A THEORETICAL MODEL OF NMR SURFACE RELAXATION IN POROUS MEDIA

by

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Abstract

A model has been developed to express the relaxation time constant of pore water hydrogen protons in porous geological materials. This model is based on the dipolar interactions of the protons with the naturally found paramagnetic ions near the surface of the solid, modulated by the diffusive motion of the pore water molecules. The effect of a uniform nonmagnetic coating on the solid, which physically separates the water molecules from the paramagnetic ions, is incorporated in the developed model of surface relaxation rate, $1/T_{1S}$.

A three-dimensional model pore space is defined as a rectangular prism in a sheet-like pore structure. The motion of the molecules is described as two-dimensional diffusion parallel to the solid pore walls, and one-dimensional diffusion perpendicular to the surfaces. The dipolar interaction is considered between hydrogen protons associated with the water molecules, and a layer of randomly distributed paramagnetic ions on the solid. The protons' distance of closest approach to the layer of paramagnetic ions is determined by the thickness of substance coating the solid surface.

The resulting expression for $1/T_{1S}$ involves a number of parameters, some of which can be eliminated by considering the normalized relaxation rates: $1/T_{1S}$ for the coated sample divided by that of the uncoated sample. Other unknown parameters are used to set bounding limits on the predicted normalized relaxation rates, $T_{1S}(\text{plain})/T_{1S}(\text{coated})$. The predicted trend in $T_{1S}(\text{plain})/T_{1S}(\text{coated})$ with increasing coating thickness can be approximated by a logarithmic decline for thicknesses up to 2nm. This predicted decay in normalized relaxation rate with increasing coating thickness is more gradual than the trend predicted by previous models. As a result, the application of the developed model to measured relaxation times reported in studies of coated and plain samples is capable of providing realistic estimates of coating thicknesses.

ii

Table of Contents

Abstract	ii
List of Tables	iv
List of Figures	v
Acknowledgements	vi
Introduction	1
Theory	10
Basic Principles of NMR	10
T ₁ Relaxation Mechanism	11
Model Description	16
Results and Discussion	23
Summary and Conclusions	34
References	

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List of Tables

Table 1: References to NMR relaxation rate experiments with different surface	ce states of porous
materials	4
Table 2: Relaxation rates and predicted coating thicknesses using models: a)	restricted rotational
diffusion; and b) 2D planar diffusion.	9
Table 3: Model Parameters	23
Table 4: Model Comparisons	

List of Figures

Figure 1:	Geometry of a point, P, at a displacement, r, from a pure magnetic dipole at the origin.
Figure 2:	Cross Section of the sheet-like pore structure
Figure 3:	Dependence of normalized relaxation rate on the coating thickness27
Figure 4:	The trend in the spectral density functions with respect to angular frequency28
Figure 5:	Dependence of Relaxation rate, $1/T_{1S}$, on proton Larmor frequency at different coating
thick	nesses
Figure 6:	Dependence of the relaxation rate, $1/T_{1S}$, on the relative diffusion coefficient, R_D 30
Figure 7:	Dependence of the relaxation rate, $1/T_{1S}$, on the thickness of solid layer containing
paran	nagnetic ions, l _p

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vi

Introduction

Proton nuclear magnetic resonance (NMR) can be used to obtain information about the molecular-scale environment of fluids in porous materials. In a typical proton NMR experiment, the sample is placed in a static magnetic field, which acts on the nuclear magnetic moments of the hydrogen nuclei (protons) associated with the pore fluid, to yield a net macroscopic magnetization at thermal equilibrium. In many experiments, the measured quantity of interest is related to the approach of this macroscopic magnetization to thermal equilibrium following a perturbation. The change in magnetization with time is commonly described as a single exponential with time constant, T_1 , referred to as the relaxation time. The main uses of NMR in the Earth sciences have involved relaxation time measurements of water or hydrocarbons in porous geological materials.

The relaxation mechanism is governed by the diffusive motion of the pore fluid molecules, and the dipolar interactions between the hydrogen protons with other protons or paramagnetic ions. The bulk fluid has a characteristic relaxation time constant associated with this mechanism, which is referred to as T_{1B} . When the pore fluid is contained in the pore space of a porous material, the chemistry and the physical structure affect the measured relaxation time of the pore fluid. This is due to the diffusive motion of the pore fluid molecules, and the interactions between the hydrogen protons and paramagnetic species such as Fe(III) and Mn(II) in the solid phase. The relaxation time associated with the effect of the paramagnetics near the solid surface is denoted by T_{1S} . Each source of dipolar interaction leading to relaxation, acts independently to yield the measured relaxation rate, $1/T_1$,

$$\frac{1}{T_1} = \frac{1}{T_{1B}} + \frac{1}{T_{1S}}.$$
 [1]

Most NMR studies use the surface relaxation rate, $1/T_{1S}$, in order to obtain information about the molecular-scale environment of the porous geologic material.

Of specific interest in my research is the use of NMR to detect, or quantify, the presence of a contaminant adsorbed to, or coating, the solid surface. The basic idea is that a surface coating will affect the interaction between the near surface paramagnetic ions and the hydrogen protons in the pore fluid. What is required is a fundamental understanding of the resulting effect on the measured relaxation rates.

Brown and Fatt (1) first demonstrated the effect of silicone coating, on the T_1 relaxation rate of water hydrogen protons in the pore space of a sample consisting of sand grains. They concluded that surface relaxation rate, $1/T_{1S}$, is reduced through physical separation of the paramagnetic ions from the diffusing pore water molecules. Since then, numerous experiments on synthetic and natural materials with various types of coatings have consistently reported a decrease in relaxation rates in the presence of the coating. Table 1 summarizes these experiments in terms of the materials, magnetic field strengths, and the saturating fluids. Although some experiments also involved deuteron T_1 , T_{1p} , and proton T_2 measurements, we only consider proton T_1 in this study.

The motivation for many of these experiments was to develop an understanding of the link between the wettability of a geological material and T_1 relaxation times. Wettability is defined as the affinity of a fluid to the solid surface. In the analysis of geologic materials, surfaces are thought of as either water-wet or oil-wet. In a water-wet system, the water in the pore space will preferentially form a coating on the pore walls. Thus, water is referred to as the wetting fluid in a water-wet system. In an oil-wet material, water is repelled by the solid surfaces, and is referred to as the non-wetting fluid. Commonly, a layer of hydrophobic substance coating the solid surface of a naturally water-wet system is associated with an oil-wet material.

Most studies in Table 1 used a coating substance to change the wettability of their sample porous material. The observed effect of wettability on the surface relaxation rate can thus be attributed to the presence of the coating. Some of the studies considered (1, 3, 4, and 8), attempted to quantify the percentage of each surface type (wettability) using proton relaxation rate measurements of water. Other studies (Table 1: 5-6,9-12, & 14) measured the relaxation rates of protons associated with both the water and oil present in the pore space, as a means to study the surface effects on oil/water saturation. While Kanters, et al. (13) studied the dependence of pore water proton relaxation rates on surface properties through varying the geometry of the pore space (Table 1: 13), Hsu (7) considered the chemistry of the samples and the material coating the solid surfaces (Table 1: 7). Of these studies, only two attempted to correlate the amount of coating on grains with measured T_1 relaxation rates (Table 1: 2 & 15). In order to do so, a theoretical model is needed to describe the effect of paramagnetic ions and coating substances on the surface relaxation rate of diffusing pore fluid hydrogen protons.

The theoretical basis for the bulk relaxation rate, $1/T_{1B}$, of water is well described by Bloembergen, et al. (16). The surface relaxation rate, $1/T_{1S}$, in geologic materials is best described by the presence of paramagnetic ions in a layer near the solid surfaces, and diffusing protons in the pore space. There are currently two models which treat such a system: one proposed by Kleinberg et al. (17) specifically for relaxation mechanism in rocks; and the other by Neue (18) for a more general model of dipolar interactions in enhancing relaxation rates.

In describing the relaxation mechanism in rocks, Kleinberg et al. (17) used the restricted rotational diffusion model for protons coordinated with paramagnetic ions on the surface of the grains. This model predicts a strong decrease in relaxation rate $1/T_{1S}$, as the distance of closest approach, r, of the proton to the paramagnetic ion increases, $1/T_{1S} \propto 1/r^6$. Based on this model, even a thin coating of 5Å, comparable to the size of a single molecule associated with the coating substance, would reduce $1/T_{1S}$ to less than 1% of its value for the uncoated sample.

Table 1: References to NMR relaxation rate experiments with different surface states of porous materials.

Re	ference	NMR	Field	Surface State	Saturating Fluid
Stu	ıdy / Year	Measurement	Strength		
1.	Brown & Fatt (1) / 1956	proton T ₁	200 G	Sand, some with Dri-film coating	Water
2.	Devereux (2) / 1967	proton T ₁	3000 G	Clean untreated sandstone; clean sandstone treated with various surfactants; clean sandstone exposed to crude oil	Distilled water
3.	Kumar, et al. (3) / 1969	proton T ₁	6600 G	glass beads and hydrophobic plastic beads (Lucites)	Distilled water with paramagnetic salts
4.	Williams & Fung (4) / 1982	proton T_1 deuteron $T_{1\rho}$	0.7 T 4.6 T	micro glass beads, some with silicone coating	water & deuterium oxide
5.	Borgia, et al. (5) / 1991	proton T ₁	0.47 T	partial oil coating oil-field & reference Berea cores	oil & 5% NaCl brine
6.	Howard (6) / 1994	proton T ₁	0.23 T	chalk samples, some treated with oil-based drilling mud	water and decane
7.	Hsu (7) / 1994	proton T_1 deuteron $T_{1\rho}$	2 T	glass beads, some with silicone coating and some with crude oil coating; polymer beads, some with silica layer; carbonate core samples, some treated with naphthenic acid	Distilled deionized water and deuterium oxide
8.	Bonalde, et al. (8) / 1995	proton T_1 deuteron T_1	2.12 T 7 T	sand and Berea sandstone samples, some with coated phenolic resin	water & deuterium oxide
9.	Bobroff, et al. (9) / 1995	proton $T_1 \& T_2$	0.1 T	natural & silanated sandstone rocks	Dodecane and deuterium oxide
10.	Bobroff & Guillot (10) / 1996	proton T ₂	0.1 T	natural & silanated Fontainebleau sandstone, glass capillary tubes	Dodecane and deuterium oxide
11.	Borgia, et al. (11) / 1997	proton T ₁	0.47 T	well-consolidated clean sandstone cores	oil & 5% NaCl brine
12.	Howard (12) / 1998	proton T ₁ , T ₂	400 G	chalk samples, some with synthetic mineral oil coating	water & synthetic mineral oil
13.	Kanters, et al. (13) / 1998	proton T ₁	2.12 T	sand, some with crude oil coating	Distilled water and NaCl brines
14.	Zhang, et al. (14) / 1999	proton T ₁	400 G	sandstone samples, some with crude oil coating	refined oil, crude oil, and water
15.	Daughney, et al. (15) / 2000	proton T ₁	2 T	silica gel, some with sorbed crude oil	Distilled de- ionized water

Neue (18) provides an explicit numerical expression for the relaxation rate in a generic model of translational diffusion of molecules on a two-dimensional surface. These mobile hydrogen protons interact through dipolar coupling with immobile paramagnetic ions at a fixed distance, r, off the plane of diffusion. If we consider the example of water in the pore space of a geological material, the model would apply to an adsorbed layer of water diffusing on the pore walls, and a random distribution of surface paramagnetic ions with constant density. The separation, z, would correspond to the sum of the coating thickness, and the minimum distance between the centres of a paramagnetic ion and a water molecule (2.95Å). The resulting calculated relaxation rate, $1/T_{1S}$, varies as $1/z^2$ to $1/z^6$ according to the field strength of the static magnetic field, the diffusion coefficient as determined by the temperature, and the separation distance, z. For a coating thickness of 5Å, this model would predict a drop in $1/T_{1S}$ to a maximum of 14% of its value for the uncoated sample at room temperature.

Let us evaluate and compare these models using experimental observations. Experiments selected are listed in Table 2, where we give surface coating and the surface relaxation rates for the plain and coated samples. In one case, the reported relaxation times corresponded to the surface relaxation time, T_{1S} (1), while for other studies, we calculated the surface relaxation times using the reported values for T_1 and T_{1B} (Eq. [1]). Kanters, et al. (13) reported that the measurements were made at a temperature of $24\pm1^\circ$ C, and similarly, Daughney et al. (15) reported a temperature of 25° C. Since the measurement temperature was not mentioned in the other three studies, we assume that those were also conducted at room temperature. Three criteria were considered in the selection process: 1) the substance coating the surfaces contained negligible amount of paramagnetic ions; and 2) the solid surface was uniformly covered by the coating substance; and 3) the geometry, or more specifically the surface area to volume ratio of the pore structure, was not altered by the addition of the coating.

It is very difficult to ascertain the above mentioned criteria for all of the studies mentioned in Table 1. It is, however, possible to eliminate those experiments in which the coating process was not well controlled. In consideration of the first criterion regarding paramagnetic ions in the coating substance, we have selected those experiments that used synthetic coating material with known chemical composition, or natural crude oils with available chemical analysis. In the study by Devereux (2), the residual crude oil remaining as surface coating on the clean sandstone after the coating treatment, was analyzed by the author and reported as asphaltene. The dominant sources of paramagnetic ions in asphaltene are vanadium and organic free radicals (19). However, the contribution of these low concentrations of ions in asphaltene to $1/T_{1S}$ is insignificant. Hsu (7) also reports the chemical analysis for two types of crude oil used in that study. One of these, referred to as Kuparuk crude oil, contained < 2ppm by weight of paramagnetic ions. The effect of such low concentrations of paramagnetics in the coating would be insignificant in a T_1 measurement. Therefore, the T_1 values in the study by Hsu (7) that uses the Kuparuk crude oil is considered in Table 2. Traci Bryar has provided chemical analysis of the crude oil used in the studies by Kanters, et al. (13) and Daughney et al. (15), which also indicated negligible amount of paramagnetic ions.

Regarding the second criterion for uniform coverage, studies were selected based on their controlled coating procedure. A dilute solution of the coating substance was applied for uniformly treating all surfaces, while providing appropriate amount of coating in the solution for complete coverage. In the case of Devereux (2), the sample was tested for maximum adsorption of the coating material by measuring the T_1 relaxation times for several days during the treatment until an equilibrium value was reached. In two other studies (1, 13), the coated samples floated in water, which is indicative of a strongly oil-wet surface.

The sample materials used by Devereux (2) and Daughney et al. (15) had a microporous structure, since their results of relaxation times indicated the sum of two exponentials with

distinct time constants, or in other words, they observed a bimodal T_1 distribution. Therefore, it is likely that these samples had not been uniformly covered by the coating material. In both cases, the authors attributed the longer relaxation times to the pore fluid contained in the macropores, and thus the values of surface relaxation rates in Table 2 correspond to the longer reported relaxation times. Uniform coverage is a reasonable assumption in the studies considered, but we acknowledge the fact that it is not conclusively established.

In consideration of the third criterion, the selected experiments had attempted to remove excess coating using a solvent, and reported leaving only a residue of the coating material. One study reported specific surface area measurements for the coated and plain silica gel samples (15). In this study, Daughney et al. (15) concluded that adsorbed oil did not affect the surface area to volume ratio of their samples. With respect to other studies in Table 2, we assume that a uniform thin coating on a molecular scale does not change the surface area to volume ratio of the studies area in the order of microns. In addition, the treatment process in selected experiments involved a dilute solution of the coating substance to ensure a thin and yet uniform coverage.

For each of these experiments, it is possible to put a lower limit on the size of the molecules associated with the coating. For the Dri-film material, 11Å corresponds to the size of the smallest hydrocarbon chain contained in the coating (7). The heavy crude oil, or asphaltene, can be characterized by hydrocarbon rings, whose thickness is greater than 5Å (20). In the case of synthetic coatings used in the study by Devereux (2), exact values were provided. These estimates of the molecular size of the coating substance impose lower limits on the expected coating thickness if uniform coating is assumed.

The dependence of $1/T_{1S}$ on coating thickness, as predicted by the above models, can be assessed using values of relaxation rates reported for coated and plain samples in Table 2. Both the rotational diffusion model by Kleinberg et al. (17), defined as model a, and the two-

dimensional diffusion model by Neue (18), model b, predict a sharp decay in $1/T_{1S}$ with increasing coating thickness. This effect is attributed to the increasing distance of separation between the interacting water molecules and the paramagnetic ions. As a result, we expect the surface relaxation rates of coated samples to fall considerably by a monolayer of molecules forming the coating substance. According to model a, the relaxation rate of the coated sample would be less than 1% of its value for the plain sample. Likewise, model b would predict a drop to a maximum of 14%. However, the relaxation rates of coated samples in the studies considered in Table 2, are within 5.7-76% of their corresponding $1/T_{1S}$ for the plain samples.

The reported relaxation rates and the field strength in each study are used to estimate the coating thickness according to models a and b. For this purpose, we have assumed the three criteria regarding the surface states, and used the diffusion coefficient at room temperature for model b. These calculated coating thicknesses are shown in Table 2 along with a lower limit on the molecular size of the coating materials. For uniformly coated samples, the molecular size of the coating substance represents a minimum coating thickness. As shown in Table 2, both models predict coating thicknesses less than the expected minimum.

There are two possible explanations for the low estimates of coating thickness by these models. One is that the assumption of uniform coverage does not apply to the studies considered. The second explanation is related to the models themselves. If models a and b are not sufficiently descriptive of the physical system, the resulting trends in relaxation rate with increasing coating thickness would be invalid. In so far as we have no evidence for the non-uniformity of the surface coverage, we plan to develop a more realistic model that would characterize the effect of coating thickness on the surface relaxation rate.

A new model is proposed that accounts for the translational diffusion of pore water molecules away from the solid surface. This model considers three-dimensional diffusion of pore water molecules in sheet-like pore structures. It is assumed that paramagnetic ions are

uniformly distributed in a layer near the surface of the grains. We consider the presence of a substance uniformly coating the surface as a physical separation between the pore water molecules and the paramagnetic ions. Translational diffusion parallel and perpendicular to the solid surfaces define the motion of the pore water molecules. The purpose of this study is to provide an expression for calculating the surface relaxation rate, $1/T_{1S}$, in the given three-dimensional pore structure. In particular, we aim to model the dependence of $1/T_{1S}$ on the coating thickness. The developed model can then be evaluated in comparison to previous models through estimates of coating thickness for experimentally measured values of relaxation times. If successful, this model can be potentially useful for the detection of adsorbed contaminants using T_1 relaxation time measurements of fluids in porous geological materials.

		Molecular Size	Plain 1/T	Coated	Predicted	Coating
Study / Year	Surface Coating	[Å]	[1/s]	[1/s]	Model a	model b
Brown & Fatt (1) / 1956	Dri-film (SF99 GE)	> 11	5.2	1.25	0.8	3.1
Devereux	Methylene blue	4.5	3.61	2.73	0.1	0.5
(2) / 1967	Dodecylammonium acetate	15	3.61	1.69	0.4	1.5
	Stearic acid	23	3.61	1.34	0.5	2.1
	asphaltene	>5	6.71	0.50	1.6	7.5
Hsu	Dri-film (SF99 GE)	> 11	0.53	0.03	1.9	7.7
(7) / 1994	Kuparuk crude oil	> 5	0.53	0.12	0.8	3.0
Kanters, et al.	Crude oil	> 5	0.88	0.20	0.8	2.9
(13) / 1998	(for various grain	> 5	0.76	0.18	0.8	2.8
	sizes ranging from 115 to 275 μm)	> 5	0.68	0.13	0.9	3.4
		> 5	0.34	0.09	0.7	2.5
		> 5	0.51	0.05	1.4	5.6
Daughney, et al. (15) / 2000	Crude oil (sample with highest relative change in relaxation rate due to sorbed crude oil)	> 5	34.1	19.7	0.3	0.9

 Table 2: Relaxation rates and predicted coating thicknesses using models: a) restricted rotational diffusion; and b) 2D planar diffusion.

 Molecular
 Plain
 Coated
 Predicted Coating

¹ Distance of closest approach of the pore water protons to the centre of paramagnetic ions in the uncoated samples is estimated to be 2.95Å.

Theory

Basic Principles of NMR

This section briefly describes some of the basic principles in NMR T₁ relaxation time measurements. In a nuclear magnetic resonance experiment, the sample is placed in a uniform static magnetic field, B₀. Nuclei in the sample with spin angular momentum, such as hydrogen protons associated with water molecules, H⁺, precess about the axis of B₀. The inherent magnetic dipole moment of a spin I particle, $\bar{\mu}_1$, is given by (21)

$$\bar{\mu}_I = \gamma_I \hbar \bar{I} , \qquad [2]$$

where \overline{I} is the spin operator with spin quantum number I, \hbar is the Planck constant divided by 2π , and γ_I is the magnetogyric ratio of the spin I particle. A magnetic field exerts a torque on the magnetic moment of nuclear spins, causing them to precess. The angular frequency of precession (Larmor frequency ω) is proportional to the magnitude of B_o ,

$$\omega_I = -\gamma_I B_{\circ}. \tag{3}$$

A nucleus of spin I=1/2 has two spin energy states. The lower energy state is associated with the z-component of spin, $I_z = +1/2$, and points in the direction of the applied field. The higher energy state with $I_z = -1/2$ points in the direction opposite B_0 . In thermal equilibrium, there is a higher population of lower energy states with $I_z = +1/2$. This population imbalance yields a net macroscopic magnetization, $\langle M_z \rangle_{eq}$, in the z-direction parallel to B_0 .

A pulse of an oscillating magnetic field, B_1 in the x-y plane, and at the protons' Larmor frequency causes $\langle M_z \rangle_{eq}$ to precess about B_1 . This precession about B_1 can be described by rotation of $\langle M_z \rangle$ away from the z-axis. The angle of rotation is linearly proportional to the duration of the pulse, where $B_1 \langle \langle B_0 \rangle$. The macroscopic magnetization, $\langle M_z \rangle$, returns back to its thermal equilibrium value after the removal of the pulse at time, t = 0. A perturbation caused by B_1 for a 180° rotation, can be described by

$$< M_z(t) > = < M_z >_{eq} (1 - 2e^{-t/T_1}).$$
 [4]

Many systems exhibit an exponential relaxation to equilibrium characterized by a single time constant, T_1 , as in Eq. [4]. The inverse of this time constant, $1/T_1$, is commonly referred to as the T_1 relaxation rate.

For the hydrogen protons of the water molecules in a pore space, their instantaneous relaxation is a function of their positions and interactions with the surrounding media. Water molecules diffusing in a pore space sample the entire volume during a T_1 measurement. This results in the detection of an average relaxation rate. A typical T_1 experiment involves a series of pulse sequences. Each sequence is a 180° rotation followed by a time delay, t, and a 90° rotation, which is referred to as a 180°-t-90° sequence. This is the inversion recovery method, where the 90° pulse brings the z-magnetization into the x-y plane for measurement (22). By varying the time delay, t, in each sequence, the z-component of magnetization can be measured with respect to time. This will allow for the determination of the time constant, T_1 , as described by Eq. [4].

T₁ Relaxation Mechanism

This section describes the mechanism by which T_1 relaxation occurs. Coupling of the nuclear spins (pore water hydrogen protons) with the surrounding medium, historically referred to as the lattice, results in the return of z-magnetization to its thermal equilibrium value. The temperature of the lattice is reflected in the distribution of water and potential energies of the constituent molecules. Therefore, the T_1 relaxation rate is also known as the spin-lattice relaxation rate (21). The coupling of the nuclear spins with the lattice is through dipolar interactions that are modulated by the random diffusive motion of the water molecules.

The master equation for relaxation of a physical variable due to a random perturbation can be used to derive an expression for the T_{1S} relaxation rate (21). In this case, the physical

variable of interest is the macroscopic z-magnetization and the perturbation is due to dipolar interactions. This treatment requires the time dependent dipolar coupling with the lattice to be represented by its Hamiltonian, $H_{dipolar}(t)$. A description of the interaction energy between two magnetic dipoles, and their relative motion, can be used to derive $H_{dipolar}(t)$.



Figure 1: Geometry of a point, P, at a displacement, r, from a pure magnetic dipole at the origin.

The electronic spins, S, of paramagnetic ions commonly found in natural materials are responsible for these interactions. The following describes the dipolar interaction energy between the magnetic dipoles of two spins, I and S. The spins associated with the hydrogen nuclei of the pore fluid are denoted by I, while S refers to the electronic spin of the paramagnetic ions. The magnetic dipole moment of a spin particle produces a local magnetic field, B_{loc} . Figure 1 depicts the geometry of a magnetic dipole moment, μ_S , of a spin S particle at the origin, whose magnetic field at point P is given by (23)

$$\vec{B}_{loc} = \left(\frac{\mu_{\circ}}{4\pi}\right) \frac{1}{r^3} [3(\vec{\mu}_{\rm S} \cdot \hat{r})\hat{r} - \vec{\mu}_{\rm S}].$$
[5]

In this equation, μ_0 is the permeability of free space and r is the displacement vector as shown in Figure 1. The interaction energy, U, between the magnetic dipole moment, μ_I , of a spin I particle with B_{loc} is

$$U = -\bar{\mu}_{I} \cdot \bar{B}_{loc} = \left(\frac{\mu_{o}}{4\pi}\right) \left(\frac{1}{r^{3}}\right) \left[\bar{\mu}_{I} \cdot \bar{\mu}_{S} - 3(\bar{\mu}_{I} \cdot \hat{r})(\bar{\mu}_{S} \cdot \hat{r})\right].$$
 [6]

The next step in deriving an expression for $H_{dipolar}(t)$ is to introduce the time dependence of the interaction energy. The diffusive motion of pore water proton results in random fluctuations in the relative positions of the interacting spins on a molecular length scale. The paramagnetic ions with electronic spins S are assumed fixed in the solid matrix. As shown in Figure 1, the fluctuating geometrical parameters are r, θ , and ϕ . The time dependence of the interaction energy is thus contained in the random diffusive motion of the pore water molecules. It is assumed that each paramagnetic spin S contributes independently to $1/T_{15}$. This assumption ignores any correlation between the spins S, which is justified by their fast return to thermal equilibrium relative to the relaxation time of the nuclear spins. The operator form of the interaction energy described above gives the expression for $H_{dipolar}(t)$. Inserting the expression for magnetic moments in terms of their spin operators (Eq. [2]) into Eq. [6] gives the dipolar coupling Hamiltonian,

$$H_{dipolar}(t) = \left(\frac{\mu_{\circ}}{4\pi}\right) \left(\frac{\gamma_{1}\gamma_{S}\hbar^{2}}{r^{3}}\right) [\bar{\mathbf{I}}\cdot\bar{\mathbf{S}} - 3(\bar{\mathbf{I}}\cdot\hat{\mathbf{r}})(\bar{\mathbf{S}}\cdot\hat{\mathbf{r}})] \cdot$$
[7]

Before applying the given expression for the dipolar interaction Hamiltonian to the master equation for relaxation, it is useful to expand it and define its correlation functions. Expansion of this random operator, $H_{dipolar}(t)$, in polar coordinates yields the sum of five terms² (21)

$$H_{dipolar}(t) = \sum_{q=-2}^{2} F^{q}(t) A^{(q)} .$$
[8]

Each of these terms is the product of the random time varying geometrical component, $F(t)^{(q)}$, with the time-independent function of spin operators, $A^{(q)}$. The functions $F^{(q)}$ are defined as the

² This is the scalar product of the irreducible rank two tensors: $F^{(q)}(t)$ and $A^{(q)}$.

normalized second order spherical harmonics divided by r^3 . The remaining time independent terms, $A^{(q)}$, involving spin operators, are then described by

$$A^{(0)} = \left(-\frac{3}{2} \gamma_{I} \gamma_{S} \hbar \sqrt{\frac{16\pi}{5}} \right) \left\{ -\frac{2}{3} I_{Z} S_{Z} + \frac{1}{6} (I_{+} S_{-} + I_{-} S_{+}) \right\},$$
[9]

$$A^{(1)} = \left(-\frac{3}{2}\gamma_{1}\gamma_{s}\hbar\sqrt{\frac{8\pi}{15}}\right)\{I_{z}S_{+} + I_{+}S_{z}\},$$
[9a]

$$A^{(2)} = \left(-\frac{3}{2}\gamma_1\gamma_5\hbar\sqrt{\frac{32\pi}{15}}\right)\left\{\frac{1}{2}I_+S_+\right\},$$
[9b]

$$\mathbf{A}^{(q)} = \mathbf{A}^{(-q)\dagger} \,. \tag{9c}$$

The spin operators in Eqs. [9] define a complete set of eigenfunctions for systems described by angular momentum. The dipolar coupling of spins, I and S, leading to relaxation, involves the energy transfer between states differing by a spin quantum number 1. Hence, each term in $A^{(q)}$ relates to a specific pair of connecting states. It is useful at this point to define the correlation functions,

$$G_{aa'}(\tau) = \overline{F^{(q)}(t)F^{(q)*}(t+\tau)},$$
[10]

for the time dependent geometrical components.

From an intuitive perspective, any perturbation to the system such as application of B₁ for rotation, or the dipolar coupling with spins S must involve the resonance frequencies for energy transfer between the spin states as given by Eqs. [9]. These resonance frequencies are described by the Larmor frequency of the protons, ω_I , and that of the electronic spins, ω_S . As an example, consider the term A⁽⁰⁾, which involves an increase in the spin quantum number of S, and a decrease for spin I. This energy difference is denoted by $\omega_S - \omega_I$. For the dipolar coupling to induce relaxation, we expect the time varying geometrical component, $G_{qq}(\tau)$, to contain the appropriate resonance frequencies.

The master equation for relaxation of a physical variable, such as the z-component of macroscopic magnetization, requires the definition of the correlation functions (Eq. [10]), and their corresponding spectral density functions:

$$J^{(m)}(\omega) = \sum_{q,q'=-2}^{2} \left\{ D_{qm}^{(2)*}(\alpha,\beta,\gamma) D_{q'm}^{(2)}(\alpha,\beta,\gamma) \int_{-\infty}^{\infty} G_{qq'}(\tau) e^{-i\omega\tau} d\tau \right\}.$$
 [11]

The spectral density functions, $J^{(m)}(\omega)$, are the Fourier transforms of the correlation functions mapped into the laboratory frame. The Wigner rotation matrices, $D_{qm}^{(2)}(\alpha, \beta, \gamma)$ (24), transform the interaction frame into a laboratory frame with the z-axis parallel to the static magnetic field. The T₁ relaxation rate due to dipolar interactions between two unlike spins, I and S, is thus given by (21)

$$\frac{1}{T_{1s}} = \gamma_I^2 \gamma_s^2 \hbar^2 S(S+1) \left\{ \frac{1}{3} J^{(0)}(\omega_I - \omega_s) + J^{(1)}(\omega_I) + 2J^{(2)}(\omega_I + \omega_s) \right\} \left(\frac{\mu_*}{4\pi} \right)^2 \left(\frac{4\pi}{5} \right)$$
[12]

where the angular frequencies, ω_I and ω_S , represent the Larmor frequencies of the spin systems I and S, respectively.³

³ Note the difference in the coefficients of the spectral density functions arise from a different definition of the geometrical $F^{(q)}$ functions by Abragam (1961).

Model Description

The relaxation rate of pore water hydrogen protons with spin I can be calculated for a given geometry and relative motion of the interacting spins according to Eq. [12]. This would require a description of the diffusive motion of the water molecules in a model representation of the pore space. The time varying position of the pore water molecules relative to that of paramagnetic ions can provide an expression for the correlation functions given by Eq. [10]. Their corresponding spectral density functions defined in Eq. [11] can then be used to calculate the relaxation rate.

The model assumes a simple pore structure in three dimensions. Figure 2 shows the cross section of the model pore structure. The pore water molecules diffuse in the rectangular prism between two slabs of the coated solid rock grains. The water thickness, L, is related to the surface area to volume ratio of the pore space and is defined by the following expression:

$$L = 2 \left(\frac{S_p}{V_p}\right)^{-1}.$$
 [13]

Of particular interest in this model is the parameter l_c , which represents the thickness of the substance coating the solid surfaces. The closest distance between the diffusing pore water molecules and the paramagnetic ions is governed by l_c . Water molecules, which contain the hydrogen nuclear spins, I, can diffuse to the surface of the solid containing paramagnetic ions with electronic spin S. In case of a metal oxide coating, for example, this model considers the surface to be the centre of the oxygen atoms covering the solid rock grains. The closest distance between I and S, y, is approximated by

$$y = l_c + r_1 + d_s,$$
 [14]

where l_c is the thickness of the coating, r_I is the bond length between hydrogen and an oxygen atom in water, and d_s is the depth of the paramagnetic ion from the solid surface. Iron oxides such as goethite and hematite are formed on the surfaces of natural geological materials due to weathering. We have found only one study with reported thickness of the iron-bearing layer, l_p on an aquifer sand (25). In this study by Coston et al. (25), various microscopy techniques were used to determine the composition and distribution of oxides on quartz grains. They found through the use of their most sensitive technique, time of flight-secondary ion mass spectroscopy (TOF-SIMS), that all surfaces were uniformly covered by aluminum and iron. Furthermore, they reported thicknesses of these iron-bearing layers to vary from <10nm to more than 30 μ m using the combination of scanning electron microscope (SEM) and TOF-SIMS depth profiles.



Figure 2: Cross Section of the sheet-like pore structure.

The next step in the derivation of the correlation functions is to express the time varying position of the pore water molecules with respect to a single paramagnetic ion. The correlation functions, $G_{qq'}(\tau)$ as defined by Eq. [10], are the ensemble average over the probability distribution of the random functions $F^{(q)}(\bar{r}, \tau)F^{(q)*}(\bar{r})$, and can be expressed as

$$G_{qq'}(\tau) = \int \cdots \int P(\vec{r} / \vec{r}_{\circ}, \tau) p(\vec{r}_{\circ}) F^{(q)}(\vec{r}, \tau) F^{(q')*}(\vec{r}_{\circ}) d\vec{r}_{\circ} d\vec{r} , \qquad [15]$$

where,

$$\overline{\mathbf{r}}(\mathbf{t}) = \mathbf{r}(\tau), \boldsymbol{\theta}(\tau), \boldsymbol{\phi}(\tau) = \mathbf{r}(\tau), \boldsymbol{\Omega}(\tau),$$

and

$$\vec{\mathbf{r}}(0) = \mathbf{r}_{\circ}, \boldsymbol{\theta}_{\circ}, \boldsymbol{\phi}_{\circ} = \mathbf{r}_{\circ}, \boldsymbol{\Omega}_{\circ}.$$

As previously mentioned, the geometrical components of the Hamiltonian for the interaction energy, $F^{(q)}$ and $F^{(q')}$, are related to the second order spherical harmonics, $Y_2^{(q)}$ as in the following expressions:

$$F^{(q)}(\vec{r},\tau) = \frac{Y_2^{(q)}(\vec{\Omega}(\tau))}{r^3(\tau)} \text{ and } [16]$$

$$F^{(q)*}(\bar{r}_{\circ}) = \frac{Y_{2}^{(q)*}(\bar{\Omega}_{\circ})}{r_{\circ}^{3}},$$
[16a]

where the orientation parameter, Ω , represents the polar angles, ϕ and θ , between a diffusing water molecule and a stationary paramagnetic ion with spin S, and r is the distance between them. The conditional probability density, P(r/r_o, τ), of finding two spins, I and S, with displacement vector, r, given their initial displacement at time zero is r_o, can be described by the solution to the diffusion equation for the fluid molecules in a given geometry.

In this model, the pore fluid molecules are allowed to diffuse in two-dimensions parallel to the surfaces, and in one-dimension perpendicular to the solid. The probability distribution function is thus expressed in two parts: 1) as the solution to the two-dimensional diffusion equation on a 2D plane parallel to the surfaces; and 2) as the solution to the one-dimensional diffusion equation on a line perpendicular to the surfaces. The former has been expressed by Neue (18) for an infinitesimal layer of diffusing water molecules at a fixed distance of separation, z', from the solid surface containing the paramagnetic ions. The latter solution to the diffusion to the solid surface paramagnetic ions.

$$P(z'/z'_{\circ},\tau) = \frac{1}{\sqrt{4\pi D_{\perp}\tau}} \sum_{l=-\infty}^{\infty} \left\{ e^{-[z'-(2lL+z'_{\circ})]^2/(4D_{\perp}\tau)} + e^{-[z'-(2lL-z'_{\circ})-2y]^2/(4D_{\perp}\tau)} \right\},$$
[17]

where the pore surfaces represent two reflective barriers at z'=y and z'=y+L. The diffusion coefficient, D_{\perp} , relates to the motion of water molecules perpendicular to the solid surfaces. Eq. [17] is the conditional probability density function for the initial condition,

 $P(z'/z'_{\circ},0) = \delta(z'-z'_{\circ})$. The probability density for the initial position is considered to be uniform across the pore space,

$$P(z'_{\circ}) = \frac{1}{L}.$$
 [18]

Thus, the probability distribution function of water molecules for the entire pore volume can be expressed as the product of the solution to the two-dimensional diffusion equation (18), with the solution to the one-dimensional diffusion equation in the presence of two reflective barriers (Eq. [17]).

The correlation function for a planar uniform distribution of paramagnetic ions on the solid surface is given by Neue (18). Allowing the separation distance, z', between the plane of diffusion and the fixed paramagnetic ions to vary according to the diffusion equation (Eq. [17] & [18]), and defining a planar density of paramagnetic ions at y, $N_p(y)$, gives the correlation function due to a planar distribution of paramagnetic ions,

$$G_{qq'}(\tau) = \delta_{qq'} \left(\frac{5N_{p}(y)}{48} \right) \left(\frac{4}{2 - |q|} \right)_{0}^{\infty} \int_{y}^{y+L} \int_{y}^{y+L} k^{3} e^{-D_{\parallel}\tau k^{2} - (z'+z'_{\circ})k} P(z'/z'_{\circ},\tau) p(z'_{\circ}) dz' dz'_{\circ} dk.$$
[19]

The wave number, k, is associated with the spatial Fourier transform in the planar geometry. The diffusion coefficient in the direction parallel to the solid surfaces is expressed as D_{\parallel} .

In order to simplify the correlation function $G_{qq'}(\tau)$, it is useful to consider only the term with l=0 in Eq. [17] defining the probability density function in the limit of y<<L. This is the

solution to the diffusion equation for a single reflective barrier at z'=y. Inserting Eq. [19] into Eq. [11] would give the spectral density functions for z' at an orientation (α,β,γ) with respect to the laboratory frame. Due to symmetry in the x-y plane, the relative orientations can be described by a single angle, β . In natural geologic materials, the pore surfaces have random orientations, β . An average over all angles for β , yields a constant value, (24)

$$\left\langle \left| D_{qm}^{(2)}(\alpha,\beta,\gamma) \right|^2 \right\rangle \Longrightarrow \int_0^{\pi} \left| D_{qm}^{(2)}(0,\beta,0) \right|^2 \sin(\beta) d\beta = \frac{1}{5}.$$
 [20]

Fourier transform of the correlation function and mapping to the laboratory frame using Eq. [20] will give the spectral density functions.

The correlation functions can be further simplified before the spectral densities are calculated. Inserting the probability density given by Eq. [18] into the expression for the correlation function expressed in Eq. [19], gives the correlation functions

$$G_{q}(\tau) = \left(\frac{5N_{p}(y)L}{48}\right) \left(\frac{4}{2-|q|}\right) \int_{0}^{\infty} \int_{0}^{1} \int_{0}^{1} k^{3} e^{-D_{\parallel}\tau k^{2} - (Lx + Lx_{*} + 2y)k} P(x / x_{*}, \tau) dx dx_{*} dk$$
[21]

with the change of variables:

$$x = \frac{z' - y}{L}$$
 and $x_{\circ} = \frac{z_{\circ}' - y}{L}$. [22]

It is useful to take the Fourier transform and its inverse with respect to the integrand variable x in order to eliminate one of the integrals:

$$P(x/x_{\circ},\tau) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{isx} \left[\int_{-\infty}^{\infty} e^{-isx} P(x/x_{\circ},\tau) dx \right] ds.$$
 [23]

Expanding Eq. [23] and inserting it in the expression for the correlation functions given by Eq. [21] yields four integrals with respect to variables: x, x_o , s, and k. The part of the integrand containing x and x_o can be evaluated analytically and is defined as

$$\xi(s,u) = \int_{0}^{1} e^{-ux} \cos(sx) = \frac{e^{-u} [-u\cos(s) + s \cdot \sin(s)] + u}{u^{2} + s^{2}}$$
[24]

with the change of variable u=kL. The correlation function thus becomes a double integral, and for the limit of one reflecting barrier is described by

$$G_{q}(\tau) = \left(\frac{5N_{p}(y)}{24\pi l^{4}}\right) \left(\begin{array}{c} 4\\ 2-|q| \end{array}\right) \int_{0}^{\infty} \int_{0}^{\infty} u^{3} e^{-(D_{\parallel}u^{2}+D_{\perp}s^{2})\tau/L^{2}-2uy/L} \xi^{2}(s,u) ds du .$$
[25]

The spectral density functions can be derived by inserting the correlation functions of Eq. [25] into Eq. [11]. The rotation matrices for mapping to the laboratory frame can be represented by an average over all orientations as given by Eq. [20]. The resulting spectral density functions for a single planar density, $N_p(y)$, of paramagnetic ions is thus given by

$$J_{p}^{(m)}(\omega, y) = \left(\frac{4N_{p}(y)}{3\pi L^{2}D_{\perp}}\right)_{0}^{\infty} \int_{0}^{\infty} u^{3} e^{-2uy/L} \xi^{2}(s, u) \frac{R_{D}u^{2} + s^{2}}{(R_{D}u^{2} + s^{2})^{2} + \frac{L^{4}\omega^{2}}{D_{\perp}^{2}}} duds, \qquad [26]$$

where R_D is defined as the ratio of the parallel to perpendicular diffusion coefficients, D_{\parallel}/D_{\perp} .

It is important to note that the above expression is for a planar distribution of paramagnetic ions, $N_p(y)$, at a distance of closest approach, y. The spectral density functions, $J^{(m)}(\omega)$, can be derived by extending the dipolar interactions to a layer of paramagnetic ions with finite thickness, l_p as in the following expression:

$$J^{(m)}(\omega) = \frac{1}{l_p} \int_{d}^{d+l_p} J_p^{(m)}(\omega, y) dy .$$
 [27]

A uniform distribution of paramagnetic ions with volume density, N_v , is assumed in a layer between y=d to y=l_p+d such that

$$N_{p}(y) = \int_{d}^{d+l_{p}} N_{v}(y') dy' = N_{v}l_{p}.$$
 [28]

The protons' distance of closest approach, d, represents the distance as given by Eq. [14], where d_s is taken as the depth of the paramagnetic ion nearest to the solid surface. Thus, inserting Eqs. [26], [28] into [27], yields the spectral density functions for the given geometry of sheet-like pore structure with translational diffusion in three-dimension as follows

$$J^{(m)}(\omega) = \left(\frac{2N_v}{3\pi LD_{\perp}}\right)_0^{\infty} \int_0^{\infty} u^2 [e^{-2ud/L} - e^{-2u(l_p+d)/L}] \xi^2(s,u) \frac{R_D u^2 + s^2}{(R_D u^2 + s^2)^2 + \frac{L^4 \omega^2}{D_{\perp}^2}} duds.$$
 [29]

The double integrals in the spectral density functions can be evaluated numerically. Consequently, the relaxation rate for hydrogen protons of water in a model pore space of Figure 2, containing a layer of paramagnetic ions, l_p, coated by a substance with thickness, l_c, can be calculated by insertion of the spectral density functions (Eq. [29]) into the expression for relaxation rate (Eq. [12]).

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Results and Discussion

The developed model can be used to estimate the effect of a coating on the relaxation rate, $1/T_{1S}$. Of specific interest is the dependence of $1/T_{1S}$ on the thickness of the coating, l_c . The model incorporates a number of parameters, all of which are listed in Table 3. Accurate values would be required for all of these parameters in order to fully characterize the dependence of relaxation rate on the coating thickness. As a mean of assessing the validity of this model, we will set values for these to compare and explain result reported in the study by Kanters et al. (13). While it is very difficult to obtain some of these parameter values, representative values for all model parameters have been selected and are given in Table 3. The model with these representative values as model parameters is referred to as the standard configuration.

Model Parameter		Description	Representative Value		
1.	l _c	thickness of surface coating	0		
2.	ω _I	2π x proton Larmor frequency	2πx90MHz (B₀=2.12T)		
3.	D_{\perp}	diffusion coefficient perpendicular to solid surfaces	2.3x10 ⁻⁹ m²/s		
4.	R _D	ratio of parallel to perpendicular diffusion coefficients	1		
5.	Spins S	properties of paramagnetic ions	FeO(OH)		
	N _v	number density	2.89x10 ²⁸ m ⁻³		
	S	spin quantum number	5/2		
	γs	magnetogyric ratio	-1.76x10 ¹¹ rad.s ⁻¹ T ⁻¹		
6.	l _p	thickness of surface layer containing paramagnetic spins, S	8.9nm		
7.	S _p /V _p	surface area to volume ratio of the porous media	0.36µm ⁻¹		

Table 3: Mode	Parameters
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Some of the parameters in the standard configuration are determined by the experimental conditions such as temperature and the field strength. The temperature dictates the bulk

diffusion coefficient of free water, which can be assigned to D_1 . The experimental data that will be used for comparison were obtained at temperature close to 25°C. The field strength specifies the resonance Larmor frequency of the protons, ω_l , and the Larmor frequency of spin S, ω_s .⁴ The resonance frequency, ω_l , is based on the field strength used in the study by Kanters, et al. (13). The representative surface area to volume ratio, $S_p/V_p=0.36\mu m^{-1}$, corresponds to that of a sand sample with average diameter of 115 μ m. This particular type of sand was used in the study by Kanters et al. (13). The specific surface area of this sand was measured by Traci Bryar using the BET Kr-adsorption with a Micromeretics ORR 2100D surface area analyzer. Therefore, three of the parameters are set to known experimental conditions for one of the studies in Table 2 (13). Since these parameters reflect the conditions for T₁ measurements of pore water in a sand sample with a particular grain size in the study by Kanters et al. (13), the absolute value of T_{1S} predicted for this configuration will be compared to their reported measurements of this specific sand sample.

The representative values of the other free parameters are based on the following assumptions. The diffusion coefficient, $D_{\parallel}=2.3 \times 10^{-9} m^2/s$, is that of free bulk water at 25°C (27). This means that the ratio of diffusion coefficients, R_D , is set to 1 indicating that diffusion parallel to the surfaces is not restricted. The properties of the paramagnetic spins S, are those of iron(III) associated with the naturally found iron oxide coating, FeO(OH) (goethite), on geological materials. A layer thickness of goethite, l_p , can be calculated from a study of goethite coating silica sand (28). This study provides the specific surface area and concentration of goethite coating a silica sand sample. These data, along with the known density of pure goethite (20), yield an estimate of l_p =8.9nm. The number density, N_v =2.89x10²⁸m⁻³, is also derived from the density of pure goethite. Free electrons associated with iron(III) give rise to the spin quantum

⁴ Given the magnetogyric ratio, γ_s , and the field strength, B_o , ω_s can be calculated by $\omega_s = -\gamma_s B_o$.

number S=5/2, and the magnetogyric ratio, γ_S =-1.76x10¹¹rad.s⁻¹T⁻¹ corresponds to that of an electron. The representative parameter values for the standard configuration are summarized in Table 3.

These values allow us to determine the absolute value of the relaxation time for a single configuration of parameters. The predicted surface relaxation time, T_{1S} =0.63s for the standard configuration is in good agreement with the calculated T_{1S} =1.1s corresponding to the measured T_1 and T_{1B} values reported in the study by Kanters et al. (13). For this comparison, the data associated with the 115µm average diameter sand sample with known surface area to volume ratio was chosen. The difference between the two values can be explained by the uncertainties associated with the properties of the paramagnetic ions near the surface and the relative diffusion coefficient R_D . The purpose of estimating the T_{1S} relaxation time was simply to verify the validity of the developed model.

While the parameter values used in the standard configuration provide an estimate of $1/T_{1S}$, we recognize that there is a high level of uncertainty in some of the selected values that could affect our predicted dependence of $1/T_{1S}$ on the coating thickness. For the purposes of our study, we choose to eliminate the need for some of these parameters by considering the normalized relaxation rate: the ratio of $1/T_{1S}$ for the coated sample with $l_c>0$, to that of the plain, or uncoated sample with $l_c=0$. This eliminates the need for four of the parameters as follows: N_v , γ_s^2 , S(S+1), and S_p/V_p . The assumption of linear dependence on S_p/V_p requires an explanation: this parameter appears in the form of water thickness, $L=2(S_p/V_p)^{-1}$, in the expression for the spectral density functions. Although it is not explicitly clear from these expressions, their dependence on S_p/V_p is effectively linear in the range of interest for all other parameters. This suggests that the model relaxation rate, which is linearly proportional to the spectral density functions, also varies linearly with S_p/V_p .

Some of the remaining parameters can be determined from the experimental conditions, while others are unknown. The representative values in Table 3 are used to predict the trend in normalized relaxation rate with respect to the coating thickness. Variation of these parameters can then be used to set bounding limits on the predicted trend of normalized relaxation rate, $T_{1S}(plain)/T_{1S}(coated)$, as l_c increases. As the physical separation between the diffusing water molecules and the paramagnetic ions grows with increasing l_c , we expect a decrease in the normalized relaxation rate.

Figure 3 shows the trend in normalized relaxation rate for increasing coating thickness, l_c . The diamonds indicate the predicted normalized relaxation rate for the standard configuration of parameters. A logarithmic trendline using least squares fit to the calculated points (diamonds) is shown by the solid line. In comparison to a power or exponential fit, this trend yields the best correlation coefficient with $R^2 = 0.9922$. The limiting bounds on the predicted trend are calculated by evaluating the dependence of the normalized relaxation rate on the free parameters: ω_{l} , l_p , and R_D . In the following sections, we consider the role of each parameter in evaluating upper and lower limits on the predicted $T_{1S}(plain)/T_{1S}(coated)$. Subsequently, the limiting values of all parameters are combined to provide the lowest bound on normalized relaxation rate with respect to the coating thickness.

Let us first consider the role of ω_I in determining the relaxation rate. Figure 4 shows the variation in the spectral density function, $J(\omega)$, predicted for the standard configuration on the Larmor frequency, ω_I . The frequency spectrum associated with the diffusive motion of the water molecules is described by the spectral density functions. These functions determine the dependence of $1/T_{1S}$ on ω_I and $\omega_I \pm \omega_S$ (Eq. [12]). These are the transition frequencies of spin energy states for the protons, leading to relaxation. The spectral density functions are characteristic of the particular type of motion involved, and are generally constant at low

frequencies. A sudden drop occurs when $\omega \tau_c \sim 1$, where the correlation time of the motion, τ_c , can be intuitively thought of as the system's memory. In other words, the positions of the diffusing particles at times greater than t+ τ_c are independent of their positions at times < t. For our model system, τ_c is in the order of 100ns with the drop off frequency of ~10MHz (Figure 4).



Figure 3: Dependence of normalized relaxation rate on the coating thickness. The diamond symbols correspond to the standard configuration, and the solid line is a logarithmic best fit given by the equation shown. The solid and open symbols represent the upper and lower bounds, respectively. The absolute lowest bound with $R_D=0.005$, $\omega_I=2\pi x90$ MHz, and $l_p=0.3$ nm is shown by the x symbols. The circles represent the bounds set by frequency (upper for 1MHz and lower corresponding to the standard configuration at 90MHz); the triangles correspond to the bounds for l_p (upper at standard configuration with $l_p=8.9$ nm and lower at $l_p=0.3$ nm); and the square symbols correspond to bounds set by R_D (upper at standard configuration with $R_D=1$ and lower at $R_D=0.005$).

The variation of $1/T_{1S}$ with frequency is similar to that of the spectral density functions, which are independent of frequency for $\omega_{I}\tau_{c} <<1$, and drop off at $\omega_{I}\tau_{c}\sim1$.⁵ The range of interest for ω_{I} is 1-90MHz. This range was chosen according to the operating frequency of typical field and laboratory instruments. Field instruments operate at frequencies in the order of 1MHz, while the operating frequencies of laboratory instruments range from 10 to 90MHz. The dependence

 $^{^{5} \}omega_{s}$ is about three orders of magnitude greater than ω_{t} and therefore the contribution of the spectral density functions evaluated at $\omega_{t}\pm\omega_{s}$ to the relaxation rate are considerably lower.

of $1/T_{1S}$ on ω_I is shown in Figure 5 for coating thicknesses of $l_c=0$, 1nm and 2nm. As the proton resonance frequency decreases, the relaxation rate tends to increase for all values of l_c . However, this increase is slightly greater at lower coating thicknesses, which leads to lower normalized relaxation rates at higher frequencies.



Figure 4: The trend in the spectral density functions with respect to angular frequency.



Figure 5: Dependence of Relaxation rate, $1/T_{1S}$, on proton Larmor frequency at different coating thicknesses. The calculated values for $l_c=0$ are shown by the diamonds; the square symbols represent values for $l_c=1$ nm; and the triangles represent $l_c=2$ nm.

The circles on Figure 3 represent the limits on predicted normalized relaxation rates for proton Larmor frequencies ranging from 1 to 90 MHz. The lower bound is associated with the highest frequency considered. As expected from the shape of the spectral density functions, this model predicts greater relaxation rates at lower frequencies. The increase in relaxation rate with decreasing frequency is slightly greater for lower l_c values (Figure 5). Therefore, for the range of $l_c = 0.2$ - 2nm, the normalized relaxation rates were consistently higher at lower frequencies.

Figure 6 shows the trend in predicted relaxation rate of the standard configuration with respect to R_D . In choosing a range of possible values for R_D , we consider changes in the parallel diffusion coefficient associated with restricted movement of the molecules near the solid surface. We expect the diffusion coefficient corresponding to the motion of the water molecules in the direction perpendicular to the solid surfaces to be that of the free bulk pore fluid at a given temperature. While there are no mechanisms that can physically account for the enhancement of diffusion, we do expect a reduction in D_{\parallel} near the solid surface. If water molecules at the surfaces are adsorbed through hydrogen bonding, their restricted motion could affect the diffusion of water well away from the surfaces. This can be described by a decrease in D_{\parallel} , and hence the ratio parameter, R_D .

As shown in Figure 6, a reduction in R_D from a value of 1 would result in a slight increase in the predicted relaxation rate, which reaches a maximum at the relative diffusion coefficient of R_D ~0.01. In selecting a minimum for R_D , its value is reduced until the relaxation rate asymptotically reaches a constant. This is achieved for R_D <0.001. The predicted increase in relaxation rate with decreasing R_D is greater for the plain, or uncoated samples. This can be qualitatively explained by considering the water molecules' closest distance to the paramagnetic spins. Parallel diffusion's contributing to the relaxation rate decreases with increasing distance to the spins, S. Therefore, the normalized relaxation rate decreases with decreasing R_D . A lower limit for R_D indicating the minimum normalized relaxation rate is estimated at R_D ~0.005.



Figure 6: Dependence of the relaxation rate, $1/T_{1S}$, on the relative diffusion coefficient, R_D .

The predicted $T_{1S}(plain)/T_{1S}(coated)$ on the limiting values of R_D , are shown by the squares on Figure 3. The lower bound, indicated by open squares, corresponds to restricted diffusion in the two dimensional plane parallel to the solid surfaces. This limit is calculated for R_D =0.005. Thus, a lower bound would result in the predicted trend of normalized relaxation rates, if diffusion parallel to the solid surfaces were restricted. The upper bound, shown by the solid squares on Figure 3, corresponds to the standard configuration.

Another parameter of interest is the thickness of solid layer containing the paramagnetic ions with spin S, l_p . In choosing the minimum value of this parameter, we consider the smallest constituent of the substance coating the surface. For an exceedingly thin layer of goethite, which has a crystal structure with orthorhombic symmetry, this thickness would correspond to its lowest length of unit cell, $l_p=0.3nm$. Another commonly found iron oxide is hematite that has rhombohedral symmetry with a greater unit cell length of about 0.5nm. Thus, we choose 0.3nm as the absolute lowest value for l_p . Figure 7 shows the trend in relaxation rate of the standard configuration for the range of l_p from 0.3 - 30nm. The relaxation rate is found to increase as the

total number of paramagnetic spins rise. However, this enhancement of $1/T_{1S}$ is limited given the decay in relaxation rate as the distance between the interacting spins, S and I, increases. As a consequence, $1/T_{1S}$ approaches a maximum value and remains constant for $l_p > 5nm$ (Figure 7).

As expected, the dependence of $1/T_{1S}$ on the near surface properties of the solid is greatest for $l_c=0$. This results in lower normalized relaxation rates as l_p decreases. The bounds on normalized relaxation rate are predicted and indicated by the triangles in Figure 3. The upper bound (solid triangle) corresponds to the predicted $T_{1S}(plain)/T_{1S}(coated)$ for the standard configuration, while the lower bound (open triangles) is found for the lowest value of $l_p=0.3$ nm.



Figure 7: Dependence of the relaxation rate, $1/T_{1S}$, on the thickness of solid layer containing paramagnetic ions, l_p .

In order to predict the absolute bounds on the trend of normalized relaxation rate, we must consider the combination of the limiting values for all three parameters, ω_I , R_D , and l_p . These limiting values for the lower bound correspond to $\omega_I = 2\pi x 90$ MHz, $R_D=0.005$, and $l_p=0.3$ nm. The predicted trend in $T_{1S}(plain)/T_{1S}(coated)$ is shown as x symbols in Figure 3. This is the absolute lowest bound on the trend for normalized relaxation rate predicted in the range of frequencies 1 to 90 MHz. The upper bound is a function of frequency, which is shown in Figure 3 as solid circles for $\omega_I = 2\pi x 1 MHz$.

A trendline that best describes the predicted normalized relaxation rate for the standard configuration is shown by the solid line on Figure 3. The developed model shows a moderate decrease in the relaxation rate as the coating thickness increases. The equation for the declining logarithmic trendline shown in Figure 3 indicates that the decrease in relaxation rate is more gradual than is predicted by previous models.

Models a and b were considered for the estimate of coating thickness of experimental studies in Table 2. The dependence of $1/T_{1S}$ on r=l_c+d, as predicted by model a, is a steep decline characterized by $1/r^6$, where d is the distance of closest approach for the plain sample. This model is based on rotational diffusion of water molecules coordinated to spin S paramagnetic ions. Model b considers two-dimensional diffusion at a fixed distance, z, from a surface distribution of spins S. This model, which better describes the physical system, still predicts a relaxation rate that varies as $1/z^2$ to $1/z^6$.

The developed model can be used to obtain an estimate of coating thickness for the studies indicated in Table 2. This can be accomplished by considering the field strength, B_o , and the normalized relaxation rates, $T_{1S}(plain)/T_{1S}(coated)$, reported in each experiment. The diffusion coefficient, D_{\perp} , for free water at room temperature applies to all experiments considered. A range of estimates is however provided which corresponds to the limiting values of R_D and l_p . The upper limit is calculated with $R_D=1$ and $l_p=8.9$ nm as for the standard configuration, and the lower limit corresponds to $R_D=0.005$ and $l_p=0.3$ nm. The ranges of coating thicknesses predicted by each of the models are summarized in Table 4. The lower R_D value indicating restricted diffusion in the planar dimension also applies to model b. For this reason, a lower limit in coating thickness for this model is calculated and shown in Table 4. In all cases

considered, the developed model consistently predicts greater and more realistic coating

thicknesses than predicted by models a and b.

		Molecular Size	1/T _{1S}	ω _i	Predicted coating thickness: [Å]		
Study / Year	Surface Coating	[Å]	Ratio	[2πxMHz]	model a	model b	Developed Model
Brown & Fatt (1) / 1956	Dri-film (SF99 GE)	> 11	0.24	1	0.8	2.6 - 3.0	6.0 – 23
Devereux	Methylene blue	4.5	0.75	13	0.1	0.31 – 0.46	0.62 – 1.8
(2) / 1967	Dodecylammonium acetate	15	0.45	13	0.4	0.92 - 1.5	1.9 - 6.7
	Stearic acid	23	0.34	13	0.6	1.3 - 2.1	2.7 – 10
	asphaltene	>5	0.075	13	1.6	3.5 - 7.5	8.5 – 39
Hsu (7) / 1994	Dri-film (SF99 GE)	> 11	0.057	85	1.9	2.5 - 7.7	7.5 – 23
	Kuparuk crude oil	> 5	0.23	85	0.8	1.2 – 3.0	3.1 - 9.3
Kanters, et al.	Crude oil	> 5	0.23	90	0.8	1.2 – 2.9	3.0 – 9.0
(13) / 1998	(for various grain	> 5	0.24	90	0.8	1.1 - 2.8	2.9 - 8.6
	sizes ranging from	> 5	0.19	90	0.9	1.3 - 3.4	3.5 – 11
	115 to 275 μm)	> 5	0.27	90	0.7	1.0 - 2.5	2.6 - 7.8
		>5	0.094	90	1.4	2.0 - 5.6	5.7 – 17
Daughney, et al. (15) / 2000	Crude oil (sample with highest relative change in relaxation rate due to sorbed crude oil)	> 5	0.58	90	0.3	0.41 - 0.88	0.94 – 2.6

 Table 4: Model Comparisons

In contrast to the previous models' estimates of coating thicknesses, those predicted by the developed model are in proper agreement with the limits imposed by the size of a single molecule forming the coating substance. Two exceptions are the experimental results of Devereux (2) and Daughney, et al. (15). It should be noted that both cases involved microporous sample materials with bimodal distribution of relaxation times. The higher normalized relaxation rates in these experiments can be explained by the existence of uncoated micropores. Diffusion of water molecules into the micropores can increase the surface relaxation rates reported for the coated larger pores. Such a shift in $1/T_{1S}$ in both coated and plain samples would increase the normalized relaxation rates. All considered, the developed model provides the most realistic estimates of coating thickness in comparison with previous models.

Summary and Conclusions

Distinct T_1 relaxation times of pore water hydrogen protons in plain and coated porous media have been reported in experimental studies since 1956. These studies have consistently shown a lower T_1 relaxation rate of pore water hydrogen protons for the coated samples. The observed relaxation rate is described as the sum of bulk water relaxation and surface relaxation, $1/T_{1S}$. The surface relaxation rate inside the pore space of geological materials has long been attributed to the dipolar interactions of the pore water hydrogen protons with the electronic spins of the paramagnetic ions near the solid pore walls. A layer of substance coating the solid surfaces physically separates the pore water molecules from the paramagnetic ions near the solid surface. This shielding effect of the surface coating results in the reduced relaxation rates reported for coated samples.

There have been no attempts to estimate the amount of substance coating the surfaces of geologic materials, based on the observed change in T₁ relaxation times. One model has been proposed to relate the relaxation rate to $r=l_c+d$, where l_c is the coating thickness, and d is the distance of closest approach of the diffusing water molecules to the paramagnetic ions in the plain sample. This model of $1/T_{1S}$, referred to throughout this thesis as model a, was described by Kleinberg et al. (17) for application in geological materials. A more general model, referred to as model b, is that proposed by Neue (18) for estimating $1/T_{1S}$ in porous media. For the purpose of evaluating these models, studies were selected with consideration to the following criteria: 1) the coating substance did not contain paramagnetic ions; 2) the surface area of the samples remained constant after the application of the coating; and 3) samples were completely covered by the coating substance. We have assessed the validity of each of these assumptions for each of the studies considered. Application of both models to the measured values of $1/T_{1S}$ in such studies provided unrealistically low estimates of coating thickness.

A new model has been developed for diffusing pore water molecules in a threedimensional pore structure. The spectral density functions have been derived for coupling of the pore water hydrogen protons with paramagnetic spins S, distributed uniformly in a layer near the surface of the solid sample. In addition to the coating thickness, this model uses a number of parameters, which include the proton Larmor frequency, parameters describing the physical geometry of the pore space, properties of the paramagnetic ions in the solid, and the diffusion coefficients related to the motion of the water molecules parallel and perpendicular to the solid surfaces. The developed model can be used to predict the relaxation rate for a known set of model parameters.

In considering the normalized relaxation rate, $T_{1S}(\text{plain})/T_{1S}(\text{coated})$, we have eliminated some of these parameters for estimating the coating thickness. The extreme values of the unknowns are then used to set bounding limits on the predicted normalized relaxation rates. The developed model shows a gradual decline in $T_{1S}(\text{plain})/T_{1S}(\text{coated})$ with increasing coating thickness, which is best approximated by a logarithmic decline. Application of this model to measured relaxation rates of coated and plain samples have provided the most realistic estimates of the coating thicknesses.

In a given experiment, with known field strength, and a priori knowledge of the paramagnetic properties of the geologic sample, the predicted bounds can be further constrained. In addition, we can remove some of the previous assumptions used for application of models a and b, if the specific surface area of the samples, or the paramagnetic content of the coating are known. If the coating substance contains paramagnetic ions, the developed model can also be used in estimating their contribution to the measured relaxation rate. This model can be potentially useful for quantitative detection of sorbed contaminants in porous geological materials.

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