

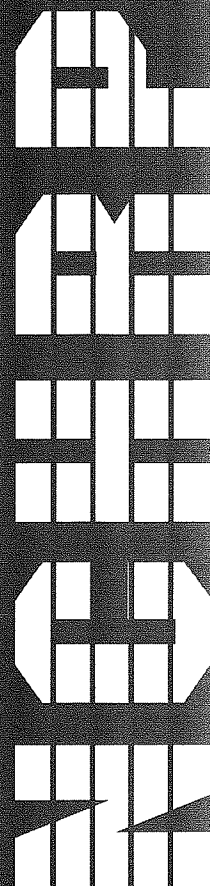
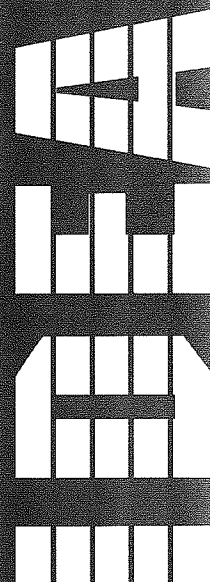
TRANSPORTATION RESEARCH BOARD
NATIONAL RESEARCH COUNCIL

IDEA *Innovations Deserving
Exploratory Analysis Project*

NATIONAL COOPERATIVE HIGHWAY RESEARCH PROGRAM



Report of Investigation



IDEA PROJECT FINAL REPORT

Contract NCHRP-5

**IDEA Program
Transportation Research Board
National Research Council**

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MAGNETIC RESONANCE FOR IN-SITU DETERMINATION OF ASPHALT AGING AND MOISTURE CONTENT

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**SUMMARY OF PHASE I
CONTRACT NO. NCHRP-92-ID005
MAGNETIC RESONANCE FOR IN-SITU DETERMINATION OF
ASPHALT AGING AND MOISTURE CONTENT**

Objectives: To assess the basic feasibility of Magnetic Resonance (MR) technology for in-situ determination of aging and moisture content of asphalt concrete pavements based on: (1) laboratory measurements using existing MR apparatus and asphalt materials from SHRP Materials Reference Library and (2) limited in-situ measurements of existing asphalt pavements using surface access MR system previously developed for FHWA. Additional objectives were to evaluate the suitability of the Trivalley MR system developed under a SHRP-IDEA contract and to provide a conceptual design and specification for a field pavement inspection system based on MR technology.

Approach: Samples of twelve (12) different asphalt materials were selected from the Materials Reference Library in Austin, Tx. to be representative of wide variations in properties that were believed to affect asphalt aging and which are either pertinent to measurement by MR or which can possibly affect MR measurements. The range of parameters for these samples include: (1) Viscosity (60°C) 363 to 3634 poises; (2) Penetration (25°C) 48 to 291 (0.1 mm); (3) Trace elements: Vanadium (V) 58 to 1484 ppm, Nickel (Ni) 25 to 142 ppm, Iron (Fe) 0 to 255 ppm and Sulphur (S) 1.2 to 8.3%; (4) Molecular weight 700 to 1300; (5) Asphaltenes 4.0 to 25.6% and (6) TFOT Aging: Mass change -0.015 to -1.335% and Viscosity ratio 1.62 to 3.25. Neat samples of each asphalt were measured in the laboratory by hydrogen transient nuclear magnetic resonance (NMR) at room temperature and at 60°C to determine the signal amplitude and the complex relaxation times (T_1 , $T_{1\rho}$, and T_2). Electron paramagnetic resonance (EPR) properties of the samples at room temperature were also measured. After simulated aging in a thermal vacuum chamber the samples were remeasured to determine the effect of loss of volatiles on the NMR parameters. The samples were then subjected to accelerated aging in oxygen at 2.03 MPa (300 psi) and at 60°C (140°F) for a total of 740 hours with NMR parameters being remeasured at intervals during this period. In-situ asphalt pavement tests were conducted using the FHWA NMR system in conjunction with available laboratory apparatus. Laboratory MR studies provided additional data on asphalt/aggregate mixes of different ages. All the MR data were examined for the suitability in determining asphalt aging, to reveal any effects of asphalt constituents that would limit the utility and to determine the requirements for an in-situ measurement system.

Results: Results of Phase I show a good correlation of MR data with asphalt aging and moisture. The T_1 NMR data, $T_{1\rho}$ in particular, and T_2 correlated very well with aging of all the asphalts. This data, which relates to the viscosity and hardness of materials, varied consistently with loss of volatiles and with oxidation aging for all asphalts. With aging, T_1 for all the asphalts, except for AAK-1 and ABL-2, varied over a similar range. For these two asphalts T_1 and $T_{1\rho}$ were substantially smaller as would be expected from the high concentration of the paramagnetic vanadium. The T_2 data consistently showed two signal components from each asphalt with one becoming harder with oxidation aging and the second becoming more fluid. The potential of EPR for measuring the vanadium and iron contents of the asphalts and for compensation of the NMR data for effects of these elements was considered.

The recommended MR system for in-situ inspection of asphalt pavement will use: (1) NMR to provide T_1 , $T_{1\rho}$, and T_2 data needed for aging and moisture measurements plus (2) EPR to detect and measure paramagnetic elements, primarily vanadium and manganese, and iron which can affect the NMR data. The MR system will utilize the same magnet for both NMR and EPR and be integrated to work in combination to provide accurate, compensated measurement of data needed to assess the aging and moisture in all asphalt pavements independently of the type of asphalt or aggregate. This trailer mounted system will be implemented in an optimum configuration for in-situ asphalt applications but can be based on MR designs previously developed for concrete moisture measurements and other in-situ inspection applications.

Recommendations: It is recommended that an experimental model of a mobile MR system for asphalt inspection be developed and evaluated. In addition, MR data should be acquired on a much wider variety of asphalt -aggregate mixes of different ages and conditions in the laboratory and roadway tests conducted at a number of sites where representative asphalt pavements of different ages are available.

I. PROBLEM STATEMENT

The maintenance of highways under ever-increasing traffic loads and accumulating deterioration is a serious problem in every state. The need for tools to detect pavement aging problems was recognized by the Strategic Highway Research Program (SHRP) as a key element in implementing timely maintenance treatments and repairs and has continued under the NCHRP-IDEA Program. Presently, inspection of highway structures and roadway pavements rely heavily on visual examinations¹ supplemented with limited non-destructive evaluation (NDE) techniques, photography, and surface profile measurements. NDE techniques that examine not only the surface, but also the interior of the pavement for distress, are needed to correctly assess roadway condition and for planning repair or rehabilitation.

Many of the properties of asphalt are understood quantitatively and have been reasonably well analyzed and controlled for many years.^{2,3} These important properties include elastic behavior, strength, elementary creep, and shrinkage characteristics.³ However, standardized destructive and non-destructive test methods used to measure asphalt properties for quality control and prediction of remaining service life³⁻⁶ often lack sufficient accuracy and reliability and are not sufficient for assessment of existing asphalt concrete pavements. From previous studies it is known that as asphalt deteriorates the elastic-like binders become more rigid and less flexible³. Innovative magnetic resonance (MR) technologies have previously been shown to have the capability to make rapid and reliable in-situ measurements of similar properties of materials for other applications. The utility, potential problems and means for best using MR for accurate assessment of asphalt pavement materials has been investigated in the present program.

II. RESEARCH APPROACH

A. BACKGROUND

Compared to other sensing methods, MR, which includes both nuclear magnetic resonance (NMR), in particular hydrogen transient NMR (HTNMR), and electron paramagnetic resonance (EPR) potentially offers significant advantages for in-situ asphalt inspection. These include:

- Non-destructive, Non-contacting, Non-intrusive
- Safe - No ionizing radiation is used or produced
- Bulk measurements - instead of surface conditions only
- Analytical - constituents and molecular binding state
- Rapid and suitable for on-line, in-motion measurements

Transient NMR measures the total quantity of a selected element (usually hydrogen) in solids, liquids and gases as well as the amounts and relative viscosities of the different components in complex materials. Preliminary tests suggested that the aging changes in the elastic-like binders of asphalts are measurable as variations in the magnitude and relaxation times characteristic of the NMR signal. Additionally, as exfoliation of the rigid structure introduces cracking in asphalt⁴ the concurrent moisture ingress⁶ increased the total NMR signal from asphalt and added another detectable component. This work implied that selectivity to aging and moisture content could be achieved by appropriate use of the signal amplitude and relaxation data. It was also found that EPR could be used with NMR to provide more specificity and freedom from the para- and ferro-magnetic effects in asphalts and aggregates.

NMR has been extensively used in laboratory studies of asphalts⁽²⁻²⁸⁾ but, except for the work of Pearson⁽²⁶⁾, these investigations have made use of high resolution ¹H NMR and ¹³C NMR. High resolution NMR is well suited for studies of asphalt chemistry but is not suited to in-situ measurements in a highway environment. Prior EPR ⁽²⁷⁻³⁸⁾ studies of asphalt have also shown promise as a means for asphaltene-preasphaltene measurements, for detection of the effects of oxidation on asphalt quality and aging and for measurement of the vanadium content (which apparently influences the rate of aging) and other paramagnetic elements. ⁽³⁸⁾

Both EPR and HTNMR are basically amenable to implementation in inspection apparatus for non-contacting, in-situ measurements from a moving vehicle. Such apparatus has been previously developed for measurement of moisture in

concrete bridge decks and in large acreages of agricultural soil, for detection of buried explosives and for measurement of the thickness of coal over-lying the rock substrates in coal mining.

B. THE CONCEPTS OF MR

To obtain MR data the material to be inspected must be located in a magnetic field H_0 and for transient MR, must be exposed to bursts (or pulses) of a radio frequency (RF) field, H_1 . Selected atomic nuclei in the sample will strongly absorb (and subsequently re-emit) energy when the frequency of the RF field, f_0 , is related to the magnetic field intensity by $f_0 = \gamma H_0/2\pi$ where γ is the gyromagnetic ratio of the particular absorbing nuclear isotopes. Hydrogen is the only element in asphalt which can be detected with adequate sensitivity for practical application of NMR to highway measurements and for this element $f_0 = 42.6$ MHz/Tesla.

Hydrogen NMR produces a signal of an amplitude proportional to the total concentration of hydrogen in the measured volume of the material. When nuclei absorb energy from the applied RF field, the thermal equilibrium is changed and the absorbed energy is exchanged exponentially with the surroundings. This results in an emitted transient signal of (nominal) frequency f_0 which is characterized by two primary time constants; the spin-lattice (T_1) and the spin-spin (T_2) relaxation times. The first, T_1 , is related to the time required for nuclei in the material being measured to become completely polarized in a magnetic field. The second, T_2 , determines how rapidly the transient NMR signal decays in a perfect magnetic field. These two relaxation times are related to the viscosity and hence, in the case of asphalt pavements, to the aging and moisture content. In complex materials both T_1 and T_2 may have multiple values with each being representative of different molecular constituents, binding states or the hardness or viscosity of the components in the material. The amplitude and time constant of all these NMR signal components are used as analytical tools for assessing physical and chemical characteristics of materials.

Electron Paramagnetic Resonance (EPR) is similar in principal to NMR but responds to the un-paired electrons instead of nuclei. Such electrons occur in many pyrolyzed and natural hydrocarbons, such as coal, crude oil and asphalts, due to free radicals or broken bonds and may also occur in many organo-metallic compounds such as those involving vanadium, nickel, manganese or other paramagnetics. EPR occurs at a nominal frequency of 2.8 MHz/oersted. Compared to NMR the frequency and sensitivity of EPR in the same magnetic field are much greater and the time constants T_1 and T_2 are generally much shorter. These factors are desirable for rapid, high sensitivity in-motion applications and make EPR attractive for in-situ highway measurements. Implementation of the EPR technology for in-situ measurements of asphalt pavements can supplement and add to the specificity of data available from NMR.

C. SAMPLES AND PROCEDURES

Samples of twelve (12) different asphalt materials as listed in Table I were selected from the SHRP Materials Reference library in Austin, Tx. to be representative of wide variations in properties that are believed to be relevant to asphalt aging and which are either pertinent to measurement by MR or which can possibly affect MR measurements. Small samples of each of these twelve neat asphalts were prepared in 25mm (nominal) glass vials for the NMR tests. The weights of these samples are listed in Table 2 and the sample thickness ranged from 4 to 6 mm in the vials. The vials were capped and remained sealed throughout the measurement process except where controlled tests to remove volatiles or to effect oxidation were underway. The samples for EPR measurement were prepared in a similar fashion in 4mm diameter samples tubes. The weights of the EPR samples ranged from 34 to 72 mg.

The asphalt samples were measured, as initially prepared, to determine the hydrogen transient NMR (HTNMR) properties and the EPR properties. Then, to simulate the initial stages of curing and aging, the NMR samples were placed in a vacuum oven at a temperature of 60°C (140°F) for a period of 20 hours to remove the volatiles. This approach allows the volatiles to be removed independently of oxidation. After the vacuum oven treatment the weight loss, Table 2, was comparable to that reported for the TFOT test, Table 1. The "volatized" samples were measured to determine the HTNMR properties. Then to simulate effects of long term aging due to oxidation, the samples were exposed to an oxygen atmosphere of 2.07 MPa (300 psig) at a temperature of 60°C (140°F) for a total of 740 hours. The samples were removed, cooled and weighted to determine the amount of oxygen which had been absorbed, Table

2, at several selected intervals and then measured by HTNMR. The total weight increase varied somewhat from sample to sample but is about 2%.

TABLE 1. Properties Of Asphalt Samples Used In Magnetic Resonance Study

Asphalt Code AC Grade	Crude Source	Viscosity 60°C Poises	Penetration 25°C 0.1 mm	Trace Elements		Molecular Weight (Toluene)	Asphaltenes (n-Heptane)	TFOT Aging	
				V/Ni ppm	Fe (ppm)/ S (%)			% Mass Change	Viscosity Ratio (60°C)
AAA-2 200/300 PEN	Lloydminster	363	291	138/27	--/6.0	790	16.2	-.537	2.39
AAB-2 AC-5	Wyoming Sour (Dist)	403	166	163/36	--/5.4	840(?)	16.7	-.015	2.66
AAC-1 AC-8	Redwater/Gulf Boundary Lake	419	133	146/63	--/1.9	870	10.1	-.259	2.42
AAD-2 AR2000	California Coastal (Dist)	600	195	266/135	--/8.3	700	21.3	-.709	2.86
AAE 60/70 PEN	Lloydminster (Air Blown)	3634	73	179/91	6/5.2	820	22.9	-.289	3.19
AAF-2 AC-10	West Texas Sour	867	82	102/22	--/4.6	840(?)	13.0	-.069	2.32
AAK-1 AC-30	Boscan (Dist)	3256	70	1480/142	24/6.4	860	20.1	-.548	2.98
AAM-1 AC-20	West Texas Intermediate (SDA)	1992	64	58/36	255/1.2	1300	4.0	-.052	1.98
AAS-2 AC-10	Arabian Heavy	1220	96	133/37	--/6.8	960(?)	17.1	-.016	3.25
ABC AC-20	Mississippi Valley	2091	76	37/25	12/6.4	870	25.6	-.219	2.40
ABL-2 EB-10	Boscan (Emulsion Based)	1097	169	1484/134	--/6.3	--	17.0	-1.335	3.37
ABM-1 AR-4000	California Valley Lime-treated crude	2230	48	63/111	--/1.3	--	7.1	-.248	1.62

The hydrogen transient NMR properties of the asphalts were measured at a frequency of 27 MHz in the SwRI laboratory NMR system. Data was acquired at room temperature (23°C nominal) and at 60°C (140°F) in keeping with the temperatures customarily used in listings of asphalt properties. The measurements included the peak free induction decay (FID) signal; solid echo; Hahn echo; CPMG; FID ratio; spin lattice relaxation time (T_1), two components, (T_{21} and T_{22}) of the spin-spin relaxation time (T_2) and the spin lattice relaxation time in the rotating frame ($T_{1\rho}$).

The EPR samples were examined only in the as-received condition and only at room temperature using a Varian EM-500 EPR spectrometer. This system operates at a nominal frequency of 10 GHz and acquires data by sweeping the magnetic field over a selected range which includes the EPR resonance. These data have been correlated with the NMR data to identify ferromagnetic and paramagnetic effects from iron, vanadium and manganese in the asphalts.

In-situ asphalt pavement data were acquired with the surface access NMR system previously developed for the U.S. Department of Transportation Federal Highway Administration (FHWA) for determining moisture in concrete bridge decks. Asphalt/aggregate mixes of different ages were also measured in the laboratory.

TABLE 2. The Sample Weights Before And After Vacuum Oven And Oxidations

Sample	Original Weight (gram)	After Vacuum		After Oxidations 1* and 5*			
		weight (gram)	weight change (%)	weight 1* (gram)	weight 1* change (%)	weight 5* (gram)	weight 5* change (%)
AAA-2	3.250	3.230	-.615	3.268	+1.176	3.291	+1.189
AAB-2	3.540	3.531	-.254	3.558	+.765	3.587	+1.586
AAC-1	2.880	2.872	-.278	2.896	+.836	2.919	+1.636
AAD-2	3.660	3.638	-.601	3.665	+.742	3.712	+2.034
AAE	2.920	2.913	-.240	2.938	+.858	2.973	+2.060
AAF-2	3.150	3.141	-.286	3.173	+.987	3.204	+2.006
AAK-1	2.960	2.945	-.507	2.970	+.849	3.013	+2.309
AAM-1	3.870	3.864	-.155	3.894	+.776	3.934	+1.812
AAS-2	3.290	3.285	-.152	3.307	+.670	3.336	+1.553
ABC	3.390	3.383	-.206	3.407	+.709	3.434	+1.508
ABL-2	2.840	2.823	-.599	2.849	+.921	2.890	+2.373
ABM-1	3.290	3.279	-.334	3.306	+.823	3.352	+2.223

1*: 60 hours at 60°C and 2.07 MPa; 5*: 740 hours at 60°C and 2.07 MPa (300 psi.).

III. RESULTS

A. INITIAL NMR DATA CONSIDERATIONS

The peak amplitude of the HTNMR signal, in volts per gram of sample, is a directly proportional to the total hydrogen content of the asphalts and ranges from 0.622 for ABM-1 to 0.802 for AAA-2. For a given type of asphalt concrete this parameter can be used to provide an accurate measure of the amount of asphalt per unit volume.

The T_1 parameter decreases with temperature for all the asphalts and ranges from 75 to 146 milliseconds at 23° (74°F) and

50 to 114 milliseconds at 60°C (140°F). This parameter is important in analyses of materials and also provides a measure of the time a material must be exposed to a magnetic field before an appreciable NMR signal may be obtained. For measurements from a moving vehicle, T_1 sets the maximum speed for a given length of magnet. For a magnetic field 1-meter long the maximum vehicular speed for NMR measurement of asphalt pavements is on the order of 2.28 m/s (5.1 mph) for an accuracy of 5%.

Figure 1 shows the HTNMR free induction decay (FID) signal traces from time zero to 300 μ s after the acquisition pulse for three of the asphalt samples. The initial part of each trace decays rapidly with a time constant T_{21} and then decays more slowly at a rate T_{22} . The T_{21} component is associated with the more solid part of a complex material while T_{22} is associated with the softer or more fluid, lower viscosity constituents. The traces for the three asphalts show substantial differences in the ratio of the solid to the more liquid components and this is reflected in the viscosity and penetration parameters, Table 1.

The T_{21} values from the harder, more solid component of the twelve asphalt samples varies, from 14.8 microseconds (μ s) for AAK-1 to 18.0 for AAB-2 at 23°C (74°F). At 60°C (140°F) all T_{21} values are increased and ranges from 22.5 μ s for AAK-1 to 27.6 for AAA-2. This indicates a softening of the more solid component. The observed value of T_{22} at 74°F ranges from 73 μ s for ABM-1 to 164 μ s for AAA-2. At 60°C (140°F) the softening of the asphalt increases the observed value of T_{22} from 237 μ s for AAK-1 to 476 μ s for AAB-2.

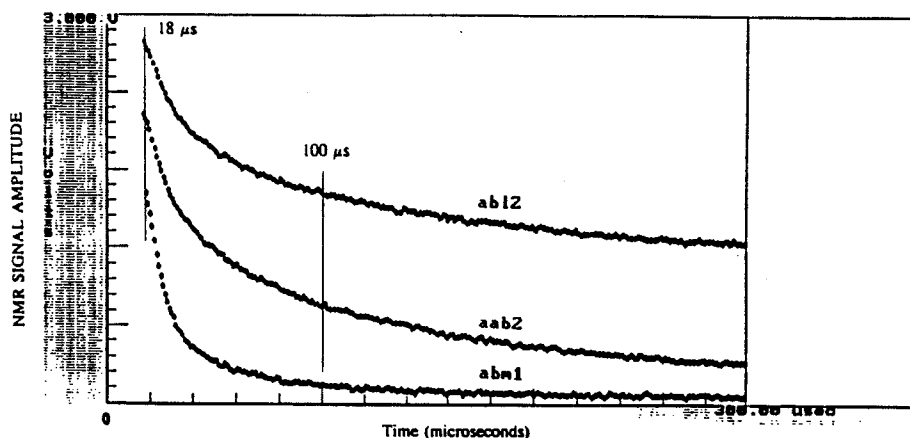


FIGURE 1. Comparison of free induction decay data from three asphalts at 23°C

B. CORRELATION WITH NEAT ASPHALT PROPERTIES

The HTNMR data for the as-received samples were correlated with the listing of several asphalt properties provided by the Materials Reference Laboratory. Figure 2 shows the scatter plots of the NMR data from the "as received" samples vs. physical parameters for each asphalt. The T_{21} component shows quite good correlation with penetration at 23°C, (74°F) Figure 2a, though the best fit is not a straight line. At 60° (140°F) the T_{21} data correlates with the viscosity, Figure 2b, but there is substantial scatter. Figure 2c shows the spin lattice, T_1 , relaxation times vs penetration at 23°C (74°F). Decreases in T_1 is generally indicative of a softer material and greater penetration and the correlation is quite good except for AAK-1 and ABL-2. The high vanadium content in these two reduces T_1 through paramagnetic effects. Similarly Figure 2d shows that T_1 increases with viscosity as measured at 60° (140°F). Here the reduction of T_1 through paramagnetic effects is evident for AAD-2 and AAE in addition to AAK-1 and ABL-2.

C. EFFECTS OF VOLATILES ON HTNMR

T_{21} was consistently reduced by removal of the volatiles, Figure 3, as would be expected from the hardening of the more solid component of the asphalts. The effect on T_{22} was not as consistent with some samples showing an increase and others, a small decrease, at both temperatures. No consistent trend was observed in the effects of volatilization on the value of T_1 .

D. EFFECTS OF OXIDATION

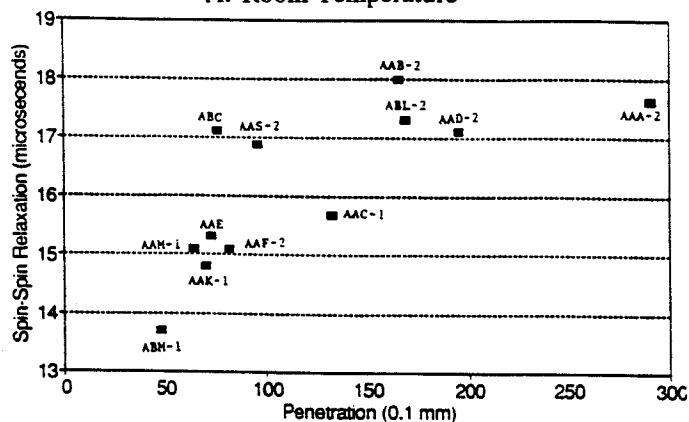
The effects of oxidation on the HTNMR properties of each asphalt sample are shown in Figures 4 and 5. For the first 100 hours of oxidation, the presence of increasing amounts of paramagnetic oxygen in the asphalts caused a consistent reduction in T_1 , Figure 4. Additional oxidation caused the trend to reverse due, apparently to hardening of the asphalt and a resultant increase in T_1 . The $T_{1\rho}$ data, Figure 4, shows a consistent increase with oxidation for all asphalts.

Two changes were observed in the T_2 of the asphalts as oxidation increased -- a hardening of the short T_{21} constituent and a softening of the long T_{22} constituent. The T_{21} data, Figure 5, shows a small but consistent decrease with oxidation which is indicative of a hardening of the more solid component of the asphalt. The increase in the hardness or rigidity of this constituent is even more evident in the T_{21} data at 60°C (140°F), Figure 5. The HTNMR data also shows an appreciable increase in T_{22} as a function of oxidation time. This indicates a softening of the long T_{22} constituent in the asphalt that is also more apparent in the T_{22} data at 60°C (140°F).

Additional oxidation time is needed to evaluate the observed trends in T_1 and T_2 to the end point. However, the results show changes in NMR parameters which are indicative of aging and which can be readily measured with an appropriate fieldable MR instrumentation system.

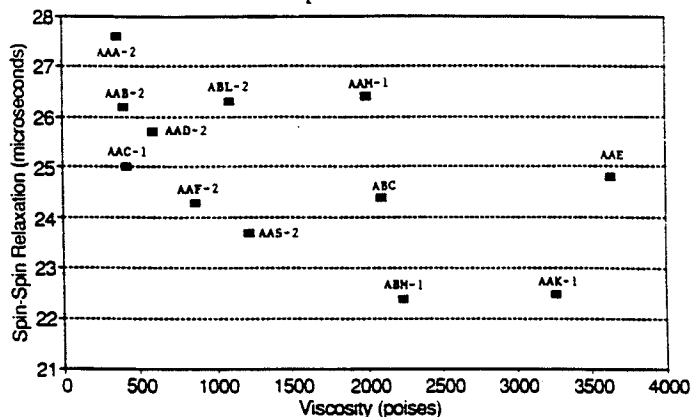
Spin-Spin Relaxation vs. Penetration

A. Room Temperature



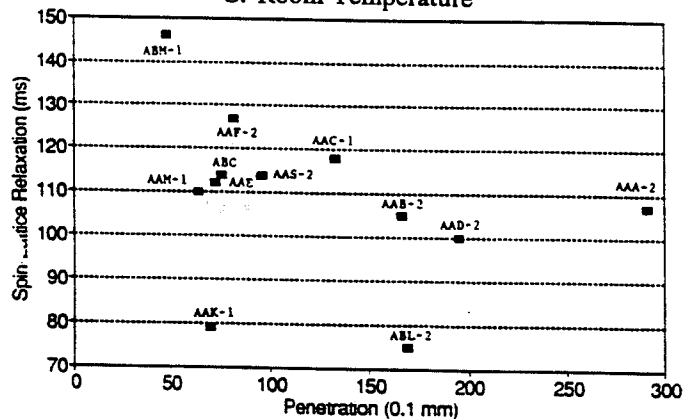
Spin-Spin Relaxation vs. Viscosity

B. Temperature 60°C



Spin-Lattice Relaxation vs. Penetration

C. Room Temperature



Spin-Lattice Relaxation vs. Viscosity

D. Temperature 60°C

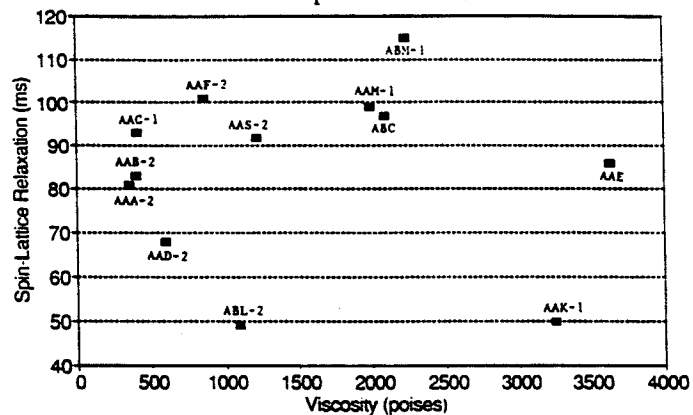
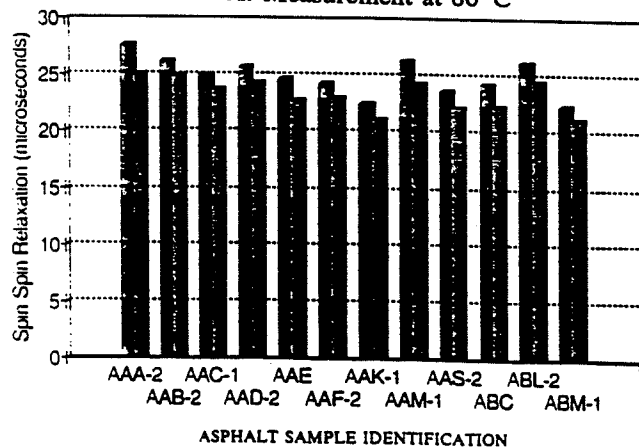


FIGURE 2. NMR data vs. physical properties of neat as-received asphalts.

A. Measurement at 60°C



B. Measurement at 23°C

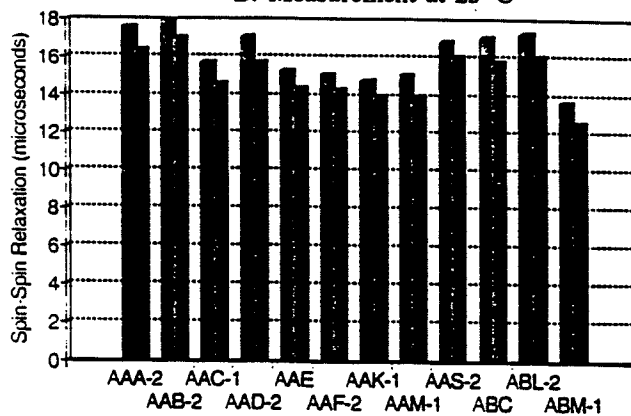


FIGURE 3. T_2 Relaxation time before and after vacuum oven heating.

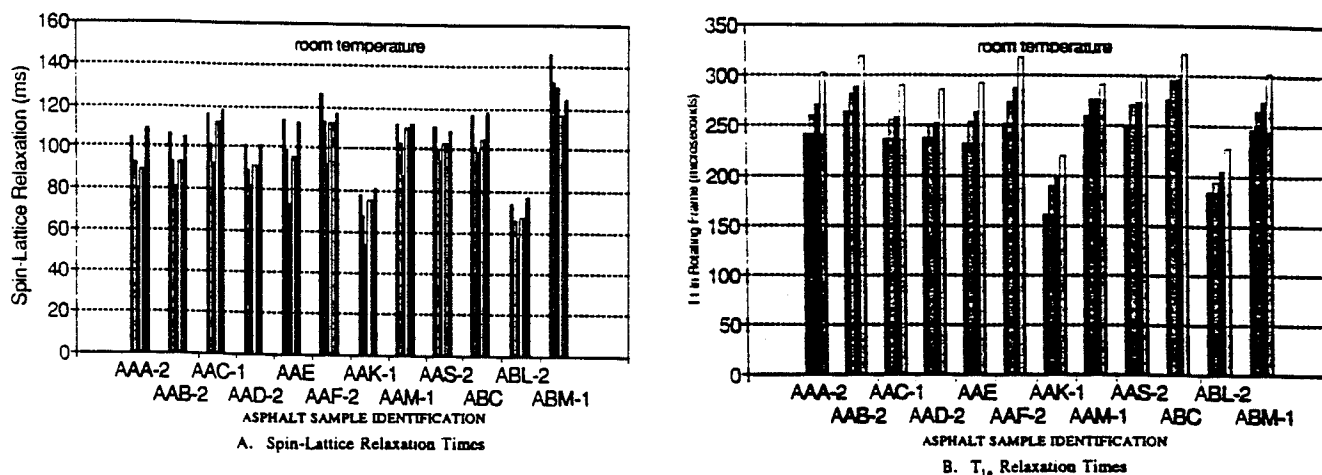


FIGURE 4. T_1 relaxation time before and after oxidation for 60, 100, 400, 570 and 740 hours at 60°C and 2.07 MPa (300 psi)

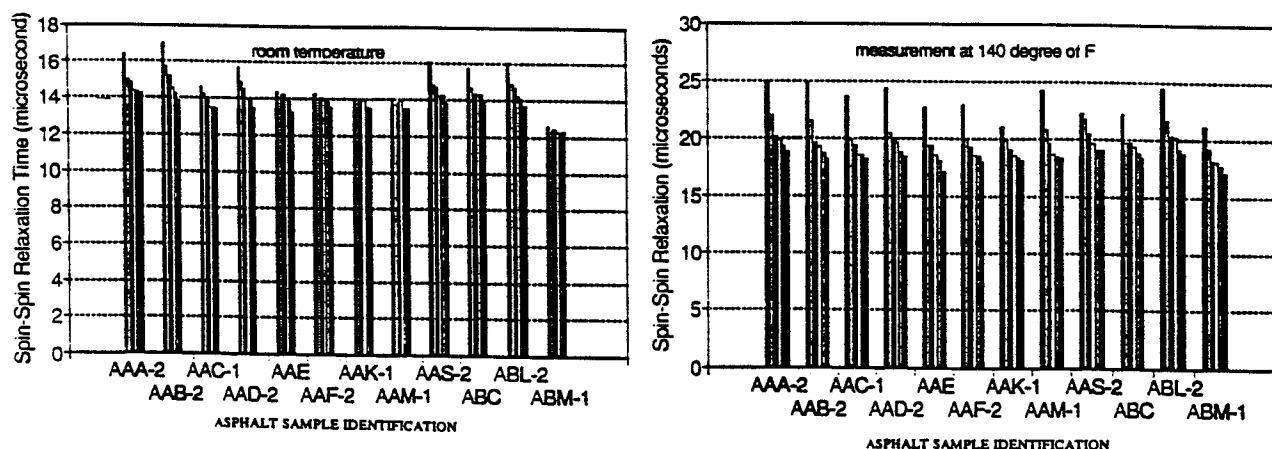


FIGURE 5. T_2 Relaxation times before and after vacuum oven and oxidation for 60, 100, 400, 570 and 740 hours at 60°C and 2.07 MPa (300 psi)

E. EPR MEASUREMENTS

Electron paramagnetic resonance (EPR) measurements were made on all the asphalts as received. EPR spectra for asphalts of AAB-2, ABM-1, AAK-1 and ABL-2 are shown in Figure 6. These spectra show the complete EPR response from the broken bonds in the hydrocarbon portion of the asphalt plus that from significant amounts of paramagnetic metals. All of the asphalts showed the typical pyrolyzed material response as shown in Figure 6a and 6b. At higher instrument gain settings, all the asphalts except, AAM-1 and ABC, showed a significant multi-peak vanadium spectra though an order of magnitude (or more) smaller than that from AAK-1 and ABL-2, Figures 6c and 6d. AAM-1 and ABC showed a small vanadium peak. These results are in agreement with the vanadium content listed in Table 1. All the EPR data in Figure 6 were obtained with the same apparatus settings. The sweep covers a nominal range of 0.2825 to 0.3575 Tesla (2825 to 3575 gauss) that centers the trace on the EPR resonance. Each small horizontal division is approximately 5.0 gauss and the total sweep time was about 10 minutes. The vertical axis is the first derivative of the EPR line spectra as obtained by A.C. modulation of the magnetic field and phase sensitive detection of the EPR signal. In addition to detection of vanadium and other paramagnetic and ferromagnetic constituents the EPR data may potentially provide direct information on asphalt aging.

F. ASPHALT AGGREGATE MEASUREMENTS

HTNMR and EPR measurements were made on two very dry samples of asphalt pavement removed from roadways many years old. Sample No. 1, exhibited weak bonding strength and some resilience. It could be broken by hand but not easily. Sample No. 2, was older, very deteriorated, easily crumbled and had little bonding strength.

TABLE 3. HTNMR Data from Aged Asphalt Concrete Pavements

SAMPLE	T_1 msec.	T_{21} μ sec.	T_{22} μ sec.	A_{22}/A_{21} Volts
#1	81	14.9	187	0.349
#2	95	14.3	129	0.198

The HTNMR FID data, Table 3, obtained from these pavement samples in the laboratory showed very weak signals with a very short decay time T_2 . The weak signal is attributable to the small amounts of hydrocarbon (asphalt) remaining in the mixes compared to the amount of aggregate. The T_{22} component of the signal for the older sample was very weak. This indicates that little of the resilient asphalt remains in this mix as is apparent from the physical characteristics. Hahn echo data for sample No. 1 showed the existence of a much larger T_{22} component in the NMR signal. An analysis of this data indicates T_2 signal components with time constants of 0.65 and 4.41 millisecond in addition to the very short (14.9 μ sec.) component determined from the FID. This indicates that T_2^* is shorter than can be attributed to magnet inhomogeneity. This suggested the presence of ferromagnetic constituents in the aggregate-asphalt mix which was confirmed by the EPR data.

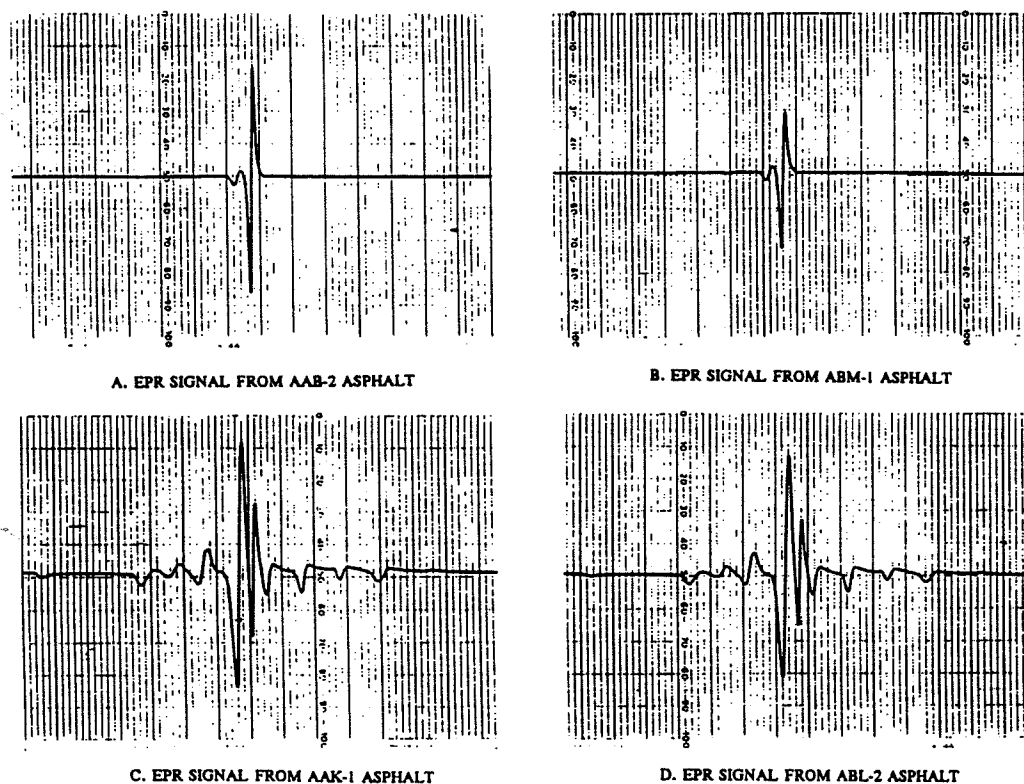


FIGURE 6. EPR Signals from four asphalts

EPR data from pavement sample No. 1, Figure 7a shows a very broad signal which is attributable to a ferromagnetic constituent in the asphalt-aggregate mix. This constituent undoubtedly accounts for the short T_2^* observed in the NMR data. The weaker fine structure on the trace is amplified and expanded in Figure 7b to show the hydrocarbon response as well as an appreciable vanadium spectra. The EPR trace from sample No. 2, Figure 7c also shows a broad iron signal component but it is much weaker than the multi-peak spectra. The expanded trace of the EPR spectra from Sample No. 2, Figure 7d, shows spectra indicative of the normal hydrocarbon signal plus a multi (6) peak spectra indicative of manganese. These results support the need for EPR data to supplement the HTNMR data and provide a basis for compensation of the NMR measurements for effects of ferromagnetic and paramagnetic constituents in asphalt-aggregate mixes.

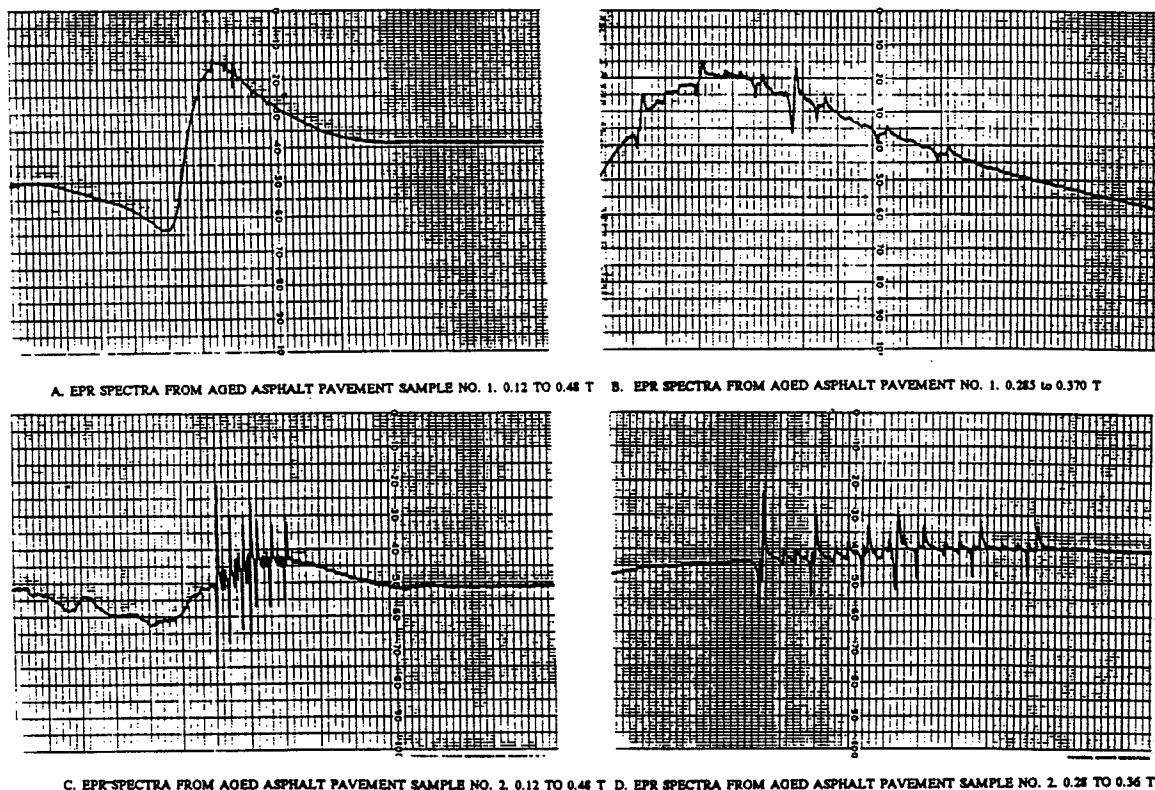


FIGURE 7. EPR spectra from aged asphalt pavement

G. IN SITU MEASUREMENTS

The NMR system as previously developed for FHWA to measure moisture in concrete bridge decks was tested for in-situ measurement of asphalt pavements. This system has a surface access (one sided) sensor to allow non-intrusive detection of hydrogen NMR signals from the interior of materials with the sensor above the surface. The magnet, sensor coil, transmitter power and detector sensitivity are adequate to obtain moisture signals at 2.1 MHz from a band of material about 2.5 mm (0.1-inch) thick at selected depths ranging from 12 to 100 mm (0.5 to 4.0) inches below the surface. However, the system does not incorporate provisions for solid echo measurements and, in addition, the combination of transmitter pulse width and receiver recovery time prevent detection of the short transient NMR signal components from aged asphalt pavements. While the system is acceptable for the relatively slowly decaying signal from moisture in concrete it could not detect the rapidly decaying ($T_{21} \approx 15 \mu s$) signal which is the primary component of the asphalt pavement response. To overcome this problem and to provide additional signal processing capability the FHWA system was temporarily interfaced with a more versatile laboratory type NMR system that was available. This combination made possible the detection of HTNMR signals from sections of the aged asphalt pavements (samples No. 1 and No. 2

previously described) in simulated in-situ tests, i.e. from the surface of materials with the detection zone set to be 25 mm (1-inch) into the pavement samples.

Figure 8a is a Hahn echo NMR signal at 80-microseconds from asphalt pavement Sample No. 1 and Figure 8b shows the solid echo NMR signal at 60 microseconds from this same asphalt pavement. The signal-to-noise voltage ratio from the asphalt pavement is on the order of 4:1 or 12 dB.

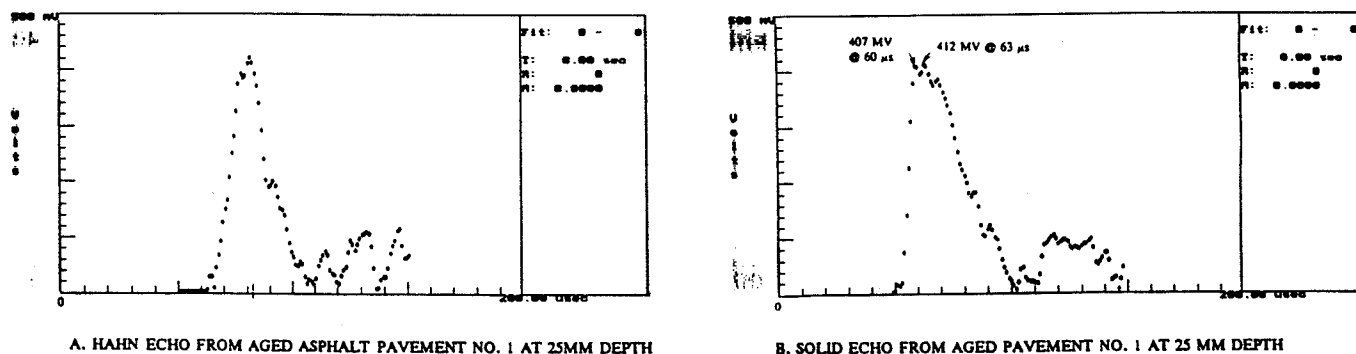


FIGURE 8. NMR signals using surface access sensor.

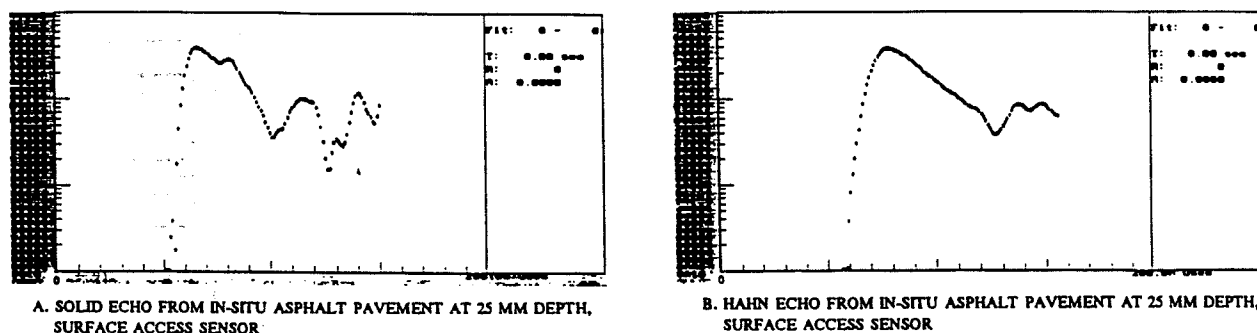


FIGURE 9. NMR signals from in-situ asphalt pavement.

The composite in-situ NMR system was also used for measurements of the asphalt pavement on a parking lot. This pavement is approximately 5-years old, in good condition and apparently not showing deterioration due to aging. The solid echo NMR signal obtained in-situ from the pavement is shown in Figure 9a. The sensitive zone was within the asphalt and 1-inch below the sensor surface. Figure 9b shows the Hahn echo signal from the same region.

H. SUMMARY AND DISCUSSION OF PHASE I RESULTS

The results of the Phase 1 study showed good correlation of the NMR T_2 (spin-spin) data with the penetration for the neat asphalts as received. The NMR T_1 data correlated well with the viscosity except for asphalts, AAK-1 and ABL-2, which have a smaller T_1 attributable to the very high vanadium (paramagnetic) content. Heating of the samples in a vacuum oven to reduce the volatiles without oxidation resulted in weight loss comparable to those reported for TFOT tests (Table 1) and the loss of the volatiles caused the short T_2 component (which is from the harder asphalt constituent) to be consistently reduced as would be expected from the hardening which occurred.

Oxidation of the samples at 60°C (140°F) and 2.07 MPa (300 psi) in an oxygen atmosphere for a period of 740 hours resulted in weight increases on the order of 2%. Significant and consistent decrease in NMR T_1 was observed during the first 100 hours of oxidation for all samples at both room temperature and at 60° (140°F). However, with additional

oxidation the trend reversed and T_1 began to increase. The initial decrease in T_1 with oxidation is apparently due to the effect of the paramagnetic oxygen being present in the asphalt but without molecular changes that cause extensive hardening. Continued oxidation did induce hardening indicative of aging and T_1 increased as is expected for harder, more brittle materials. The $T_{1\rho}$ (T_1 in the rotating frame) data increased consistently for all samples over the entire aging period. The changes in T_2 with oxidation were consistent with the shorter signal component decreasing, indicating additional hardening, while the longer T_2 component increased as is indicative of a softening of the more fluid constituents. Oxidation for longer time periods are believed to be needed to reach an equilibrium.

In-situ NMR tests using the previously developed FHWA system produced weak but detectable signals from dry asphalt pavements. The weak signals result from the low concentration of asphalt in the pavement, from the limited sensing volume in the magnet used with this instrument and from limitations in instrument capability to adequately sense the very short T_2 component of the asphalt-aggregate mix. These limitations are correctable in a system appropriately designed for asphalt inspection. Tests of aged asphalt pavement in the laboratory confirmed the very short T_2 , attributable to iron and paramagnetic elements (vanadium and manganese) in the aggregates or asphalts, which is characteristic of the asphalt in these mixes. This short T_2 factor was addressed in development of the instrument specifications and design concept - Appendix A. EPR studies of the neat asphalts showed the typical hydrocarbon response from all samples plus a large, multi-peak vanadium spectra from some samples particularly AAK-1 and ABL-2. Vanadium spectra of lower amplitude were observed in most other samples in proportion to the concentration of this element in the different asphalts. The EPR vanadium signal can be used to provide a basis for correction of the NMR data for the effects of paramagnetic elements on T_1 . An inspection system based on a combination of EPR and NMR, using the same magnet and other apparatus common to the two methods, is believed to offer the potential for in-situ pavement inspection that is substantially immune to the variations in the different asphalts and aggregates.

The recommended system design configuration and specifications, Appendix A, incorporates both HTNMR and EPR sub-systems in an integrated, trailer mounted configuration using a common magnet. The automated data acquisition and data processing makes use of the NMR data as the primary pavement condition sensor and the EPR data to provide corrections for the effects of ferro- and paramagnetic constituents in the asphalt. These data are used to provide an indication and recording of asphalt aging and moisture under static or in-motion conditions. In addition, the system acquires and stores complete NMR and EPR data for future use or for any additional processing that may be applicable. An integral engine-generator provides electrical power for the system. The design is expected to permit in-motion data acquisition and processing at vehicular speeds up to about 10 kmh (6 mph). The system measures the MR properties of asphalt pavement in a band about 2.5 mm (0.1-inches) thick and 100 mm (4-inches) wide located from 12.5 to 25 mm (0.5 to 1.0 inches), as selected, below the top surface. The data is time averaged for selected periods, ranging from 10 to 100 seconds, prior to readout. It is recommended that this system be fabricated in experimental form and used to evaluate the technology and system performance over a variety of asphalt concrete roadways.

IV. CONCLUSIONS

Conclusions from the Phase 1 efforts are as follows:

1. Useful hydrogen transient NMR (HTNMR) data can be obtained from all asphalts.
2. The signal amplitude and NMR time constants T_1 and T_2 varies with asphalt type.
3. The T_1 and T_2 data correlate with the viscosity and penetration of the different neat asphalts.
4. The T_1 is decreased by paramagnetic, particularly vanadium, and ferromagnetic constituents in asphalts.
5. The removal of the volatiles affects the spin-spin, T_2 , relaxation time of all the neat asphalts.
6. Oxidation of the neat asphalts to simulate accelerated aging affects both T_1 and T_2 . T_1 , provides the most consistent indication of oxidation aging. Oxidation over longer time periods is needed to reach equilibrium.
7. The effects of oxidation aging are rapidly measured by HTNMR in a non-intrusive manner.
8. The T_1 of the asphalts is amenable to in situ HTNMR measurements from a moving vehicle.
9. Electron paramagnetic resonance (EPR) can provide a non-contacting, non-intrusive measure of the paramagnetic (vanadium and manganese) and ferromagnetic (iron compounds) in asphalt and other data.
10. Mixtures of asphalt and aggregates may introduce bonding effects and constituents (paramagnetic and ferromagnetic) that affect the HTNMR relaxation times. Additional studies are needed in this area.
11. In-situ asphalt measurements have been found feasible but improved apparatus is needed to increase the sensitivity to the rapidly decaying, short T_2 , component of the asphalt pavement NMR signal.
12. The recommended mobile inspection system for asphalt inspection includes optimized HTNMR and EPR sub-systems in an integrated configuration with automated data acquisition and processing. The system is trailer mounted with an integral engine generator to provide the required electrical power. The system is suitable for acquiring asphalt data while stationary or in-motion at slow speeds, 5 to 10 kmh (3 to 6 mph).

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APPENDIX A - SYSTEM DESIGN AND SPECIFICATIONS

The MR system for in-situ inspection of asphalt concrete pavement incorporates features and capabilities required for operation in the highway environment and to provide data needed for assessment of asphalt aging, moisture and possibly other asphalt conditions. The entire system is mounted in an enclosed trailer to provide the mobility and convenience required for extensive evaluation of the apparatus and technology in the inspection of asphalt concrete roadways.

Figure A-1 shows a block diagram of the system that includes both NMR and EPR sub-systems. Both sub-systems make use of the same U-shaped magnet to provide the field required for resonance. The field from a magnet of this general configuration extends from the open poles of the magnet into the pavement. Though the field has an

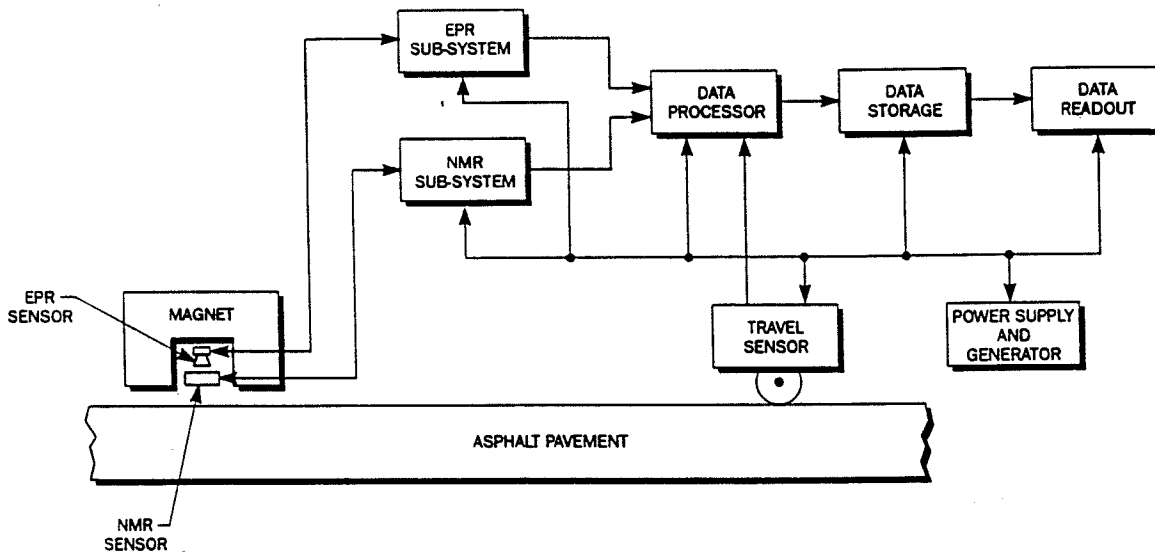


Figure A-1. MR system for in situ asphalt pavement inspection.

appreciable gradient, there is a well defined region (the sensitive region) at a selected distance below the pole faces where the field intensity is proper for NMR detection of hydrogen and EPR detection of un-paired electrons at a selected operating frequencies. The magnet design provides a sensitive region that is located 38 mm (1.5-inches) below the pole faces and which extends across 100 mm (4-inches) of the pavement and 900 mm (36-inches) in the direction of travel. The nominal field intensity of 0.0875 T (875 gauss) produces hydrogen NMR at 3.73 MHz and EPR at 2450 MHz. The magnet pole faces will be 13 to 25 mm (0.5 to 1.0 inches) above the average pavement surface for non-contact operation at the speeds of 5 to 10 km/h (3 to 6 mph). The system will be usable for static as well as in-motion measurements. Means to raise the magnet vertical position are incorporated to allow higher speed transportation from site to site, to dislodge debris which may collect and to permit acquisition of data from different depths in the pavement.

