unusual NMR properties but not the pressed OBMF, it means that the paramagnetic materials in the filtered OBMF must accumulate in the mud cake formed in the pressing process of getting the pressed OBMF. Indeed, the magnetic susceptibility of the mud cake is $+17.7 \times 10^{-6}$ cgs/g, indicating the presence of paramagnetic material. For
comparison, diamagnetic material such as Kaolinite has a negative magnetic susceptibility of \(-0.34 \times 10^6\) cgs/g. Moreover, XRD analysis of the heavy components of the mud cake (Shafer et al., 2004) indicated that they are mainly magnetite (77%). Other heavy components include pyrite (15%) and siderite (8%).

6.2.1.4 Duplication of the Unusual NMR Properties of the Filtered OBMF with Precipitated Magnetite

A model system of precipitated magnetite ferrofluid was synthesized to duplicate the unusual NMR properties as observed for the filtered OBMF. First, the synthesis procedures of the ferrofluid are as follows (Lisensky, 2003).

1. Add 4 ml of 1 mol/l FeCl\(_3\) (freshly prepared in 2 mol/l HCl) and 1 ml of 2 mol/l FeCl\(_2\) (freshly prepared in 2 mol/l HCl) solution to a 100 ml beaker and stir the mixture with a magnet stirring bar,

2. Slowly add 50 ml of 1 mol/l NH\(_4\)OH solution (in water) over a period of 5 minutes, observe the magnetite precipitation after an initial brown precipitate,

3. Stop stirring and take out the magnet bar,

4. Discard the clear supernatant after the magnetite settles down, transfer the magnetite precipitate to a weighing boat,

5. Attract the ferrofluid to the bottom of the weighing boat by a strong magnet, rinse it with DI water for three times and discard the clear supernatant liquid phase each time,
6. Add 1~2 ml of 25% tetramethylammonium hydroxide and stir with a glass rod, attract the ferrofluid to the bottom of the weighing boat and discard the dark liquid.

7. The finely dispersed magnetite precipitate left in the weighing boat is the ferrofluid we used in this study.

A trace amount of the aqueous ferrofluid magnetite particles were then added in SB, together with 3% OBM surfactant of NOVA to make the magnetite particles disperse in the oil phase. For this model system of SB plus 3% NOVA plus a trace amount of ferrofluid magnetite particles, the three unusual NMR properties of the filtered OBMF were duplicated (Figure 6.2.1.11),

1. $T_1$, $T_2$ relaxation time shorter than that of SB ($T_1$ and $T_2$ is 24% and 8% that of SB, respectively),

2. $T_1/T_2$ ratio of about 3,

3. Deviation from the correlation between diffusivity and $T_2$.

![Figure 6.2.1.11: $T_1$, $T_2$ relaxation times of SB and SB + 3% NOVA + ferrofluid](image_url)

FIGURE 6.2.1.11 $T_1$, $T_2$ relaxation times of SB and SB + 3% NOVA + ferrofluid
6.2.1.5 \( T_1/T_2 \) Ratio and Echo Spacing Dependence of \( T_2 \) of the Filtered OBMF

The \( T_1/T_2 \) ratio and echo spacing dependence of \( T_2 \) of the filtered OBMF was further investigated. Figure 6.2.1.12 compares the filtered OBMF with two other systems which also contain paramagnetic materials. For a \( 3.2 \times 10^{-4} \) mol/l solution of Fe\(^{3+} \) in 1M HCl, \( T_1/T_2 \) ratio is 1 and there is no echo spacing dependence of \( T_2 \). For a fresh-state reservoir core #199 containing magnetite at \( S_{\text{swr}} \) with base oil, \( T_1/T_2 \) ratio is 2.0 and there is large echo spacing dependence of \( T_2 \). As a comparison, for a filtered OBMF, \( T_1/T_2 \) ratio is 1.9 but there is no echo spacing dependence of \( T_2 \).

![Graph showing \( T_1/T_2 \) ratios and echo spacing dependencies for different systems](image)

**FIGURE 6.2.1.12** \( T_1/T_2 \) ratio and echo spacing dependence of \( T_2 \) for three systems: Fe\(^{3+} \) in HCl, filtered OBMF and fresh-state reservoir core #199 at \( S_{\text{swr}} \) with base oil.

The comparison shown in Figure 6.2.1.12 raises a question: why the systems with iron paramagnetic material show different behaviors of \( T_1/T_2 \) ratio and echo spacing dependence of \( T_2 \)? In order to gain more understanding of these different behaviors, \( T_1 \),
$T_2$ relaxation times of water solutions with a series of concentrations of the magnetite ferrofluid particles were investigated. The concentration of iron element in each sample was measured by ICP measurement.

Figure 6.2.1.13 shows that the effective relaxation rate $(1/T_{1,2})_{\text{eff}}$ (Table 6.2.1.2) increases linearly with the concentration of iron element in water. The effective relaxation rate is defined as follows,

$$
\left(\frac{1}{T_{1,2}}\right)_{\text{eff}} = \left(\frac{1}{T_{1,2}}\right)_{\text{total}} - \left(\frac{1}{T_{1,2}}\right)_{\text{WB}}
$$

(6.2.1.1)

Where the index "total" and "WB" stand for total relaxation rate and that of pure bulk water, respectively. The linear correlation as shown in Figure 6.2.1.13 is similar to the trend of change of $(1/T_{1,2})_{\text{eff}}$ with respect to concentration of Fe$^{3+}$ in acid solution (Figure 6.2.1.14). However, unlike the acid solution of Fe$^{3+}$, Figure 6.2.1.15 shows that for water solution of magnetite ferrofluid particles, from high to low concentration, $T_1/T_2$ ratio first keeps constant at about 1.6 and then increases to about 2.2. Afterwards $T_1/T_2$ ratio drops to about 1 at very dilute concentration. Moreover, there is no echo dependence for $T_2$ at any concentration. Table 6.2.1.2 summarizes the $T_1$, $T_2$ data at different concentration.

The above observations suggest that water solution of magnetite ferrofluid particles also behaves similarly to the filtered OBMF in $T_1/T_2$ ratio and echo dependence of $T_2$. This provides model systems for further investigation as recommended in Chapter 7.
TABLE 6.2.1.2 $T_1$, $T_2$ and $T_1/T_2$ ratio at different concentration of magnetite ferrofluid particles

<table>
<thead>
<tr>
<th>Conc. (mol/l)</th>
<th>$T_2$ (ms)</th>
<th>$T_1$ (ms)</th>
<th>$T_1/T_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.78E-04</td>
<td>12.8</td>
<td>20.2</td>
<td>1.57</td>
</tr>
<tr>
<td>2.69E-04</td>
<td>21.3</td>
<td>33.0</td>
<td>1.55</td>
</tr>
<tr>
<td>1.58E-04</td>
<td>35.3</td>
<td>55.5</td>
<td>1.57</td>
</tr>
<tr>
<td>9.38E-05</td>
<td>56.5</td>
<td>88.3</td>
<td>1.56</td>
</tr>
<tr>
<td>5.78E-05</td>
<td>91.8</td>
<td>141.9</td>
<td>1.55</td>
</tr>
<tr>
<td>3.62E-05</td>
<td>142.8</td>
<td>222.7</td>
<td>1.56</td>
</tr>
<tr>
<td>2.54E-05</td>
<td>206.8</td>
<td>352.9</td>
<td>1.71</td>
</tr>
<tr>
<td>2.05E-05</td>
<td>214.6</td>
<td>463.9</td>
<td>2.16</td>
</tr>
<tr>
<td>1.57E-05</td>
<td>262.9</td>
<td>584.8</td>
<td>2.22</td>
</tr>
<tr>
<td>9.42E-06</td>
<td>432.9</td>
<td>894.9</td>
<td>2.07</td>
</tr>
<tr>
<td>5.30E-06</td>
<td>555.4</td>
<td>1155.7</td>
<td>2.08</td>
</tr>
<tr>
<td>2.72E-06</td>
<td>989.8</td>
<td>1720.8</td>
<td>1.74</td>
</tr>
<tr>
<td>1.93E-06</td>
<td>1251.6</td>
<td>1819.0</td>
<td>1.45</td>
</tr>
<tr>
<td>1.26E-06</td>
<td>1682.6</td>
<td>2179.3</td>
<td>1.30</td>
</tr>
<tr>
<td>0.00E+00</td>
<td>3017.0</td>
<td>3003.0</td>
<td>1.00</td>
</tr>
</tbody>
</table>

FIGURE 6.2.1.13 Effective $T_1$, $T_2$ relaxation rate versus iron concentration in water solution of magnetite ferrofluid particles.
FIGURE 6.2.1.14 Effective $T_2$ relaxation rate versus concentration of Fe$^{3+}$ in HCl, pH = 2

FIGURE 6.2.1.15 $T_1/T_2$ ratio versus iron concentration in water solution of magnetite ferrofluid particles.
6.2.2 Interactions of OBMF with Reservoir Cores and Outcrop Berea Cores

The previous section showed that it was the paramagnetic particles in the filtered OBMF that caused its unusual NMR bulk properties. Moreover, it also showed that the paramagnetic particles accumulated onto the mud cake during the pressing process. In addition, OBMF is known to have some surfactants additives. Therefore, qualitatively speaking, the potential interactions of OBMF with core samples may include adsorption of OBM surfactants onto the core surface causing wettability alteration (water-wet to intermediate-wet or oil-wet), and adsorption or precipitation of paramagnetic particles onto the core surface causing higher surface relaxivity and internal gradient strength. If taken place, all of these three interactions can cause the shortening of the hydrocarbon $T_2$ peak. The following sections quantitatively examine the interactions of OBMF with the core samples including reservoir cores from the cored well and outcrop Berea cores.

6.2.2.1 Wettability Alteration by OBMF

The potential of wettability alteration by the OBMF was examined by Amott-Harvey wettability index measurements of both fresh-state and extracted-state reservoir cores. The two fresh-state core measured had Amott-Harvey indices of -0.35 and -0.36; while the two extracted-state cores measured had Amott-Harvey indices of 0.83 and 0.12. Because the hydrocarbon centrifuged out of the fresh-state core typically contains about 20% to 25% OBMF and 75% to 80% dead reservoir crude oil, which means that the fresh-state cores were invaded by OBMF, the slight oil-wetness of the fresh-state cores is likely due to the adsorption of surfactants in the OBMF. Moreover, the decrease of oil-
wetness from the fresh-state to extracted-state core is possibly due to the removal of the adsorbed surfactants from the surface.

$T_1$, $T_2$ measurements of the fresh-state and extracted-state cores as well as the centrifuged oil were performed to show the consistency to the Amott-Harvey wettability index measurements. Figure 6.2.2.1 shows that oil $T_1$ peak in the fresh-state core (the larger peak at longer relaxation time of the solid black curve) is about 100 ms smaller that that of the bulk oil centrifuged out of the same core, indicating that the fresh-state core is not water-wet. Similarly, consistence with the Amott-Harvey wettability index measurement of the extracted-cores, Figure 6.2.2.2 shows that $T_1$, $T_2$ peak of decane for core #477 (Amott-Harvey: 0.12) at $S_{wir}$ with decane shifts more to the shorter relaxation time from that of bulk decane than that for core #200 (Amott-Harvey: 0.83). The consistency between $T_1$, $T_2$ relaxation time and Amott-Harvey wettability index suggests that the apparent hydrocarbon $T_2$ shift to shorter relaxation time between the CMR and LWD logs could be due to the wettability alteration by the surfactants in the OBMF.

![Graph](image)

**FIGURE 6.2.2.1** Comparison of $T_1$ of bulk centrifuged oil and the fresh-state core #196 at $S_{wir}$. 
(Core #200: water-wet, $I_{AH} = 0.83$)

---

(Core #477: intermediate-wet, $I_{AH} = 0.12$)

---

FIGURE 6.2.2.2 $T_1$ and $T_2$ (at multiple echo spacing) of core #200 (water-wet) and core #477 (intermediate-wet) at $S_{wi}$ with decane.
Figure 6.2.2.2 also shows that the $T_2$ peak of decane inside the core shifts to shorter relaxation time from that of bulk decane even for the water-wet core #200 (Amott-Harvey: 0.83). This is an indication of high internal gradient. $T_2$ at multiple echo spacing (TE = 0.3 and 0.6 ms) calculates an internal gradient strength of 146 and 188 G/cm for core #200 and #477, respectively. The issue of internal gradient will be illustrated in more detail in the following section.

6.2.2.2 Enhanced Surface Relaxation and Increased Internal Gradient Strength by OBMF

The potential interaction of enhanced surface relaxation and increased internal gradient strength from adsorption or precipitation of the paramagnetic particles in the OBMF onto the mineral surface was examined. In all the following cases, the internal gradient strength was calculated by $T_2$ relaxation times at multiple echo spacing (TE = 0.3 and 0.6 ms), and/or by $D$-$T_2$ map to obtain a distribution of internal gradient strength.

First, extracted core #206 at $S_{wir}$ with base oil was flushed with 2.5 PV filtered OBMF at reservoir temperature of 71 °C, aged at room temperature for 2 months, and then the OBMF displaced with base oil. Figure 6.2.2.3 shows that $T_2$ of the base oil shifts to shorter relaxation time after OBMF flushing and aging. This is similar to what was observed for the hydrocarbon $T_2$ peak during the time period between CMR and LWD logs. Consistent with this, the internal gradient strength from $T_2$ at multiple echo spacing increases from 74 G/cm to 152 G/cm after OBMF flushing and aging.
FIGURE 6.2.2.3 $T_2$ relaxation time distributions of core #206 before and post OBMF flushing

Figure 6.2.2.4 shows an illustration example of the process of obtaining the distribution of internal gradient strength from the $D-T_2$ measurement. The $D-T_2$ map is for core #206 at $S_{wir}$ with base oil after OBMF flushing and aging. The apparent diffusivity distribution is the projection of the $D-T_2$ map onto the diffusivity axis. From the diffusivity distribution, the distribution of the local gradient strength was calculated as follows (Hürlimann, M. D., et al., 2003),

$$g_{loc} = \sqrt{\frac{D_{app}}{D_0}} \cdot g_{ext} \quad (6.2.2.1)$$

Where $D_0$ is the self diffusion coefficient, $g_{ext}$ is the applied gradient strength in the $D-T_2$ measurements (13.2 G/cm in this study). A diffusivity cutoff of $1.0 \times 10^{-3}$ cm$^2$/sec was used to separate water and oil relaxation time for this sample.
FIGURE 6.2.2.4 (a) $D-T_2$ map of core #206 at $S_{wir}$ with base oil post OBMF flushing

FIGURE 6.2.2.4 (b) Distributions of diffusivity (left) and local gradient strength (right) experienced by oil
Secondly, to look in more detail at the effect of OBMF flushing and aging on the $T_2$ peak shift of base oil, as shown above for core #206, two more extracted cores #140 and #165 at $S_{wir}$ with base oil were flushed at 71 °C with 3 PV filtered OBMF or pressed OBMF, respectively. This gives a comparison between the interaction of the filtered OBMF with the core samples and that of the pressed OBMF with the core samples. After the OBMF flushing, the core was aged at 71 °C and $T_2$ relaxation time monitored with respect to time.

Figure 6.2.2.5 shows the oil $T_2$ peak with respect to aging time. Core #165 has a $T_2$ peak of 568 ms for the base oil before flushing. After flushing with 3 PV pressed OBMF (which has a $T_2$ peak of 647 ms at room temperature), $T_2$ peak of the base oil decreases from 567 ms at time zero to 276 ms at time 108 hours. Core #140 has a $T_2$ peak of 631 ms for the base oil before flushing. After flushing with 3 PV filtered OBMF (which has a $T_2$ peak of 182 ms at room temperature), $T_2$ peak of the base oil decreases from 181 ms at time zero to 57 ms at time 550 hours. Compared with the pressed OBMF, the filtered OBMF has a stronger effect on shortening the $T_2$ peak of the base oil, as shown by the larger slope of $T_2$ decrease with respect to time.

Figure 6.2.2.6 shows the $D-T_2$ maps of core #165 and #140 at $S_{wir}$ with base oil before and after OBMF flushing and aging. Generally, the apparent diffusivity of base oil is higher after OBMF flushing and aging, indicating an increase of internal gradient strength experienced by base oil (Figure 6.2.2.7). In comparison, filtered OBMF has a stronger effect on the increase of internal gradient strength than the pressed OBMF.
FIGURE 6.2.2.5 Monitor of oil $T_2$ peak with respect to aging time after flushing with filtered OBMF (core #140) and pressed OBMF (core #165).

Before flushing

Sample #140

After flushing

Sample #165

FIGURE 6.2.2.6 $D-T_2$ maps of sample #140 and #165 at $S_{wir}$ with base oil before and after OBMF flushing.
FIGURE 6.2.2.7 Internal gradient strength distributions of sample #140 (left) and #165 (right) at $S_{\text{wir}}$ with base oil before and after OBMF flushing

Finally, the effect of the filtered OBMF and the model system of magnetite ferrofluid particles on internal gradient was examined with Berea cores which have an original internal gradient strength smaller than that of the extracted reservoir cores. Berea core B83 at $S_{\text{wir}}$ with base oil was flushed with 7.7 PV of the filtered OBMF and aged at 90 °C for 6 days. Figure 6.2.2.8 and Figure 6.2.2.9 shows the $D-T_2$ maps and the internal gradient strength distribution, respectively. It indicates an increase in internal gradient strength with flushing and aging. Similarly, Berea core B71 was flushed with 10 PV of (base oil + 2% NOVA + magnetite ferrofluid) and aged for 6 days at 90 °C. Figure 6.2.2.10 and Figure 6.2.2.11 shows the $D-T_2$ maps and the internal gradient strength distribution, respectively. It also indicates an increase in gradient strength with flushing and aging.
FIGURE 6.2.2.8 $D-T_2$ maps of Berea B83 at $S_{\text{wir}}$ with SB (left), after flushing (middle) and after aging (right). The flushing fluid was 7.7 PV filtered OBMF.

FIGURE 6.2.2.9 Internal gradient strength of Berea B83 at $S_{\text{wir}}$ with SB, after flushing and after aging. The flushing fluid was 7.7 PV filtered OBMF.
FIGURE 6.2.2.10 $D$-$T_2$ maps of Berea B71 at $S_{wir}$ with SB (left), after flushing (middle) and after aging (right). The flushing fluid was 10 PV (SB + 2% NOVA + magnetite ferrofluid).

FIGURE 6.2.2.11 Internal gradient strength of Berea B71 at $S_{wir}$ with SB, after flushing and after aging. The flushing fluid was 10 PV (SB + 2% NOVA + magnetite ferrofluid).
6.3 Conclusions

The methods of filtration to obtain OBMF from the mud sample have a big effect on the relaxation time of the OBMF. While the pressed OBMF (whole mud pressed with 5 \( \mu \text{m} \) filter paper) behaves similarly to the corresponding base oil, three unusual NMR properties were observed for the filtered OBMF (supernatant oil phase filtered with 0.22 \( \mu \text{m} \) filter paper) as follows,

1. Relaxation time much shorter than that of the corresponding base oil,
2. \( T_1/T_2 \) ratio different from unity,
3. Deviation from the correlation between diffusivity and \( T_2 \).

The reason for the unusual NMR properties of the filtered OBMF was hypothesized and proved to be the unexpected presence of trace amount of paramagnetic submicron particles. Precipitated magnetite ferrofluid was shown to be a reasonable model system for these paramagnetic particles, because addition of small amount of precipitated magnetite ferrofluid in base oil surfactant solution duplicates all the three unusual NMR properties of the filtered OBMF. The filter cake in a laboratory pressing process has the potential of removing the paramagnetic particulates. However, filtration of the supernatant with 0.22 mm filter paper was not effective in removing the paramagnetic particles.

Interactions between the filtered OBMF (surfactants and paramagnetic particles) and rock sample can cause wettability alteration (water-wet to intermediate-wet or oil-wet), enhanced surface relaxation and increased internal gradient strength. All three mechanisms may contribute to the apparent hydrocarbon \( T_2 \) shift to shorter relaxation time during the period between LWD and CMR logs.
Chapter 7  Conclusions

Mineralogy affects surface relaxation. Surface relaxivity of water in the 100% $S_w$ Berea cores is about 2.3 times that of the Texas Cream limestone cores used in this study.

Paramagnetic ions are a very important factor of surface relaxation. $\rho_1$ and $\rho_2$ decreases with respect to acid washing as more and more ions are washed off the surface. However, $\rho_1$ and $\rho_2$ goes to a finite plateau value at the end of washing, accounting for about 10% and 17% of the original value, respectively. In addition, $\rho_2/\rho_1$ ratio generally increases and deviates further from the mean value of natural rocks with respect to acid washing, while $\rho_2/\rho_1$ ratio is close to the mean value for both the original or coated samples.

Mechanism of the surface enhanced dipole-dipole is negligible when paramagnetic ion mechanism is strong. In such case, surface relaxivity of both water and oil depends only weakly on temperature. However, in cases when paramagnetic ion mechanism is weak, the contribution from surface enhanced dipole-dipole interaction could dominate the total surface relaxation rate. In such case, surface relaxivity of both water and oil decreases with temperature.

Diffusion coupling between the micro-pores and macro-pores is observed for unconsolidated silica gel and North Burbank Sandstone. The combined effect of surface
relaxation and diffusion coupling on the relaxation time distribution depends on surface relaxivity, fluid diffusivity and pore structure.

$T_1, T_2$ bulk relaxation time distributions of the OBM surfactants generally range over two or three orders of magnitude, indicating that the OBM surfactants are mixture of many components. Moreover, their short $T_1, T_2$ relaxation times and $T_1/T_2$ ratio being larger than unity suggest that the OBM surfactants are composed of heavy components.

Originally water-wet Berea and Texas Cream limestone are altered to be at least intermediate-wet or even oil-wet by the OBM surfactants, depending on the type, the flushing volume and their concentration in the flushing fluid. These wettability alteration determined by Amott-Harvey wettability index measurements is also visualized by the NMR $D-T_2$ measurements.

$T_{2,\text{cutoff}}$ model works well for the Berea and Texas Cream limestone when they are at their original water-wet condition. However, for an oil-bearing rock, $S_{\text{wir}}$ from $T_{2,\text{cutoff}}$ model after flushing generally underestimates the measured value of $S_{\text{wir}}$ due to wettability alteration from water-wet to intermediate-wet or oil-wet. The magnitude of underestimation correlates with the Amott-Harvey index.

A larger value of $T_{2,\text{cutoff}}$ can be used to estimate $S_{\text{wir}}$ when wettability alteration occurs. Because the actual $S_{\text{wir}}$ after OBM flushing for an oil-bearing rock does not
change much but is underestimated by the default $T_{2, \text{cutoff}}$ at water-wet condition. The modified value of $T_{2, \text{cutoff}}$ correlates with the Amott-Harvey index.

For the crude/brine saturated Berea, $T_{2, \text{cutoff}}$ model overestimates the measured value of $S_{\text{wir}}$. This is due to the interference of bulk relaxation time of the crude oil used in this study with that of the irreducible water. It suggested that in crude oil bearing zone/formation, $T_{2, \text{cutoff}}$ for $S_{\text{wir}}$ estimation may need to be modified.

Wettability alteration of silicate and calcite surface by the model surfactant DDA and SA or the OBM surfactants was evaluated. 0.74% wt DDA in the oil phase alters the preferential water-wet glass slide surface but not the marble surface; while 0.50% wt SA in the oil phase alters the preferential water-wet marble surface but not the glass slide surface. The addition of 0.50% wt LLD, BOO, VERSA and NOVA alters both the preferential water-wet glass slide and marble surface. All these wettability alterations refer to the surface which is in contact with the oil.

Wettability effect on NMR relaxation time was quantified by $\rho_{2, \text{eff}}$, the effective surface relaxivity. The quantitative change of $\rho_{2, \text{eff}}$ of either water or oil was shown to be directly related with wettability alteration. For water/oil partially saturated silica flour, the effective surface relaxivity of water decreases and the effective surface relaxivity of oil increases with the addition of 0.74% wt DDA or 1% wt OBM surfactants in the oil phase. Similarly, for water/oil partially saturated calcite, the effective surface relaxivity of water decreases and the effective surface relaxivity of oil increases with the addition of
0.50% SA in the oil phase. These changes are directly related with the wettability alteration. By contrast, the effective surface relaxivity of either water or oil remains unchanged when there is no wettability alteration.

A novel model of NMR wettability index was proposed and tested based on the concept of effective surface relaxivity. NMR water, oil and the combined wettability indices correlate with the independent Amott-Harvey wettability index, suggesting that quantitative information about rock wettability can be obtained from NMR measurements.

The methods of filtration to obtain OBMF from the mud sample have a big effect on the relaxation time of the OBMF. While the pressed OBMF (whole mud pressed with 5 μm filter paper) behaves similarly to the corresponding base oil, three unusual NMR properties were observed for the filtered supernatant OBMF (supernatant oil phase filtered with 0.22 μm filter paper) as follows,

1. Relaxation time much shorter that that of the corresponding base oil,
2. $T_1/T_2$ ratio different from unity,
3. Deviation from the correlation between diffusivity and $T_2$.

Unexpected presence of trace amount of paramagnetic submicron particles is the reason for the unusual behaviors of the filtered OBMF. Precipitated magnetite ferrofluid is a reasonable model system for these paramagnetic particles. The filter cake in a laboratory pressing process has the potential of removing the paramagnetic particulates.
However, filtration of the supernatant with 0.22 mm filter paper was not effective in removing the paramagnetic particles.

Interactions between the filtered OBMF (surfactants and paramagnetic particles) and rock sample can cause wettability alteration (water-wet to intermediate-wet or oil-wet), enhanced surface relaxation and increased internal gradient strength. All three mechanisms may contribute to the apparent hydrocarbon $T_2$ shift to shorter relaxation time during the period between LWD and CMR logs.
Chapter 8  Future Work

This study suggests the following future work:

1. Test the conclusion of temperature dependence of surface relaxation with calcite samples,

2. Test the model of NMR wettability indices with carbonate cores. The $D-T_2$ data of the Texas Cream limestone cores were not available when the wettability studies were carried on with the Texas Cream limestone cores due to Maran 2 equipment not functioning at that period of time.

3. Investigate the diffusion coupling of bi-modal pore structure systems by varying parameters such as pore sizes, fluid diffusivity (water and different hydrocarbon), surface relaxivity, temperature and pressure,

4. Identify the mechanisms for $T_1/T_2$ ratio being deviated from unity with no echo dependence of $T_2$ relaxation time for oil solution with dispersed submicron paramagnetic particles.
Reference


Coates, G.R., Xiao, L, and Prammer, M.G.: NMR Logging, Principles and Applications (1999), Houston, TX.


Zhang, Y.: Spin Relaxation and Molecular Dynamics in Hydrocarbon Gases and Liquids (2003), Ph.D. Thesis, Rice University, Houston, TX.


APPENDIX

Part A. Determination of Surface Relaxivity and Pore Size Distribution by Comparison between Mercury Capillary Pressure Curve and NMR Relaxation Time Distribution

This part first describes three commonly used models of capillary pressure curves: Thomeer model, Log Normal model and Bimodal Log Normal model, and then demonstrates the model fitting of the measured capillary pressure curves for both Berea and limestone, and finally illustrates the determination of surface relaxivity by comparison between mercury capillary pressure curve (either measured or model calculated) and NMR relaxation time distribution, as well as the resulting pore size distributions.

A.1 Descriptions of Capillary Pressure Models

The following capillary pressure models describe the relationship between Leverett $J$ function and reduced wetting phase saturation $S$. $S$ and $J$ are defined as follows,

$$ S = \frac{S_w - S_{wr}}{S_{wi} - S_{wr}} $$

(A.1)

$$ J = \frac{0.2166}{\sigma \cos \theta} \sqrt{\frac{k}{\phi}} \cdot P_c $$

(A.2)

Where $S_w$ is wetting phase saturation. $S_{wr}$ is the residual or asymptotic saturation when the capillary pressure approaches infinity. $S_{wi}$ is the initial saturation. $P_c$, $k$ and $\phi$ are capillary pressure (psi), permeability (md) and porosity, respectively. $\theta$ and $\sigma$ are the
contact angle and surface tension (dyne/cm) between non-wetting and wetting fluids. For mercury/air system, \( \sigma = 480 \) dyne/cm and \( \theta = 180^\circ \).

A.1.1 Thomeer Model

Thomeer model is described as follows,

\[
S = \begin{cases} 
1 & \text{when } J < J_e = C_1 \\
1 - \exp[C_2 / \ln(\frac{C_1}{J})] & \text{when } J > J_e = C_1 
\end{cases} \tag{A.3}
\]

Where \( J_e \) is the entry value of Leverett \( J \) function. \( C_2 \) is the pore geometry factor.

Thomeer model has three parameters: \( C_1 \), \( C_2 \) and \( S_{wr} \).

A.1.2 Log Normal Model

Log Normal model is described as follows,

\[
S = \begin{cases} 
1 & \text{when } J < J_e = C_1 \\
\frac{1}{2} \text{erfc}\left[\frac{\ln(J - C_1) / C_3}{C_2}\right] & \text{when } J > J_e = C_1 
\end{cases} \tag{A.5}
\]

Where \( C_2 \) is the median value of the Leverett \( J \) function subtracted by \( C_1 \). \( C_3 \) is the width of the distribution of the logarithm of the Leverett \( J \) function. Log Normal model has four parameters: \( C_1 \ldots C_3 \) and \( S_{wr} \).

A.1.3 Bimodal Log Normal Model

Bimodal Log Normal model is described as follows,
\[ S_1 = \begin{cases} -1 & \text{when } J < C_1 \\ \text{erf}\left[\frac{\ln(J - C_1)/C_3}{C_4}\right] & \text{when } J > C_1 \end{cases} \quad (A.7) \]

\[ S_2 = \begin{cases} -1 & \text{when } J < (C_1 + C_2) \\ \text{erf}\left[\frac{\ln(J - C_1 - C_2)/C_5}{C_6}\right] & \text{when } J > (C_1 + C_2) \end{cases} \quad (A.9) \]

\[ S = 0.5 \times [1 - C_7 \times S_1 - (1 - C_7) \times S_2] \quad (A.11) \]

Where \( C_1 \) and \( C_2 \) are the entry values of Leverett \( J \) function for the first and second lognormal distribution, respectively. \( C_3 \) and \( C_5 \) are the median values of Leverett \( J \) function for the first and second lognormal distribution subtracted by \( C_1 \) and \( C_2 \), respectively. \( C_4 \) and \( C_6 \) are the width of the first and second lognormal distribution, respectively. \( C_7 \) reflects the dominance of the first lognormal distribution. Bimodal Log Normal model has eight parameters: \( C_1 \), \( \ldots \), \( C_7 \), and \( S_{wr} \).

### A.2 Model Fitting of the Mercury Capillary Pressure Curves

Figure A.2.1 and Figure A.2.2 show the measured mercury capillary pressure curves for three selected Berea cores (out of total 115 samples) and three selected Texas Cream limestone cores (out of total 100 samples), respectively. Refer to Chapter 4 section 4.2.1 for properties of the Berea and Texas Cream limestone cores. The standard of selection is to choose cores whose air permeability is the mean value of the total samples, or plus/minus the standard deviation of the air permeability. The porosity and permeability of these six cores are listed in table A.2.1.
TABLE A.2.1 Porosity and permeability of Berea and Texas Cream limestone cores

<table>
<thead>
<tr>
<th>Core</th>
<th>Type</th>
<th>Porosity</th>
<th>Air permeability (md)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B18</td>
<td>Berea</td>
<td>0.174</td>
<td>69.0</td>
</tr>
<tr>
<td>B53</td>
<td>Berea</td>
<td>0.179</td>
<td>95.8</td>
</tr>
<tr>
<td>B69</td>
<td>Berea</td>
<td>0.186</td>
<td>120.0</td>
</tr>
<tr>
<td>L84</td>
<td>Limestone</td>
<td>0.211</td>
<td>4.3</td>
</tr>
<tr>
<td>L24</td>
<td>Limestone</td>
<td>0.234</td>
<td>6.6</td>
</tr>
<tr>
<td>L61</td>
<td>Limestone</td>
<td>0.249</td>
<td>9.0</td>
</tr>
</tbody>
</table>

FIGURE A.2.1 Hg capillary pressure curves for Berea B18, B53 and B69.

FIGURE A.2.2 Hg capillary pressure curves for limestone L84, L61 and L24.
Figure A.2.3 shows an example of model fittings of Leverett J function for Berea core B18 by the three models described in section A.1. In comparison of the three models, Bimodal Log Normal model is the best fitting of the measured data, except that there is a slight deviation when the wetting phase saturation is close to zero. Similarly, Figure A.2.4 shows an example of model fittings of Leverett J function for limestone core L24. In comparison, the Log Normal model fits measured data the best. Table A.2.2 and A.2.3 summarize the parameters of model fitting for Berea (Bimodal Log Normal) and limestone (Log Normal), respectively. The averaged values of the parameters were used for other cores which do not have the measured capillary pressure data.
TABLE A.2.2 Parameters of model fitting (Bimodal Log Normal) for Berea cores

<table>
<thead>
<tr>
<th>Core</th>
<th>B18</th>
<th>B53</th>
<th>B69</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{nr}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$C_1$</td>
<td>0.11</td>
<td>0.24</td>
<td>0.11</td>
<td>0.14</td>
</tr>
<tr>
<td>$C_2$</td>
<td>0.80</td>
<td>0.84</td>
<td>0.79</td>
<td>0.81</td>
</tr>
<tr>
<td>$C_3$</td>
<td>0.13</td>
<td>0.18</td>
<td>0.12</td>
<td>0.14</td>
</tr>
<tr>
<td>$C_4$</td>
<td>1.08</td>
<td>1.45</td>
<td>1.03</td>
<td>1.17</td>
</tr>
<tr>
<td>$C_5$</td>
<td>25.23</td>
<td>52.76</td>
<td>11.66</td>
<td>24.94</td>
</tr>
<tr>
<td>$C_6$</td>
<td>3.98</td>
<td>3.44</td>
<td>4.69</td>
<td>4.00</td>
</tr>
<tr>
<td>$C_7$</td>
<td>0.63</td>
<td>0.61</td>
<td>0.62</td>
<td>0.62</td>
</tr>
</tbody>
</table>

TABLE A.2.3 Parameters of model fitting (Log Normal) for Texas Cream limestone cores

<table>
<thead>
<tr>
<th>Core #</th>
<th># 24</th>
<th># 61</th>
<th># 84</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{nr}$</td>
<td>0.025</td>
<td>0.016</td>
<td>0.014</td>
<td>0.018</td>
</tr>
<tr>
<td>$C_1$</td>
<td>0.093</td>
<td>0.097</td>
<td>0.081</td>
<td>0.090</td>
</tr>
<tr>
<td>$C_2$</td>
<td>0.26</td>
<td>0.34</td>
<td>0.28</td>
<td>0.29</td>
</tr>
<tr>
<td>$C_3$</td>
<td>2.12</td>
<td>2.11</td>
<td>2.19</td>
<td>2.14</td>
</tr>
</tbody>
</table>

A.3 Comparison between Mercury Capillary Pressure Curve and Relaxation Time Distribution: Surface Relaxivity

Surface relaxivity of a single fluid in 100% saturated core can be determined by the comparison between mercury capillary pressure curve and NMR relaxation time distribution. Capillary pressure curve is related to the pore throat size distribution as follows,

$$P_c = \frac{2\sigma \cos \theta}{r_t}$$  \hspace{1cm} (A.12)

Where $r_t$ is the pore throat size, $\theta$ and $\sigma$ are the same as in equation (A.2).
NMR relaxation time distribution is a mapping of the pore body size distribution as follows,

\[
\frac{1}{T_{1,2}} - \frac{1}{T_{1,2,B}} = \rho_{1,2} \frac{S}{V_p} = \rho_{1,2} \frac{\alpha}{r_b}
\]

(A.13)

Where \( r_b \) is the specific pore body size, \( \alpha \) is the geometrical constant (\( \alpha = 1, 2, 3 \) for slab, cylinder and spherical pore geometry, respectively. Tube-like model was used in this study so \( \alpha = 2 \)).

The ratio of pore throat size to pore body size \( \frac{r_i}{r_b} \) does not vary very much from pore to pore for sandstone. Combine equation (A.12) and (A.13), we get,

\[
\rho_{1,2,\text{eff}} = \frac{\sigma \cos \theta}{T_{1,2,\text{eff}} P_c}
\]

(A.14)

Where \( \rho_{1,2,\text{eff}} \) and \( T_{1,2,\text{eff}} \) are the effective surface relaxivity and effective relaxation time, respectively.

\[
\rho_{1,2,\text{eff}} = \rho_{1,2} \frac{r_i}{r_b}
\]

(A.15)

\[
\frac{1}{T_{1,2,\text{eff}}} = \frac{1}{T_{1,2}} - \frac{1}{T_{1,2,B}}
\]

(A.16)

To numerically determine \( \rho_{1,2,\text{eff}} \), we can rearrange equation (A.14) to be,

\[
\frac{1}{P_{c,i}} = C \cdot T_{1,2,\text{eff},i}
\]

(A.17)

Where \( P_{c,i} \) corresponds to cumulative capillary pressure distribution \( P_{c,i} \sim F_{1,2,P} \), \( T_{1,2,\text{eff},i} \) corresponds to cumulative relaxation time distribution \( T_{1,2,\text{eff},i} \sim F_{1,2,T} \), \( C \) is a constant defined as follows,
\[ C = \frac{\rho_{1,2,\text{eff}}}{\sigma \cos \theta} \quad (A.18) \]

\[ \chi^2 = \sum_i \left( \log_{10} \left( C \cdot T_{1,2,\text{eff},i} \right) - \log_{10} \left( \frac{1}{P_{c,i}} \right) \right)^2 \quad (A.19) \]

That is,

\[ C = 10^{\left( \frac{\sum \log_{10} \left( \frac{1}{P_{c,i}} \right) - \sum \log_{10} \left( T_{1,2,\text{eff},i} \right) }{n} \right)} \quad (A.20) \]

Where \( n \) is the number of data points in the neighborhood of the median values of the cumulative distribution (in this study, the region of 0.35 \sim 0.85 was used for Berea cores and 0.20 \sim 0.80 used for limestone cores). Having determined \( C \), \( \rho_{1,2,\text{eff}} \) can be calculated from equation (A.18).

## A.4 Pore Size Distributions of Berea and Texas Cream limestone Cores from NMR and Hg Capillary Pressure Curves

Pore size distributions are obtained in the process of determining surface relaxivity. Rearrange equation (A.12) and (A.13), we can get the pore size distributions from capillary pressure and relaxation time distribution, respectively.

\[ r_i = \frac{2 \sigma \cos \theta}{P_c} \quad (A.21) \]

\[ r_i = \frac{\alpha \cdot \rho_{1,2,\text{eff}}}{\frac{1}{T_{1,2}} - \frac{1}{T_{1,2,b}}} \quad (A.22) \]

Figure A.4.1 shows an example of the incremental and cumulative pore size distributions of Berea core B18. In getting Figure A.4.1 (a) and (b), Hg capillary pressure
curve calculated from Bimodal Log Normal model was used. Since there is a slope discontinuity at one point of the Bimodal Log Normal fitting curve (Figure A.4.2), there is an artifact of little peak in the incremental pore size distribution (Figure A.4.1 (a)). As a comparison, in getting Figure A.4.1 (c), measured Hg capillary pressure curve was used, and there is no such artifact of little peak in the pore size distribution.

Similarly, Figure A.4.3 shows an example of the incremental and cumulative pore size distributions of Texas Cream limestone core L2 from NMR $T_2$ relaxation time and Hg capillary pressure curve calculated from Log Normal model.
FIGURE A.4.1 Incremental and cumulative pore size distributions for Berea B18, (a) and (b): from $T_2$ and Hg capillary pressure curve calculated by Bimodal Log Normal model, (c): from $T_2$ and measured Hg capillary pressure curve.
FIGURE A.4.2 Bimodal Log Normal fitting of the measured data for Berea core B18
FIGURE A.4.3 Incremental and cumulative pore size distributions for Texas Cream limestone L2 from $T_2$ and Hg capillary pressure calculated by Log Normal model.
Part B  \( T_1, T_2 \) Relaxation time distributions of OBM surfactants
FIGURE B.1 $T_1$, $T_2$ distributions of LE SUPERMUL, BIO COAT, OMNI MUL, OMNI TEC, NOVA MUL, NOVA WET, VERSA MUL and VERSA COAT.
### Part C  Data Summary

**TABLE C. 1**  $T_2$, cutoff of the Berea cores at the original water-wet condition

<table>
<thead>
<tr>
<th>core #</th>
<th>$S_{wir}$, weighing air/brine</th>
<th>$S_{wir}$, 33 ms 100% Sw</th>
<th>T2,cutoff, weighing 100% Sw</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>0.223</td>
<td>0.211</td>
<td>36.6</td>
</tr>
<tr>
<td>27</td>
<td>0.230</td>
<td>0.236</td>
<td>31.2</td>
</tr>
<tr>
<td>30</td>
<td>0.205</td>
<td>0.211</td>
<td>31.1</td>
</tr>
<tr>
<td>36</td>
<td>0.221</td>
<td>0.199</td>
<td>39.4</td>
</tr>
<tr>
<td>98</td>
<td>0.224</td>
<td>0.226</td>
<td>32.6</td>
</tr>
<tr>
<td>14</td>
<td>0.224</td>
<td>0.223</td>
<td>33.2</td>
</tr>
<tr>
<td>10</td>
<td>0.224</td>
<td>0.211</td>
<td>36.3</td>
</tr>
<tr>
<td>29</td>
<td>0.242</td>
<td>0.241</td>
<td>33.4</td>
</tr>
<tr>
<td>21</td>
<td>0.208</td>
<td>0.218</td>
<td>30.4</td>
</tr>
<tr>
<td>16</td>
<td>0.218</td>
<td>0.237</td>
<td>28.0</td>
</tr>
<tr>
<td>45</td>
<td>0.211</td>
<td>0.200</td>
<td>36.2</td>
</tr>
<tr>
<td>58</td>
<td>0.210</td>
<td>0.194</td>
<td>38.1</td>
</tr>
<tr>
<td>66</td>
<td>0.218</td>
<td>0.211</td>
<td>35.0</td>
</tr>
<tr>
<td>56</td>
<td>0.212</td>
<td>0.215</td>
<td>32.1</td>
</tr>
<tr>
<td>57</td>
<td>0.209</td>
<td>0.228</td>
<td>27.2</td>
</tr>
<tr>
<td>107</td>
<td>0.206</td>
<td>0.212</td>
<td>31.4</td>
</tr>
<tr>
<td>28</td>
<td>0.236</td>
<td>0.257</td>
<td>27.2</td>
</tr>
<tr>
<td>34</td>
<td>0.239</td>
<td>0.225</td>
<td>36.7</td>
</tr>
<tr>
<td>35</td>
<td>0.232</td>
<td>0.231</td>
<td>33.4</td>
</tr>
<tr>
<td>23</td>
<td>0.245</td>
<td>0.251</td>
<td>31.4</td>
</tr>
<tr>
<td>31</td>
<td>0.236</td>
<td>0.242</td>
<td>31.4</td>
</tr>
<tr>
<td>1</td>
<td>0.220</td>
<td>0.231</td>
<td>30.0</td>
</tr>
<tr>
<td>90</td>
<td>0.216</td>
<td>0.203</td>
<td>37.2</td>
</tr>
<tr>
<td>4</td>
<td>0.233</td>
<td>0.24</td>
<td>31.0</td>
</tr>
<tr>
<td>38</td>
<td>0.214</td>
<td>0.214</td>
<td>32.9</td>
</tr>
<tr>
<td>39</td>
<td>0.228</td>
<td>0.228</td>
<td>33.0</td>
</tr>
<tr>
<td>6</td>
<td>0.206</td>
<td>0.221</td>
<td>27.7</td>
</tr>
<tr>
<td>9</td>
<td>0.212</td>
<td>0.212</td>
<td>33.1</td>
</tr>
<tr>
<td>3</td>
<td>0.214</td>
<td>0.22</td>
<td>31.3</td>
</tr>
<tr>
<td>19</td>
<td>0.242</td>
<td>0.244</td>
<td>32.5</td>
</tr>
<tr>
<td>20</td>
<td>0.222</td>
<td>0.214</td>
<td>35.2</td>
</tr>
<tr>
<td>13</td>
<td>0.223</td>
<td>0.225</td>
<td>32.3</td>
</tr>
<tr>
<td>22</td>
<td>0.220</td>
<td>0.216</td>
<td>34.0</td>
</tr>
<tr>
<td>32</td>
<td>0.243</td>
<td>0.236</td>
<td>34.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Arithmetic</th>
<th>Mean</th>
<th>Std.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometric</td>
<td>Mean</td>
<td>Std.</td>
</tr>
</tbody>
</table>

182
### Table C.2 Contact angles of water/glass slide/oil and water/marble/oil systems with model surfactants DDA and SA

<table>
<thead>
<tr>
<th>Contact angle (degree)</th>
<th>Glass slide</th>
<th>Marble</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Escaid</td>
<td>+0.74% DDA</td>
</tr>
<tr>
<td>Receding</td>
<td>15</td>
<td>132.4</td>
</tr>
<tr>
<td>Advancing</td>
<td>31</td>
<td>145.9</td>
</tr>
</tbody>
</table>

### Table C.3 Contact angles of water/glass slide/oil and water/marble/oil systems with OBM surfactants LLD, BOO, VERSA and NOVA

<table>
<thead>
<tr>
<th>Contact angle (degree)</th>
<th>Glass slide</th>
<th>Marble</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SB</td>
<td>+0.5% LLD</td>
</tr>
<tr>
<td>Receding</td>
<td>15</td>
<td>34</td>
</tr>
<tr>
<td>Advancing</td>
<td>31</td>
<td>155.5</td>
</tr>
<tr>
<td>Receding</td>
<td>19</td>
<td>146.5</td>
</tr>
<tr>
<td>Advancing</td>
<td>21</td>
<td>153.3</td>
</tr>
</tbody>
</table>
Table C.4 Summary of surface relaxivity of water and oil in 100% $S_w$, 100% $S_o$ and water/oil partially saturated silica flour and calcite

<table>
<thead>
<tr>
<th>Silica flour # 1</th>
<th>Oil phase</th>
<th>$S_w$</th>
<th>$\rho_{2,W,eff}$ (µm/s)</th>
<th>$\rho_{2,O,eff}$ (µm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-</td>
<td>100%</td>
<td>1.56</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>escaid</td>
<td>0%</td>
<td>-</td>
<td>0.56</td>
</tr>
<tr>
<td></td>
<td>escaid</td>
<td>30%</td>
<td>1.69</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>escaid + 0.74% DDA</td>
<td>30%</td>
<td>0.78</td>
<td>0.24</td>
</tr>
<tr>
<td>Silica flour # 2</td>
<td>-</td>
<td>100%</td>
<td>1.64</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>escaid</td>
<td>0%</td>
<td>-</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>escaid</td>
<td>21%</td>
<td>1.03</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>escaid + 0.5% SA</td>
<td>21%</td>
<td>0.96</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>SB</td>
<td>0%</td>
<td>-</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>SB</td>
<td>18%</td>
<td>1.06</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>SB + 0.12 LLD</td>
<td>18%</td>
<td>0.89</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>SB + 0.24% LLD</td>
<td>18%</td>
<td>0.50</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>SB + 0.98% LLD</td>
<td>18%</td>
<td>-</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>SB</td>
<td>40%</td>
<td>1.60</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>SB + 1% BOO</td>
<td>40%</td>
<td>1.07</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>SB + 1% VERSA</td>
<td>40%</td>
<td>1.13</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>SB + 1% NOVA</td>
<td>36%</td>
<td>-</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>SB + 1% LLD</td>
<td>40%</td>
<td>1.20</td>
<td>0.14</td>
</tr>
<tr>
<td>Calcite # 1</td>
<td>-</td>
<td>100%</td>
<td>1.28</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>SB</td>
<td>0%</td>
<td>-</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>SB</td>
<td>38%</td>
<td>1.20</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>SB + 0.74% DDA</td>
<td>43%</td>
<td>1.24</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>SB</td>
<td>40%</td>
<td>1.31</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>SB + 0.50% SA</td>
<td>43%</td>
<td>0.98</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>100%</td>
<td>1.91</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>SB</td>
<td>0%</td>
<td>-</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>SB</td>
<td>49%</td>
<td>2.04</td>
<td>2.4E-03</td>
</tr>
<tr>
<td></td>
<td>SB + 1% LLD</td>
<td>50%</td>
<td>2.174</td>
<td>3.4E-03</td>
</tr>
<tr>
<td></td>
<td>SB + 1% BOO</td>
<td>55%</td>
<td>1.941</td>
<td>2.0E-03</td>
</tr>
<tr>
<td></td>
<td>SB + 1% VERSA</td>
<td>52%</td>
<td>1.75</td>
<td>4.6E-03</td>
</tr>
<tr>
<td></td>
<td>SB + 1% NOVA</td>
<td>61%</td>
<td>2.07</td>
<td>2.3E-03</td>
</tr>
</tbody>
</table>

184
TABLE C.5 NMR water wettability index, $T_2$ log mean values are used in the calculation.

<table>
<thead>
<tr>
<th>Core #</th>
<th>$I_{AH}$</th>
<th>$T_{2,w}$ (ms)</th>
<th>$S_w = 1$</th>
<th>$T_{2,w}$ (ms)</th>
<th>$S_{or}$</th>
<th>$T_{2,w}$ (ms)</th>
<th>$I_{w,NMR}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
<td>0.93</td>
<td>75.3</td>
<td>49.8</td>
<td>0.33</td>
<td>2837.6</td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.92</td>
<td>79.3</td>
<td>69.8</td>
<td>0.25</td>
<td>2837.6</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>0.93</td>
<td>80.6</td>
<td>71.9</td>
<td>0.31</td>
<td>2837.6</td>
<td>0.78</td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>0.08</td>
<td>84.2</td>
<td>108.9</td>
<td>0.10</td>
<td>2837.6</td>
<td>0.69</td>
<td></td>
</tr>
<tr>
<td>107</td>
<td>0.03</td>
<td>78.01</td>
<td>118.9</td>
<td>0.08</td>
<td>2837.6</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>-0.10</td>
<td>64.60</td>
<td>139.2</td>
<td>0.13</td>
<td>2837.6</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>-0.12</td>
<td>72.24</td>
<td>167.8</td>
<td>0.09</td>
<td>2837.6</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>-0.35</td>
<td>76.54</td>
<td>132.2</td>
<td>0.18</td>
<td>2837.6</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>-0.52</td>
<td>89.52</td>
<td>180.3</td>
<td>0.17</td>
<td>2837.6</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>66</td>
<td>-0.51</td>
<td>82.09</td>
<td>190.9</td>
<td>0.18</td>
<td>2837.6</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>91</td>
<td>-0.50</td>
<td>81.16</td>
<td>203.2</td>
<td>0.18</td>
<td>2837.6</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>-0.57</td>
<td>70.99</td>
<td>285.5</td>
<td>0.25</td>
<td>2837.6</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>-0.59</td>
<td>86.06</td>
<td>246.5</td>
<td>0.23</td>
<td>2837.6</td>
<td>0.25</td>
<td></td>
</tr>
</tbody>
</table>

TABLE C.6 NMR water wettability index, $T_2$ mode values are used in the calculation.

<table>
<thead>
<tr>
<th>core #</th>
<th>$I_{AH}$</th>
<th>$T_{2,w}$ (ms)</th>
<th>$S_w = 1$</th>
<th>$T_{2,w}$ (ms)</th>
<th>$S_{or}$</th>
<th>$T_{2,w}$ (ms)</th>
<th>$I_{w,NMR}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
<td>0.93</td>
<td>196.4</td>
<td>121.7</td>
<td>0.33</td>
<td>2837.6</td>
<td>1.12</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.92</td>
<td>190.2</td>
<td>159.6</td>
<td>0.25</td>
<td>2837.6</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>0.93</td>
<td>226.5</td>
<td>175.2</td>
<td>0.31</td>
<td>2837.6</td>
<td>0.81</td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>0.08</td>
<td>178.0</td>
<td>243.1</td>
<td>0.10</td>
<td>2837.6</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>107</td>
<td>0.03</td>
<td>170.7</td>
<td>284.8</td>
<td>0.08</td>
<td>2837.6</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>-0.10</td>
<td>187.6</td>
<td>360.1</td>
<td>0.13</td>
<td>2837.6</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>-0.12</td>
<td>201.2</td>
<td>408.5</td>
<td>0.09</td>
<td>2837.6</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>-0.35</td>
<td>183.2</td>
<td>343.2</td>
<td>0.18</td>
<td>2837.6</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>-0.52</td>
<td>213.4</td>
<td>467.2</td>
<td>0.17</td>
<td>2837.6</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>66</td>
<td>-0.51</td>
<td>230.0</td>
<td>444.2</td>
<td>0.18</td>
<td>2837.6</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>91</td>
<td>-0.50</td>
<td>207.0</td>
<td>490.1</td>
<td>0.18</td>
<td>2837.6</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>-0.57</td>
<td>167.0</td>
<td>612.3</td>
<td>0.25</td>
<td>2837.6</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>-0.59</td>
<td>199.9</td>
<td>561.3</td>
<td>0.23</td>
<td>2837.6</td>
<td>0.24</td>
<td></td>
</tr>
</tbody>
</table>
TABLE C.7  NMR oil wettability index, $T_2$ mode values are used in the calculation.

<table>
<thead>
<tr>
<th>core #</th>
<th>$I_{AI}$</th>
<th>$T_{2,o}$ (ms) after F.D.</th>
<th>$S_o$ after F.D.</th>
<th>$T_{2,o}$ (ms) bulk</th>
<th>$I_{o,NMR}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>0.95</td>
<td>557.5</td>
<td>0.77</td>
<td>701.4</td>
<td>0.25</td>
</tr>
<tr>
<td>30</td>
<td>0.92</td>
<td>567.2</td>
<td>0.76</td>
<td>701.4</td>
<td>0.22</td>
</tr>
<tr>
<td>72</td>
<td>0.93</td>
<td>575.1</td>
<td>0.79</td>
<td>701.4</td>
<td>0.21</td>
</tr>
<tr>
<td>56</td>
<td>0.08</td>
<td>562.0</td>
<td>0.77</td>
<td>701.4</td>
<td>0.23</td>
</tr>
<tr>
<td>57</td>
<td>0.05</td>
<td>541.9</td>
<td>0.78</td>
<td>701.4</td>
<td>0.28</td>
</tr>
<tr>
<td>107</td>
<td>0.03</td>
<td>545.8</td>
<td>0.78</td>
<td>701.4</td>
<td>0.27</td>
</tr>
<tr>
<td>28</td>
<td>-0.10</td>
<td>453.2</td>
<td>0.84</td>
<td>701.4</td>
<td>0.56</td>
</tr>
<tr>
<td>16</td>
<td>-0.12</td>
<td>504.3</td>
<td>0.80</td>
<td>701.4</td>
<td>0.38</td>
</tr>
<tr>
<td>34</td>
<td>-0.35</td>
<td>443.1</td>
<td>0.88</td>
<td>701.4</td>
<td>0.63</td>
</tr>
<tr>
<td>45</td>
<td>-0.38</td>
<td>484.9</td>
<td>0.78</td>
<td>701.4</td>
<td>0.43</td>
</tr>
<tr>
<td>58</td>
<td>-0.52</td>
<td>456.6</td>
<td>0.81</td>
<td>701.4</td>
<td>0.54</td>
</tr>
<tr>
<td>66</td>
<td>-0.51</td>
<td>426.6</td>
<td>0.86</td>
<td>701.4</td>
<td>0.68</td>
</tr>
<tr>
<td>91</td>
<td>-0.50</td>
<td>439.6</td>
<td>0.84</td>
<td>701.4</td>
<td>0.62</td>
</tr>
<tr>
<td>26</td>
<td>-0.57</td>
<td>386.9</td>
<td>0.86</td>
<td>701.4</td>
<td>0.86</td>
</tr>
<tr>
<td>77</td>
<td>-0.59</td>
<td>420.7</td>
<td>0.88</td>
<td>701.4</td>
<td>0.72</td>
</tr>
<tr>
<td>80</td>
<td>-0.68</td>
<td>407.7</td>
<td>0.87</td>
<td>701.4</td>
<td>0.77</td>
</tr>
<tr>
<td>40</td>
<td>-0.66</td>
<td>403.2</td>
<td>0.84</td>
<td>701.4</td>
<td>0.77</td>
</tr>
<tr>
<td>69</td>
<td>-0.67</td>
<td>430.0</td>
<td>0.87</td>
<td>701.4</td>
<td>0.68</td>
</tr>
<tr>
<td>64</td>
<td>-0.72</td>
<td>427.5</td>
<td>0.92</td>
<td>701.4</td>
<td>0.73</td>
</tr>
<tr>
<td>51</td>
<td>-0.60</td>
<td>428.8</td>
<td>0.87</td>
<td>701.4</td>
<td>0.68</td>
</tr>
<tr>
<td>96</td>
<td>-0.69</td>
<td>433.9</td>
<td>0.87</td>
<td>701.4</td>
<td>0.66</td>
</tr>
</tbody>
</table>

TABLE C.8  $T_2$ mode values of Berea cores at 100% $S_o$

<table>
<thead>
<tr>
<th>Core #</th>
<th>37</th>
<th>41</th>
<th>51</th>
<th>64</th>
<th>69</th>
<th>96</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{2,0, S_o = 1}$ (ms)</td>
<td>411.6</td>
<td>378.9</td>
<td>407.8</td>
<td>366.2</td>
<td>384.1</td>
<td>374.6</td>
</tr>
<tr>
<td>Mean (ms)</td>
<td></td>
<td>387.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Std. (ms)</td>
<td></td>
<td>18.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Core #</td>
<td>$I_{AH}$</td>
<td>$I_{W,NMR}$</td>
<td>$I_{O,NMR}$</td>
<td>$I_{C,NMR}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>----------</td>
<td>-------------</td>
<td>-------------</td>
<td>-------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.92</td>
<td>0.85</td>
<td>0.22</td>
<td>0.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>0.93</td>
<td>0.78</td>
<td>0.21</td>
<td>0.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>0.08</td>
<td>0.69</td>
<td>0.23</td>
<td>0.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>107</td>
<td>0.03</td>
<td>0.59</td>
<td>0.27</td>
<td>0.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>-0.10</td>
<td>0.39</td>
<td>0.56</td>
<td>-0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>-0.12</td>
<td>0.38</td>
<td>0.38</td>
<td>-0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>-0.35</td>
<td>0.46</td>
<td>0.63</td>
<td>-0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>-0.52</td>
<td>0.40</td>
<td>0.54</td>
<td>-0.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>66</td>
<td>-0.51</td>
<td>0.34</td>
<td>0.68</td>
<td>-0.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>91</td>
<td>-0.50</td>
<td>0.31</td>
<td>0.62</td>
<td>-0.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>-0.57</td>
<td>0.17</td>
<td>0.86</td>
<td>-0.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>-0.59</td>
<td>0.25</td>
<td>0.72</td>
<td>-0.47</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE C.9 Combined NMR wettability indices, $T_2$ mode values are used in the calculation