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Methane Absorption in Oil Shale and Its Potential Mine Hazard

UNITED STATES DEPARTMENT OF THE INTERIOR

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CONTENTS

ILLUSTRATIONS

TABLE

METHANE ABSORPTION IN OIL SHALE AND ITS POTENTIAL MINE HAZARD

by

J. E. Matta,[1] J. C. LaScola,[2] and Fred N. Kissell[3]

ABSTRACT

The Bureau of Mines made laboratory absorption measurements on oil shale samples, which showed that the amount of methane absorbed is proportional to pressure and oil yield, and can be much larger than would be predicted based solely on porosity.

Oil shale cores collected in the field were also measured for their gas content using the Bureau of Mines direct method. Cores taken from deep locations and far from outcrops yielded more gas than cores from shallower locations or at outcrops, when taking into account variations in oil yield, and all data indicate that oil shale mines that are both deep and far from an outcrop will emit low levels of methane gas.

INTRODUCTION

One of the many difficulties faced by any prospective oil shale mine is the possibility that methane gas may seep into the mine, creating an explosion hazard and causing the mine to be classified as gassy under State or Federal laws. Methane has never been detected at existing oil shale mines in Colorado. However, the early history of oil shale mining indicates that at least in some cases methane was detected.

Near the turn of the century oil shale was being mined actively in several parts of the world, most notably in Scotland, where for many years it was the basis of a large industry (4).[4] In 1912, Caldwell (2) reported that "The gases found in shale workings, though not of the volume of those in coal seams, are of an explosive and dangerous character." In Colorado mining officials,

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[2]Mathematician.

[3]Physical research scientist.

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[4]Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

anticipating the possibility of encountering methane, wrote a fire boss inspection requirement for oil shale mines into the State mining regulations of 1919 (9). However, because no methane was ever detected, this requirement was eventually dropped.

Recently, Kissell recognized that the nongassy nature of the existing oil shale mines in Colorado, which are all located at outcrops, might not be a very good indicator of what could be expected for a deeper mine located far from any outcrop. Coal mines located close to or at an outcrop are known to be less gassy than mines in the same bed that are deeper and far from the outcrop. The situation might be the same for oil shale. A preliminary study (7) gave some support to this reasoning, based on three main observations:

1. Drillers working at exploration holes located far from outcrops had observed methane emissions, often from the tuff layers near the oil shale.

2. The trona mines in southwestern Wyoming are gassy, and the gas is thought to originate in the oil shales located near the trona.

3. The Bureau of Mines direct method (8) was applied to two fresh oil shale cores, and both were found to contain low levels of methane. Although their methane contents were considerably less than would be found in fresh coal cores taken from a deep coalbed, they were not negligible.

However, this preliminary study left many questions unanswered. For example, much of the methane might be associated with the porous tuff layers rather than with the oil shale. Nor was it clear to what extent the differences in the methane contents measured by the direct method were due to location (depth, distance to outcrop) and/or to changes in the oil yield of the sample tested. This might be an important factor, since in the case of coal, McCulloch and Diamond (10) have linked increased methane content to an increase in the fixed-carbon content. For other sediments, organic richness is currently used as an indicator of the hydrocarbon source potential, providing information in oil and gas exploration (5).

In this current study, direct-method tests were conducted in the field to measure the methane levels in fresh oil shale cores. In addition, laboratory absorption measurements were made to determine if much more methane is absorbed than can be accounted for by the low oil shale porosity. If this is the case, it would indicate that the oil shale at least had the capacity to act as a source of gas. Moreover, if methane is absorbed, a correlation between methane absorption and oil yield would be sought, because this would be necessary in interpreting results from direct-method tests in the field.

LABORATORY RESULTS

Details of the laboratory experiments are presented in the appendix. The results of these experiments may be summarized as follows:

1. Methane is absorbed by the oil shale. In figure 1 a sample which had been pressured to 200 psig and then reduced to atmospheric pressure released

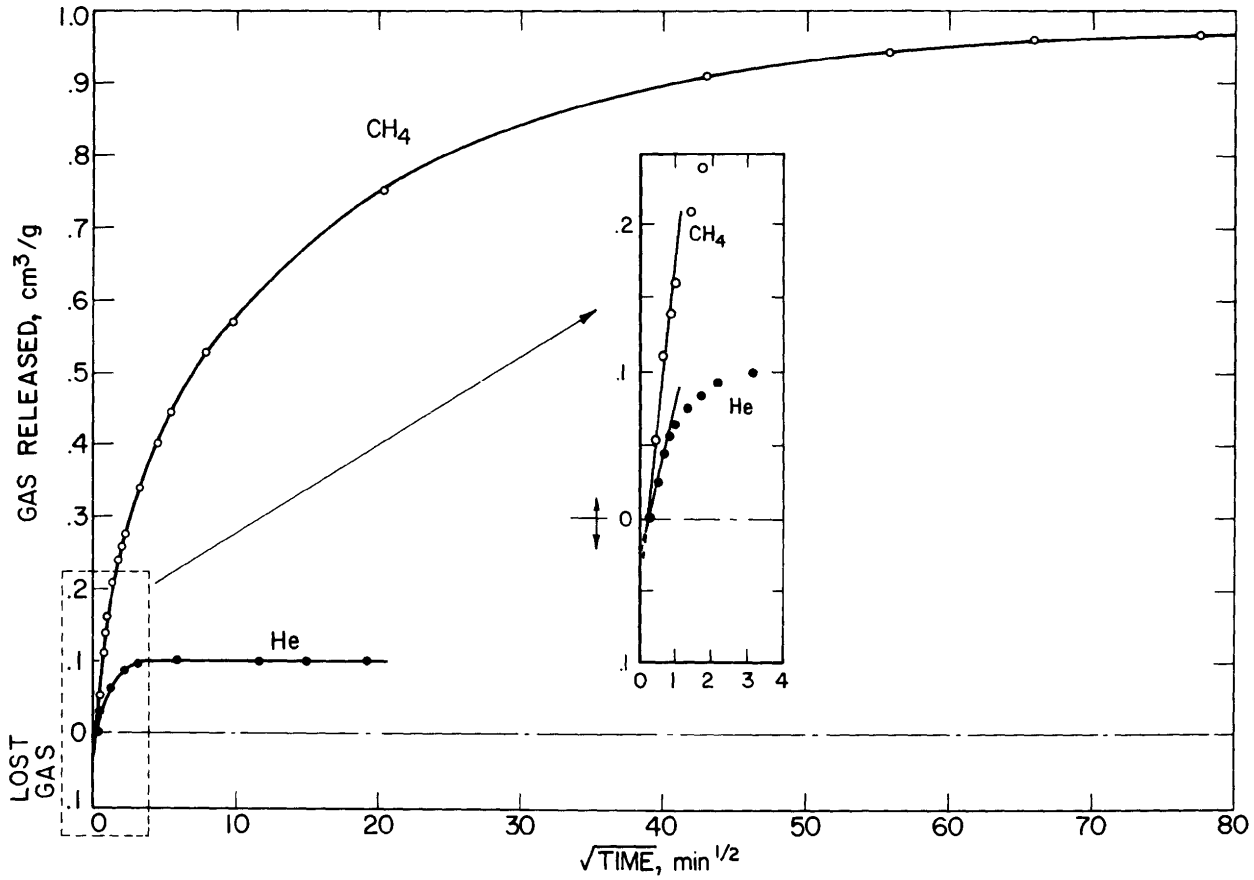

FIGURE 1. - Emission curve for a 50.8-gal/ton oil shale pressured with methane and helium.

10 times more methane than helium under the same conditions. Since helium does not absorb under these conditions, the difference must be attributed to absorption of methane. The amount of methane released from this sample is equivalent to what would be released from a nonabsorbing material with approximately 15 pct porosity.[5]

2. For a given pressure, the quantity of methane released when the pressure is reduced to atmospheric varies linearly with the oil yield of the sample, as measured by the standard Fischer retort method (fig. 2). This indicates that for direct-method samples, the depth and distance to outcrop are not the only factors to be considered in assessing the gas content. Oil yield is also important.

3. For a given oil yield, the quantity of methane released varies linearly with pressure, at least up to about 350 psig (fig. 3).

The results from figures 2 and 3 are combined in figure 4, in which the methane released is given as a function of pressure and oil yield, with the pressure shown as a series of isobars.

[5]For samples with a lower oil yield, the equivalent porosity would be proportionally lower, as indicated by the second result.

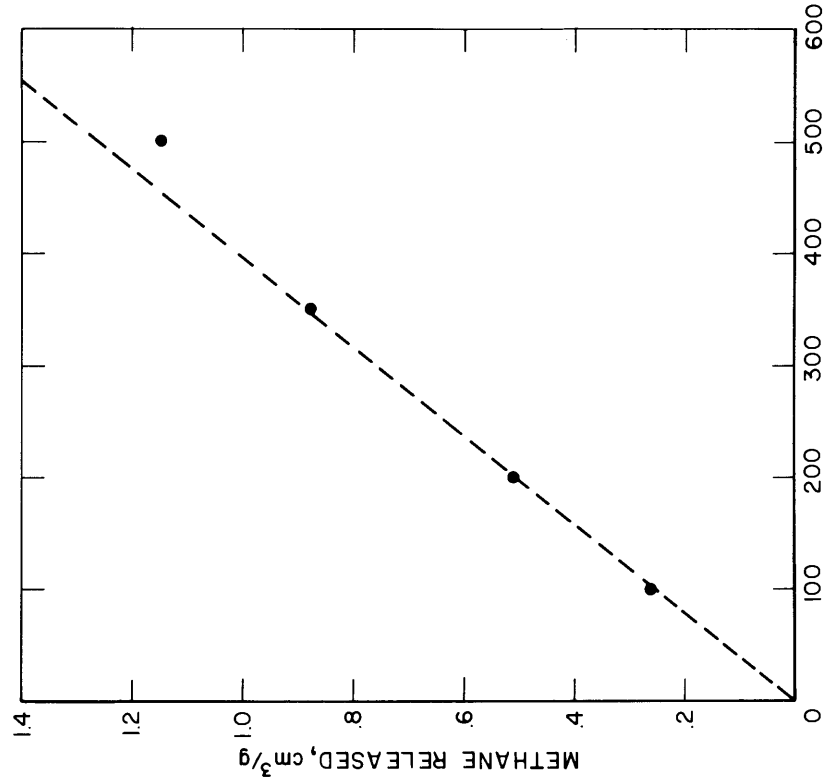

FIGURE 3. - Methane released versus pressure for oil shale with an oil yield of 30.3 gal/ton.

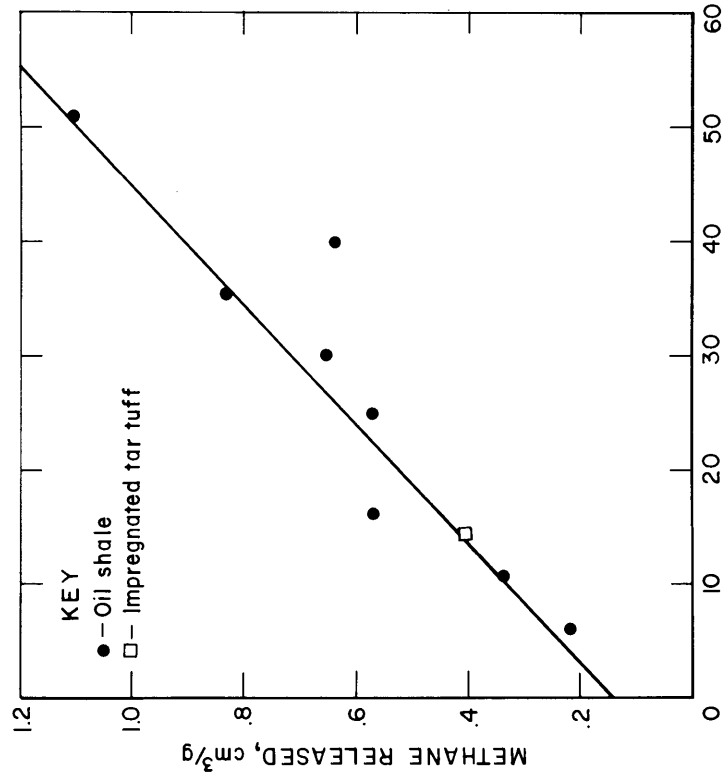

FIGURE 2. - Methane released versus oil yield content for samples pressured to 200 psig.

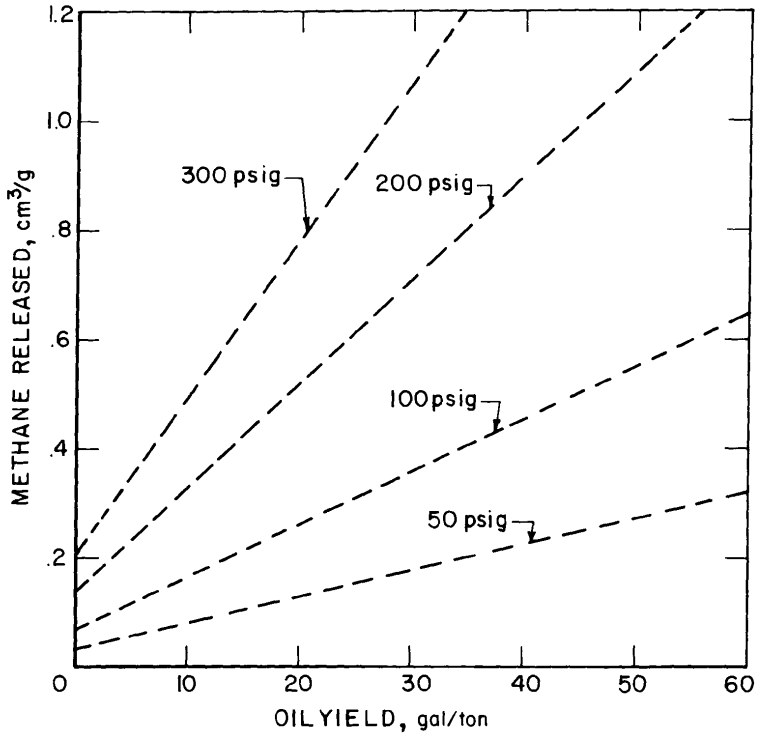

FIGURE 4. - Methane released as a function of oil yield and pressure.

The mechanism by which the methane is held in the oil shale remains unclear, but it is probable that the gas absorbs in the organic material of the shale. The linear relationship between methane released and the oil yield (fig. 2) supports this explanation. One of the laboratory tests was conducted on an impregnated tar tuff which had been ground to a powder. Interestingly, when plotted against oil yield it corresponds with the oil shale samples (fig. 2).

The amount absorbed is also roughly comparable to the methane held in solution in crude oil under similar conditions. For example, results in figure 4 indicate that a 1-ton shale sample with a kerogen yield of 42 gal/ton (1 bbl) will contain,

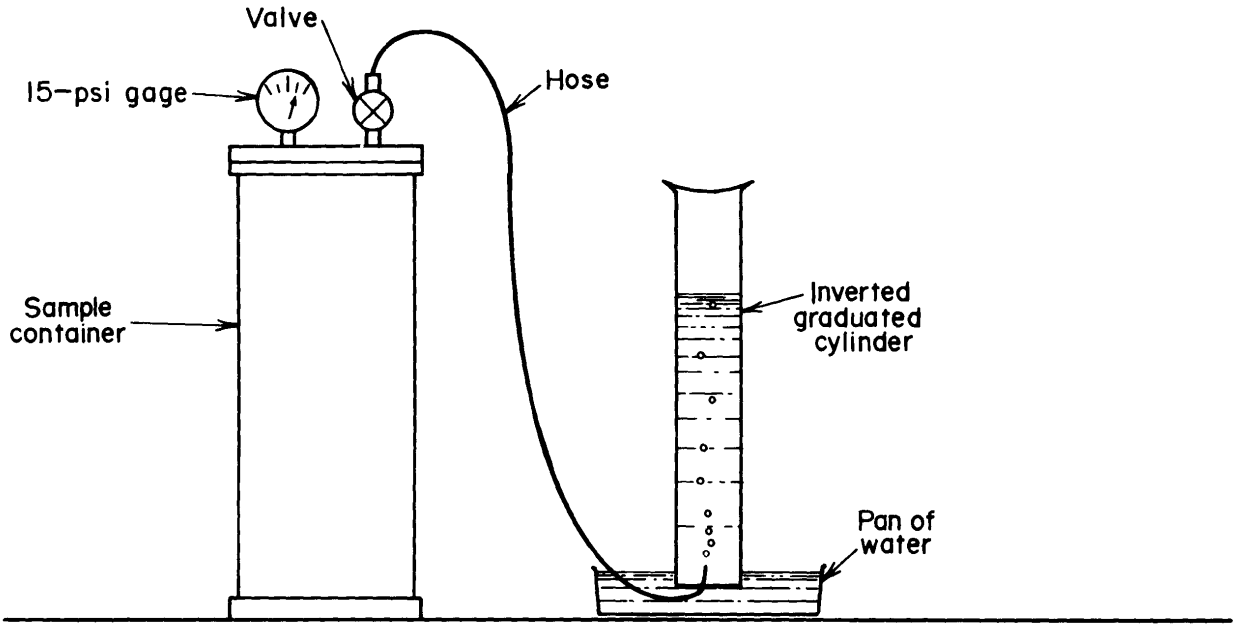

FIGURE 5. - Sample container–gas emission by displacement of water.

at 200 psig, about 0.95 cm^3/g or 30 ft^3 of methane. If, on the other hand, one assumes that the ton of shale contained 42 gal (1 bbl) of crude oil instead of kerogen, the amount of methane held in solution at 200 psig would range from about 15 ft^3 for crude oil with an API gravity of 10 to about 160 ft^3 for crude oil with an API gravity of 60 (12).

FIELD TESTS AND RESULTS

Explanation of the Direct Method

The direct method developed in 1973 by the Bureau was designed as a simple method of estimating the gas content of coalbeds by testing cores taken during exploration drilling (8). The procedure follows:

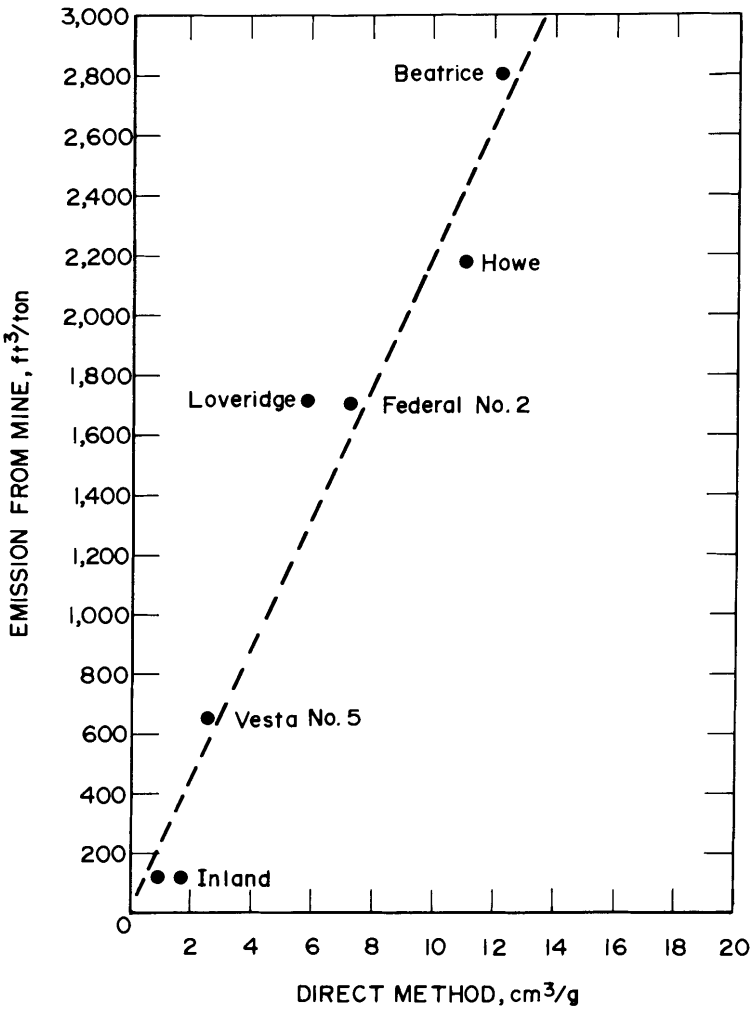

FIGURE 6. - Coalbed gas amount via the direct method versus actual mine emission.

1. A 1-foot piece of coal core is placed in a small container as soon as the core is brought out of the hole.

2. Methane bleeding from the core is measured immediately by bubbling it into an inverted water-filled graduated cylinder (fig. 5).

3. The methane "lost" from the core while it was being brought out of the borehole is calculated by plotting the amount of gas released from the container versus the square root of time, and extrapolating back.

4. Eventually, the core essentially stops bleeding methane, but its residual gas can be measured by crushing the core to a fine powder.

Cores have been desorbed from virgin coal in the vicinity of coal mines to obtain a rough correlation between the gas content of the core and the amount of methane emerging from the nearby mine (fig. 6). Thus

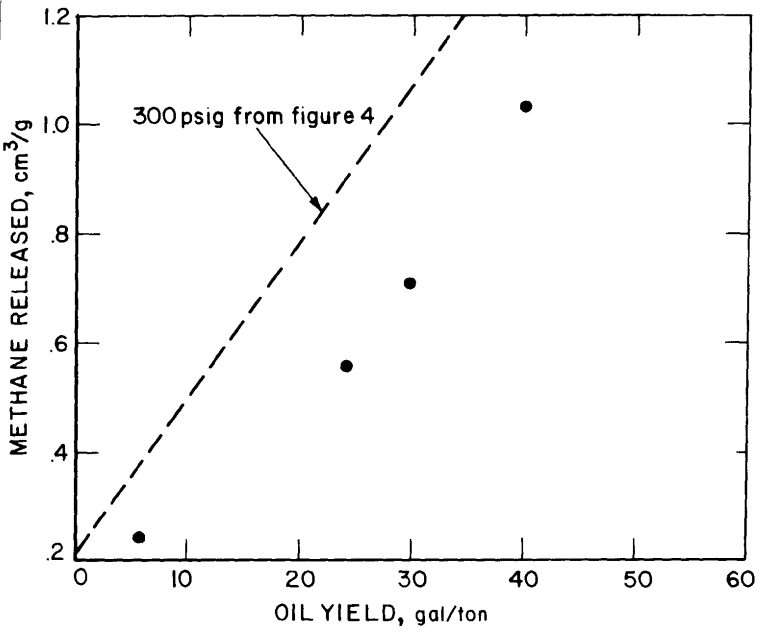

FIGURE 7. - Direct-method field results for cores taken from the same hole out of the Uinta basin.

the direct method can be used to roughly forecast the methane emission of a prospective coal mine when it has reached full production. By analogy, the method was also applied to oil shale cores to obtain some very rough indications of how gassy an oil shale mine might be.

Cores From the Same Hole

Results in the laboratory had indicated that at a given pressure, the amount of methane released was proportional to the oil yield. To determine whether the same would be true of cores taken in the field, the direct method was applied to four oil shale cores taken from a single corehole in the Uinta basin. All were within 20 feet of the Mahogany Marker, which was the mining zone of interest. The overburden depth to the marker was approximately 1,020 feet, and the location was about 5-1/2 miles from an outcrop. After completion of the corehole, the mining zone was partitioned off with packers, and a drill stem equilibrium pressure of approximately 300 psig was measured. Since these cores were all within 20 feet of one another, it was assumed that they all were subjected to about 300 psig pressure. The total[6] gas released for each of the core samples is plotted versus oil yield in figure 7. As in the laboratory test, results from these field samples again indicate that, for a given pressure, the methane released varies linearly with the oil yield of the samples.

The 300-psig isobar from figure 4 is also shown in figure 7 to indicate how much gas would be released from laboratory samples that have been pressured to 300 psig. The direct method samples taken in the field yielded about two-thirds of the gas in this instance.

[6]Of the total gas, the lost gas was 5 pct or less. The gas released from the container in 3 weeks was about 35 pct, and the remaining 60 pct was residual gas released during crushing. The low permeability of the oil shale does not prevent a substantial portion of the gas from seeping from the solid core.

Cores From Different Locations

The four cores from the same location had all presumably been subjected to 300 psig before extraction. Cores taken from shallower depths or locations closer to an outcrop will probably have been subjected to lower methane pressures. Figure 8 gives the methane contents and oil yields of seven additional cores taken at other locations.

Using figure 4 as a guide, various isobars are drawn on figure 8 to represent the results that would be obtained for samples subjected to various pressures in the laboratory. The core that contained the most gas would fall on a 200-psig isobar, the intermediate cores on 65- and 45-psig isobars, and the least gassy on a 0-psig isobar.

It seems from figure 8 that core samples taken from locations that are deeper and farther from outcrops are subjected to higher pressures, and that this, in conjunction with the oil yield, affects the amount of methane released.

A specific example of the effect of overburden depth is shown in figure 8 by the samples taken from the Green River basin. All were taken approximately 20 miles from an outcrop and have roughly the same oil yield, but the gas content of the shale increases markedly with increasing overburden depth.

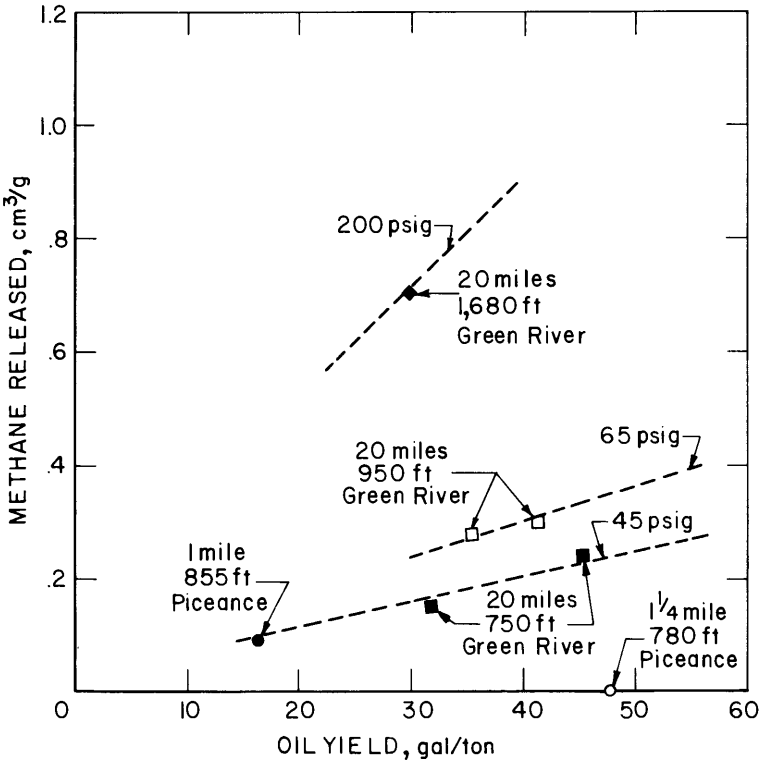

FIGURE 8. - Direct-method field results for seven cores from five locations. (Distance to outcrop, overburden depth, and basin are given for each location.)

Cores From Trona Regions

Methane has been encountered in the trona mines at Green River, Wyo. (7). These mines are classified as gassy and may serve as an indication of what might be expected at certain oil shale mines, since the trona is interbedded with oil shales moderately rich in carbonaceous matter. Most of the gas is encountered when the roof is caved, indicating that it is emitted by the adjacent strata rather than by the trona. Table 1 gives the methane emission characteristics of two of these mines, both of which are about 20 miles from the nearest outcrop.

TABLE 1. - Methane emission characteristics of two gassy trona mines in southwestern Wyoming

	Mine 1	Mine 2
Approximate depth.....feet..	800	1,500
Daily tonnage.....	8,000	10,000
Daily methane.....MMcf..	0.4	2.6
Methane concentration (main returns).....pct..	0.1	0.2
Direct-method results for adjacent shale in 30- to 45-gal/ton range.....cm^3/g..	0.15-0.30	0.70

Of the seven direct-method samples shown in figure 8, five (shown as Green River) were collected near these two trona mines. The sample at 1,680 feet was taken from below the trona at mine 2. The samples at 950 feet were taken from below the trona, and the samples at 750 feet were taken above the trona at mine 1. The fact that mine 1 is shallower and does not intentionally cave the roof could account for its lower gas emission. However, the direct method does indicate that the shale beds adjacent to mine 1 are about a third as gassy as the bed adjacent to mine 2 (table 1).

These Green River samples may be compared with the others collected at different locations. For instance, the two samples listed as Piceance (fig. 8) have less gas, and the four samples listed as Uinta (fig. 7) have similar or higher gas contents.

CONCLUSIONS

Based on this laboratory and field study, the following conclusions can be drawn:

1. Much more methane is absorbed by oil shale than can be accounted for by the low oil porosity. The amount absorbed is proportional to the pressure to which the sample has been subjected and to its oil content. The probable mechanism is absorption in the organic material.

2. The amounts of gas released from oil shale samples in laboratory experiments are roughly comparable to the amounts of gas released from direct-method samples taken in the field.

3. Cores taken from locations that are deeper and far from outcrops yield more gas than those taken at or near outcrops, even after variations in oil yield have been taken into account.

While the present information is hardly conclusive, all the data continue to indicate that oil shale mines that are both deep and far from an outcrop will emit low levels of methane gas. Just what the measured concentrations will be remains to be seen. Since the measured concentrations also depend on the quantity of ventilation air provided for dilution, it would seem that some good ventilation planning is appropriate.

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APPENDIX.--LABORATORY EQUIPMENT AND PROCEDURE

In designing the experiment to measure absorption on oil shale, the approach used by many investigators to measure absorption[1] on coal samples (1, 11) was considered first. In this standard absorption procedure the "dead space," which is the pore volume of the coal plus the "free volume" of the sample chamber, is determined by helium pressure-volume measurements because helium does not absorb. The amount of gas actually absorbed by coal is the total gas released minus the amount of gas that can be accounted for by compression into the dead space. This technique is useful for coal where the amount of methane absorbed is much higher than the quantity compressed into the dead space. However, it was anticipated that only a small quantity of methane would be absorbed by oil shale and that this would be difficult to determine accurately by the standard procedure because of the proportionally larger dead space correction. Accordingly, a simpler apparatus and procedure were developed which also have more inherent accuracy for samples which emit low methane quantities.

The procedure used is an adaptation of the direct-method test used in the field (8). Rather than attempt to measure the amount of gas compressed in the dead space, the approach was to simply bleed it off quickly. Naturally, while the dead space gas is being bled off, the sample begins to lose its absorbed gas. However, if the absorbed gas does not come off too quickly, then the quantity lost during bleed-off is calculated in the same way as the "lost gas" in the direct method.

This approach has the advantages that the free volume of the container does not enter directly into the sorption calculation and that no elaborate sorption apparatus is necessary. Rapid depressurization of the sample canister eliminates the gas that was compressed in the free volume from the sorption measurement, and thus the error associated with its determination. The method has the disadvantage that it only works for materials with very low permeability. If the permeability is too high, the lost gas is too high a proportion of the total. Errors in calculating the lost gas then become dominant.

Rapid depressurization of the sample cylinder causes a temperature drop that can also be a source of error. If the methane in the dead space is cooled slightly, then it will expand as the cylinder returns slowly to room temperature and be measured along with the absorbed gas being released from the sample. To minimize this error, the sample cylinders were filled completely with oil shale, so that the free cylinder volume was usually less than 250 cm^3. Under these conditions, a temperature change of 1° C would correspond to less than a cm^3 change in volume. Tests indicated that rapid depressurization of the cylinder caused less than a 3° C change in the internal temperature, so methane from expansion during warming was less than 3 cm^3. Since the gas released from the samples was in the range 125 to 250 cm^3, the 3 cm^3 was considered to be negligible.

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[1]Strictly speaking, methane is adsorbed in coal rather than absorbed. For a definition, see Jolly (6).

Apparatus

The apparatus consisted of a 500-cm^3 aluminum sample cylinder which could be pressurized to several hundred pounds per square inch, and a common laboratory buret filled with water and inverted into a pan of water. Connected to the sample cylinder along with the buret were helium and methane tanks, an accurate pressure gage, and a vacuum pump (fig. A-1).

Procedure

All eight samples were from the Uinta basin, Utah. Preliminary experiments indicated that if the oil shale was crushed to less than 4 mesh, the samples could reach absorption equilibrium within a few days, yet the lost gas would not be too high.

A crushed sample was placed in the cylinder, which was then evacuated and pressurized with methane to a selected pressure. A valve between the methane tank and the sample cylinder was then closed. As the sample absorbed gas, the pressure in the sample cylinder dropped. Periodically, the valve was reopened to restore the initial pressure. Generally 3 to 4 days were required to complete the absorption, but the sample was always pressurized for at least a week.

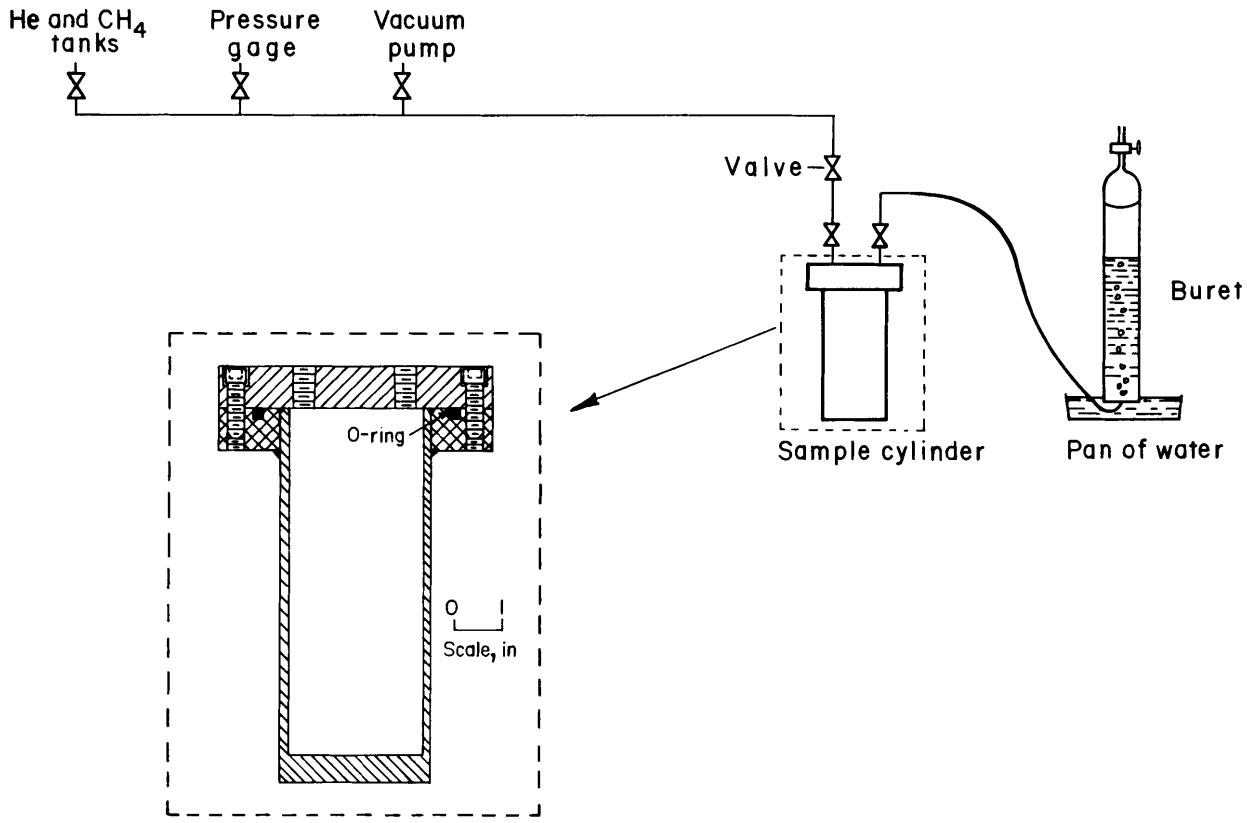

FIGURE A-1. - Apparatus to measure gas in oil shale.

After absorption was complete, the desorption was measured. A second valve on the sample cylinder was opened, and the gas inside was bled into the air through a hose for 5 sec. This was more than enough to bring the internal pressure in the sample cylinder down to atmospheric. Then, the hose was inserted into the water-filled buret so the gas being released from the sample could be measured.

A key assumption of the direct method is that the methane release rate from the sample follows the diffusion equation for spherical particles (3). If this is the case, then the amount released varies linearly with $(\text{time})^{1/2}$ if the time is not too large. This was shown to be true for coal cores extracted from the ground, and was found to be true for the oil shale samples. Therefore, by plotting the amount of gas released versus $(\text{time})^{1/2}$ and extrapolating the initial portion of the curve linearly backwards to zero time (when depressurization began), one can account for the gas lost from the sample during depressurization. The loss was not large; for example, it was about 0.025 cm^3/g for the sample in figure 1. The "methane released" values in figures 2, 3, and 4 include this "lost" methane. Results from repeated tests were within 5 pct.

To determine whether the methane released could be accounted for by porosity rather than actual absorption, the procedure was repeated using helium, which is known not to absorb. The helium released was much less, indicating that methane is absorbed by the oil shale.

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