

## EFFECTS OF MAGNETIC SUSCEPTIBILITY CONTRASTS ON OIL AND WATER SATURATION DETERMINATIONS BY NMR $T_2$ LABORATORY AND WELL LOG MEASUREMENTS

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### ABSTRACT

Nuclear Magnetic Resonance (NMR) longitudinal and transverse relaxation measurements yield, respectively,  $T_1$  and  $T_2$  distributions, i. e., the distributions of time constants observed in the relaxations. For water-wet samples containing brine and light oil, the  $T_1$  and  $T_2$  distributions typically exhibit two distinct peaks, one for the oil and the other for the brine.  $T_1$  measurements on core containing both oil and brine are shown to correspond closely to carefully made Dean-Stark saturation determinations. The correspondence of brine saturations determined from  $T_2$  measurements is shown to be noticeably reduced when the rock grains are coated with significant amounts of paramagnetic ions such as ferric iron. For the case of a homogeneous static magnetic field, gradients are induced at the pore scale by magnetic susceptibility contrasts between the grain surfaces and the pore fluids. These gradients shift both the oil and brine signals to lower  $T_2$  values (higher relaxation rates). When an external gradient is applied, the  $T_2$  values are reduced to even smaller values, i. e., the effects of the induced and applied gradients are additive. The use of short echo spacings (e. g. 0.2 ms @2 MHz) in clastics usually ensures that the oil and brine signals produce two distinct peaks in the  $T_2$  distribution. However, if paramagnetic minerals are present, the brine peak can be shifted to time constants that are too short to measure, and the oil signal can be shifted so far that the oil and brine peaks merge and become indistinct. We conclude, therefore, that  $T_1$  measurements are preferred for laboratory determinations of brine and oil saturations in preserved core.

NMR well logging tools measure transverse relaxation which yields  $T_2$  distributions. The  $T_2$  data can be acquired while the tool is moving. ( $T_1$  measurements are slow and station stops are usually needed.) Thus, accurate saturation determinations from NMR logs require that diffusion from induced and applied gradient be minimal such that no brine signal is lost and that the oil and brine  $T_2$  distributions are resolvable. Well log examples from a gas reservoir drilled with oil based mud are shown. For these examples, where the magnetic susceptibilities of the formation are significantly paramagnetic, the  $T_2$  values for the oil filtrate are shifted to shorter time constants than they are in less paramagnetic zones. High magnetic susceptibility are proposed to be the reason why algorithms successful in estimating saturation and permeability in other zones fail to accurately estimate brine saturation and permeability in a chlorite rich, low permeability zone.

## INTRODUCTION

Magnetic susceptibility contrasts between rock surfaces and saturating fluids have been shown to cause induced magnetic field gradients when a sample is placed in a magnetic field (Jerosch-Herold and Thomann, 1991, and Brown and Fantazzini, 1993). Paramagnetic compounds on the surfaces of rock grains are assumed to cause these gradients. The objectives of this study were to document such magnetic susceptibility effects: on the NMR  $T_2$  relaxation rates of both the wetting and non-wetting fluid phases, and on the estimations of permeability and oil and brine saturation from  $T_2$  Distributions.

### $T_2$ measurements on rock

To measure nuclear magnetic resonance (NMR)  $T_2$  on rock samples saturated with brine, oil, or both fluids, the samples are placed in a static magnetic field which polarizes the chosen nuclei (usually hydrogen) such that the nuclear spin precesses about the magnetic field direction. Then, a series of radio frequency pulses, called the Carr-Purcell-Meiboom-Gill or CPMG sequence, are applied to alter the spin directions and measure the relaxation of the spins back to their initial state (precessing about the magnetic field direction). This measurement is called spin-spin or transverse relaxation. For simple fluids, the transverse relaxation (perpendicular to the static magnetic field) is an exponentially decaying signal with a single time constant " $T_2$ ". For rocks, the transverse relaxation can be represented by a sum of exponentially decaying signals, and  $T_2$  is taken to be the distribution of time constants of these signals.

### Reductions in $T_2$ due to Diffusion

The CPMG sequence is a single polarizing pulse followed by a series of "echo" pulses designed to remove the effects of heterogeneity in the static magnetic field provided that the nuclei do not move (diffuse) very far between echo pulses. The time between echo pulses is made as short as possible to minimize the time for diffusion of nuclei during the measurement. In the presence of heterogeneity in the magnetic field, diffusion has the effect of shortening the measured  $T_2$  values, i. e., the transverse relaxation proceeds at a higher rate. Two major sources of magnetic field heterogeneity are applied gradients and induced, pore scale gradients caused by magnetic susceptibility contrasts between rock surfaces and pore fluids. The reduction in  $T_2$  caused by induced gradients also increases as the strength of the static magnetic field is increased.

## Diffusion Effects on Saturation Determinations

Both the brine and oil relaxation  $T_2$  values are decreased by diffusion when the measurements are made in a gradient magnetic field that is either applied or induced. In the presence of such gradient fields, the hydrogen in the brine and oil is subjected to changes in magnetic field strength as it diffuses between measurement pulses. The changes in the magnetic field strength cause the precession frequencies of the hydrogen to vary, resulting in subsequent loss in signal coherency. The loss of coherency is seen as a faster relaxation (shorter  $T_2$  values) for both the brine and oil signals.

## $T_1$ Measurements on Rocks

The " $T_1$ " time constant, or more generally, the distribution of  $T_1$  time constants is a measure of how long it takes to fully polarize hydrogen nuclei after they have been placed in a static magnetic field. The distribution of  $T_1$  time constants is most often determined by a simple though time consuming pulse sequence called "inversion recovery". This sequence measures the longitudinal (along the magnetic field direction) or "spin-lattice" relaxation from which the  $T_1$  distribution is determined. Though requiring significantly more time to acquire than  $T_2$  measurements,  $T_1$  measurements have the advantage that they are largely insensitive to diffusion.

## $T_1$ and $T_2$ Distributions

The  $T_1$  and  $T_2$  distributions are obtained by fitting the NMR relaxation curves by sums of exponentially decaying signal components with time constants  $T_1$  or  $T_2$ . The ordinate of the distribution plot is the normalized amplitude, and the abscissa is the logarithm of the  $T_1$  or  $T_2$  time constants used in the fitting process. The amplitudes are often normalized such that they sum to one or to the porosity.

To analyze the lab and well log data, we have tested three regularization procedures: curvature smoothing with the regularization term set by empirical methods, norm smoothing with the regularization term set by the Butler-Reeds-Dawson (1981) method (BRD), and Singular Value Decomposition (SVD) where the eigenvalue cutoffs are set by the signal to noise ratio (Prammer, 1994). We found that all three methods yield consistent results with high S/N ratio data, such as that obtained from laboratory measurements. However, for well log analysis, we found that methods including S/N based determinations of the regularization term (the BRD and SVD methods) are necessary for consistent results.

## CORE MEASUREMENTS

In preparation for NMR  $T_2$  logging runs for a North Sea gas field, we ran a series of laboratory NMR measurements on core and fluids from existing wells in the field. Like all the wells to be drilled, the cored wells were cut using light, oil based mud. Our goals were to determine whether we could estimate brine and filtrate saturation from lab NMR measurements on preserved core, to establish the potential accuracy of NMR log porosity estimates, to develop protocols for estimating irreducible brine saturation from NMR logs, and to develop permeability predictors. As described in the following sections, in the process of achieving these goals, we learned that estimates of porosity, saturation, and permeability from  $T_2$  measurements could be significantly distorted by the presence of small amounts of paramagnetic ions on the rock surfaces.

### Saturation Determinations from Core Cut with Oil Base Mud

In our initial core study, NMR  $T_1$  and  $T_2$  measurements were made on 10 core plugs cut and preserved in oil. Dean Stark extraction was then used to determine the brine saturations. The NMR measurements were made with a homogeneous magnetic field so that only induced gradient fields would influence the response. Figure 1 is a crossplot of brine saturation by NMR versus brine saturation by Dean-Stark extraction. Estimates obtained for both  $T_1$  and  $T_2$  measurements are shown. The  $T_2$  measurements were made at 2 MHz with an echo spacing of 0.35 ms. Note that the  $T_1$  estimates correspond closely with the Dean-Stark determinations over the complete range of brine saturation. The  $T_2$  estimates, however, are similar to the Dean-Stark values for smaller values of brine saturation, but deviate significantly at larger values of brine saturation. We believe that even an echo spacing as short as 0.35 ms was insufficient to eliminate the effects of diffusion on the  $T_2$  measurement. The  $T_1$  and  $T_2$  distributions for a sample with a high brine saturation is shown as Figure 2. Note that the brine and oil peaks have a distinct separation for the  $T_1$  measurement but overlap for the  $T_2$  measurement. Additionally, some of the water signal appears to have been lost because the echo spacing of 0.35 ms was too long to detect all of the rapidly decaying signal components.

To test the hypothesis that short echo spacings are needed for accurate saturation estimates, we saturated a chlorite rich, unpreserved sample in brine and decane. The  $T_1$  and  $T_2$  distributions for this sample are shown in Figure 3. These measurements were also made at 2 MHz without a gradient field. Echo spacings (TE) of 0.2 ms and 0.5 ms were used. The  $T_1$  distribution clearly shows a separation in the oil and brine signals which can be readily used to calculate the brine saturation. The  $T_2$  distributions, on the other hand, show a clear delineation of the brine and oil signals only at the shorter echo spacing where the effects of diffusion are minimized. The brine saturations determined from the areas under the short time peaks of the  $T_1$  and  $T_2$  (TE=0.2 ms) distributions were both 31% while the brine saturation determined from sample weights was slightly higher at 34%. Because the  $T_2$  distribution at TE=0.5 ms has no clear minimum, the choice of

cutoffs for calculating water saturation would be somewhat arbitrary. A choice of 10 ms for the cutoff would have to be used to get the 31% brine saturation determined from the  $T_1$  measurement. Note: the reduction in  $T_2$  due to diffusion is proportional to the square of the frequency times the echo spacing. Thus, for gradients induced by magnetic susceptibility contrasts, an operating frequency of 2 MHz and  $TE=0.5$  ms is equivalent to  $TE=1.3$  ms at 750 kHz, the nominal frequency of the MRIL logging tool.

We conclude, therefore, that very short echo spacings are needed even at the low frequencies of the logging tools to get the full  $T_2$  signal so that porosity, saturation, and permeability can be accurately determined.

### **Magnetic Susceptibility and Mineralogy Measurements**

To corroborate the idea that the source of the distortions in the  $T_2$  signals was paramagnetic ions on the rock surfaces, the chemical composition, mineralogy, and magnetic susceptibilities were measured on samples from the North Sea gas reservoir. Figure 4 is a plot of the measured magnetic susceptibilities versus the highly paramagnetic, ferric oxide concentration. Note the strong correlation between the magnetic susceptibilities and the ferric oxide. In a similar plot (Figure 5), the magnetic susceptibility and chlorite fractions are nearly as strongly correlated, suggesting that almost all of the paramagnetic ions are in the chlorite.

### **Magnetic Susceptibility and Permeability**

Because we suspected that chlorite was a major factor in permeability reduction, and that the magnetic susceptibility was proportional to the amount of chlorite, we crossplotted the two of them and found the strong correlation exhibited in Figure 6. The samples plotted were largely from an iron-rich, low permeability zone in the gas reservoir. Note that as the magnetic susceptibility increases, the permeability decreases suggesting that the chlorite concentration is inversely correlated with permeability.

## **WELL LOG MEASUREMENTS**

When we ran NMR logging tools in the North Sea gas field, algorithms based on  $T_2$  logging measurements could be used to accurately determine porosity, brine saturation, and permeability through all but one zone in the reservoir. In this low permeability zone, which contained significant amounts of ferric iron in chlorite, our saturation and permeability estimates were inconsistent with core measurements. As indicated by our laboratory measurements, our estimation difficulties were caused by distortions of both the brine and oil NMR signals due to diffusion.

## Saturation Determinations from NMR Logging Measurements

In the gas field in question, we got sufficient invasion such that the filtrate replaced the gas near the borehole and NMR logging tools saw distinct differences in the relaxation time constants ( $T_2$ ) for the brine and oil filtrate. This distinction usually allowed us to accurately determine saturations from the NMR logs.

An example of log data showing the separation between the brine and oil  $T_2$  time constants is shown as Figure 7 for a well log measurement at a single depth. The  $T_2$  distribution consists of two peaks: one at short time constants centered at about 10 ms and the other at much longer time constants centered at 400 ms. For this normalization and assuming zero residual gas saturation, the area under the short  $T_2$  peak is taken to be equal to the brine saturation, and the area under the long  $T_2$  peak to be equal to the oil filtrate saturation. The effects of an applied gradient are also indicated in Figure 7 by the reduction in the  $T_2$  time constant of the oil based mud filtrate. Note that the  $T_2$  of the oil at its relaxation peak is 400 ms. The independently determined, bulk  $T_2$  of the filtrate at reservoir temperature is approximately 3 s and the reduction of the  $T_2$  value is consistent with the MRIL gradient at reservoir temperature.

## Diffusion Effects on Well Logs

The effects of magnetic susceptibility contrasts causing a further reduction in the brine and oil  $T_2$  values is shown in Figure 8 where the oil peak is reduced from 400 to 250 ms and the brine from about 10 ms to about 8 ms over the distance of a few feet. The  $T_2$  distribution with the shorter oil filtrate  $T_2$  is from the chlorite rich zone. There the gradients induced by the strongly paramagnetic, ferric iron are sufficient to reduce the brine and oil  $T_2$  values.

## CONCLUSIONS

In reservoirs with high oil saturations and high ferric iron content, magnetic susceptibility contrasts between the grain surfaces and the wetting fluid can induce large, pore scale gradient magnetic fields which distort NMR  $T_2$  logging measurements such that brine saturations are incorrect and usually underestimated.

The pore scale, induced fields cause reductions in the  $T_2$  values of both the wetting and non-wetting fluids.

For the reservoir studied, magnetic susceptibility was inversely correlated with permeability due to pore filling chlorite.

The  $T_2$  distribution for rock samples saturated with oil and brine are consistently shifted to shorter time constants than the  $T_1$  distributions on the same samples. We speculate

that at least part of this shift is due to gradients induced by magnetic susceptibility contrasts between the rock grains and pore fluids.

#### ACKNOWLEDGMENTS

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### $S_w$ Estimates from Area of Short Time Peak in $T_1$ and $T_2$ Distributions

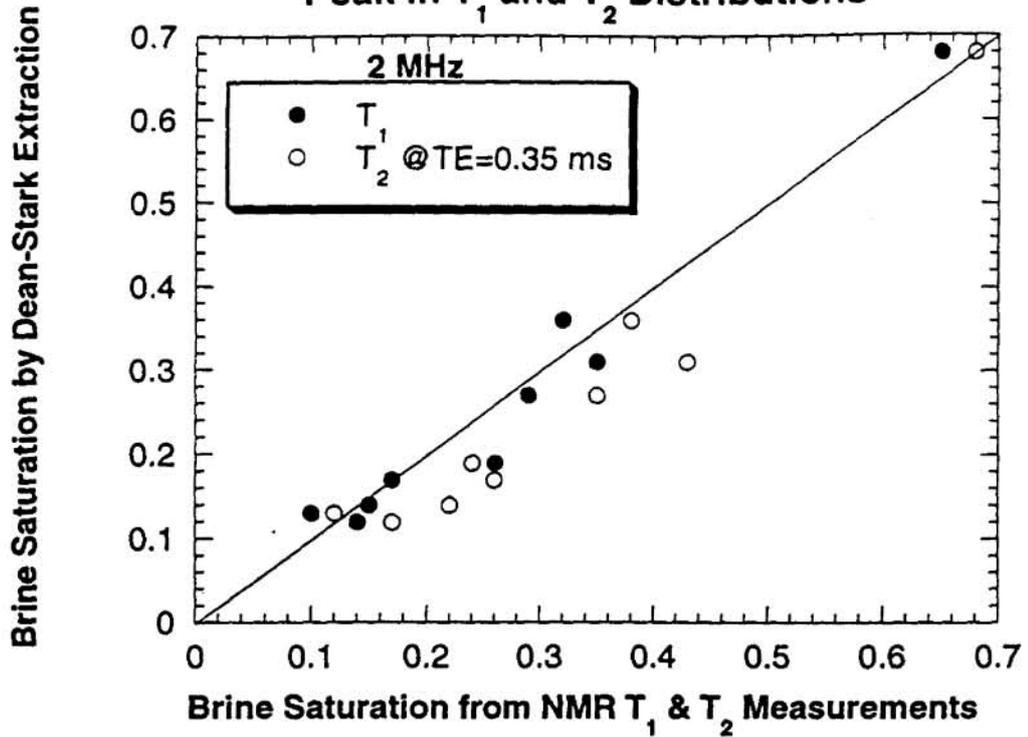


Figure 1  $T_1$  Saturation Estimates Coorespond with Dean\_Stark Values

### $T_1$ and $T_2$ Distributions for Chlorite Rich Core Sample

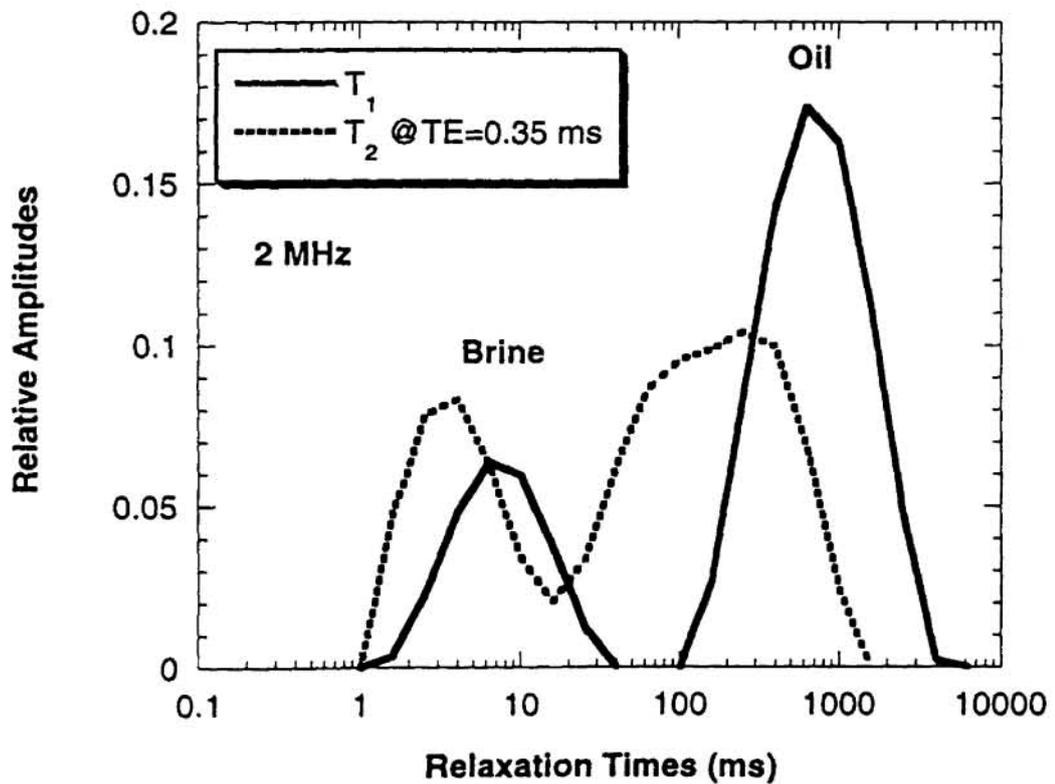


Figure 2  $T_2$  Distribution Distorted by Induced Gradients

**T<sub>1</sub> Distribution and T<sub>2</sub> Distributions  
at Two Echo Spacings for Sample  
Saturated with Oil and Brine**

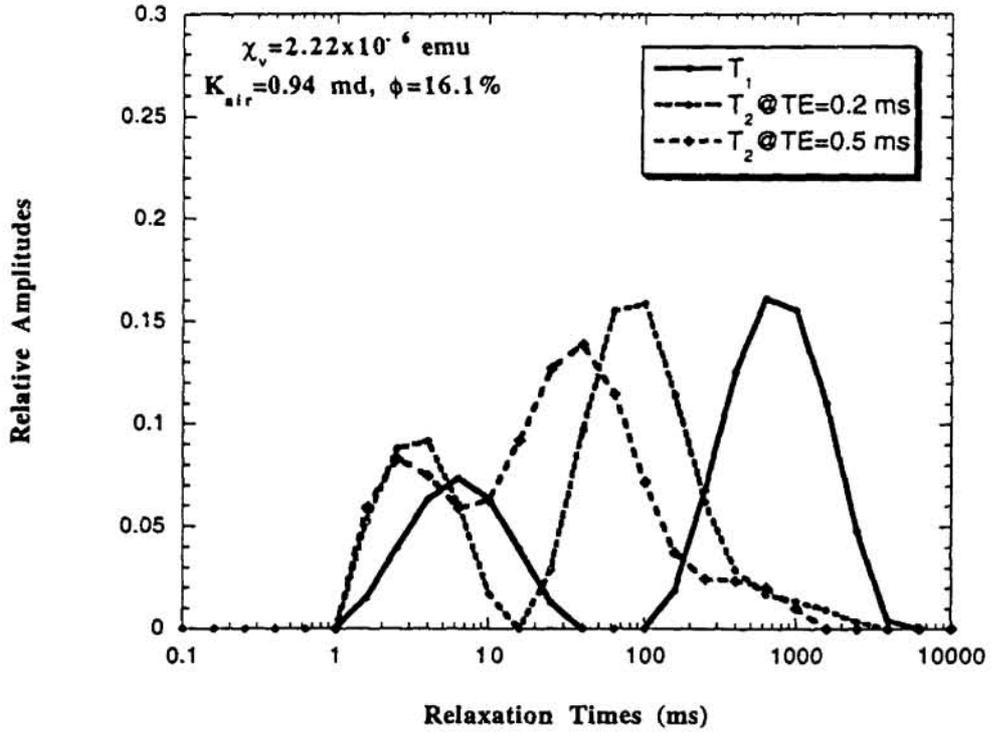


Figure 3 T<sub>1</sub> and T<sub>2</sub> Distributions Showing Induced Gradient Effects

**Magnetic Susceptibility is Strongly  
Correlated with Ferric Oxide**

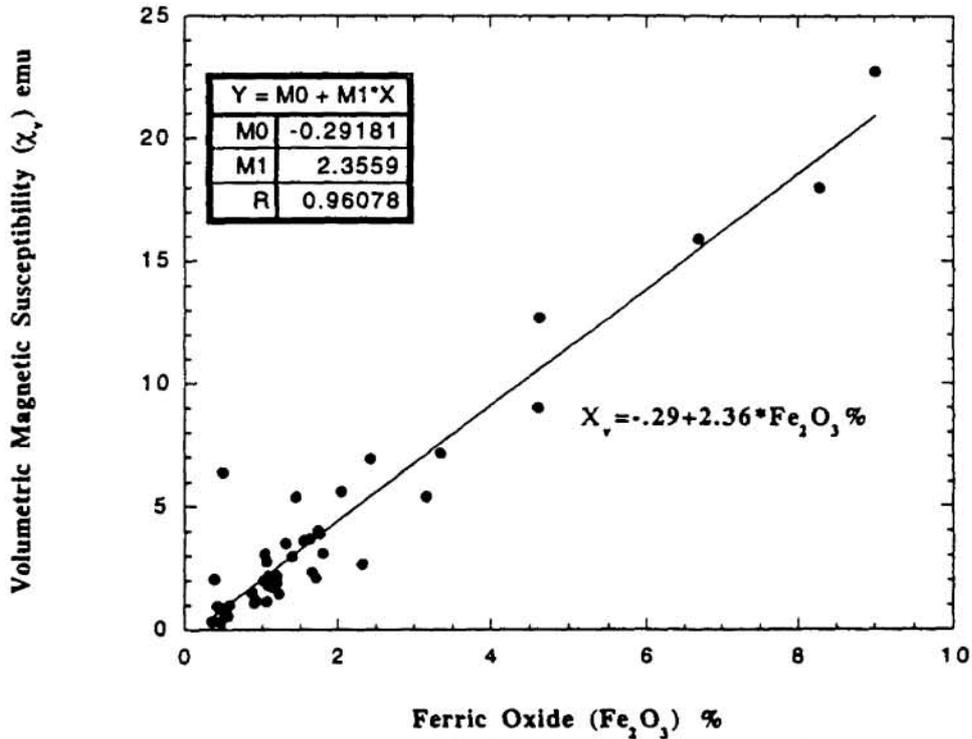


Figure 4 Correlation Between Magnetic Susceptibility and Ferric Iron

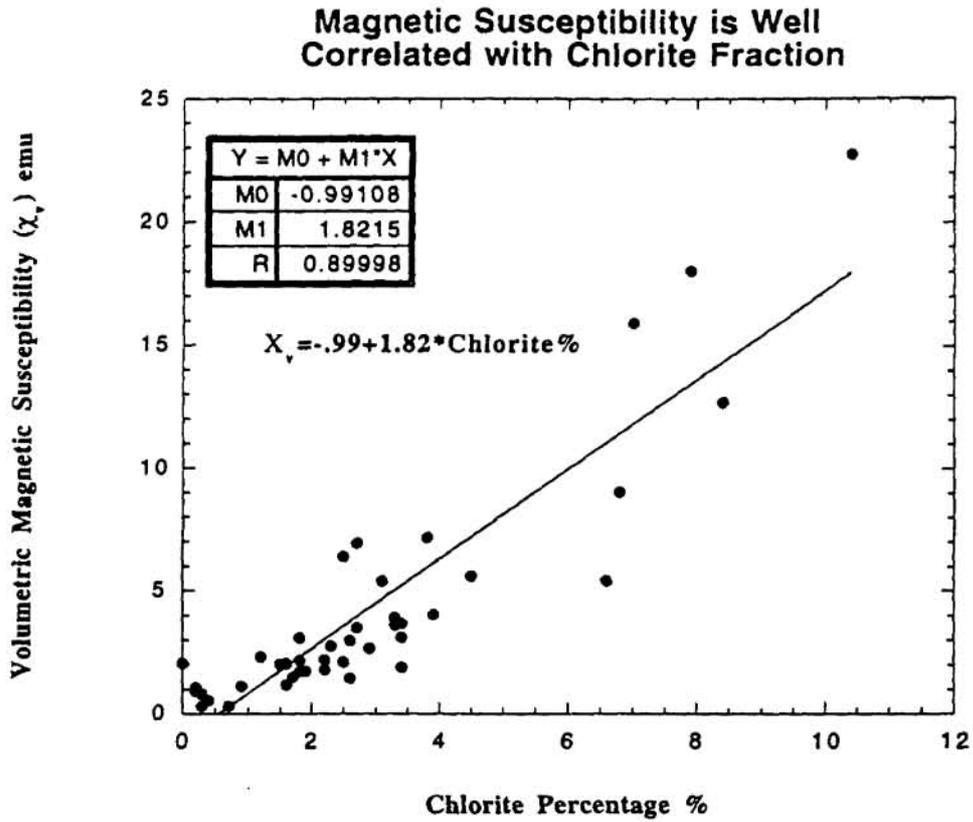


Figure 5 Magnetic Susceptibility Correlation with Ferric Iron

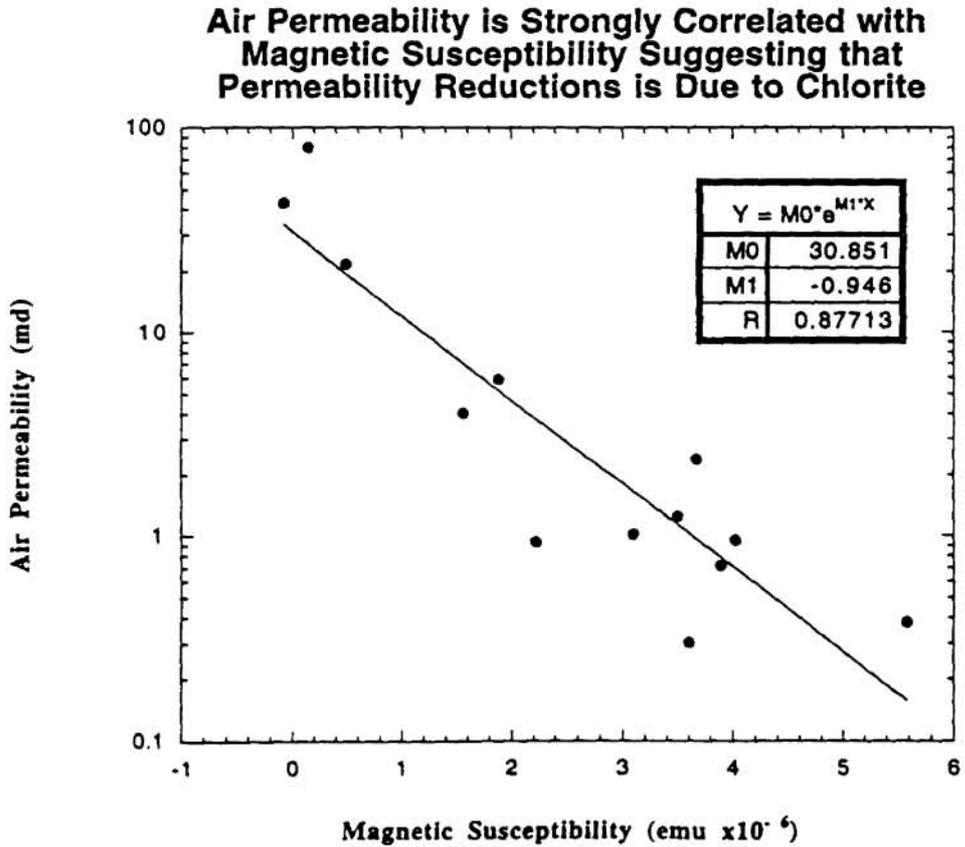


Figure 6 Correlation Between Air Permeability and Magnetic Susceptibility

**Brine and Oil Filtrate Signals Can be Clearly Distinguished in  $T_2$  Distribution**

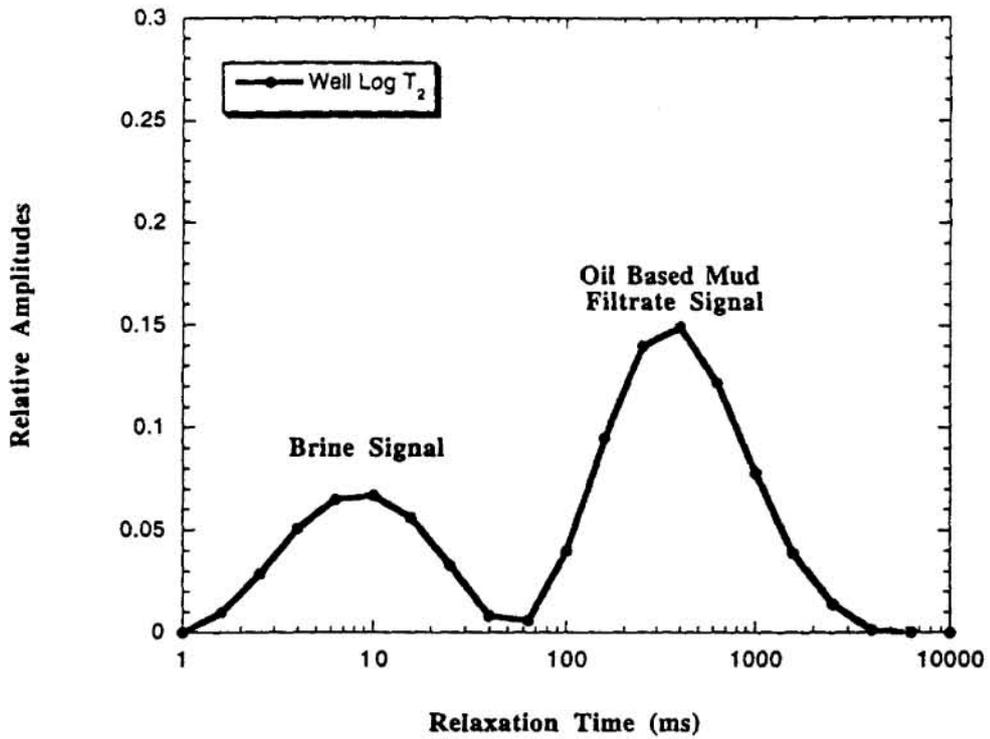


Figure 7 Well Log  $T_2$  Distribution Shows Distinct Oil and Brine Peaks

**Both Oil Filtrate and Brine Peaks are Shifted to Shorter Time Constants**

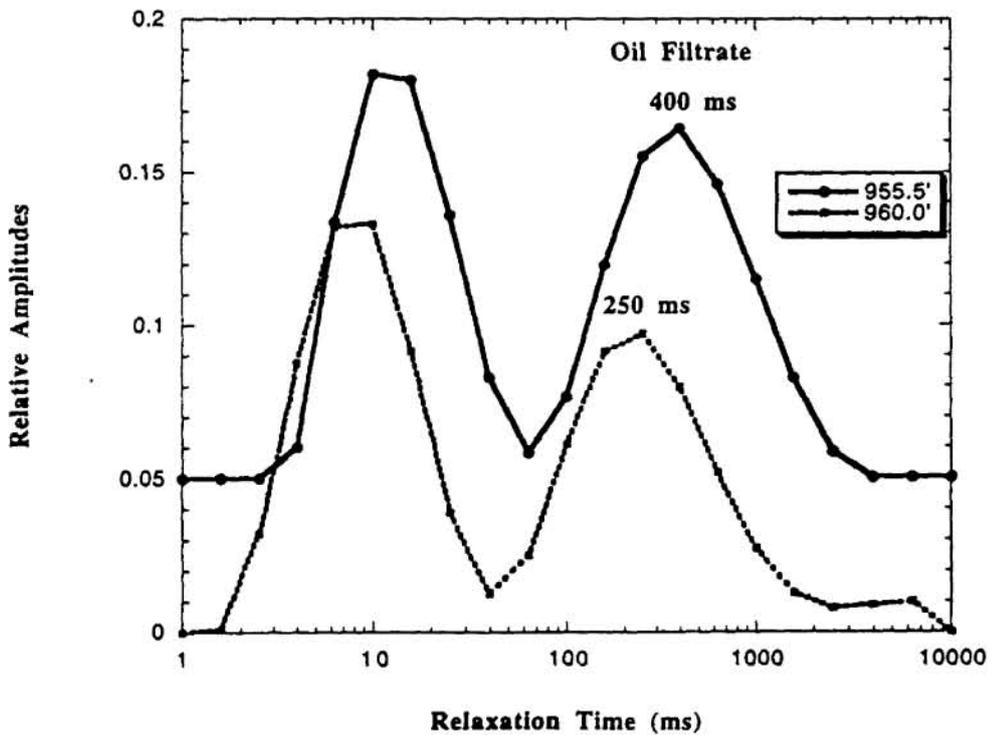


Figure 8 Both Oil and Brine Peaks are Shifted To Shorter Times in Chlorite Rich Zone