Determination of Asphalt Contents in a Paving Mixture by Thermal Neutrons

MAN MOHAN VARMA and GEORGE W. REID
Tufts University, Medford, Massachusetts

The purpose of this research was to determine the feasibility of measuring the asphalt content of bituminous paving by the neutron bombardment counting technique. The correlation of neutron count and asphalt percentages depends primarily on the chemical content of the asphalt. Because the chemistry of asphalt is that of a variable mixture, it can be expected that data collected will fluctuate to some degree with changes in the asphalts tested.

• ALTHOUGH the use of asphaltic paving has increased appreciably during the past twenty years, asphaltic pavement design is still more an art than a science. Of the several design parameters that may be varied, the asphalt content is probably the most important. Since asphalt controls the workability and durability of the pavement, a slight change in asphalt content can vary its performance markedly. Should the pavement fail, the entire cost of the paving is usually lost, because, in general, none of the materials, especially the asphalt, can be recovered. Also, in many cases the asphalt cost is high—even more expensive than the aggregate, sand and filler. These reasons, then, make it extremely desirable for the asphalt content of paving mixture to be optimum.

At present, the asphalt content of all asphaltic pavement must be determined in a laboratory, either during construction or after the completion of the paving. The American Society of Testing Materials (ASTM) (3) has described the complete procedure for this laboratory testing. The usual method is to extract the asphalt from the sample by centrifugation and then calculate the weight percent asphalt of the mixture. It is a time-consuming and cumbersome operation.

The purpose of this research program was to determine if a neutron probe can be used successfully in determining the amount of asphalt in an asphaltic pavement.

CHEMISTRY OF ASPHALTS

Although the usefulness of asphalt has a long history (2), little is known about the exact composition of asphalt molecules. This particular aspect of the material has remained essentially unexplored, primarily because asphalt is a complicated variable mixture seldom found in a pure state. Most research performed to date provides only average values of the chemical composition.

Basically, asphalt is a mixture of hydrocarbons varying chemically and in molecular size. The hydrocarbons sometimes contain sulfur, oxygen and nitrogen. Asphalt may belong to any of the four basic groups shown in Figure 1.

Theoretically, a paraffinic series may be formed with any number of carbon atoms, and the number of hydrogen atoms will always remain two more than twice the number of carbon atoms. However, the heavier organic molecules belonging to the paraffinic group usually do not form asphaltic substances without extra treatment.

Polymerized naphthenic and aromatic structures have higher carbon-to-hydrogen ratios (C/H ratios) than do their unpolymerized molecules. Although the presence of

Paper sponsored by Special Committee on Nuclear Principles and Applications.

TABLE 1

PERCENT HYDROGEN IN AROMATIC ASPHALT

No. of Rings	No. of C Atoms/Mol	At. Wt of C Atoms	No. of H Atoms/Mol	Mol Wt	Percent H
10	42	504	24	528	4.55
12	50	600	28	628	4.46
14	58	696	32	728	4.40
16	66	792	36	828	4.35
18	74	388	40	920	4.30
20	82	984	44	1,028	4.26
22	90	1,090	48	1,138	4.22
24	98	1,186	52	1,238	4.20
26	106	1,282	56	1,338	4.18
28	114	1,378	60	1,438	4.16
30	122	1,474	64	1,538	4.15

TABLE 2

PERCENT HYDROGEN IN NAPHTHENIC ASPHALT

No. of Rings	No. of C Atoms/Mol	At. Wt of C Atoms	No. of H Atoms/Mol	Mol Wt	Percent H
10	42	504	66	570	11.6
12	50	600	78	678	11.5
14	58	696	90	786	11.42
16	66	792	102	894	11.41
18	74	888	114	1,006	11.39
20	82	984	126	1,110	11.36
22	90	1,090	138	1,228	11.25
24	98	1,186	150	1,335	11.23
26	106	1,282	162	1,466	11.20
28	114	1,378	174	1,552	11.19
30	122	1,474	186	1,660	11.00

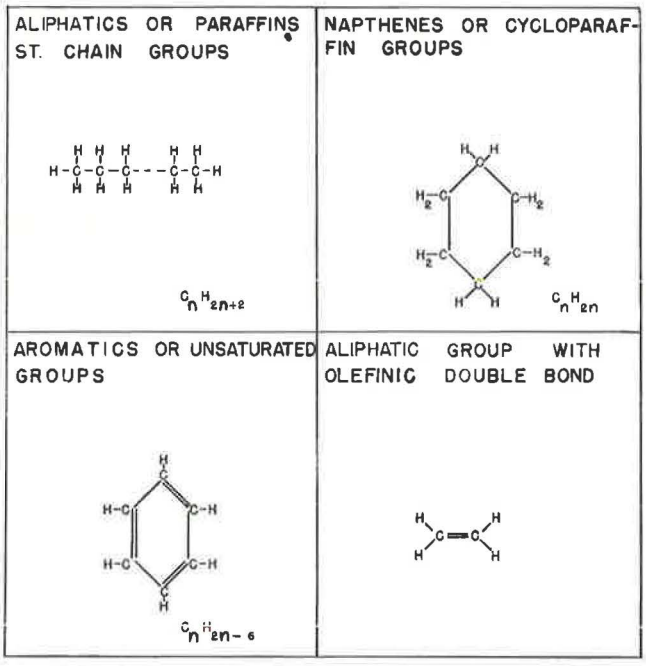

Figure 1. Possible linkage in carbon and hydrogen atoms in asphalt.

double bonds in the aromatic configuration shows that the compound is unsaturated, Pauling (10) has shown that, due to the principle of resonance, these compounds are as stable and unreactive as those of the naphthenic series.

Hydrogen in Asphalt

The composition of asphalt can be approximated by assuming that the constituents of asphalt are carbon and hydrogen atoms plus a percentage of sulfur atoms which must be measured in each case. With this assumption, the number of carbon atoms can be computed and the molecular weights of the naphthenic and aromatic groups present may be found. From these computations, the percent of hydrogen by weight in each of the two groups can be determined. In this determination the sulfur content of the asphalt must be known because, though the atomic percentage of hydrogen present is much greater than that of sulfur, the greater weight of sulfur disrupts the correlation of carbon-hydrogen weight ratios. Results of calculations made, without sulfur content, are shown in Tables 1 and 2. In Figure 2 it can be seen that hydrogen never falls below 10 percent by weight of naphthenes. Hydrogen in the aromatic group varies from 4.15 to 4.55 weight percent. Possibly the range of hydrogen content in asphalt will vary approximately from 6 to 11.4 percent.

THEORY OF NEUTRON SCATTERING METHOD

Since asphalt is formed principally by aromatic and naphthenic groups, it is expected that the number of carbon nuclei exceeds that of hydrogen nuclei. The carbon to hydrogen ratio will be higher in naphthenic groups than in aromatic groups. A reasonably accurate approximation of this proportional amount of hydrogen, coupled with the knowledge of the physical characteristics of the hydrogen atom, creates a basis for identifying asphaltic substances by radioactive bombardment. As all hydrogen in an asphalt

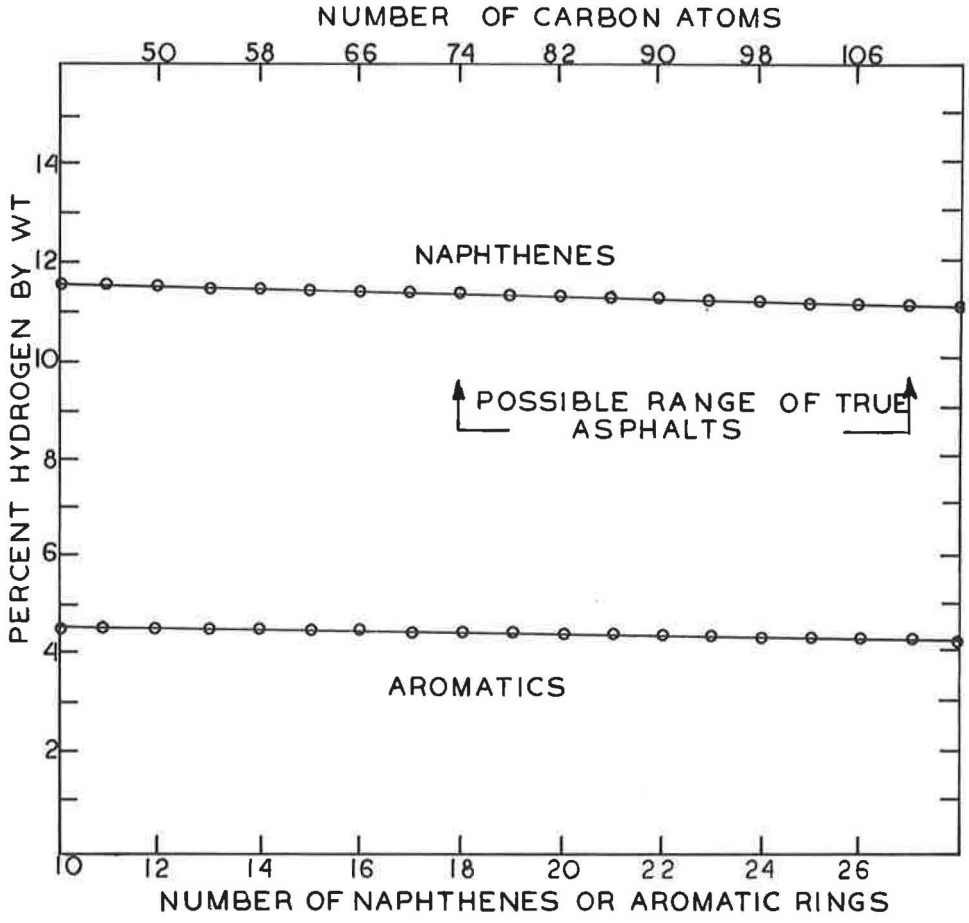

Figure 2. Percent hydrogen in naphthenes and aromatic groups.

pavement is present in the form of asphalt and because hydrogen slows down fast neutrons more effectively than any other element, a review of the theory of this process is necessary.

The use of radioactivity, such as alpha and beta particles, gamma rays and neutrons, appears practical as a method for determining asphalt content. Gerdel, Hansen and Cassidy (7) have successfully used the absorption of gamma rays for measuring the quantity of water in snow peaks, but the application of gamma rays for measuring asphalt contents would be unsatisfactory because the aggregate in an asphaltic mixture would probably absorb the radiation more than the asphalt. The ranges of alpha and beta particles are too small to be considered for this purpose. Neutrons have been used successfully in well logging (4) and in determining soil moisture (5, 6, 11). Because hydrogen slows down the fast neutrons more effectively than any other element and all hydrogen in an asphaltic pavement is present in the form of asphalt, the use of fast neutrons seems a promising solution of the problem. Properly calibrated, the number of slowed-down neutrons from a fast-neutron source would be a measure of the hydrogen content from which asphalt content can be calculated.

A neutron may be described as an uncharged subatomic particle, the mass of which is approximately equal to that of a proton or a hydrogen nucleus. The interaction of neutrons with matter usually results in elastic or inelastic scattering—the probability of neutron capture is very small. Experiments have shown that fast neutrons lose a

considerable amount of energy in collisions with protons. If this collision is repeated several times, the energy of the neutron may be reduced to the thermal energy range (approximately $\frac{1}{40}$ ev). This phenomenon is expressed by Orear, Rosenfeld, and Schluter (10) as:

$$\epsilon = \ln \frac{E_2}{E_1} = 1 - \frac{(A-1)^2}{2A} \times \ln \frac{A+1}{A-1} \quad (1)$$

and

$$En = Eo\, e^{-n\epsilon} \quad (2)$$

where

e = base of natural logarithm,
A = mass number, and
n = number of collisions.

Those neutrons not absorbed as fast neutrons will be reduced to thermal energies due to collision with carbon and hydrogen atoms. It can be estimated that in carbon, a 1-mev neutron will need approximately 110 collisions to reach the thermal energy level. In hydrogen, only 17.6 collisions will produce the same reduction in energy. Since 6.25 times as many collisions are required in carbon as in hydrogen, hydrogen is regarded as a good moderator of fast neutrons.

The collision of neutrons with nuclei may also be described in terms of collision probability (σ) which is usually expressed as a cross-sectional area, expressed in barns (1 barn = 10^{-24} sq cm). The average values of scattering cross-section of various elements are given by Adair (1), who shows that the cross-section of hydrogen increases 18.6 times as the energy of the neutrons decreases, whereas in carbon and phosphorus it increased by only 2.88 and 1.33 times, respectively. In contrast, the σ decreases in the presence of silica, sodium and magnesium. Thus, if a source emitting fast neutrons is lowered in a mixture of asphalt and aggregate, the neutrons will be slowed down primarily by the hydrogen present in the asphalt.

Other sources of hydrogen in a bituminous pavement could be the organic soil and water due to rain and seepage. However, hydrogen content in organic soil is always less than 5 percent its weight, and most specifications in this country do not allow a mixture of organic soil in any type of road pavement. The presence of water due to rain and seepage may be avoided by carefully drying the pavement before taking the reading. Chlorine may also slow down the neutrons, but its presence in significant amounts is unlikely.

Neutron Source Apparatus

The basic components of the equipment used in this program were a probe unit and a counting unit. The probe should consist of a fast-neutron source and a detector tube designed to intercept and count the neutrons which pass through the scattering medium sample. Theoretically, the detector should be as near the source as possible because the density of slow neutrons decreases with growing radial distance from the source (13). A small detector tube, 10 to 17 mm long and approximately 10 mm in diameter, is ideally suited to this research program. With such a detector, the necessary sample size would have been reduced and progress thus accelerated; however, due to limited funds, this type of instrument was unobtainable and a Nuclear-Chicago Model P-19 was used.

Model P-19 houses the neutron source and detector in a single unit. The source and detector materials were those recommended by Stone, Kirkham and Read (11): a 5-mc Ra-Be mixture and an enriched $B^{10}F_3$ tube, respectively. The electrical pulses produced by the detector tube passed directly to an amplifier, then through a cable (graduated in inches) to the counting unit where they were recorded. The counting unit consisted mainly of five glow counter tubes with associated timer and high-voltage supply (Nuclear-Chicago Model 2800). The probe, after connection to the counting unit, is lowered in the hydrogenous material through an access tube. The total counts are recorded on the scaler and counts per minute are determined.

Determining Sample Size

For neutrons to be detected and counted by the materials of the detector tube, their energy must be low, approximately at the thermal level. Therefore, to count the neu-

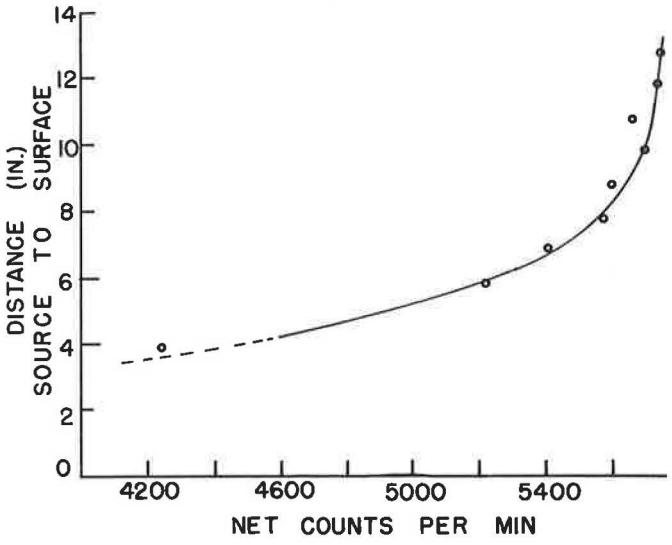

Figure 3. Sample size determination in sand and water (19.04 percent water by weight).

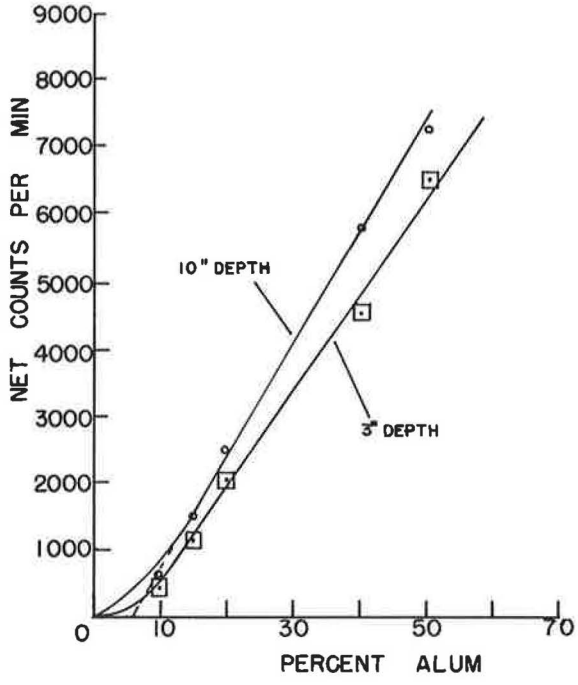

Figure 4. Percent alum vs counts per minute using $12\frac{1}{4}$-in. diameter container.

TABLE 3

COUNTS PER MINUTE AT VARIOUS DEPTHS IN DIFFERENT CONTAINERS

Diam of Container (in.)	Depth (in.)	Slope of Line (cpm/% Alum)
$12\frac{1}{4}$	10[a]	171
	3[b]	146
$10\frac{1}{2}$	10[a]	157
	4[b]	134
$8\frac{1}{2}$	7[a]	121
	3[b]	87
6	$2\frac{7}{8}$[a]	50

[a]Maximum. [b]Minimum.

trons emitted from a high-energy source, they must be first slowed down (reduced in energy) by a scattering medium. Because the sensitivity of the counting method for any concentration of scattering medium increases with the number of neutrons counted, it is desirable for the sample to be of such a size that a large number of neutrons will be slowed to thermal energy by the scattering medium.

The optimum sample size for a hydrogenous scattering medium was determined by placing the neutron source in a sample scattering medium of known concentration and obtaining data concerning sensitivity of testing as the radius of the sample was varied. The first scattering medium used was water. The neutron source probe was lowered in an access

tube and extended to the bottom of a 55-gal barrel three-fourths filled with water. The probe was raised in increments of 1 in. until appreciable loss of neutrons was detected. All distances were measured from the effective center of the probe, that is, 4 in. from the bottom. The minimum radius between probe and detector may be observed as a clear break point in the graph of Figure 3. This radius is called "sample size".

Since the sample size increases with decrease in hydrogen content, similar experiments were performed with different mixtures of sand and water. The sample size in water alone was 7 in. and in 19.04 percent water, 11 in. (Fig. 3). Hydrogen content in pure water is about 11 percent by weight. Assuming about 7 percent asphalt in an aggregate mixture and an average of 6 percent hydrogen in asphalt, the hydrogen content in an asphaltic pavement will be in the vicinity of 0.42 percent. This quantity is much less than the hydrogen in the experiment with 19.04 percent water. Hence, it was necessary to find a sample size that would provide a linear correlation in counts per minute and hydrogen content at low hydrogen levels. Such a sample size—though less than the actual sample size—should be adequate for the investigation and is referred to here as effective sample size.

Therefore, to achieve a sample with hydrogen concentration analogous to that of asphalt, ammonium alum, $NH_4Al(SO_4)_2 \cdot 12\ H_2O$, was used in various proportions with 20 to 30 mesh sand (pure alum contains about 6.63 weight percent hydrogen). This procedure furnished samples with even lower hydrogen concentrations than those usually found in paving asphalt mixtures.

Using the method of varying radii, effective sample sizes for use in this program were found. Experiments were conducted in different size containers, with the dimensions $12\frac{1}{4}$ in. diam, $15\frac{1}{2}$ in. high; $10\frac{1}{2}$ in. diam, $15\frac{1}{4}$ in. high; $8\frac{1}{2}$ in. diam, $12\frac{3}{4}$ in. high; and 6 in. diam, 7 in. high.

Figures 4, 5, and 6 indicate that the counts recorded per minute increase proportionately as the alum concentration is increased. A summary of results is given in Table 3. Hydrogen concentration (weight percent) is plotted vs counts per minute in Figures 7, 8, and 9. The slopes of the plotted lines are indicative of the sensitivity of the test: the steeper the slope, the more accurate are the results.

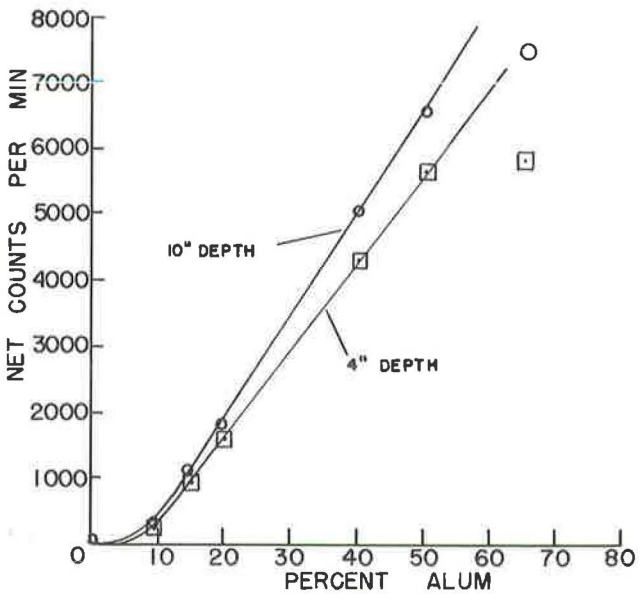

Figure 5. Percent alum vs counts per minute using $10\frac{1}{2}$-in. diameter container.

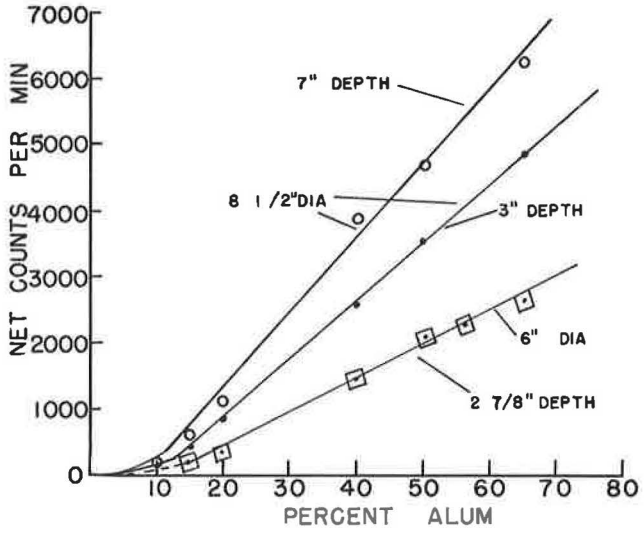

Figure 6. Percent alum vs counts per minute using $8\frac{1}{2}$- and 6-in. diameter containers.

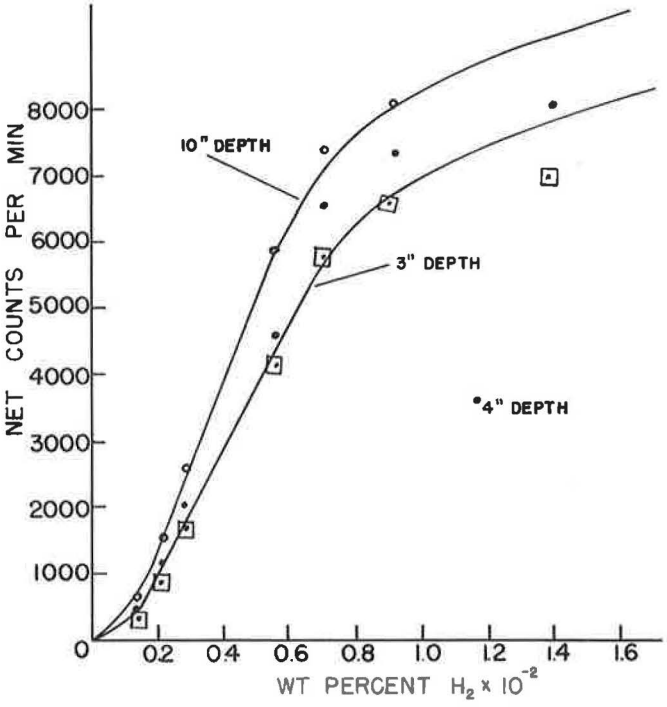

Figure 7. Weight percent hydrogen vs counts per minute using $12\frac{1}{4}$-in. diameter container.

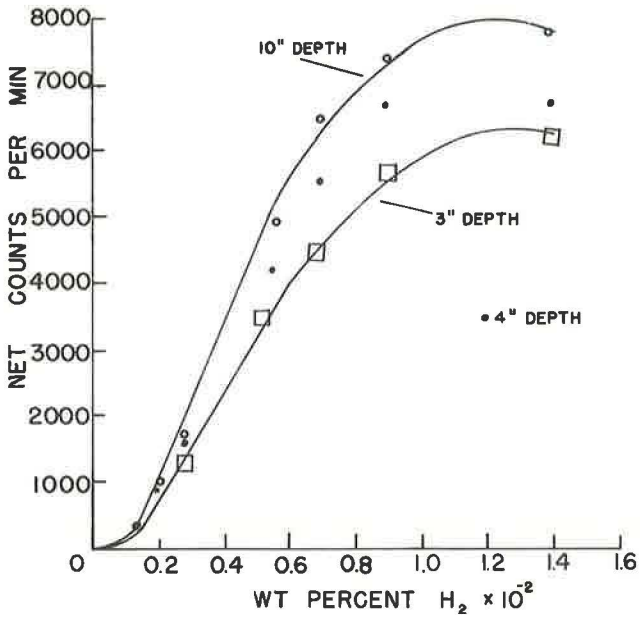

Figure 8. Weight percent hydrogen vs counts per minute using $10\frac{1}{2}$-in. diameter container.

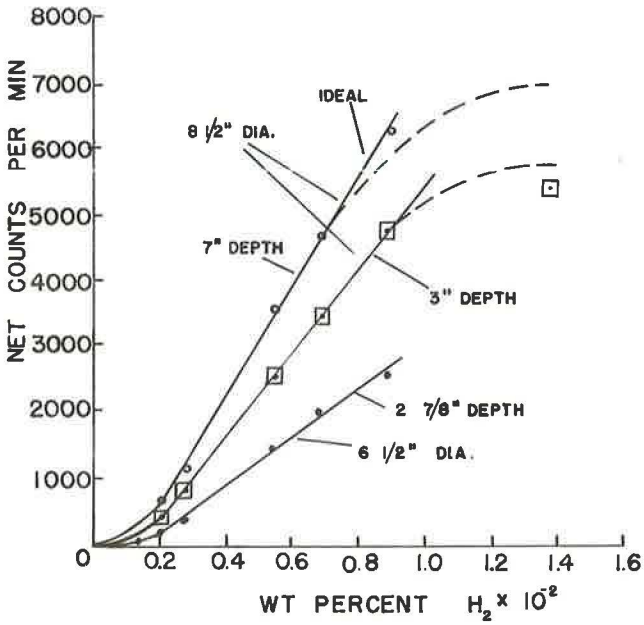

Figure 9. Weight percent hydrogen vs counts per minute using $8\frac{1}{2}$- and $6\frac{1}{2}$-in. diameter containers.

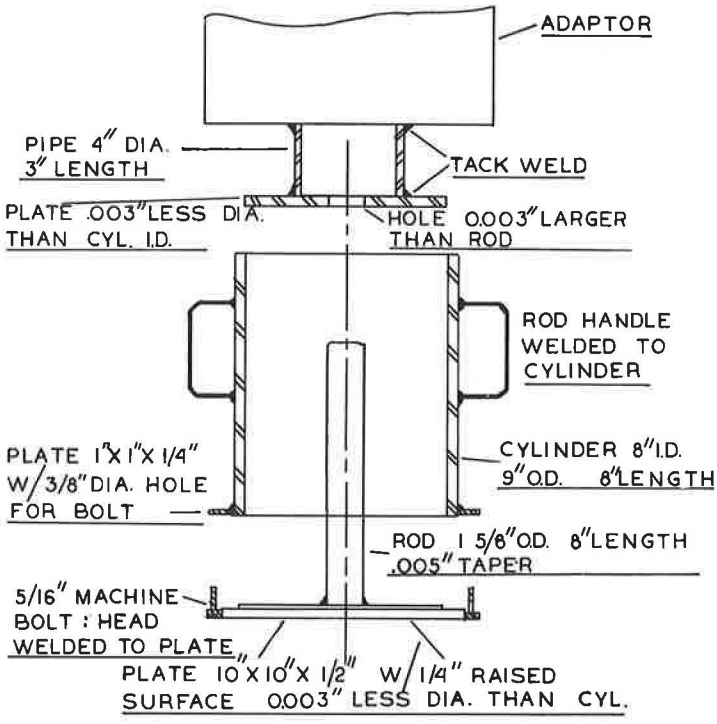

Figure 10. Details of 8-in. diameter cylinder for making asphalt aggregate samples.

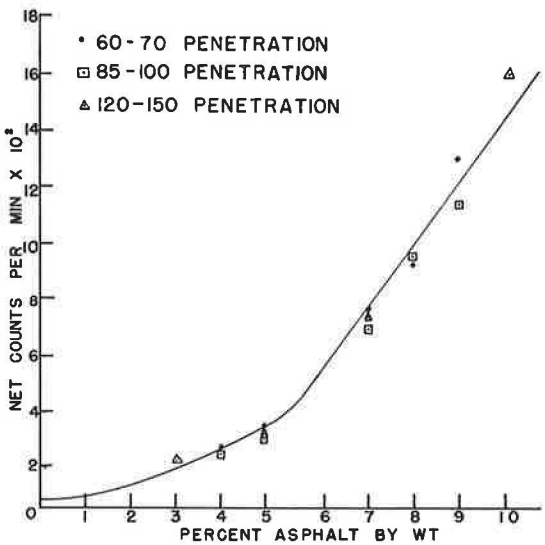

Figure 11. Counter per minute vs asphalt content using different penetration asphalt.

From these studies, it was concluded that an 8-in. diameter, 8-in. high, solid cylinder would be the most economical sample for performing the tests. A cylinder with a larger diameter would be more accurate but is not economical or practical.

The sample determination arrived at should describe not only a relation between the asphalt content in an asphaltic mixture, but also will be indicative of the hydrogen content in the asphalt sample, if properly calibrated. In addition, using an activation analysis, it may be possible to arrive at an empirical chemical formula for the asphalt.

Studies of Asphaltic Mixtures

Details of the mold used for fabricating samples of the asphaltic mixtures are shown in Figure 10. To lower the probe, a $1\frac{5}{8}$-in. diameter rod was permanently fixed in the center of the mold.

Aggregates for making samples were obtained through the Oklahoma State Highway Department. Because

the aggregate did not meet the specifications of The Asphalt Institute (12), it was passed through different sieves.

Three samples each of various asphalt concentrations using different penetration asphalt were compacted. Aggregates and asphalt were heated as specified by The Asphalt Institute, placed in the cylinder in two approximately equal layers, and compacted under 210 psi pressure. After compaction, the top of the cylinder was leveled. The molded sample was allowed to cool before being taken from the cylinder; then the probe was lowered, and testing was performed. A plotting of asphalt content vs counts per minute is shown in Figure 11.

The curvature in the lower portion of the plot indicates that the sample size is small, and if the size of the probe is reduced, the resulting plot will pass through the origin. It was also observed that the height of the mold is very critical, and a small change in height altered the counts of the thermal neutrons appreciably. However, Figure 11 shows a high degree of correlation between the quantities and confirms the validity of the proposed method.

As explained in this paper, the correlation of neutron count and asphalt percentage depends primarily on the chemical content of the asphalt. Because the chemistry of asphalt is that of a variable mixture, it can be expected that data collected may fluctuate to some degree with changes in the asphalts tested. It is proposed that additional tests, of the same nature as previously tested, be performed with different types of asphalt to further establish the validity of the technique proposed.

The density of the compressed samples as yet has not been correlated closely with the chosen sample dimensions. It has also been pointed out that theoretically a more sensitive test can be made with small probe dimensions. This idea must be correlated with the density and asphalt concentration of the compressed sample so that high rate of neutron scattering can be maintained. This correlation has not been made in the past because the smaller probe and counting instruments have not been available. It is proposed that these instruments be obtained so that the reliability of the testing method can be substantially improved.

CONCLUSIONS AND RECOMMENDATIONS

The purpose of this research was to develop a feasible method of determining asphaltic content in bituminous paving by neutron bombardment counting method.

The following extensions to the present program are suggested:

1. Statistical data for different types of asphalt should be collected to establish firmly the validity of the test.
2. The feasibility of using high-energy neutron activation analysis for the determination of asphalt content should be determined.
3. It may be possible to increase the sensitivity of the neutron bombardment method by using a more prolific source of high-energy neutrons.
4. Similar experiments should be performed with a smaller neutron source and detector tube.

ACKNOWLEDGMENTS

The authors thank William J. Brown, Jr., Paul Sheffert, and Ashok Kapur for their help in performing many of the laboratory tests.

This research was supported by a joint research grant from the U. S. Bureau of Public Roads and the Oklahoma State Highway Department.

REFERENCES

1. Adair, R. K., "Neutron Cross Sections of the Elements." Rev. Mod. Phys. 22: 249-289 (1950).
2. Abraham, H., "Asphalt and Allied Substances." Van Nostrand Co. (1938).
3. "ASTM Standard of Bituminous Materials for Highway Construction, Waterproofing Roofing." ASTM, Philadelphia, Pennsylvania (1957).
4. Fearor, R. E., "Neutron Well Logging." Nucleonics 4:30-42 (1949).

5. Feustal, I. C., and Byers, H. G., "Comparative Moisture-Absorbing and Moisture-Retaining Capacities of Peat and Soil Moistures." U. S. Dept. of Agri. Tech. Bull. 532.
6. Gardner, Wilford, and Kirkham, Don, "Determination of Soil Moisture by Neutron Scattering." Soil Sci. 73:391-401 (1952).
7. Gerdel, R. W., Hansen, E. L., and Cassidy, W. C., "Use of Radio-Isotopes for the Measurement of Water Equivalent of Snow Pack." Trans. Amer. Geophys. Union 31:449-708 (1950).
8. Gruse, W. A., "Petroleum and Its Products." McGraw-Hill, New York (1928).
9. Orear, J., Jr., Rosenfeld, A. H., and Schluter, R. A., "Nuclear Physics Notes from a Course by Enrico Fermi." Univ. of Chicago Press (1949).
10. Pauling, L. "Nature of the Chemical Bond." Cornell Univ. Press (1940).
11. Stone, J. F., Kirkham, D., and Read, A. A., "Soil Moisture Determination by a Portable Neutron Scattering Moisture Meter." Proc. Soil Sci. Soc. of Amer. 19:419-423 (1955).
12. "Mix Design Methods for Hot-Mix Asphalt Paving. Manual Series No. 2." The Asphalt Institute, Univ. of Maryland.
13. Wallace, P. R., "Neutron Distribution in Elementary Diffusion Theory." Nucleonics 4:30-55 (1949).