

SHRP-A-382

**The Application
of Small Nuclear Magnetic Resonance
Spectrometers to Quality Control
Measurements of Asphalt
and Asphalt-Aggregate Mixes**

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Abstract

Classic wide-line nuclear magnetic resonance techniques are used to measure the quantitative amounts of asphalt in asphalt-aggregate mixtures, including full 4-inch highway cores. It is shown how wide-line NMR can be used to measure and study the physical properties of both neat asphalts and asphalt in mixtures. A correlation relating known physical property measurements to NMR parameters is given for a wide range of neat asphalts. It is also shown how interactions between the asphalt and the aggregate in a mixture influence the physical properties of the asphalt and determine the physical properties of the mix.

Executive Summary

The primary goal of this work is to demonstrate that wide-line nuclear magnetic resonance (NMR) techniques can be used to measure the amount of asphalt in asphalt-aggregate mixes as they are being prepared and used in the field. This was accomplished by showing in phase I that good NMR spectra can be obtained on both the neat asphalts and small asphalt-aggregate mixes. In phase II of the program, a magnet large enough to accommodate a full 4-inch highway core was obtained and a new spectrometer was assembled. This spectrometer was used to demonstrate the feasibility of using NMR techniques to quantitatively determine the amount of asphalt in 4-inch cores.

This report shows calibration curves for determining the asphalt content of highway cores; however, a finding at least as interesting is that wide-line NMR can be used to determine NMR relaxation times of neat asphalts, and that these relaxation times can be related to measured asphalt physical properties. We show how NMR relaxation times, as measured on a small wide-line NMR spectrometer, can be related to known tan-delta measurements on neat asphalts, how glass transition temperatures of asphalt can be measured by NMR, and, more important, that a reaction occurs between the asphalt and the aggregate of a mixture that profoundly changes the physical properties of the asphalt.

In our studies of the neat asphalts, we demonstrate the use of two different NMR techniques to look at the "flexibility" of an asphalt. These techniques are free induction decay studies, which measure the relative amounts and relaxation times of three hydrogen populations that exist in most asphalts, and the use of second moment analysis of the off-resonance NMR signal after Fourier transformation, which measures the presence of molecular motion in the asphalt (i.e., its flexibility). These NMR properties are related to known methods of determining physical properties for a wide range of asphalts.

The identification of the reaction between asphalt and aggregate and how it affects asphalt physical properties in the mix has important implications for the use of NMR to quantitatively measure the amount of asphalt in a mix. A good understanding of this interaction, how it changes the physical properties of the mix, and how it affects the NMR signal of a mix must be obtained before the technique can be reliably used in the field.

At present, it is felt that good quantitative determinations of asphalt in mixtures can be achieved by running the analysis at elevated temperatures and flowing the sample through the NMR magnet so that the NMR data are the accumulation of spectra from a large sample. Such a system could be used to gather data from a large set of hot-mix samples either at a hot-mix plant or in an asphalt laboratory.

This report shows how wide-line NMR can be used to measure asphalt physical properties such as tan-delta and glass transition temperatures. Simple free induction decays followed by computer fitted deconvolution techniques are used to measure the relative amounts of the three different hydrogen populations found in most asphalts. These three phases consist of a stiff phase, a flexible phase, and a fluid phase. Tan-deltas are shown to be a linear combination of the relative concentration of these three phases plus their measured spin-spin relaxation times. Glass transition temperature measurements are made by determining the off-resonance free induction decay of the asphalt and using a computer program to calculate the second-moment of this absorption mode NMR spectrum. We also show how NMR intensities can be used to measure glass transition temperatures of asphalts, both neat and in mixtures, and how the aggregate influences these measurements.

Introduction

Nuclear magnetic resonance (NMR) has become the premier spectroscopic technique to determine the structure of most organic compounds. The Strategic Highway Research Program (SHRP) has funded, under contract A-002C, a comprehensive study of asphalt and asphalt-aggregate mixtures. This work consisted primarily of determining asphalt structure and its effect on asphalt physical properties.

The primary goal of our work was to develop NMR methods to quantitatively determine the amount of asphalt in an asphalt-aggregate mixture. These methods were to be capable of making these measurements in the field as the mixtures were being prepared. The equipment would need to be operated by plant personnel who have no knowledge of NMR. Our work in the aluminum industry convinced us that this could be done if the proper NMR methods for the determination of asphalt in these mixtures could be developed (1, 2).

A major impact on the NMR results was found during the development of the necessary NMR methods for determining asphalt in hot mix, when we realized that there was an interaction between the asphalt and the aggregate in the mix. This interaction affected the physical properties of the asphalt in the mix and, therefore, its NMR spectrum. A better understanding of this reaction was needed if we were to achieve our goal. That is, we needed a better understanding of the relationship between asphalt physical properties and NMR relaxation times of asphalt in both mixtures and in the neat asphalt.

There is a long history in the use of wide-line NMR in studying the relationships between NMR relaxation times and physical properties of organic materials, and abundant literature exists on the use of NMR relaxation times to study molecular motion in a wide range of organic materials (3, 4, 5, 6, 7, 8). In the past workers have shown the usefulness of NMR when applied to such studies. It is especially useful when materials are studied over a wide temperature range, much like the range of temperatures that are important in the use of asphalts in highway construction. Thus, the use of wide-line NMR to study asphalt physical properties is a natural extension of past NMR efforts.

In SHRP contract A-002C, high resolution NMR techniques were used to help understand the chemical structure of the core asphalts and how changes in this structure affect asphalt rheology. We approached this problem from a different direction. Asphalts are large, diverse organic molecules whose chemical structures are very complex. It is probable that asphalt physical properties are determined by very small changes in their chemical structure. Relating physical properties of an asphalt to its chemical structure is much like attempting to measure the molecular weight of a polymer by measuring its functional groups (the molecular weight of a polymer is

determined by the last few functional groups that react; functional group concentrations need to be determined with great accuracy if they are to relate to polymer physical properties).

Likewise, asphalt chemical structures need to be determined with great accuracy in order to relate them to asphalt physical properties.

The fact that NMR relaxation times of the asphalt in a mix are modified by the presence of the aggregate has important implications for this study. It means that after a proper understanding of the relationship between NMR relaxation times and asphalt physical properties is obtained, it should be possible to develop NMR methods that would measure not only the amount of asphalt in a mix but also the physical condition of the asphalt in the mix without removing it from the aggregate. Indeed, it may even be possible to use flat magnet technology to make these measurements in situ in the pavement. This could have a profound impact on quality control measurements in the highway industry.

Calibration curves relating asphalt concentrations in 4-inch cores are presented here. It is shown that the effect of the aggregate on asphalt physical properties profoundly affects their NMR spectra. Using a smaller 1-inch core, we were able to determine NMR spectra on portions of these cores as a function of temperature. These temperature data show that quantitative results are obtained for these mixes when the NMR spectra are determined at temperatures above about 125°C. At these temperatures, the hardening effects of the aggregate on the asphalt is minimized, and quantitative NMR spectra are obtained.

Instrumentation

Two NMR spectrometers were used during phases I and II of this work. Both these spectrometers were designed so that the majority of the digital electronics needed for an NMR spectrometer is contained on the bus of a personal computer. Commercially available parts were used when ever possible. The basic design concept of this spectrometer is shown in Figure 1-1. Tri-Valley Research (TVR) owned a spectrometer of this type before the contract with SHRP was signed, and all the phase I (proof of concept) work was done on this spectrometer. This includes the asphalt physical properties work described in the experimental section of this report.

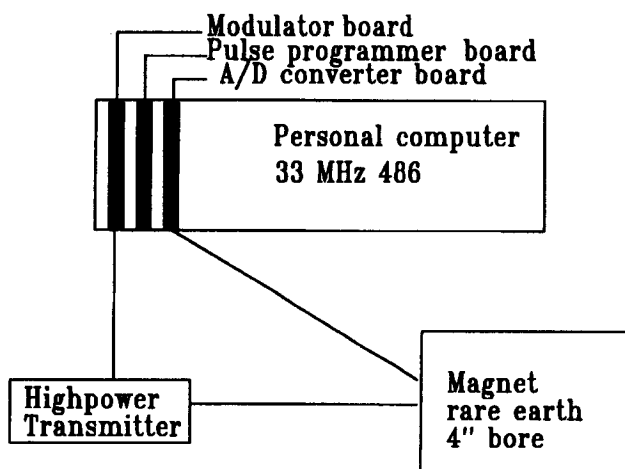


Figure 1-1. Block diagram of Tri-Valley Research NMR spectrometer

When the feasibility of studying both neat asphalt and asphalt-aggregate mixtures with NMR spectroscopy was established SHRP funded a phase II effort that included constructing a new spectrometer capable of running NMR spectra of full-size, 4-inch, highway cores.

The large-bore instrument obviously had to be designed around a much larger magnet than the one owned by TVR. Because we had a great deal of experience designing and using standard H-type magnets for NMR applications, we realized that their use in this application would present some significant problems, not the least of which is their size and weight. Because of this, and with the advice of our magnet maker, we decided to base the large-bore SHRP spectrometer on the use of a Halbach condensed-field magnet. This type magnet was first suggested by Klaus Halbach (9) as a focusing magnet for particle accelerators. It has been well studied and discussed in the open literature (10,11). This magnet is essentially a permanent magnet that returns the magnetic flux lines inside its magnetic material. That is, it does not use a heavy steel yoke as magnetic flux return lines. This means they are a fraction of the weight and cost of a standard H-type magnet. The concept is illustrated in Figure 1-2, which is from Marinescu and Marinescu (11).

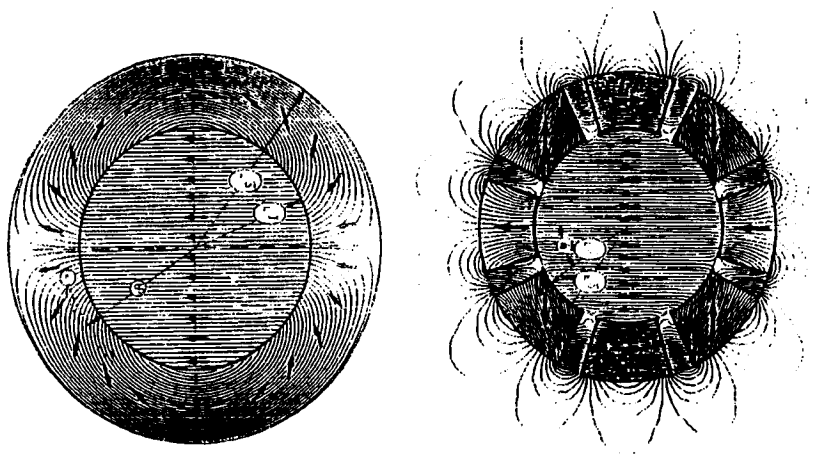


Figure 1-2. Concept of the Halbach dipole magnet

The weight and cost of the magnet are important design concepts in any NMR spectrometer that will eventually be used as a quality control device in the highway industry. This magnet also has other significant advantages for use in an NMR spectrometer, which have to do with the fact the magnet's field axis is transverse to the direction of its bore. This means that it can be extended to any length for flowing applications and that a solenoid can be used as the NMR coil.

In addition to the NMR spectrometer already owned by TVR, which is based on a standard H-type magnet and is limited to the use of 15 mm samples and smaller, we obtained a smaller Halbach dipole to prove the feasibility of its use before the full-size Halbach dipole was ordered. This smaller Halbach was used to optimize the design and prove the concept.

Magnet temperature control has always been a problem with present, commercially available, small NMR spectrometers. We solved this problem by enclosing the small Halbach dipole in a piece of PVC pipe fitted with large end caps. A smaller piece of PVC pipe was passed through the middle of the magnet and became the bore tube that housed the NMR probe. The magnet was placed in this PVC enclosure and the whole thing fitted into an anodized aluminum housing. Figure 1-3 illustrates how this was done. A temperature-controlled solution from a Cole-Parmer circulating bath was passed through the PVC portion of the enclosure.

The above arrangement gave us magnet temperature control better than $\pm 0.1^{\circ}\text{C}$ and produced a stable NMR magnet. This magnet was interfaced to our existing NMR electronics and used to show NMR spectra on 1-inch mix samples.

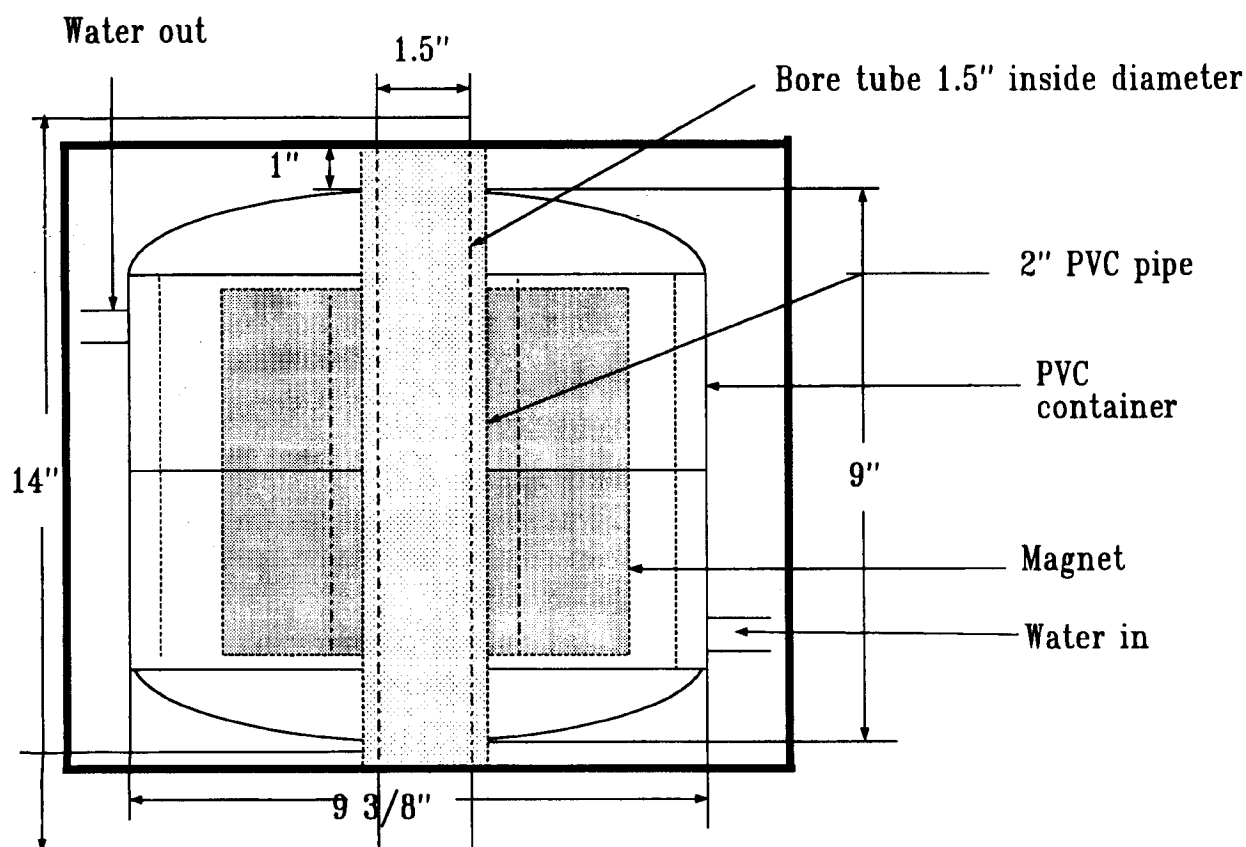


Figure 1-3. Housing for model Halbach dipole magnet

Full-Size Halbach Dipole

After proving the feasibility of using a Halbach dipole in an NMR system, we ordered the full-size, 6-inch bore Halbach magnet. Our experience with the model Halbach convinced us that the larger magnet needed to be end corrected to improve the magnetic field gradients that exist along the axis of the dipole. (We arbitrarily designate the two axes perpendicular to the axis of the bore of the dipole as the X and Z axes of the magnet and the direction along the bore as the Y axis.) This end correction, which was suggested by the magnet maker, consisted of reducing portions of the inside diameter of the magnet by a half inch. The full-size Halbach contains four layers of magnetic material consisting of twenty segments per layer, each layer being 4 inches in length. The two middle layers are 13 inches outside diameter and 6 inches inside diameter, whereas the top and bottom segments are 13 inches outside diameter and 5.5 inches inside diameter. This assembly is enclosed in a 17 inch aluminum tube 14 inches in diameter and 1 inch thick. This makes the magnet 17 inches long and 15 inches in diameter. It weighs about 300 lbs. Figure 1-4 is a drawing of the large Halbach enclosed in its aluminum container.

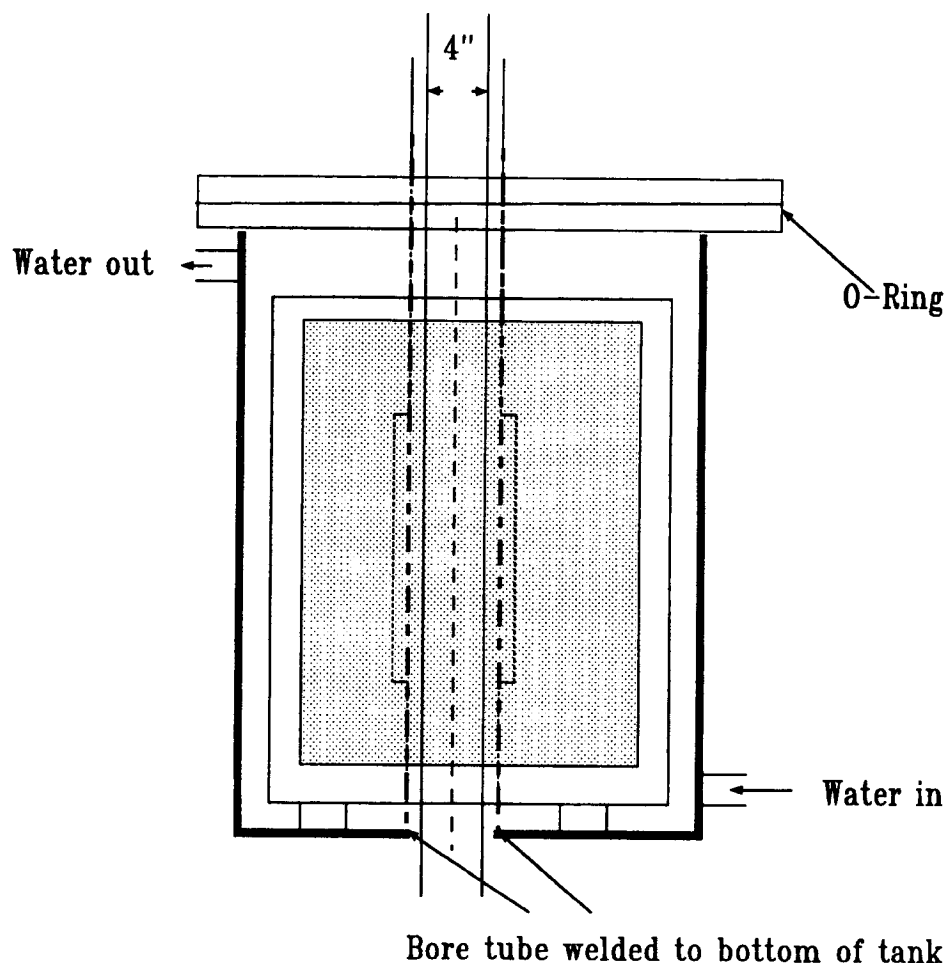


Figure 1-4. Housed large Halbach dipole magnet

Figure 1-5 is a drawing of the assembled magnet, container, probe, and temperature controlled circulating bath.

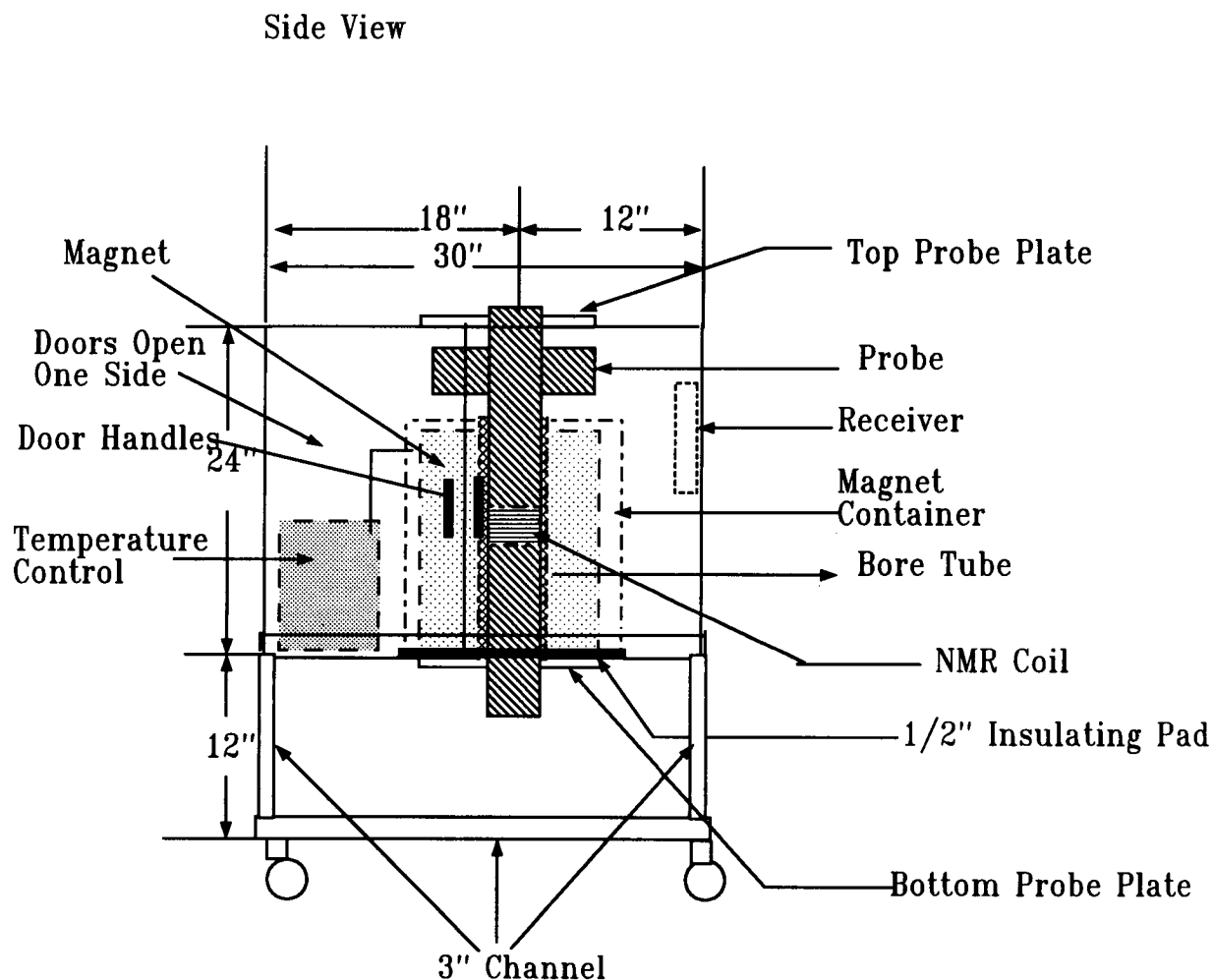


Figure 1-5. Halbach magnet assembly

Modifications of this system were used not only to determine hydrogen NMR spectra of 4-inch highway cores, but also used to satisfy our cost sharing commitments to our cost-sharing partners, Archer Daniels Midland Company for solids/liquid ratio of edible oils and Gilroy Foods for a solids-in-onions application.

A probe, which can accommodate a 4-inch sample, was ordered from CCMR Enterprises. This probe was small enough to accommodate shim coils wrapped on the outside of the probe that fit inside the bore tube of the magnet.

In addition to the described spectrometer and its probe, we designed and built a temperature-controlled NMR probe that can accommodate a 1-inch sample tube. This probe consisted of a copper bore tube fitted with an external copper jacket, which allowed the passage of a temperature-controlled solution from a Cole-Parmer circulating bath to be passed through it. This arrangement provides good sample temperature control over the temperature range accommodated by the circulating bath. In our case, this amounted to a temperature range of from -7°C to +100°C. Samples were also heated to 160°C in an oven and placed into the hot probe, and NMR spectra were determined at this temperature.

All temperature studies were made on samples sealed in glass tubes to minimize the effects of oxidation on the asphalt in the sample.

Experiments

NMR of Neat Asphalts

In order to show that good wide-line NMR spectra can be determined on our existing NMR spectrometer, a series of asphalt samples was obtained from the SHRP Materials Reference Library at the University of Texas and used to conduct the following research.

Free Induction Decays

If a hydrogen containing material is placed in the coil of an NMR spectrometer and treated with a proper radio frequency (RF) pulse, the spins of the hydrogen atoms in the sample will assume a high-energy orientation (i.e., the sample will be magnetized). At the end of the pulse, the magnetization of the sample will decay. Such a decay, if free to decay at its own natural rate, is called a *free induction decay* or FID. This decay will induce a voltage in the coil used to pulse the sample. This voltage is detected by the spectrometer and becomes the NMR spectrum. Thus, the NMR spectrum obtained in such an experiment is the decay of the magnetization in the sample as a function of time. Such a spectrum, a FID of asphalt AAG-2, is shown in Figure 2-1.

The sharp spike on the left side of the spectrum in Figure 2-1 is a breakthrough caused by the RF pulse. The receiver is saturated at this point. The usable data start just to the right of this spike at the peak of the decaying magnetization. Care must be taken in interpreting data from such FIDs such as shown in Figure 2-1. All small, low-field NMR spectrometers use magnets with limited field homogeneity. Inhomogeneities in the magnet field can cause demagnetization in the sample, and proof has to be obtained that the decay is the natural decay rate of the hydrogens in the sample and is not caused by the quality of the magnet.

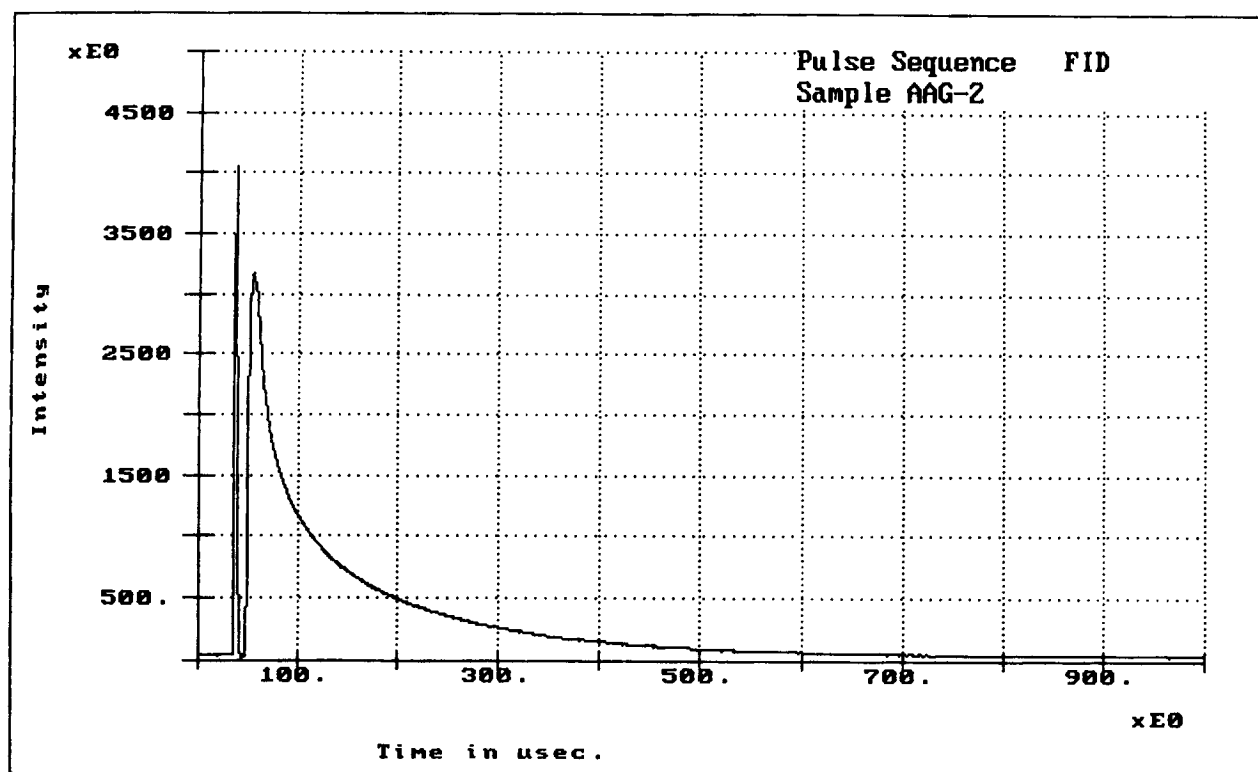


Figure 2-1. FID of asphalt AAG-2

FIDs of neat asphalt samples can be shown to be the true decay of the hydrogens in the sample by looking at a FID of a vegetable oil, in which the decay rate is known to be determined by magnet quality. Since the FID of an oil decays much more slowly than that of an asphalt, the asphalt FID shows that NMR spectra, such as exemplified in Figure 2-1, represent the true decay rate of the hydrogen atoms in the asphalt and are a measure of the spin-spin relaxation time, T_2 .

It is known that a plot of the log of the intensity of the FID as a function of time will be a straight line if all the hydrogen atoms in the sample belong to one population. If more than one population of hydrogen atoms is present, each will produce a straight-line decay, and the \ln plot will be an overlap of these decays. Figure 2-2, the \ln plot for a typical asphalt FID, shows that the decay can be fairly well divided into three straight-line segments, each representing a unique hydrogen population.

These populations are unique in the sense that hydrogens do not exchange between them faster than their corresponding line widths in Hz. For these samples, this means that the hydrogens do not exchange between populations faster than at about 10,000 Hz. The separation shown in Figure 2-2 seems arbitrary, and to some extent it is; but we will see that data such as these seem to measure the relative physical states (i.e., stiffness of a broad range of asphalt samples).

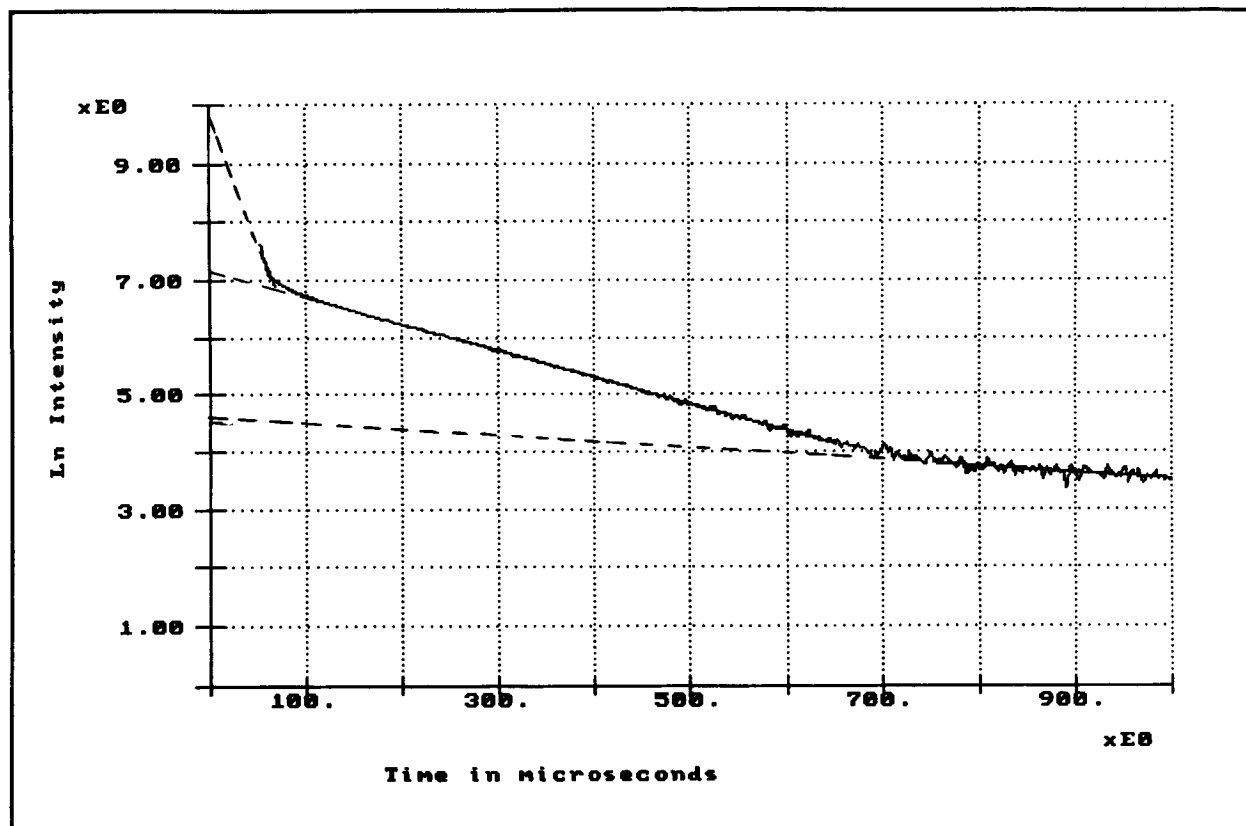


Figure 2-2. Log plot for asphalt FID

Each of the straight-line portions of the decay shown in Figure 2-2 represents a different hydrogen population in the asphalt. Each is a collection of molecules that share a unique hydrogen population. Populations with steeper slopes have faster NMR relaxation times caused by the presence of more rigidly bound hydrogen atoms. That is, hydrogen populations with faster NMR decay rates contain more rigidly bound hydrogen atoms (i.e., they are stiffer). Thus, the asphalt whose NMR data are shown in Figure 2-2 contains three hydrogen populations that differ in relative stiffness; a stiff fraction, a flexible fraction, and a fluid fraction.

FIDs were obtained for a wide range of asphalt samples. Log plots were computed for each FID and computer-fitted to estimate the relative concentration of each of the three hydrogen populations present and their spin-spin relaxation times. A regression analysis was done on this data using tan-delta values determined by researchers at Pennsylvania State University, under contract A-002A, as the dependent variable. The results of this analysis are shown in Figure 2-3.

The data used to generate Figure 2-3 are shown in Table 2-1. Standard deviations were calculated for these data and are shown in Table 2-2.

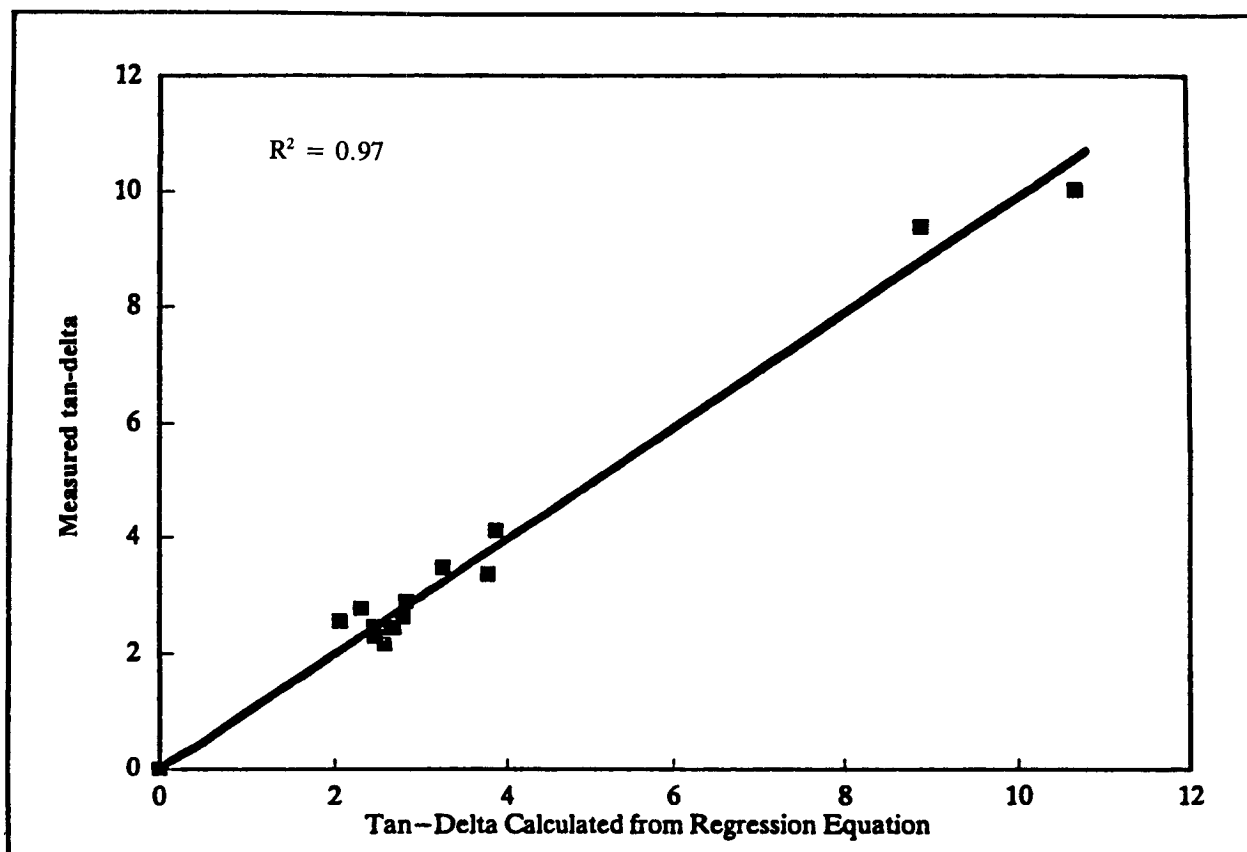


Figure 2-3. Regression analysis results-NMR versus tan-delta

Table 2-1. Data for tan-delta regression

Asphalt	Tan-delta ¹	[Fast] ²	T ⁵	[Inter] ³	T ⁵	[Slow] ⁴	T ⁵	Moment
AAG-2	10.68	82.51	124.00	13.90	754.00	3.58	3,384.00	13.01
AAG-2	10.68	82.62	132.00	15.48	769.00	4.46	2,984.00	10.42
AAG-1	8.91	82.62	123.00	13.86	795.00	3.51	3,870.00	13.00
AAG-1	8.91	81.60	126.00	14.67	774.00	3.73	3,587.00	11.56
AAZ	5.77	75.85	151.00	15.95	859.00	8.20	2,102.00	6.00
AAZ	5.77	72.44	154.00	17.57	801.00	9.99	1,628.00	7.40
AAV	4.78	61.67	194.00	20.79	815.00	17.53	1,426.00	3.01
AAV	4.78	62.27	197.00	21.16	870.00	21.16	1,576.00	2.43
AAF	3.87	68.97	175.00	18.02	899.00	13.01	1,719.00	3.19
AAF	3.87	68.89	176.00	18.91	895.00	12.19	1,776.00	3.60
AAC-1	3.78	63.89	199.00	19.46	947.00	16.65	1,691.00	2.36
AAC-1	3.78	63.25	198.00	18.94	906.00	17.80	1,494.00	NA
AAX	3.71	69.97	170.00	20.03	858.00	10.00	2,132.00	4.94
AAX	3.71	69.01	170.00	18.08	892.00	12.91	1,732.00	4.71
AAN	3.26	65.09	190.00	19.26	895.00	15.64	1,639.00	3.62
AAN	3.26	64.47	192.00	19.43	905.00	16.10	1,648.00	2.97
AAJ	2.83	60.89	200.00	21.11	890.00	19.00	1,515.00	2.64
AAJ	2.83	62.43	194.00	19.58	891.00	17.99	1,430.00	3.26
AAK-2	2.79	50.26	251.00	28.06	822.00	28.06	1,424.00	2.83
AAK-2	2.79	51.21	248.00	27.82	823.00	20.47	1,429.00	2.34
AAD-2	2.69	47.20	291.00	19.24	1,094.00	33.56	1,559.00	1.62
AAD-2	2.69	47.22	293.00	20.27	1,105.00	32.51	1,634.00	1.48
AAD-1	2.66	53.56	249.00	20.05	1,017.00	26.38	1,544.00	2.00
AAD-1	2.66	54.06	245.00	21.38	1,010.00	24.56	1,622.00	2.07
AAW	2.66	63.27	192.00	19.50	944.00	16.23	1,759.00	2.46
AAW	2.66	58.56	212.00	19.29	965.00	22.15	1,536.00	NA
AAS	2.58	59.20	205.00	24.00	810.00	16.77	1,417.00	1.46
AAS	2.58	60.21	210.00	21.00	918.00	18.79	1,599.00	1.97
AAM-2	2.51	59.42	213.00	21.31	873.00	19.26	1,478.00	1.28
AAM-2	2.51	60.67	210.00	23.78	871.00	15.55	1,723.00	NA
AAK-1	2.47	61.47	197.00	26.99	748.00	11.60	1,694.00	5.42
AAK-1	2.47	61.17	198.00	27.47	747.00	11.36	1,709.00	4.23
AAH	2.46	46.91	266.00	14.39	1,022.00	38.17	1,277.00	1.70
AAH	2.46	47.49	261.00	14.79	1,014.00	37.73	1,283.00	1.53
AAM	2.31	63.16	195.00	22.65	845.00	14.17	1,730.00	3.09
AAM	2.31	63.26	195.00	22.49	837.00	14.24	1,677.00	3.67
AAE	2.07	57.04	231.00	20.95	1,014.00	22.00	1,701.00	2.25
AAE	2.07	54.73	231.00	18.51	905.00	26.75	1,257.00	2.09

¹ Furnished by Dr. David Anderson, Pennsylvania State University² Concentration of fast portion of FID; NMR data generated at 35°C³ Concentration of intermediate portion of FID; NMR data generated at 35°C⁴ Concentration of slow portion of FID; NMR data generated at 35°C⁵ Spin-spin relaxation time of preceding population

NA = Not Available

Table 2-2. Averages and standard deviations for tan-delta regression

Asphalt	Tan-delta ¹	[Fast] ²	T ⁵	[Inter] ³	T ⁵	[Slow] ⁴	T ⁵	Moment
AAG-2	10.68	82.57	128.00	14.69	762.00	4.02	3,184.00	11.71
std.		0.08	5.70	1.12	10.60	0.62	283.00	1.83
AAG-1	8.91	82.11	125.00	14.27	785.00	3.62	3,729.00	12.28
std.		0.72	2.12	0.57	14.84	0.16	200.00	1.01
AAZ	5.77	74.15	153.00	16.76	830.00	9.10	1,865.00	6.70
std.		2.41	2.12	1.14	41.00	1.27	335.00	0.99
AAV	4.78	61.97	196.00	20.98	843.00	19.35	1,451.00	2.72
std.		0.28	2.12	0.26	38.90	2.57	176.80	0.41
AAF	3.87	68.93	176.00	18.47	897.00	12.60	1,748.00	3.40
std.		0.06	0.71	0.63	2.83	0.58	40.30	0.28
AAC-1	3.78	63.57	199.00	19.20	927.00	17.23	1,593.00	2.36
std.		0.45	0.71	0.37	29.00	0.81	139.00	NA
AAX	3.71	69.49	170.00	19.06	875.00	11.46	1,932.00	4.11
std.		0.68	0.00	1.38	23.30	2.05	283.00	0.84
AAN	3.26	64.78	191.00	19.35	900.00	15.87	1,644.00	3.29
std.		0.44	1.41	0.12	7.07	0.32	6.36	0.45
AAJ	2.83	61.66	197.00	19.85	891.00	18.50	1,523.00	2.95
std.		1.09	4.24	0.37	0.71	0.71	10.60	0.43
AAK-2	2.79	50.74	150.00	27.94	823.00	24.27	1,427.00	2.58
std.		0.67	2.12	0.17	0.71	5.36	3.53	0.34
AAD-2	2.69	47.21	292.00	19.76	1,100.00	33.04	1,597.00	1.55
std.		0.01	1.41	0.73	7.78	0.74	53.00	0.10
AAD-1	2.66	53.81	247.00	20.72	1,008.00	25.47	1,583.00	2.04
std.		0.35	2.83	0.94	4.95	1.28	55.20	0.05
AAW	2.66	60.92	202.00	19.40	955.00	19.19	1,648.00	2.46
std.		3.33	14.14	0.14	14.84	4.18	157.00	NA
AAS	2.58	59.71	207.00	22.50	864.00	17.78	1,508.00	1.71
std.		1.06	3.53	2.12	76.40	1.42	129.00	0.36
AAM-2	2.51	60.05	212.00	22.55	873.00	17.41	1,601.00	1.28
std.		0.88	2.12	1.74	3.53	2.61	173.00	NA

continued on the next page

Table 2-2. Averages and standard deviations for tan-delta regression (continued)

Asphalt	Tan-delta ¹	[Fast] ²	T ⁵	[Inter] ³	T ⁵	[Slow] ⁴	T ⁵	Moment
AAK-1	2.47	61.41	198.00	27.23	748.00	11.48	1,702.00	4.83
std.		0.16	0.71	0.34	0.71	0.16	10.60	0.84
AAH	2.46	47.20	264.00	14.69	1,018.00	37.95	1,280.00	1.62
std.		0.41	3.53	0.28	5.65	0.31	4.24	0.12
AAM	2.31	63.22	195.00	22.57	841.00	14.21	1,704.00	3.38
std.		0.06	0.00	0.09	5.66	0.05	37.50	0.41
AAE	2.07	55.89	231.00	19.73	960.00	24.38	1,479.00	2.17
std.		1.63	0.00	1.72	77.10	3.36	314.00	0.11
Avg.	3.82	62.60	196.00	19.98	889.00	17.73	1800.00	3.84
Avg. Std.		0.78	2.60	0.74	19.2	1.50	127.00	0.54
Std. as % of avg.		1.240	1.320	3.700	2.160	8.460	7.060	13.900

¹ Furnished by Dr. David Anderson, Pennsylvania State University

² Concentration of fast portion of FID

³ Concentration of intermediate portion of FID

⁴ Concentration of slow portion of FID

⁵ Spin-spin relaxation time of preceding population

NA = Not Available

The results of the regression analysis shown in Figure 2-3 and data given in tables 2-1 and 2-2 demonstrate the good relationship that exists between NMR relaxation times and measured tan-delta values. Correlations between NMR data and other measures of asphalt stiffness, such as penetration, were done, but none were nearly as successful as the one shown here for tan-delta.

The ability to use NMR relaxation times as a measure of asphalt stiffness is not surprising. It is as one would expect from NMR theory. NMR relaxation times have been used for many years to study polymer physical properties, and books have been written on the subject. The correlation given in Figure 2-3 is one of the two most important findings of this work.

Another important finding in this work is the identification of the interaction that occurs between asphalt and aggregate when they are mixed. We will discuss this interaction later in this report.

Frequency Domain NMR Spectra and Second-Moments

Conventional NMR spectroscopy uses the Fourier transform of a time domain spectrum to produce the familiar frequency domain NMR spectrum. In order to see frequencies both above and below the resonance frequency, one must offset the frequency. These are called "off-resonance" conditions. Figure 2-4 shows an off-resonance FID of an asphalt sample.

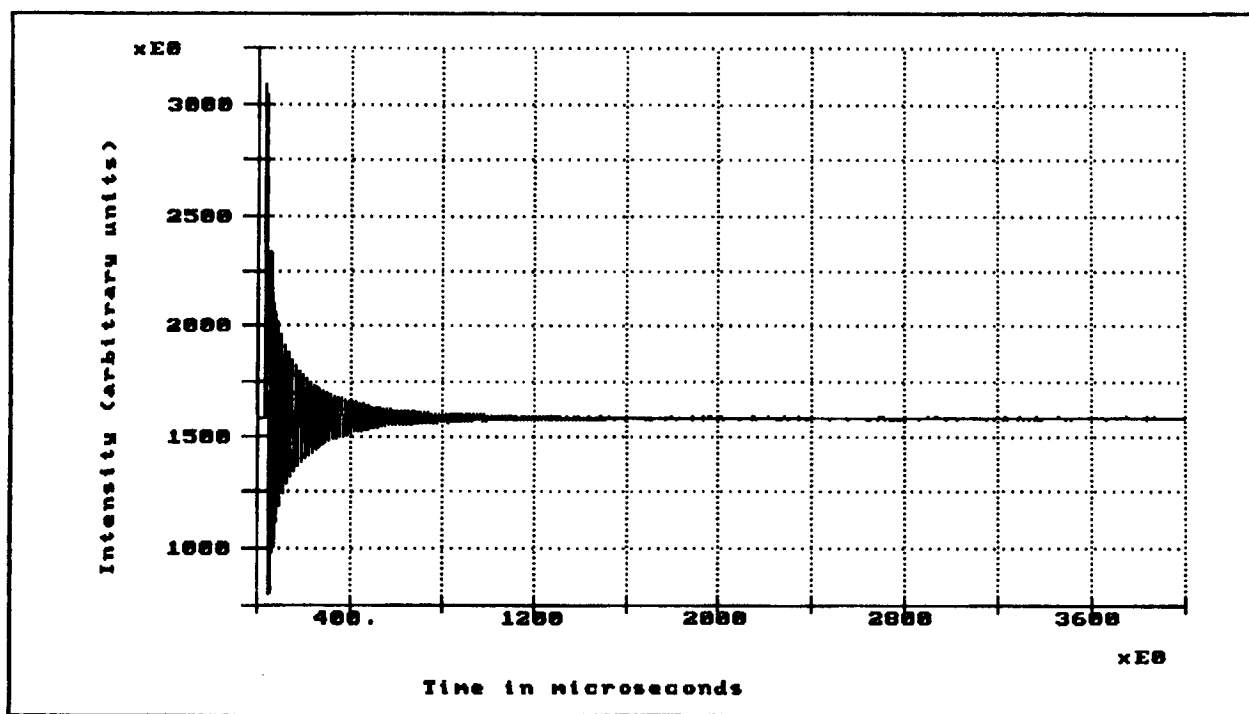


Figure 2-4. Asphalt off-resonance FID

The Fourier Transform of these data produces the frequency domain NMR spectrum shown in Figure 2-5.

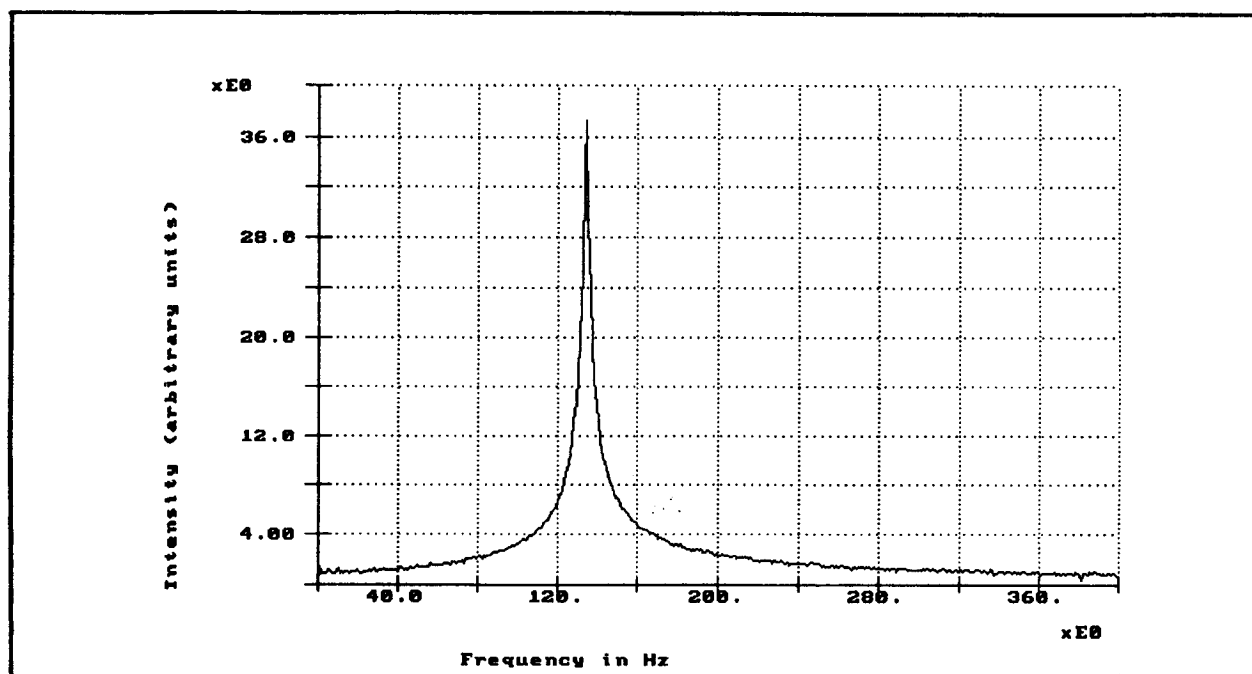


Figure 2-5. Asphalt frequency domain NMR spectrum

Careful examination of the NMR spectrum shown in Figure 2-5 indicates that the spectrum is composed of several overlapping spectra of different line widths. In fact, frequency domain NMR spectra of asphalts can be deconvoluted into their constituent parts. These parts can then be integrated to estimate the relative concentrations of the various hydrogen populations in the asphalt. These data should be equivalent to the previously described FID analysis.

The Asyst software package has a deconvolution routine capable of separating out the various overlapping NMR lines found in a frequency domain spectrum. This Asyst routine first fits the frequency domain spectrum to a specified number of hydrogen populations. It then displays the fit, which can then be integrated to measure the relative concentrations of the hydrogen populations found in the asphalt. Difficulties were encountered in using the Asyst software to separate frequency domain NMR spectra of asphalts into three hydrogen populations, but it did well in fitting it to two hydrogen populations. Figures 2-6 and 2-7 show such an analysis for asphalt AAG-1. This is a particularly stiff asphalt, and the above analysis indicates that it contains some 76% immobile component.

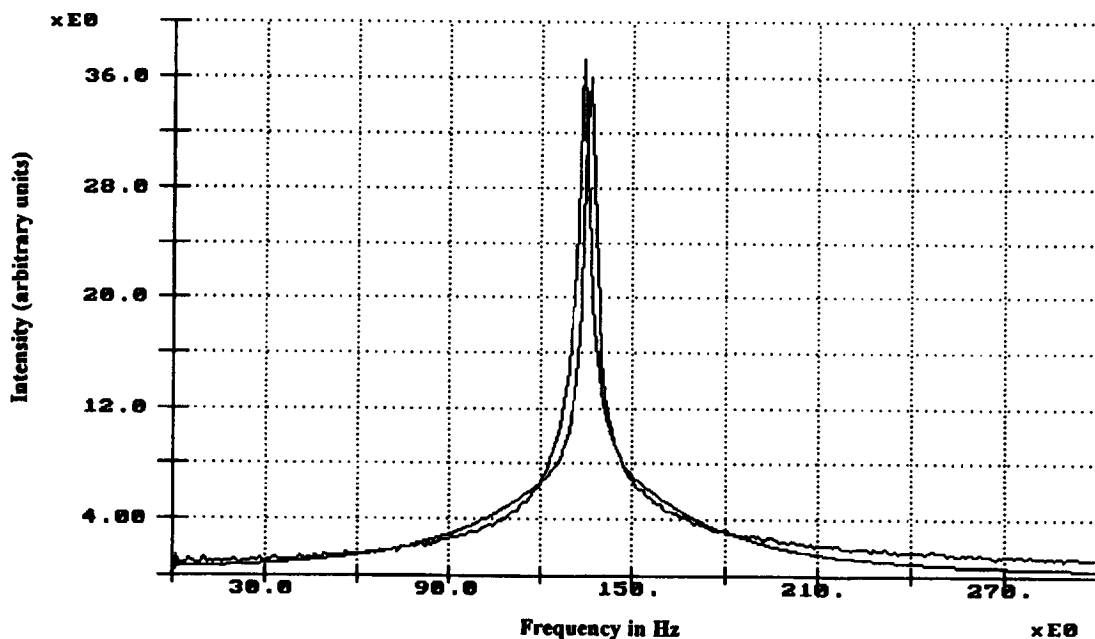


Figure 2-6. Deconvoluted asphalt frequency domain NMR spectrum

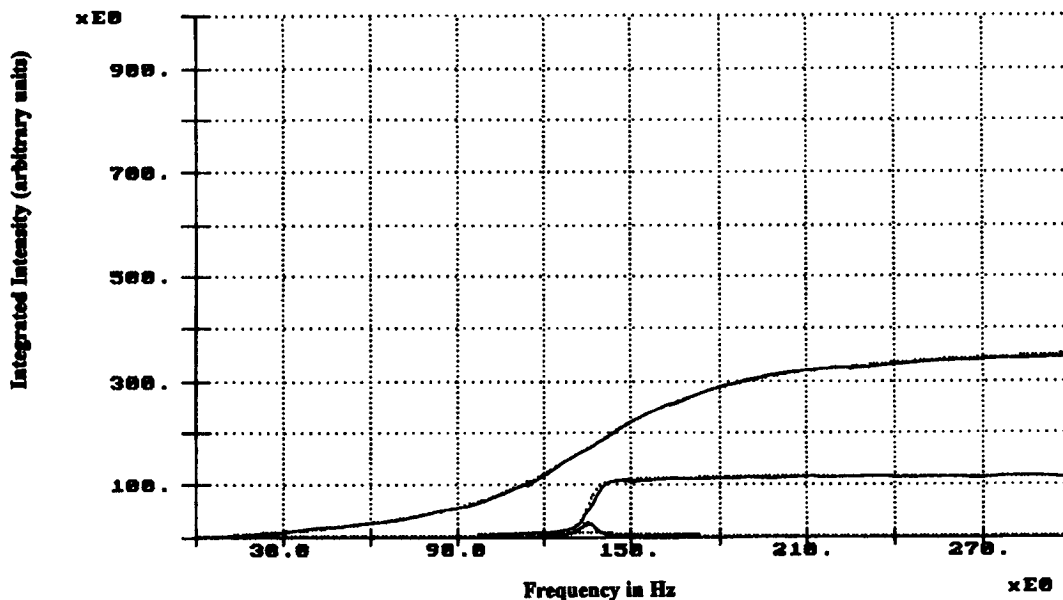


Figure 2-7. Integrated asphalt frequency domain NMR spectrum

Frequency domain NMR spectra were determined on all the samples used in the above tan-delta correlation, but the results did not produce a correlation of the quality as had the on-resonance analysis. This is probably due to the difficulty in deconvoluting the frequency domain NMR spectra into their constituent parts. The Asyst software seems to do a better job of separating the log plots than it does the frequency domain spectra.

Second-Moment Analysis

It is obvious that since NMR relaxation times, or line widths for asphalts, are determined by the mobility of the hydrogen atoms in the sample, they will change with sample temperature. We used a second-moment analysis of NMR spectra as a function of sample temperature to measure the effect of temperature on the SHRP core asphalts. The second-moment of an NMR spectra is

$$\Delta H = \int_{-\infty}^{\infty} (X - X_0)^2 g(X) dX$$

This equation shows that if the intensity of the frequency domain NMR spectrum at a particular point on the curve is multiplied by the square of this point's distance from the center of the spectrum, and these points are summed over the entire spectrum, a measure of the weighted width of the spectrum will be obtained. This makes second-moments very sensitive to the wings of the

NMR spectrum. In fact, for a Lorentzian curve the second-moment is infinite. Lorentzian and Gaussian line shapes are compared in Figure 2-8.

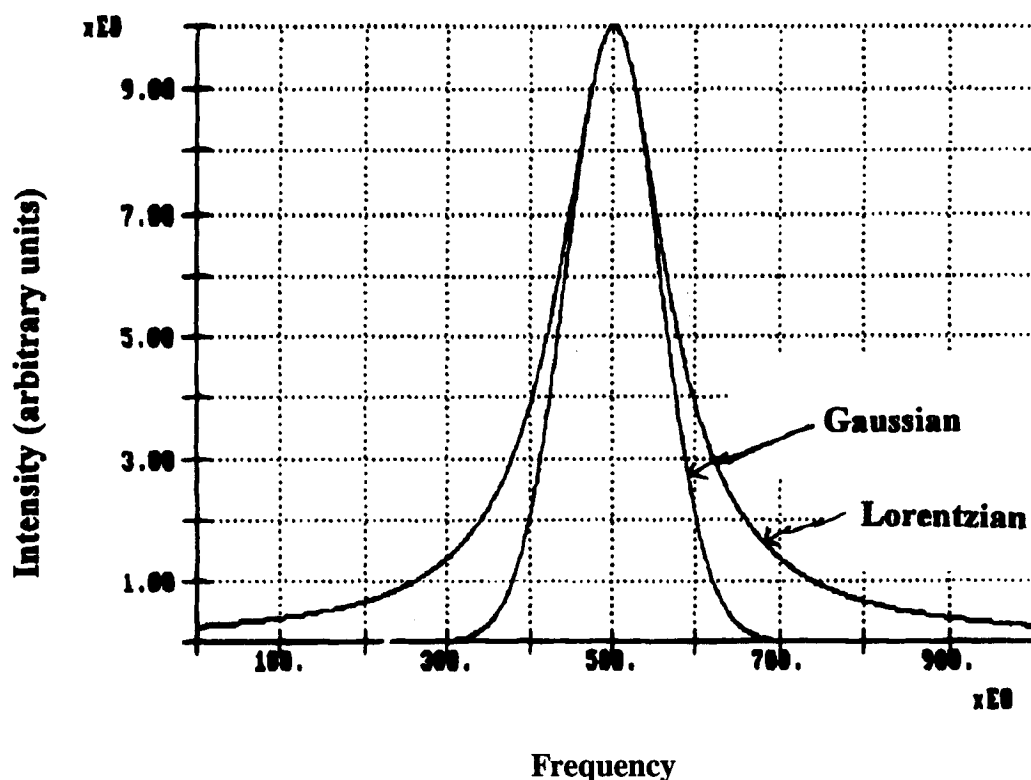


Figure 2-8. Lorentzian and Gaussian line shapes

The extended wings of the Lorentzian line shape make a second-moment calculation possible only if the intensity is truncated at a given point on the wings. Our computer was programmed to truncate the spectrum when the wings reached 5% of the peak intensity.

A temperature probe was assembled for the smallest of the three magnets used in this study and frequency domain NMR spectra were determined for the core asphalts. Figures 2-9 and 2-10 show second-moments as a function of temperature for two asphalts in which the hydrogen atoms had different mobilities.

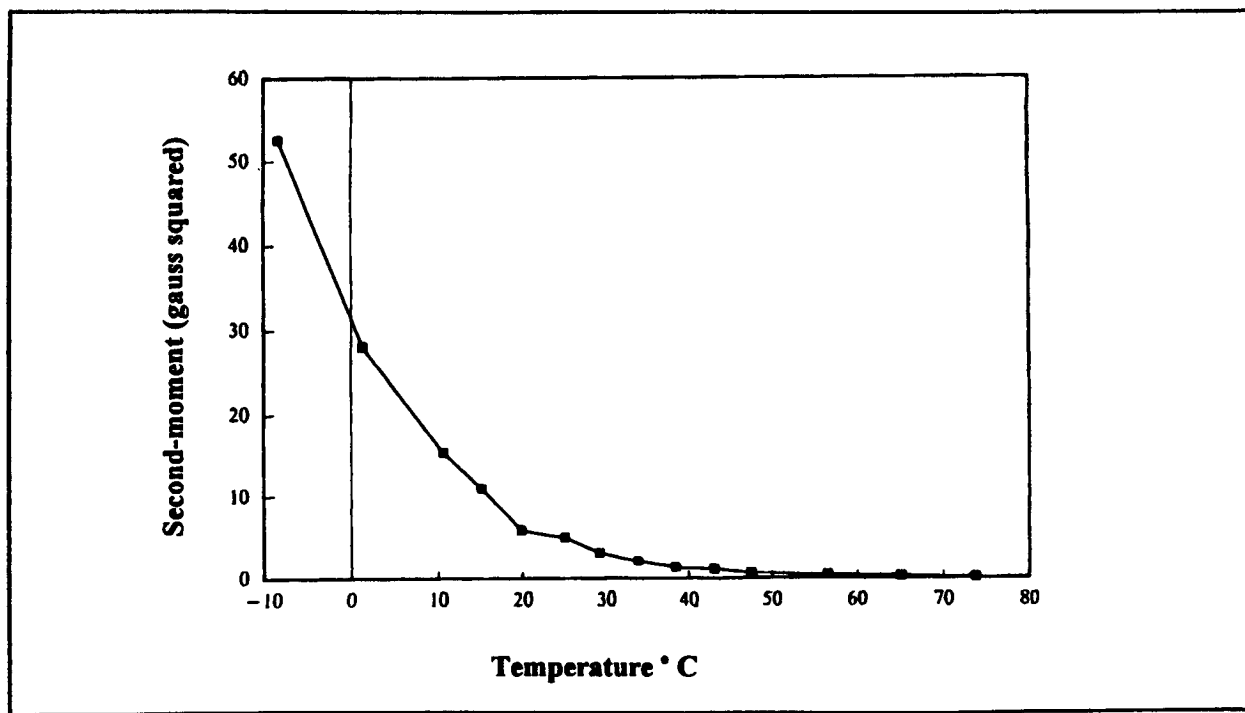


Figure 2-9. Second-moment versus temperature-asphalt AAM

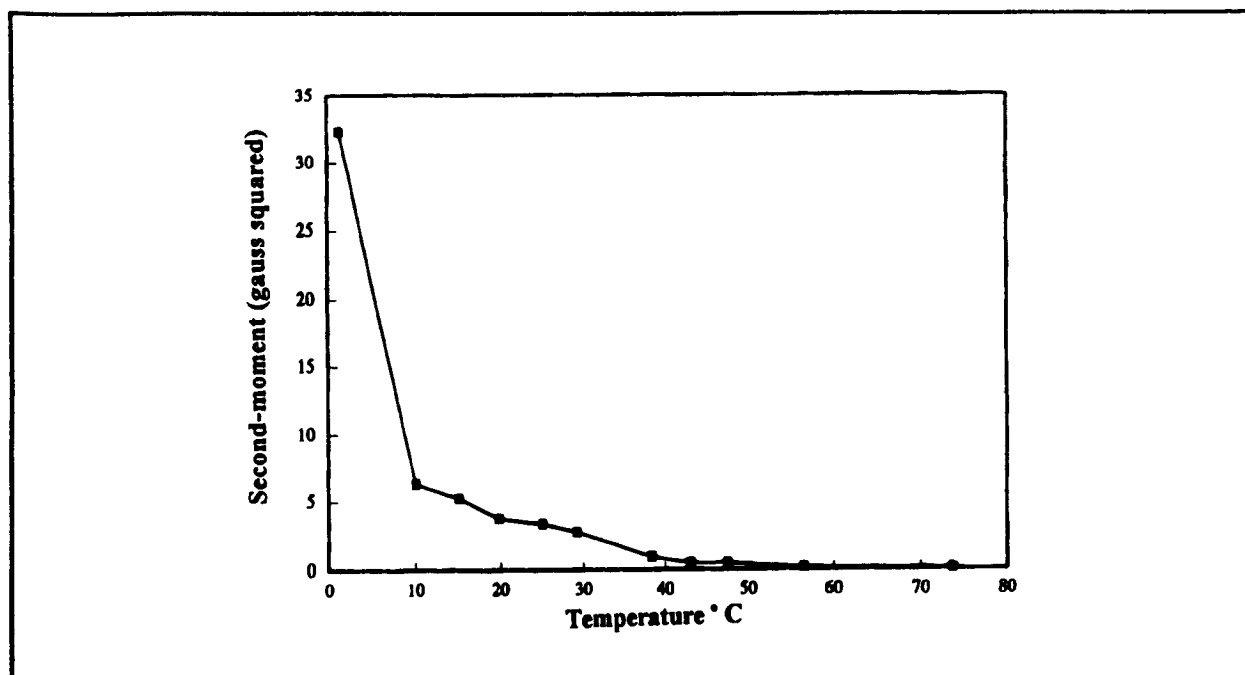


Figure 2-10. Second-moment versus temperature-asphalt AAD

Professor Norman Garrick of the Civil Engineering Department of the University of Connecticut ran solution viscosities of eight asphalts on which we had run second-moments as a function of temperature. He compared his data with our second-moments and generated the data shown in Figure 2-11 for six of these asphalts (12).

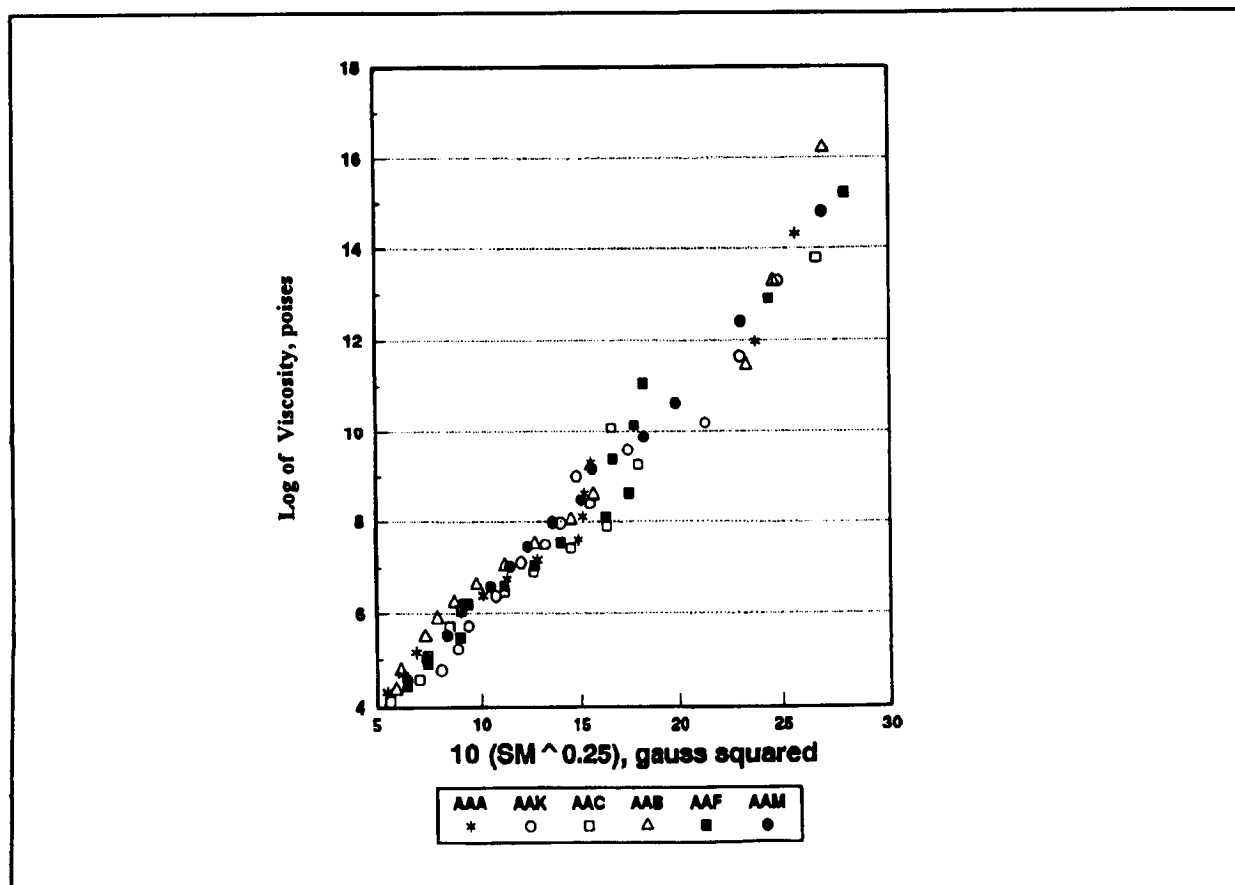


Figure 2-11. Solution viscosities versus second-moments

For the core asphalts shown in Figure 2-11, a good correlation between solution viscosity and NMR second-moments is seen. However, the two asphalts AAG and AAD did not fit well in the above correlation. This could easily be due to the difficulty of calculating good second-moments of the NMR spectra of these two asphalts. It is very possible that these two asphalts have physical characteristics that affect the results in a manner we do not as yet understand.

The work described here is only preliminary. Although it demonstrates that NMR second-moments do in fact measure the molecular motion of the hydrogen atoms in the asphalt, as measured by their solution viscosities, much more effort is needed before good analytical techniques can be expected from comparisons of this type.

NMR of Mixes and Cores

The overall goal of this project is to demonstrate the use of NMR as an asphalt quality control device for hot mix. The ability to obtain good NMR spectra on neat asphalts does not mean that similar results can be obtained on asphalt-aggregate mixes. To study the NMR of mixes, we prepared a series of asphalt-aggregate mixes by heating aggregate fines and asphalt to 160°C and mixing them by hand in a Pyrex dish. The NMR spectra of these mixes consisted of a very fast decaying FID such as that shown in Figure 2-12.

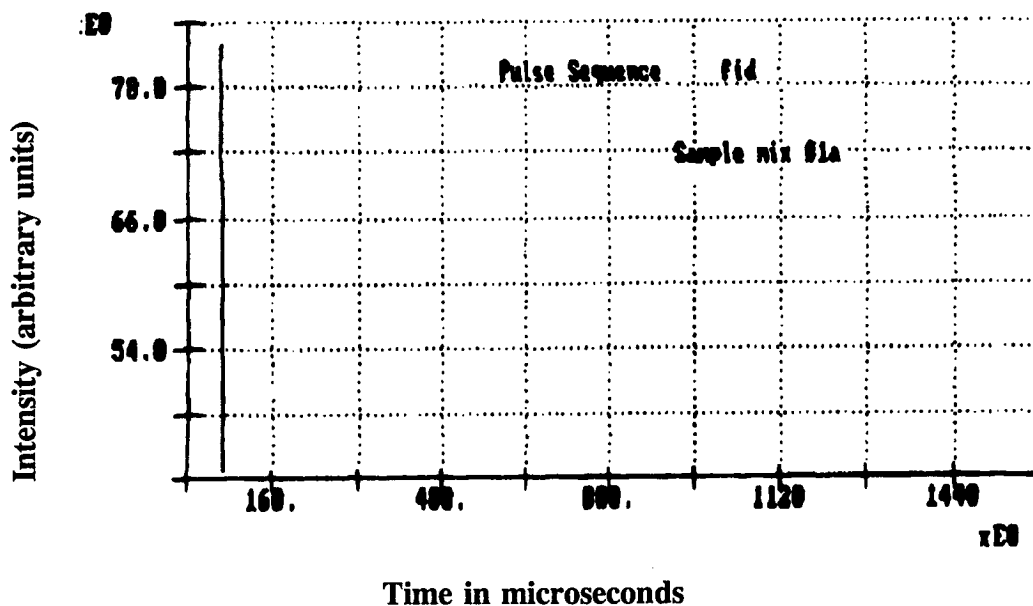


Figure 2-12. FID of asphalt-aggregate mixture

The aggregate used to make the mixture, whose FID is shown in Figure 2-12, was dried at 150°C overnight, and it showed negligible hydrogen signal before the asphalt was added. Therefore, the fast decay seen in Figure 2-12 is from the asphalt in the mix. This very fast decay rate is in part attributable to magnetic properties of the aggregate affecting the homogeneity of the spectrometer's magnetic field. It is not the inherent decay rate for the asphalt.

This is not uncommon in NMR: for example, paramagnetic iron in chocolate has the same effect on its NMR signal. These homogeneity effects can be overcome by using a more complex pulse sequence to obtain the NMR signal.

Carr-Purcell-Meiboom-Gill Pulse Sequence

All small NMR spectrometers use magnets with limited homogeneity. This limited magnetic field homogeneity makes it impossible for these spectrometers to produce a FID that decays slowly enough to measure the true relaxation time for any sample that has a narrow NMR line. Thus, any FID of material that has a long T_2 , such as vegetable oil, will decay at a rate determined by the magnet homogeneity rather than its own natural decay rate. This problem can be overcome by using a pulse sequence that will average out magnetic field inhomogeneities. The Carr-Purcell Meiboom-Gill (CPMG) is such a pulse sequence.

The CPMG pulse sequence consists of a 90° X pulse followed by a series of 180° Y pulses. An appropriate time delay is used between the X and Y pulses. This time delay, by convention, is called the *tau time* of the experiment. Various tau times are used, depending on the true T_2 of the sample being studied. This experiment produces a series of NMR echoes, the intensity of which is a measure of the true magnetization of the sample at that point in time. We use the NMR spectrum of peanut oil to illustrate the CPMG method.

Figure 2-13 is a simple FID of peanut oil obtained on TVR's smaller NMR spectrometer. Note that the FID shown in Figure 2-13 decays in of about 2 milliseconds.

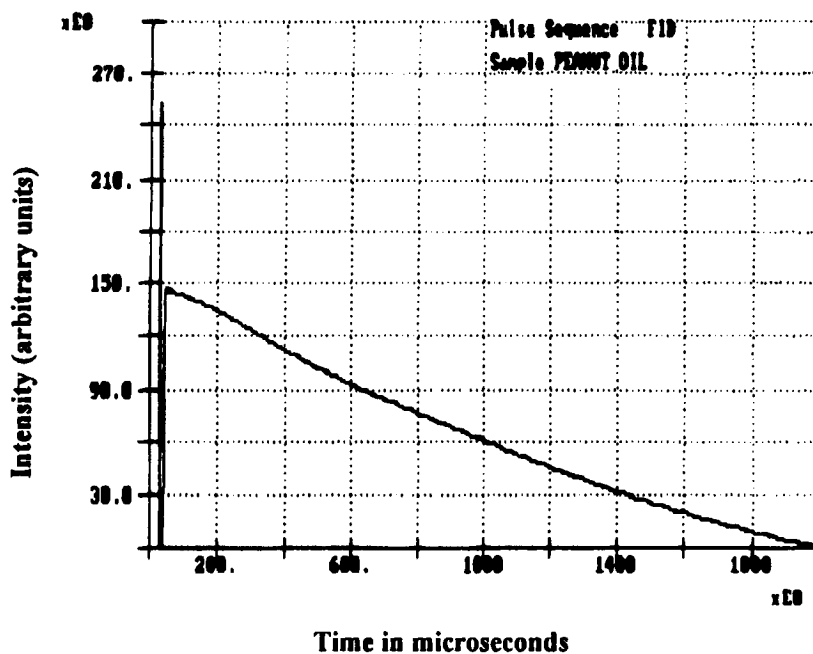


Figure 2-13. FID of peanut oil

It can be shown that this decay rate is a measure of the homogeneity of the magnet by doing a CPMG experiment with this sample in the same magnet. The results of this experiment are shown in Figure 2-14.

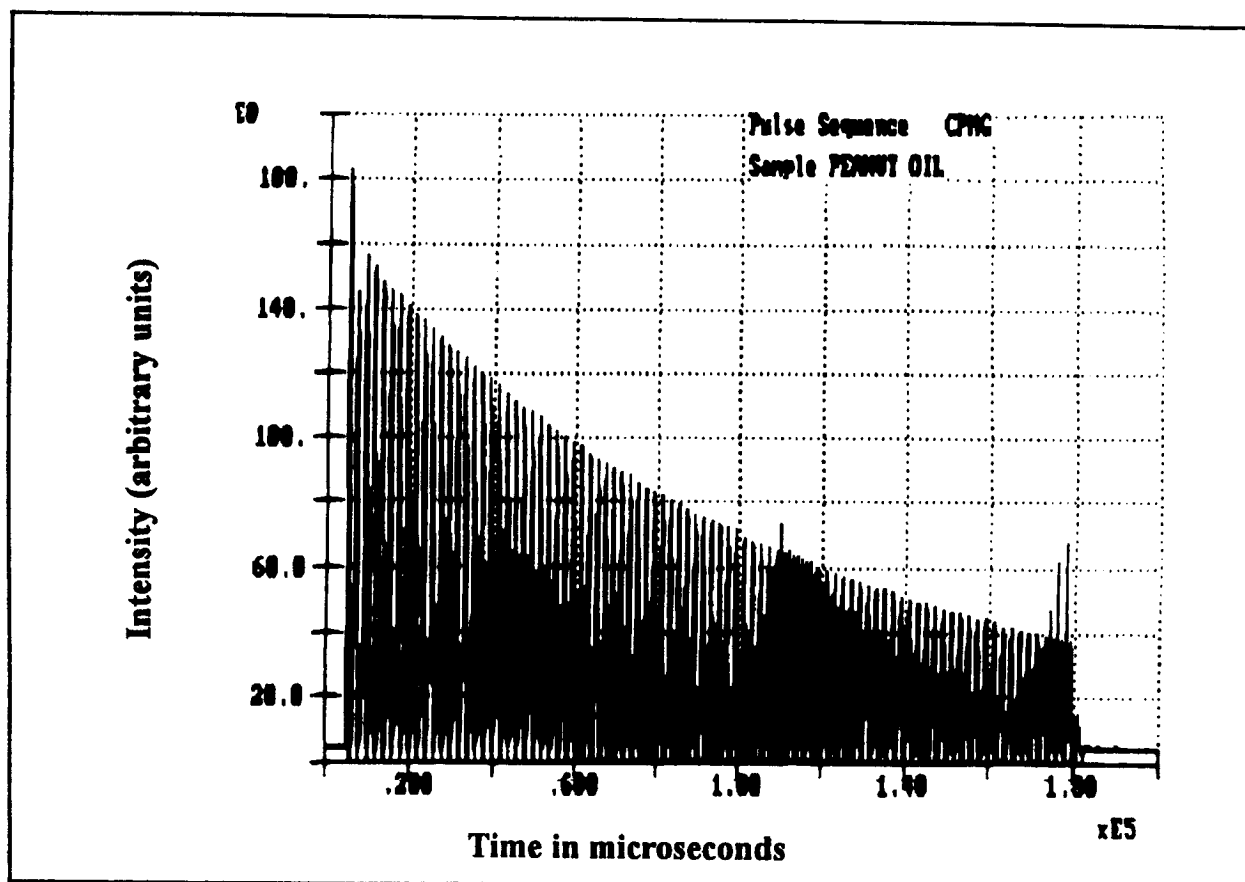


Figure 2-14 CPMG data for peanut oil

Figure 2-15 shows an expanded portion of the first few echoes in the CPMG data of Figure 2-14

Note that true echoes are present, the peak intensity of which is a measure of the magnetization of the peanut oil at that point in time. Also note in Figure 2-14 that even after 200 milliseconds, the intensity of the echoes had still not decayed to zero. This experiment illustrates the extreme effect of magnetic field inhomogeneity on the NMR spectra of a material containing mobile hydrogen atoms and shows how the CPMG pulse sequence can be used to average out magnetic field effects caused by the aggregate in an asphalt-aggregate mixture.

A CPMG data set is shown for one of the hand mixed asphalt-aggregate mixtures in Figure 2-16. Data such as shown in Figure 2-16 were obtained for a series of asphalt-aggregate mixtures that varied in asphalt concentration. Although the intensity of the first echo showed a straight line correlation with known asphalt content, each different combination of asphalt and aggregate produced a radically different calibration curve. This was especially noticeable for a set of mixtures we obtained from Auburn University. The Auburn mixtures produced very different NMR data than did the mixtures made by hand at TVR. All these mixtures produced NMR data that showed a great deal of intensity variation when different asphalts were mixed with different aggregates. It would be tempting to relate these differences to paramagnetic impurities found in the aggregate, but no such correlation could be found.

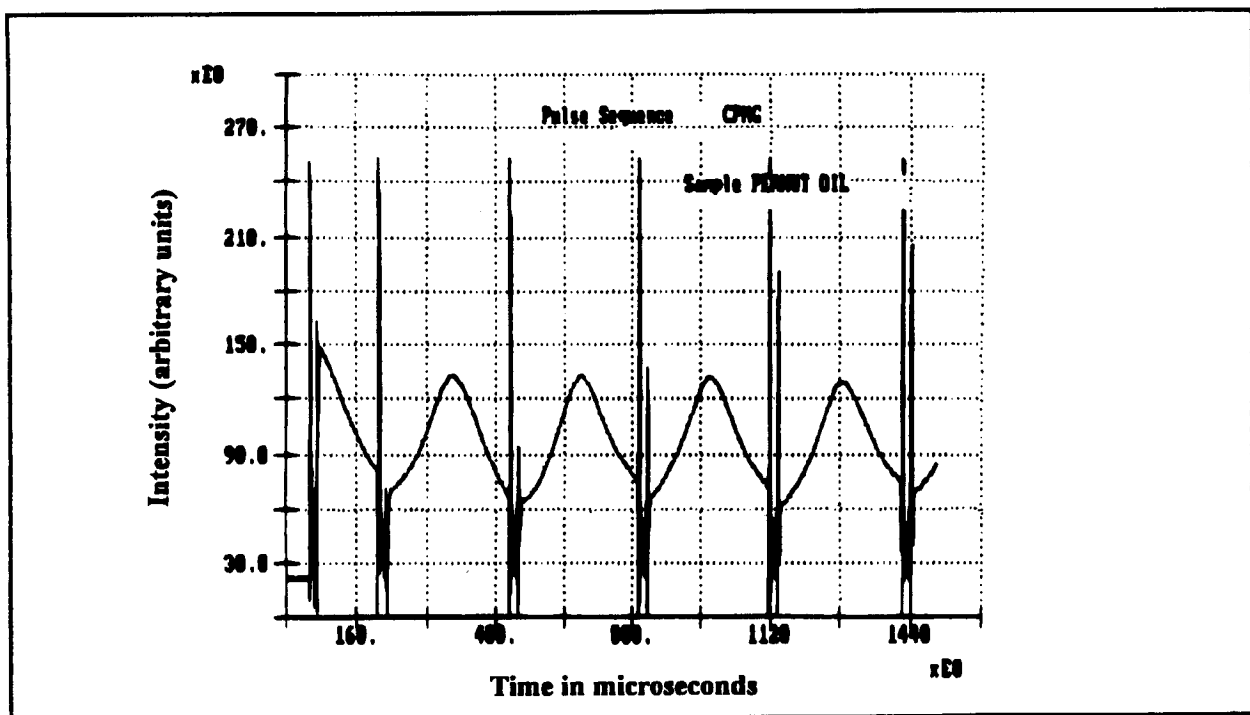


Figure 2-15. Expanded CPMG data

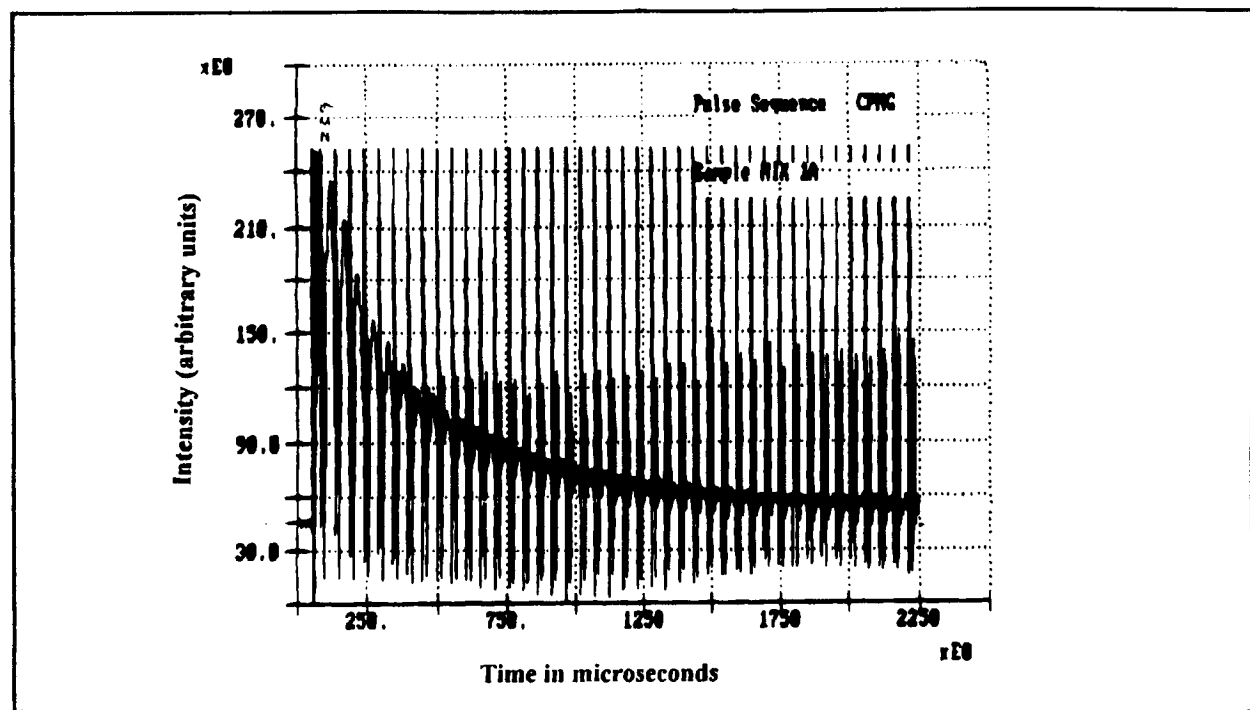


Figure 2-16. CPMG data for asphalt-aggregate mixture

Because of the variation in the NMR data for these mixtures, it was decided that full 4-inch cores made under standard conditions would be necessary to fully understand the NMR of these mixtures.

NMR of 4-inch Cores

In order to achieve our objective of measuring the amount of asphalt in 4-inch cores made under standard conditions, we visited scientists at the Caltrans Asphalt Laboratory in Sacramento and requested sets of cores that varied in asphalt content. They furnished us with several sets, including one made from asphalt AR-4000 and one made from this asphalt modified by adding 5% natural rubber and 15% rubber from used tires. All cores were 4 inches in diameter and 2.5 inches long. They had asphalt concentrations ranging from 2% to 8%. The 8% cores were sticky, whereas the 2% cores were crumbly. A modified CPMG pulse sequence was used in conjunction with the large Halbach magnet to determine the intensity of a single echo in the NMR data of these cores. Figure 2-17 shows an NMR spectrum taken in such a manner.

Other pulse sequences can be used to obtain NMR spectra of these cores. One of the most useful of these is the solid echo sequence. This sequence consists of a 90° X pulse followed by a 90° Y pulse. That is, there are two 90° pulses, the second of which is phase shifted. The advantage of the solid echo pulse sequence is that it echoes the magnetization such that spin-spin relaxation decay is regained, and, in theory, one can use this pulse sequence to refocus all the magnetization in the sample and recover the true intensity of the signal. Figure 2-18 shows a solid echo spectrum of the same core used to obtain the CPMG data of Figure 2-17.

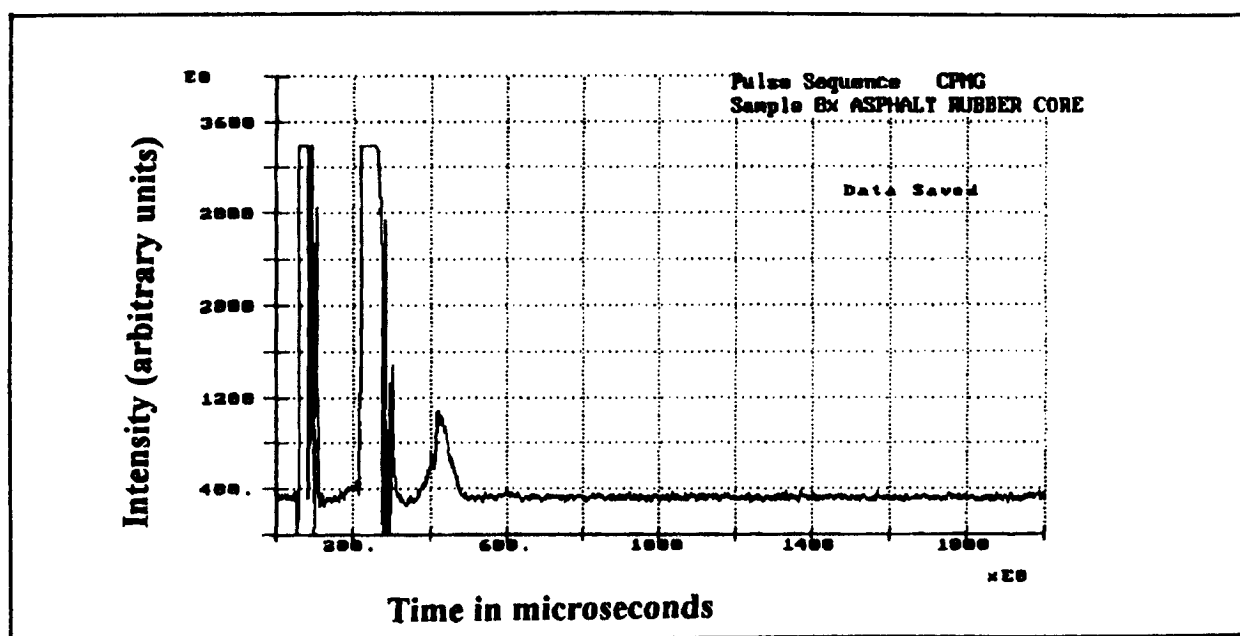


Figure 2-17. CPMG echo of 8% asphalt rubber core

It appears that the solid echo technique has no advantages in our case. This is probably due to the H_1 homogeneity of the RF coil in our probe. The results obtained with these two pulse sequences are comparable.

In the presentation of data and the discussion that follows, data for both the CPMG pulse sequence and the solid echo are used. It is felt that these two pulse sequences produce comparable results. At first glance, the echoes shown in Figures 2-17 and 2-18 appear small in intensity. The small size of these echoes is caused by the intensity of the pulse break through saturating the

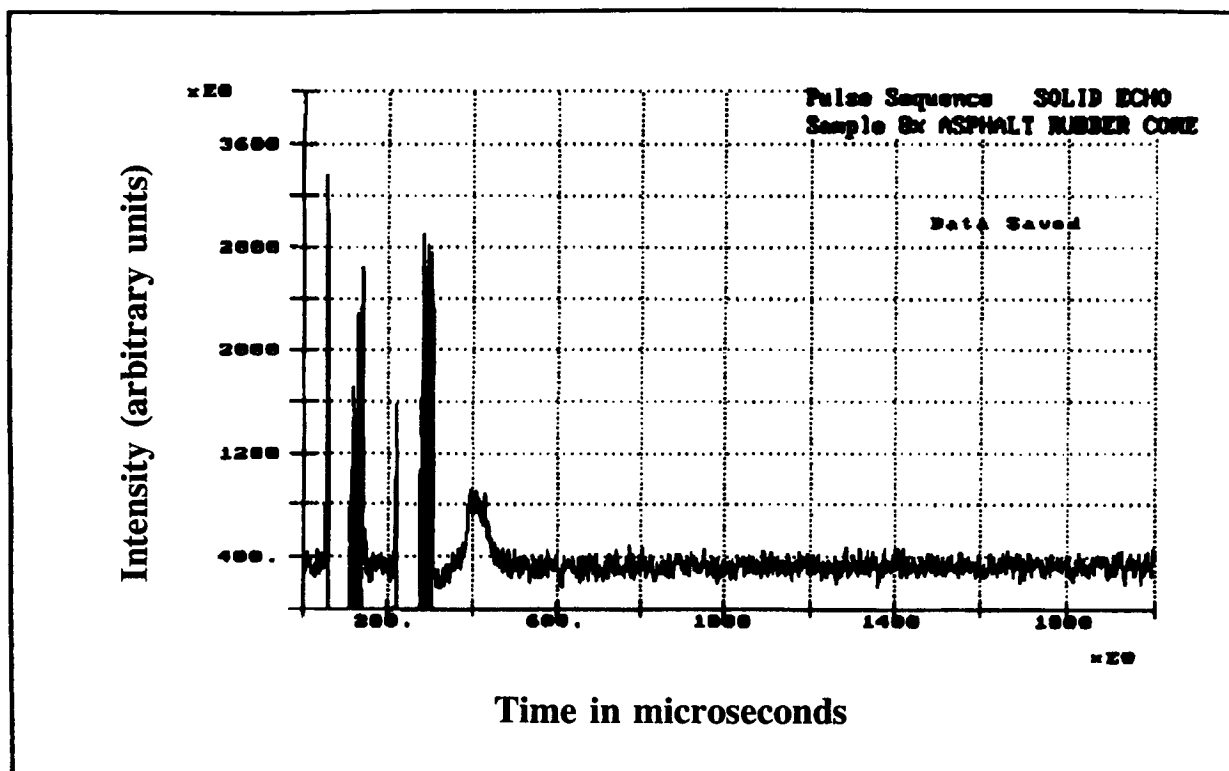


Figure 2-18. Solid echo of 8% asphalt rubber core

analog to digital (A/D) converter. This limits the physical size of the actual spectrum. The appearance of the spectrum can be changed by starting the spectrum just before the appearance of the echo and eliminating the effect of the pulse breakthrough. This allows the computer to expand the intensity of the echo to the point that its true intensity is apparent. Figure 2-19 shows such a display on a core that has only 2% asphalt concentration and illustrates that echoes of adequate intensities can be obtained on 4-inch cores with this technique.

Our next experiment was to determine solid echoes on a series of cores that varied in asphalt concentration from 2% to 8% asphalt. These data were collected by placing each core in the magnet and determining the intensity of the solid echo as fast as possible. The results of this experiment are shown in Figure 2-20.

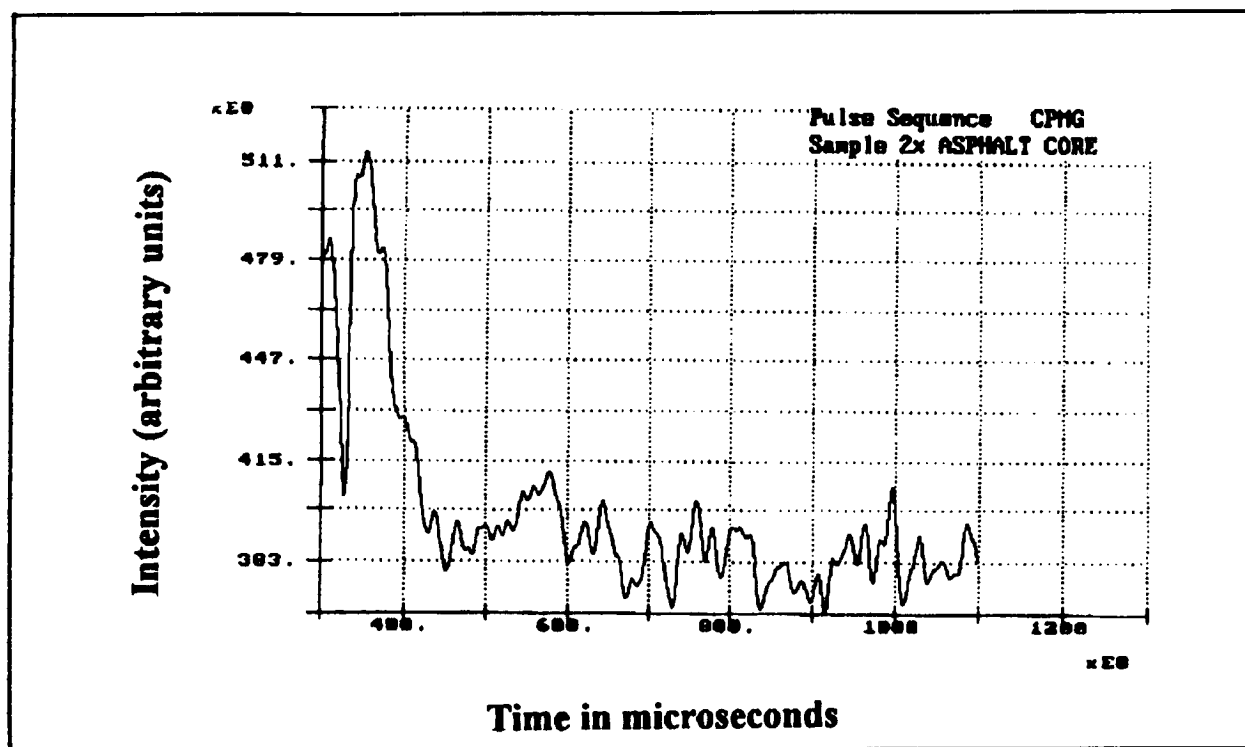


Figure 2-19. Solid echo of 2% asphalt core

Figure 2-20 shows that the intensities of the solid echoes run under these conditions do not produce a straight line. This is disturbing; NMR calibration curves should be straight lines. These cores were placed in the magnet and their intensity determined right away under ambient temperature conditions. The magnet was being operated at 35°C, which is considerably above room temperature. This means that the sample is heated once it is placed in the magnet and increases in average temperature; this increases the mobility of the hydrogen atoms in the sample, reduces its NMR line width, and increases the intensity of its NMR spectrum. This effect was studied by placing a core in the magnet and measuring the intensity of the echo as a function of time. The results of this study are shown in Figure 2-21.

The data in Figure 2-21 clearly show the intensity of this core sample increasing with time in the magnet. This is undoubtedly caused by the increase in mobility of the asphalt in the core as the asphalt's temperature increases with time in the magnet. Both the solid echo and the CPMG pulse sequence show the same effect. This is easier to understand for the CPMG method. The magnetization decays as a function of time. The decay rate is determined by the mobility of the hydrogen atoms in the asphalt of the core and this mobility is a function of temperature. This is better illustrated in the data shown in Figure 2-22.

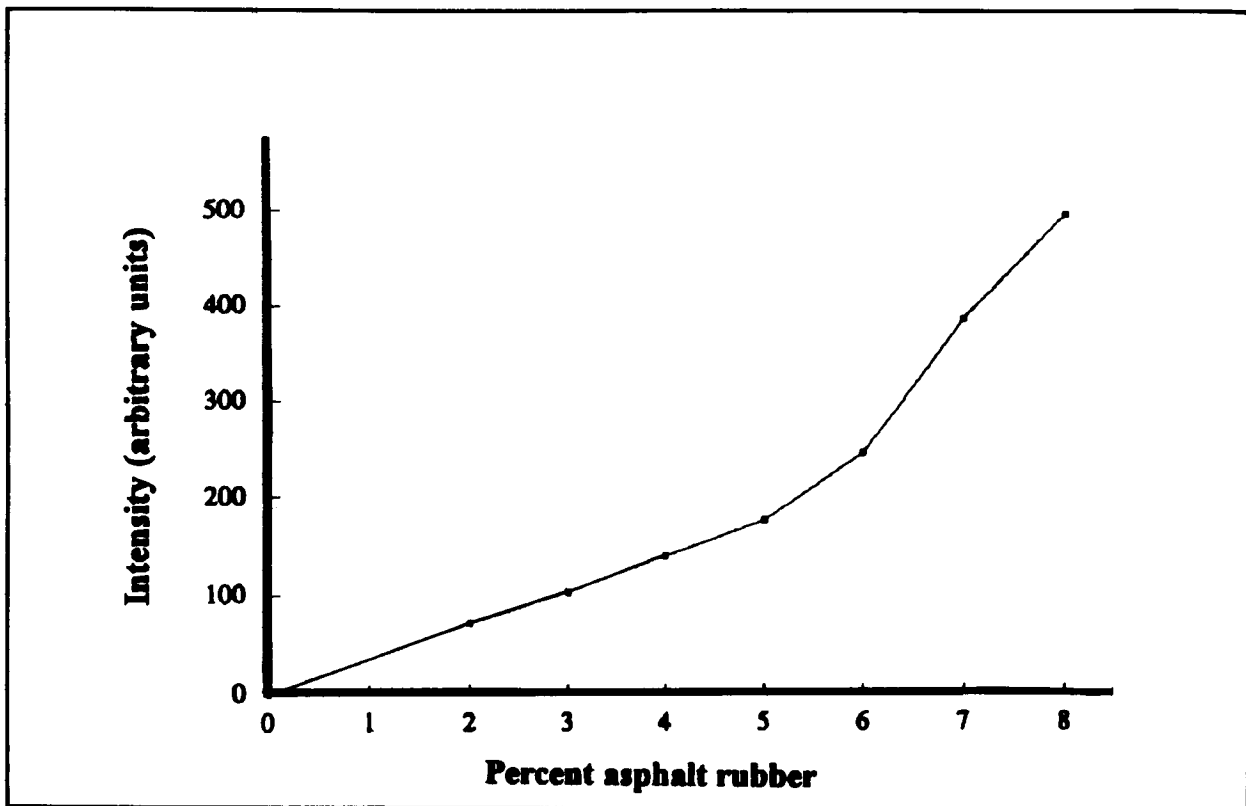


Figure 2-20. Intensities of solid echo--asphalt cores

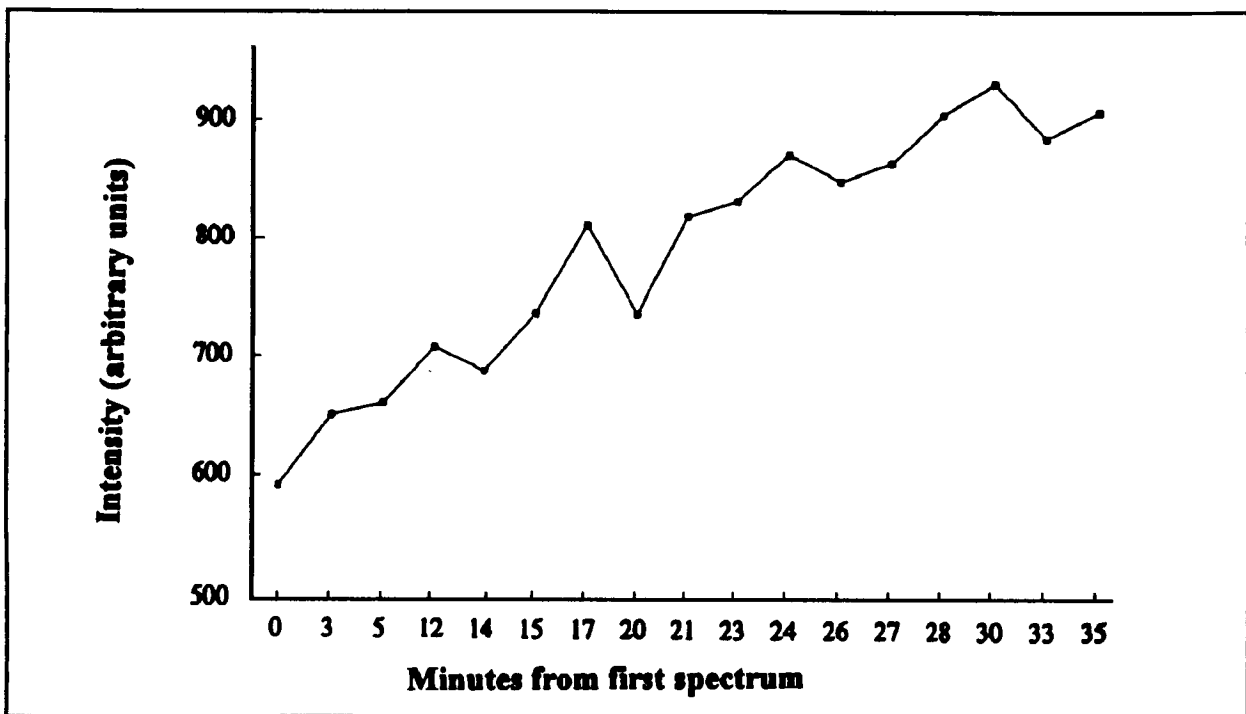


Figure 2-21. Echo intensity versus time--8% asphalt core

This experiment measured the equilibrium intensity of the echo as a function of temperature. It was done using a new probe built to accommodate 1-inch samples. The probe is described later in this report.

Figure 2-22 shows that the intensity of the NMR spectrum of the asphalt in the core increases with temperature, but that the curve tends to flatten out at temperatures above 100°C. The data in Figure 2-22 are a little like using the intensity of the NMR echo to measure the glass transition

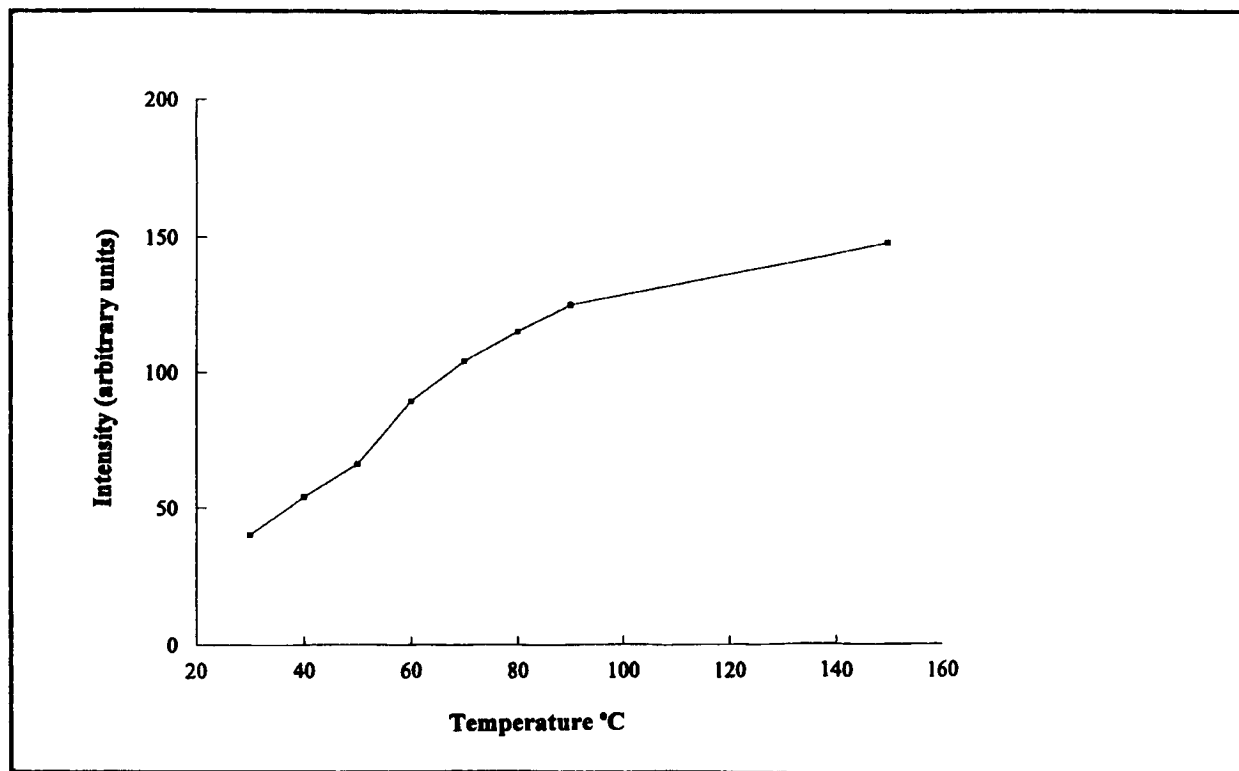


Figure 2-22. Echo intensity of asphalt in core versus equilibrium temperature

temperature of the asphalt in the core. This is an important finding because it is the first time, to our knowledge, that a technique has been demonstrated that can directly measure the physical properties of the asphalt in the presence of the aggregate in the core. It would appear obvious that it is important to compare such data with similar data for the neat asphalt in order to study the effects of aggregate on asphalt physical properties.

Figure 2-23 gives similar data for the neat asphalt used to prepare the cores studied here. The echo intensity versus temperature data for the neat asphalt given in Figure 2-23 show a sharp break in the increase in intensity at about the glass transition temperature of the asphalt. It is important to reiterate that the intensity of this echo is a measure of the magnetization in the sample at the point in time of the echo. Therefore, as the viscosity of the asphalt decreases with temperature, the magnetization will decay more slowly. At temperatures about or above the glass transition temperature of the asphalt, the viscosity of the asphalt will not show appreciable

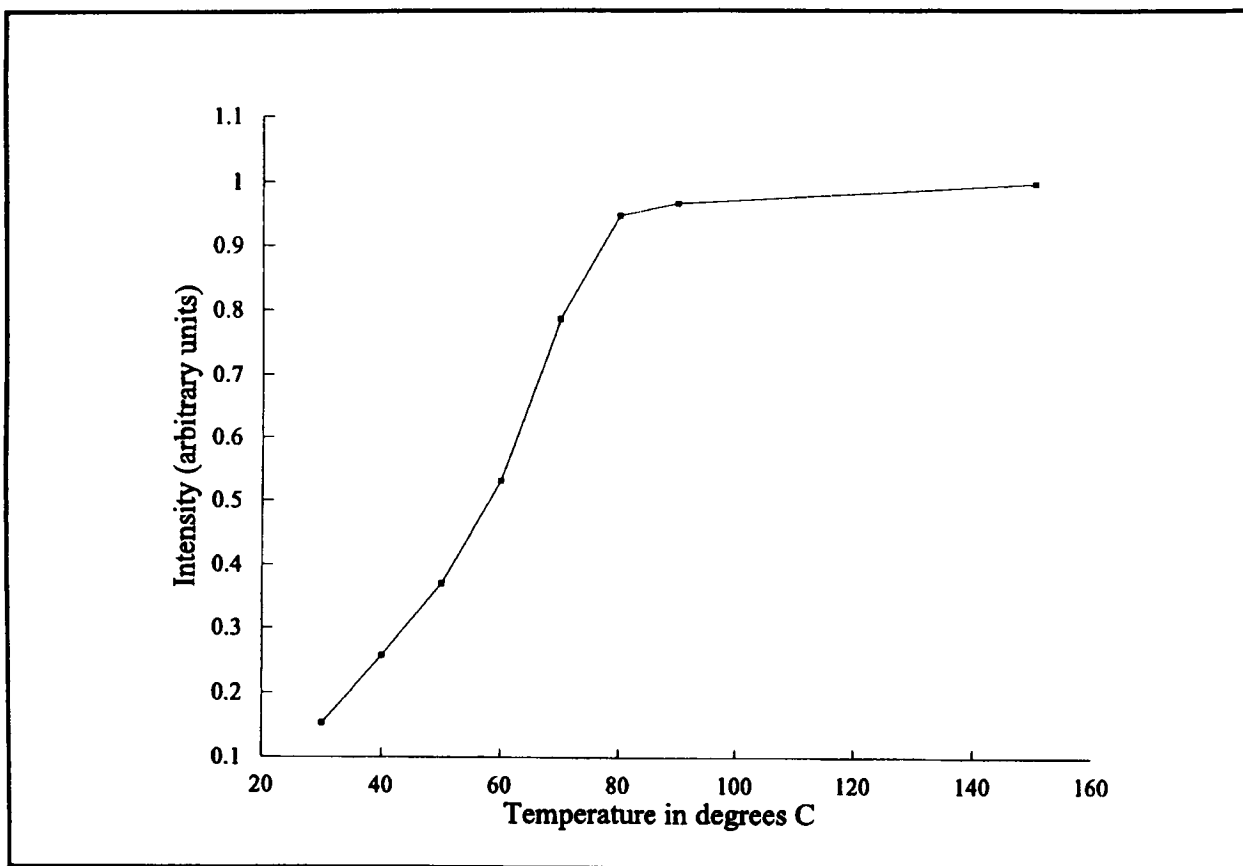


Figure 2-23. Echo intensity as a function of temperature for neat asphalt AR-4000

change. Thus, above the asphalt glass transition temperature, the decay of the magnetization will slow with time, and such data as shown in Figures 2-22 and 2-23 will be obtained.

It is informative to compare the temperature data for the neat asphalt and a core made from that asphalt. Such a comparison is shown in Figure 2-24. The data given in Figure 2-24 show that echo intensities of the neat asphalt are lower at low temperatures and higher at high temperatures than the intensity of the echo in a core. Remember that these changes in intensity are caused by changes in the viscosity of the asphalt, both neat and in the core. Thus, the asphalt in the core is softer at low temperatures and stiffer at high temperatures than is the neat asphalt. We have seen this effect before.

Each set of mixtures on which we have done NMR has shown this same effect. That is, when the asphalt is mixed with the aggregate, a more flexible asphalt phase appears in the mix, and the intensity of the first echo of the CPMG train shows variable intensity when the same asphalt is mixed with different aggregates. This means that if calibration curves are run for the same asphalt mixed with different aggregates at magnet temperature, these calibration curves will differ depending on the effect each individual asphalt has on the viscosity of the asphalt as a function of temperature (see Figures 2-25 to 2-29).

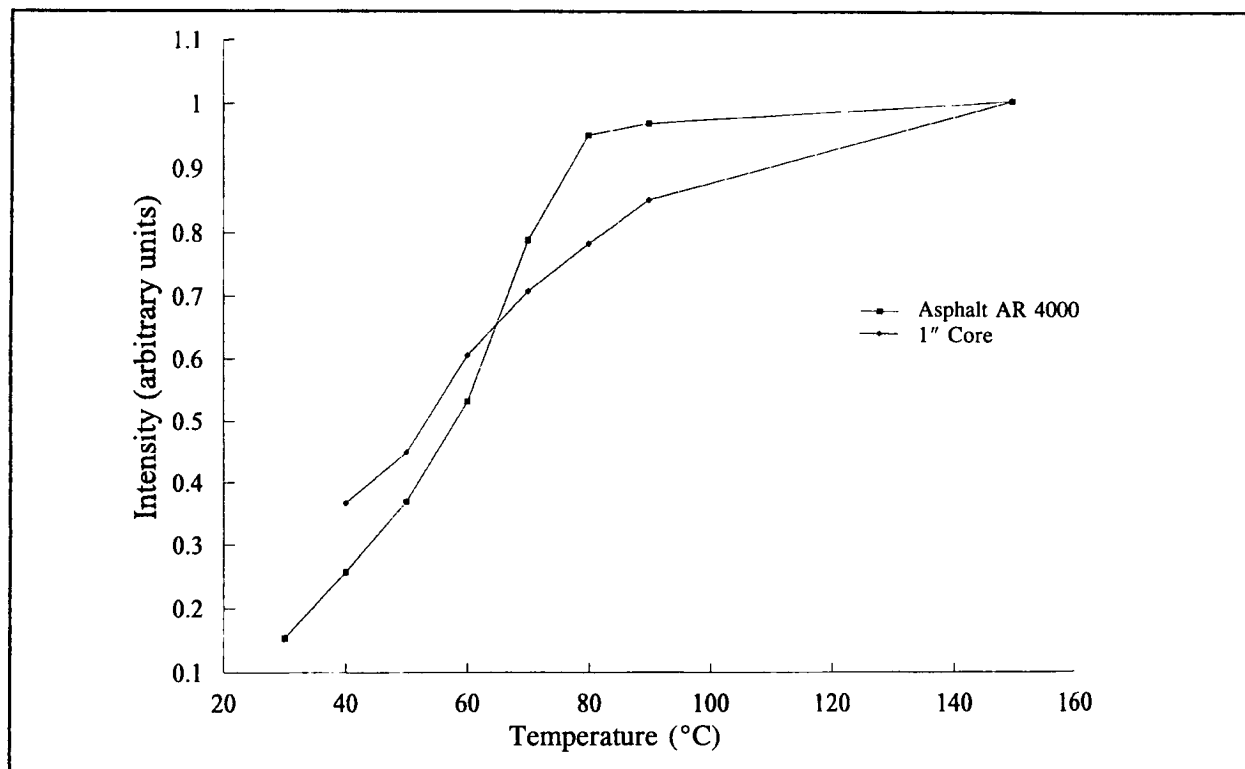


Figure 2-24. Echo intensities of neat asphalt compared to intensity of asphalt in core

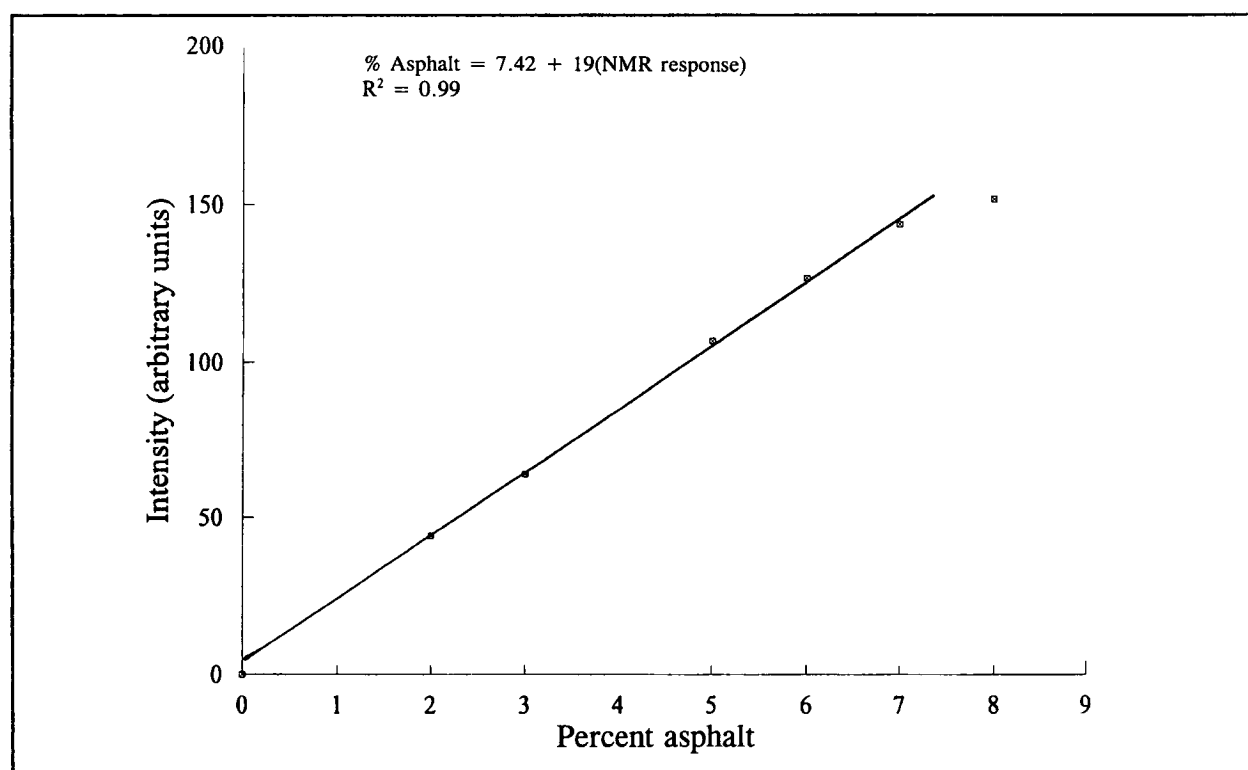


Figure 2-25. Calibration curve—aggregate 1813

1-inch Sample Cores

The results reported in Figures 2-22, 2-23 and 2-24 were obtained using a new NMR probe built to accommodate a 1-inch sample. This smaller sample limits the NMR experiment to the middle of the magnet, where the magnetic field is more uniform. This fact and the smaller sample size allow the use of shorter pulses. The new probe had better temperature control for temperatures up to 100°C. This control was obtained by circulating temperature-controlled ethylene glycol solution through the probe. A sample temperature of about 150°C was obtained by heating the sample in an oven and then placing it in the heated probe.

A 6% asphalt core was heated to 160°C in an oven. At this temperature, the core becomes soft and can be taken apart. Material from this core was pressed into a smaller core. This 1-inch core was sealed into a Pyrex test tube to minimize oxidation of the asphalt in the core. The core was then placed in the new probe, and the intensity of the NMR signal was determined as a function of temperature. The intensity of the asphalt in the core was compared with the intensity of the neat asphalt under the same conditions. The results of this comparison are shown in Figure 2-30 which shows that the expected results were obtained. At lower temperatures, intensities corresponding to greater than 6% are seen due to the aggregate creating a less viscous asphalt phase in the core. As the temperature of the core increases, these intensities go through a minimum of less than the known asphalt content of the core and approach quantitative values as the temperature approaches mix temperatures.

These results are consistent with those shown in Figure 2-24. Note that both sets of data show quantitative results both at the high temperature and at about 60 °C.

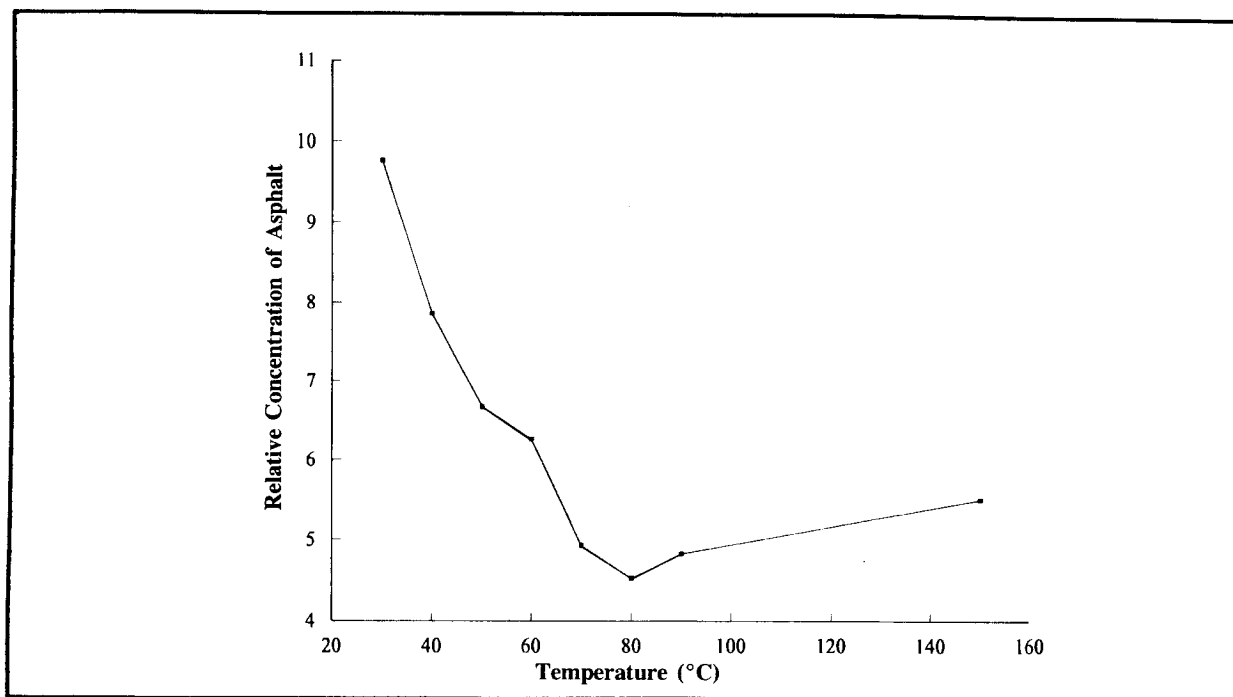


Figure 2-30. Relative concentration of asphalt seen as a function of core temperature

Conclusions and Suggestions for Further Work

The first important finding of this study is the ability to use wide-line NMR spectroscopy to determine and study the physical properties of both neat asphalt and, more important, asphalt in a mixture including full-size highway cores. The importance of the latter finding should not be underestimated. It means that any interactions between the asphalt and the aggregate of a mixture can be studied directly in that mixture without first separating the asphalt from the aggregate. This leads to the second important finding of this study.

It has been shown in this report that when an asphalt and aggregate are mixed, an interaction between the two takes place. This interaction modifies the physical properties of the asphalt to an extent that depends on the particular combination of the two ingredients. The importance of this finding is that it is now possible to study, in situ, the interactions in asphalt-aggregate mixtures. It must be emphasized that these studies are preliminary and were not the main emphasis of this work. Time and funding did not permit us to pursue this line of inquiry to the extent it deserves.

It must be pointed out that the use of wide-line NMR to determine and study the physical properties of the asphalts may seem straightforward after reading this report--and in fact it is. However, it was not predicted nor pursued by the academic type spectroscopists who conducted NMR studies under the SHRP program. Instead those workers concentrated on the more conventional, at least by modern standards, high-resolution NMR techniques to study the chemical structure of the SHRP core asphalts. This is a result of the radical change in NMR in the early 1970s from continuous-wave techniques to modern pulsed NMR.

The advent of the modern pulsed NMR spectrometer caused a radical change in the way spectroscopists approached problems. I would argue, however, that there is still a place for wide-line NMR applications that concentrate on the measurement of relaxation times instead of chemical shifts. The study of asphalt physical properties is an excellent example of such an opportunity. It would be both shortsighted and tragic if this is not done. However, it is doubtful that it will be done in any of the so-called "modern" NMR facilities; they are too dedicated to the "conventional" as they see it.

The primary goal of showing that NMR can be used to quantitatively measure the amount of asphalt in asphalt-aggregate mixes has been achieved, but we did not have time to actually put the spectrometer in a hot mix plant. We had intended to do this, but feel that such an effort is premature. There are two things that we feel need to be done before a field test of this equipment is appropriate.

The first of these efforts has to do with gaining a better understanding of the NMR of asphalt-aggregate mixes. The other problem, yet unsolved, is an adequate sample handling procedure, especially for mixes containing large size aggregate.

The importance of showing how NMR can be used to measure the physical properties of both neat asphalt and asphalt-aggregate mixes should not be underestimated. This could easily be the most important product of our work in asphalt, and it has to be completed before we can hope to be successful in a field application of this technology. The reason for this importance has to do with better hot mix quality control and better mix design. Various aggregates mixed with the same asphalt require different concentrations of asphalt to obtain optimum pavement physical properties, probably because different aggregates react with the asphalt differently and modify its physical properties as was shown in this study.

It is probable that the changes in asphalt concentration required for the attainment of optimum pavement properties are caused by the reactions that occur between the aggregate and the asphalt. Thus, the asphalt aggregate ratio used to achieve this optimum condition can only be determined by the physical properties of the mixture. This is, in fact, how these ratios are determined when mix design studies are done. The advantage to the NMR method is that it is possible this could be done by measuring the NMR signal of the mix at some temperature, not necessarily mix temperature. Doing this in a plant would allow the operator to adjust the mix ratio in a continuous manner to keep the physical properties of the hot mix at the optimum level.

Before the present SHRP NMR spectrometer is placed in a field trial it should be converted to a flowing system. The Halbach magnet design is ideal for such a system which could accommodate a sample of almost unlimited size. NMR data can be collected and averaged over the whole sample. This would give much better sampling statistics, especially for mixtures that contain large size aggregate.

This conversion and a better understanding of the asphalt-aggregate interaction that would result from further work in this field would make possible successful introduction of wide-line NMR technology into the highway industry.

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