

Evaluation of Devonian Shale With New Core and Log Analysis Methods

D.L. Luffel, SPE, and F.K. Guildry, SPE, ResTech Houston, and J.B. Curtis,* SPE, Consultant

Summary. Results of this study of Appalachian basin Devonian shale show that all porosity exceeding 2.5% is occupied by free hydrocarbon (mostly gas). From analyses of logs and 519 ft of conventional core in four wells, reservoir porosity averages 5% and free-gas content averages 2% by bulk volume.

Introduction

There is a growing interest in shale formations in selected areas of the U.S. as potential commercial gas and oil reservoirs. An example is the Devonian shale in the Appalachian basin, which is considered a major potential gas source. The Gas Research Inst. (GRI) sponsored a research program to improve the understanding of formation evaluation and reservoir description in shales and to enhance well productivity and gas recovery through better well completions and stimulation methods. Four air-drilled wells were completed recently in the Devonian shale. Extensive formation evaluation data, including 519 ft of conventional cores, were collected from these wells. Designated comprehensive study wells (CSW's), the four wells are located in Kentucky and West Virginia.

One purpose of the CSW program was to develop new formation evaluation methods to identify gas-producing intervals both for deliverability and reserves with logging tools. Significant progress has been made.¹⁻⁴ A key element of these new evaluation methods is to establish the reservoir rock and fluid properties through careful core analyses and then to develop the log interpretation methods necessary to match core and production results. New core analysis methods had to be developed to provide accurate measurements of reservoir porosity, gas, oil, and water content.⁴⁻⁶ These new methods involve crushing the rock samples before extraction, drying, and measuring porosity. In the black, organic-rich shales present in these wells, porosities measured with the new methods were higher by more than a factor of 3 and free-gas contents were higher by up to a factor of 20 compared with conventional methods.

Through use of these new core and log analysis methods, an extensive database was developed for reservoir description in the four CSW wells. Several important features have emerged from interpretation of these data. Results are presented from a relatively new plotting method that relates bulk volume of hydrocarbon to porosity. This valuable

tool has provided useful insight into the fluid distribution present in the reservoir and clearly indicated the minimum porosity required to store free hydrocarbons. Also, this plotting method leads to a means of determining formation resistivity factor as related to porosity and of controlling quality to monitor core and log analysis results.

In the Devonian shale, an important part of formation evaluation by log analysis is to determine the amount of kerogen present because kerogen appears as hydrocarbon-filled porosity on conventional logs. In this study, total organic carbon (TOC) and pyrolysis analyses were made on 93 core samples from the four CSW wells. A new method was used to derive volumetric kerogen and oil content. Results (shown here) then were used to derive kerogen from the uranium response of the spectral gamma ray log. In addition, free-oil content is shown to relate to kerogen content. This is useful in partitioning the reservoir free gas and oil because they are indistinguishable from logs in the Devonian shale.

Finally, results of salinity measurements made directly on 50 core samples from the CSW wells are shown to determine formation water salinity for log analysis. This information is very important because formation water rarely is produced from the Devonian shale.

Porosity and Fluid Content

In the new method of core analysis,⁶ a whole core piece (about 300 g) is weighed, bulk volume is measured by immersion in mercury, and bulk density with contained fluids is calculated. The core piece is then crushed and blended, and a measured weight of about 100 g is taken with a sample splitter. The crushed sample is extracted with toluene (Dean Stark) for 1 to 2 weeks and dried at 230°F for 1 to 2 weeks until stable. The grain volume is then measured with helium. Crushed-sample bulk density is presumed to be the same as that measured on the whole core piece. The bulk volume of the crushed sample is

$$V_b = W_w / \rho_b \quad (1)$$

Porosity is then calculated from

$$\phi = (V_b - V_g) / V_b \quad (2)$$

*Now at the Colorado School of Mines.

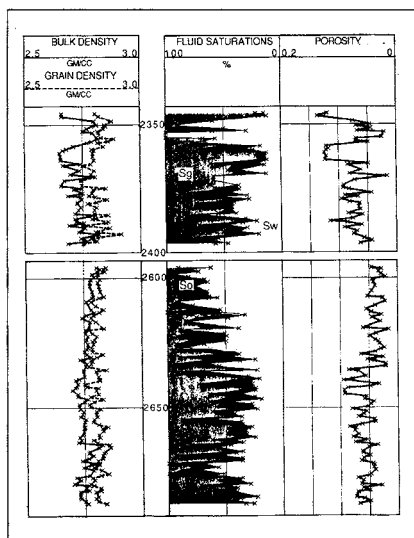


Fig. 1—Core analysis results, CSW No. 4A.

Note that the calculated porosity is at ambient conditions and needs to be decreased somewhat to correct to overburden stress.⁵ Water saturation is calculated from the water collected in the Dean Stark apparatus. Oil content is determined by subtracting the weight of distilled water collected from the total weight loss of the crushed sample after drying. In these analyses, oil density, which is not known, was presumed to be 1.0 g/cm³ to calculate volume. Because all the CSW wells were drilled with air-mist and the cores were preserved at the wellsite, the fluid saturations in the core should represent those in the reservoir after appropriate correction for compaction to reservoir stress.

Overall Core Analysis Results. Fig. 1 shows an example of the core analysis results from the new procedure for ϕ , S_o , S_w , S_g , ρ_b , and ρ_g done foot-by-foot in the Ashland-Evans No. 91 (CSW No. 4A), Breathitt County, KY, for the cored sections in the Cleveland shale and the Middle and Lower Huron members of the Ohio shale. The reservoir property of most economic interest is bulk volume content of hydrocarbon, which is $\phi(S_o + S_g)$. This is presented as a function of porosity alone in Fig. 2. The plot is a variation of one found useful in presenting results from capillary pressure measurements on cores.^{7,8} Note that bulk volume of water can be shown as the difference $\phi - V_{bh}$. These core data show an excellent correlation with the best-fit reduced-major-axis (RMA) line shown and display a relatively constant value of bulk volume of water independent of porosity and depth over the cored intervals. The extrapolated best-fit line suggests that, for porosity less than 2.5% on average no free hydrocarbons are present, and on average all porosity greater than 2.5% is occupied by hydrocarbons. These results also suggest that the water saturations present are at irreducible levels and, from previous limited data,⁵ capillary pressures of about 1,000 psi are present.

Fig. 3 is a similar plot of bulk volume of gas as related to porosity, based on core analyses, for CSW No. 2 in the Lower Huron formation. In this well, very little kerogen and free oil are present, so the bulk volume of gas is identical to the bulk volume of hydrocarbon. Although the data show more scatter, the RMA line shows a trend similar to that in Fig. 2 with irreducible bulk volume of water of about 3% on average. Fig. 4 shows the core analysis results for CSW No. 5. Again, a similar trend is evident with irreducible bulk volume of water of about 2% to 2.5% on average.

Fig. 5 presents core analysis results from CSW No. 1A, the fourth well drilled and analyzed, with best-fit line as shown. Because this trend is different from the others, companion sample splits were rerun with extra care taken with the laboratory procedures. Fig. 6 shows the new results. The data now show the best correlation of any of the four wells with an irreducible bulk volume of water of 2.5% on average. Scatter in the other three wells probably would also improve with the revised laboratory procedures now used.

Comparison of Log and Core Analyses.

Log analysis methods have been developed especially for the Devonian shale.⁴ Because most of the wells in the Appalachian basin are air-drilled, an empty-hole logging program must be used, which limits the number of log measurements. The 13 constituents (including porosity) of the Devonian shale were grouped into five major components: quartz, illite, pyrite, kerogen, and porosity. These can be determined from the density, sidewall neutron, photoelectric effect, and natural gamma ray uranium log responses. Water saturation is then determined from the induction log resistivity with the standard Archie equation. Values of 1.7 for the cementation and saturation exponents have been found to give the best results compared with core analysis water saturations. Formation-water salinity, discussed shortly, also is an important component of the calculation of water saturation.

Fig. 7 compares log and core analysis results for the cored sections of CSW No. 4A. The mineral fraction makeup of the rock determined from logs is also shown. There is generally good agreement between log and core analyses, with best agreement for the bulk volume of water. However, the core analysis results shown were measured at ambient conditions, so both ϕ and bulk volume of gas need to be decreased about 0.5 to 1.0 porosity unit to correct to reservoir stress.⁵ Average ϕ , bulk volume of hydrocarbon, and bulk volume of water from core analyses, ambient and adjusted to reservoir stress, are compared with results from log analyses in all CSW wells in Table 1. There is generally good agreement, especially considering the low porosity values involved.

Kerogen and Free Oil

Kerogen, a major constituent of the Devonian shale, is important to determine because

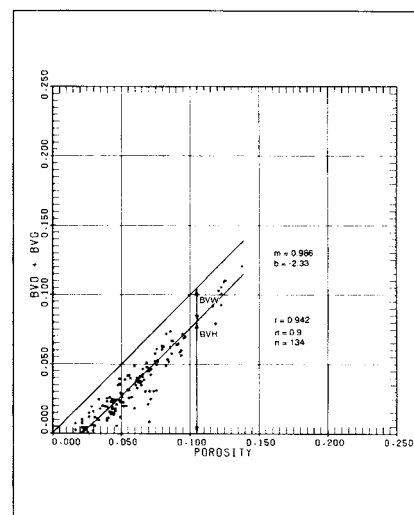


Fig. 2—Relationship of bulk volume of hydrocarbon to porosity from core analyses, CSW No. 4A.

it appears as hydrocarbon-filled porosity on conventional logs. One task in this study was to determine kerogen quantitatively from core analyses and then to develop a reliable log analysis method to solve for the kerogen volume. The kerogen volume was determined initially from thin-section point count of core plug end trims. Geochemical measurements of TOC and rock evaluation pyrolysis were made simultaneously on a wide range of core samples to evaluate source rock potential of the basin.⁹⁻¹² These measurements generally have not been used to determine precise kerogen volumes. However, a fairly simple relationship of kerogen volume to TOC was developed in this study. It involves a small correction based on the free oil present, S_1 , determined by pyrolysis.¹³ Eq. 3 is used to solve for kerogen volume:

$$V_k = [(C_t - S_1 C_{s1}) / C_k] \rho_b / \rho_k \quad \dots \dots (3)$$

Values for C_{s1} , C_k , and ρ_k are not yet well-established for the Devonian shale, so they were approximated with 0.87, 0.78, and 1.0, respectively. In general, these values are likely to depend on the level of thermal maturity and the source of the kerogen.

Through use of Eq. 3, kerogen volume was calculated on 93 samples from the four CSW wells. Table 2 summarizes results of the TOC and free oil from pyrolysis measurements, along with calculated kerogen volumes. Bulk volume of oil was derived directly from S_1 , which is the oil distilled during pyrolysis below 572°F, where $V_{bo} = \rho_b S_1 / \rho_o$, with ρ_o presumed to be 1.0. Kerogen volume in some of the black, organic-rich shales ranges from 8% to 26%. On one set of 10 samples from the CSW No. 4A, V_k calculated from Eq. 3 averaged 17.1%, whereas kerogen volume from thin-section on companion samples averaged only 10.7%. Reasons for this difference are not clear. When measured values of C_{s1} , C_k , and especially ρ_k are better established, some of this difference may be resolved.

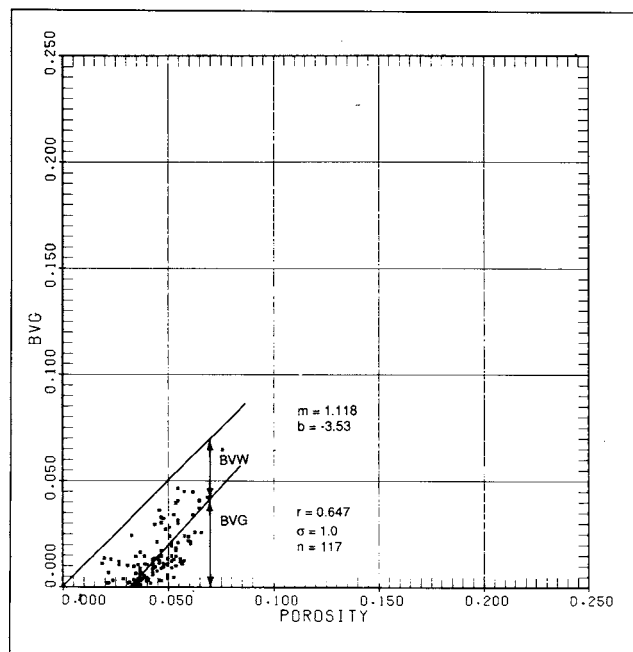


Fig. 3—Relationship of bulk volume gas to porosity from core analyses, CSW No. 2.

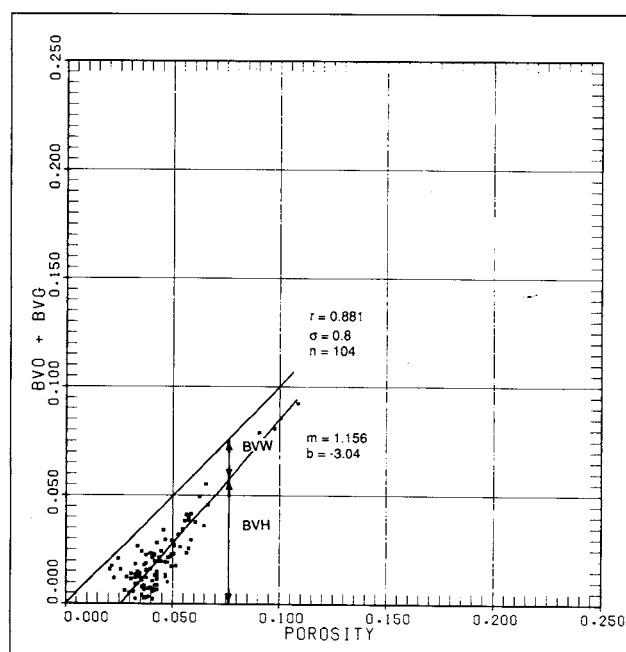


Fig. 4—Relationship of bulk volume of hydrocarbon to porosity from core analyses, CSW No. 5.

There appears to be a fairly good relation of bulk oil volume to kerogen volume within each well or within formation units. From Table 2, the ratio of bulk volume of oil to V_k varies over a fairly narrow range of 0.05 to 0.1. Because this ratio is important to partition the oil and gas present in the bulk hydrocarbons as determined from log analysis, work is in progress to map TOC and S_1 information in the study area.

To determine kerogen volume from log responses, the kerogen volume determined from core samples was correlated with uranium response from the natural spectral

gamma ray log on several wells in the study. Fig. 8 shows this correlation, which is similar to one reported previously.⁴

Formation-Water Salinity

To calculate water saturation from log analysis, it is important to establish formation-water salinity. Because formation water rarely is produced from the Devonian shale, water salinity is essentially unknown. Through use of the cores from the air-drilled CSW's, the water salinity was measured directly on crushed core samples. A sample split of 20 g of crushed rock was mixed and equilibrat-

ed with 100 mL of ion-free distilled water. Chloride ion was then measured on a water sample with an ion chromatograph and, in some cases, by titration. This chloride content was then converted to sodium chloride and allocated back to the bulk volume of formation water measured in a companion crushed sample with the analysis procedures described previously.

Table 3 summarizes the salinities determined for each CSW. For CSW No. 2, the data are less precise because chloride measurements were made on samples adjacent to the whole core pieces used for water-content

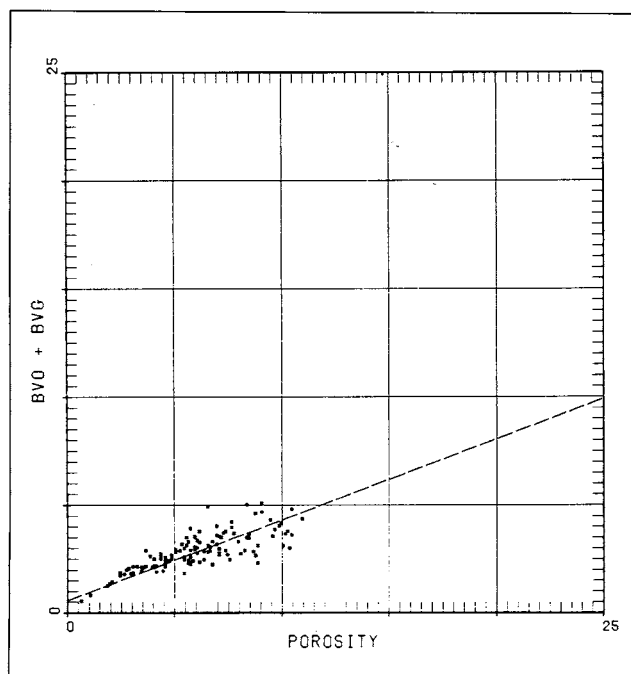


Fig. 5—Relationship of bulk volume of hydrocarbon to porosity from core analyses, CSW No. 1A.

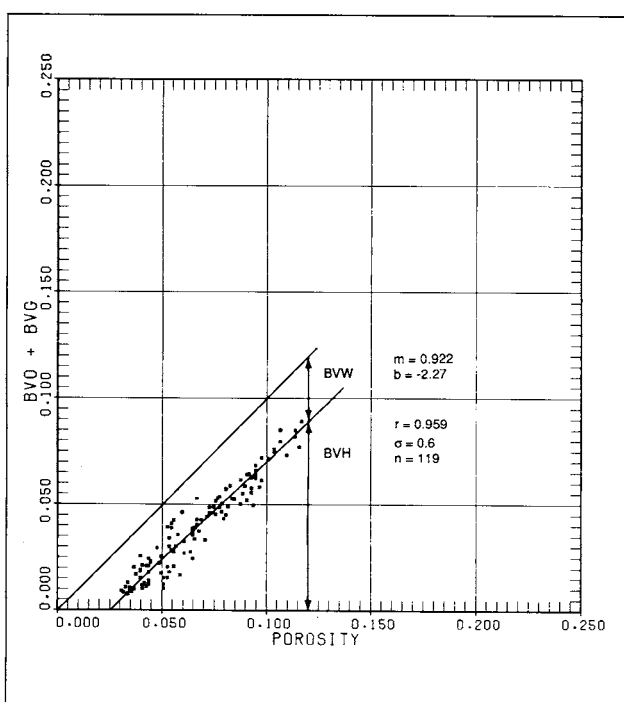


Fig. 6—Results from rerun of core analyses, CSW No. 1A.

measurements rather than on a companion crushed sample. Overall, a wide range of water salinities is present. Results for CSW Nos. 2 and 4A initially were thought to vary because of experimental uncertainties. In CSW Nos. 5 and 1A, however, it became evident that real differences are present. This is illustrated for CSW No. 1A in Fig. 9, which shows water salinity measured throughout the cored interval from 15 core samples. Also shown for comparison are the gamma ray and induction log curves, as well as kerogen calculated from log analysis. Water salinity varies from 19,000 to 222,000 ppm NaCl and seems to be linked with changes in formation resistivity, R_f , and kerogen volume. Especially surprising is the rapid change in salinity over very short distances, such as from 3,179 to 3,185 ft.

Fig. 10 shows the apparent linkage of water salinity to R_f . This relates formation-water conductivity, C_w , at 125°F from the salinity measured on 35 crushed core samples to R_f from logs at the same depth as the core samples for CSW Nos. 1A, 4A, and 5. Data from CSW No. 2 are not included because data quality is poorer. Although there is substantial scatter about the best-fit line in Fig. 10, the correlation is significant. Because core analyses showed water content (bulk volume of water) to vary only over a fairly limited range, the primary cause in variation of R_f seems to be variation in C_w . For these same 35 core samples, TOC and pyrolysis measurements were performed on companion sample splits. Kerogen volumes were calculated as described previously. Fig. 11 shows the relation of C_w to V_k for these data. Correlation of C_w to V_k , although still significant, is not as strong as for C_w to R_f . Currently, the cause of this salinity variation and its correlation with V_k are not understood. As a corollary to the linkage of C_w to R_f , and C_w to V_k , Fig. 12 shows the relation of R_f from log response to V_k calculated from the uranium curve of the spectral gamma ray log (with the correlation in Fig. 8) for the Devonian shale sections logged in CSW Nos. 1A, 4A, and 5. The general trend is that, for black, organic-rich shales (high V_k), there is high R_f that is related to low salinity (low C_w); for gray shales with low organic content (low V_k), there is low R_f that is related to high salinity (high C_w). From the linkage of R_f to C_w and from the fact that bulk volume of water is relatively constant, there is also information implied regarding rock electrical properties. This is currently under study.

Conclusions

1. In the Devonian shale in the Appalachian basin, all porosity greater than about 2.5% is occupied by hydrocarbons, mostly gas. Reservoir porosities average about 5% and free-gas contents average about 2%.
2. The Devonian shale appears everywhere to be at irreducible water content.
3. A new method was developed to determine kerogen volume from TOC and pyrolysis of core samples, with kerogen of

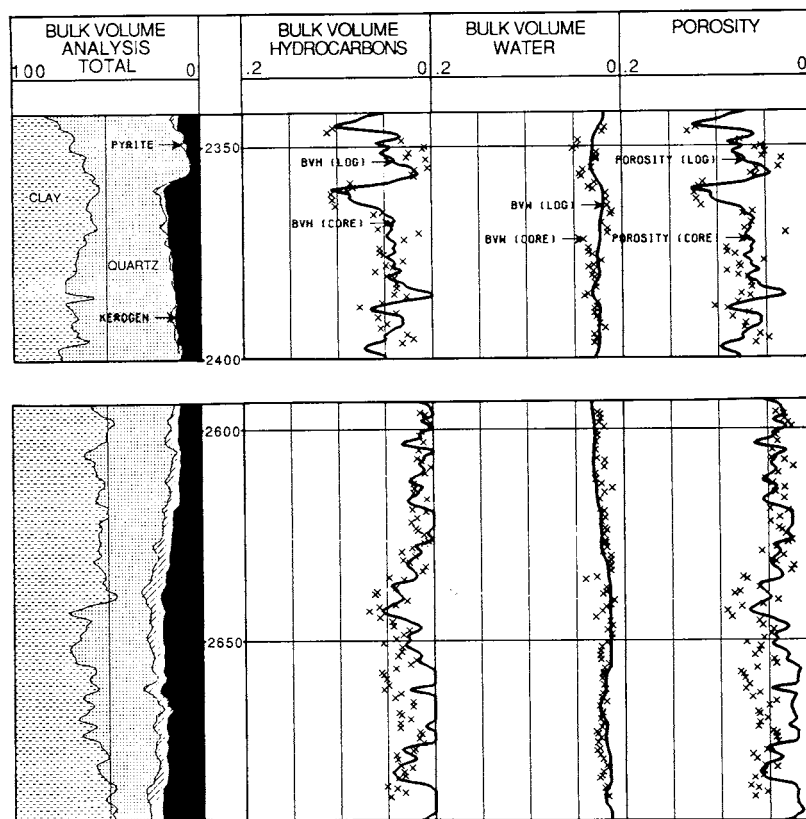


Fig. 7—Comparison of core and log analysis results, CSW No. 4A.

TABLE 1—COMPARISON OF LOG AND CORE ANALYSES

	Core		Log
	Ambient	Adjusted	
CSW No. 2			
Lower Huron			
Bulk volume of hydrocarbon, %	1.5	0.8	0.7
Bulk volume of water, %	3.0	3.0	3.2
ϕ , %	4.5	3.8	3.9
CSW No. 4A			
Cleveland			
Bulk volume of hydrocarbon, %	4.9	4.2	4.5
Bulk volume of water, %	2.8	2.8	2.6
ϕ , %	7.7	7.0	7.1
Lower Huron			
Bulk volume of hydrocarbon, %	3.0	2.3	1.6
Bulk volume of water, %	2.2	2.2	2.2
ϕ , %	5.2	4.5	3.8
CSW No. 5			
Lower Huron			
Bulk volume of hydrocarbon, %	2.3	1.6	2.0
Bulk volume of water, %	2.2	2.2	2.7
ϕ , %	4.5	3.8	4.7
Java			
Bulk volume of hydrocarbon, %	1.4	0.7	1.2
Bulk volume of water, %	2.8	2.8	2.4
ϕ , %	4.2	3.5	3.6
CSW No. 1A			
Middle Huron			
Bulk volume of hydrocarbon, %	3.0	2.3	2.3
Bulk volume of water, %	2.5	2.5	2.5
ϕ , %	5.5	4.8	4.8
Lower Huron			
Bulk volume of hydrocarbon, %	5.3	4.6	4.0
Bulk volume of water, %	3.3	3.3	2.2
ϕ , %	8.6	7.9	6.2

TABLE 2—SUMMARY OF GEOCHEMICAL PROPERTIES FOR DEVONIAN SHALES

	Samples	TOC (wt%)	S ₁ (g/g)	Kerogen (vol%)	Bulk Volume of Oil (%)
CSW No. 2					
Lower Huron	15	0.34	0.00021	1.1	0.1
CSW No. 4A					
Cleveland	10	5.08	0.00324	15.0	0.8
Lower Huron	25	5.04	0.00435	15.0	1.1
CSW No. 5					
Lower Huron	13	3.60	0.00246	10.9	0.8
Java	7	0.71	0.00057	2.2	0.2
CSW No. 1A					
Middle Huron	14	1.72	0.00180	5.2	0.5
Lower Huron	9	4.45	0.00490	12.9	1.2

TABLE 3—SUMMARY OF FORMATION-WATER SALINITY MEASUREMENTS FROM CORE ANALYSES

	Samples	Salinity (1,000 ppm NaCl)	
		Average	Range
CSW No. 2			
Lower Huron	10	49	12 to 102
CSW No. 4A			
Cleveland	2	71	57 to 85
Lower Huron	13	72	32 to 114
CSW No. 5			
Lower Huron	7	71	41 to 92
Java	3	192	161 to 210
CSW No. 1A			
Middle Huron	9	136	85 to 222
Lower Huron	6	48	19 to 90

up to 26% in this study. Kerogen volume correlates well with uranium response from the spectral gamma ray log.

4. Formation-water salinity was measured directly on core samples and ranges from 19,000 to 222,000 ppm NaCl. Salinity variations correlate well with formation resistiv-

ity and to some extent with kerogen volume, but reasons for these variations are unclear.

Nomenclature

b = intercept of regression line
 C_k = carbon in the kerogen, weight fraction

C_{s1} = carbon in the free oil, weight fraction
 C_t = TOC in the rock sample, weight fraction
 C_w = formation-water conductivity, Ω/m
 m = slope of regression line
 n = number of data points
 r = correlation coefficient
 R_t = formation resistivity, $\Omega \cdot \text{m}$
 S_g = gas saturation, fraction
 S_o = oil saturation, fraction
 S_w = water saturation, fraction
 S_1 = free oil in the rock sample, weight fraction
 V_b = bulk volume of crushed sample, mL
 V_{bh} = bulk volume of hydrocarbon, fraction
 V_{bo} = bulk volume of oil, fraction
 V_g = grain volume of crushed sample, mL
 V_k = kerogen volume in rock sample, fraction
 W_w = weight of wet, crushed rock sample, g
 ρ_b = bulk density, g/cm^3
 ρ_g = grain density, g/cm^3
 ρ_k = density of kerogen, g/cm^3
 ρ_o = density of oil, g/cm^3
 σ = standard deviation
 ϕ = porosity, fraction

Acknowledgment

This work was performed for and funded by the GRI under Contract No. 5086-213-1390, supervised by Richard J. Scheper under the management of Rich A. McBane.

References

1. Campbell, R.L. and Truman, R.B.: "Formation Evaluation in the Devonian Shale," paper

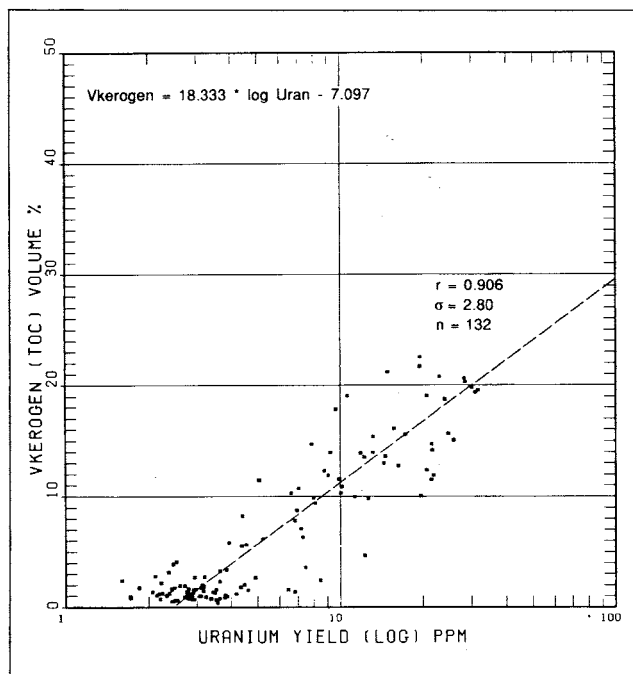


Fig. 8—Volume of kerogen from core analyses (TOC) vs. the uranium yield from the spectral gamma ray log.

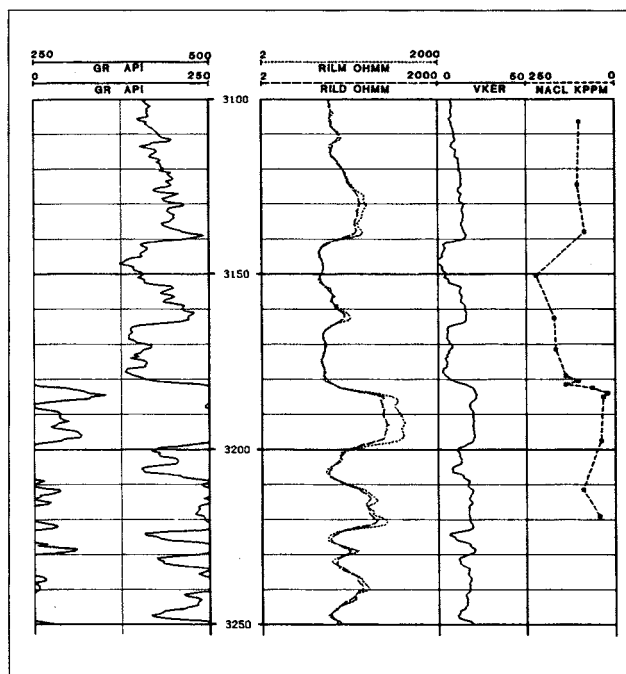


Fig. 9—Comparison of formation-water salinity from core analyses with R_t and V_k from logs, CSW No. 1A.

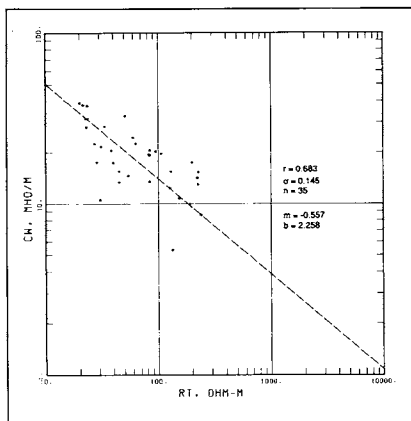


Fig. 10—Formation-water conductivity from core analyses as related to formation resistivity from logs, data from CSW Nos. 1A, 4A, and 5.

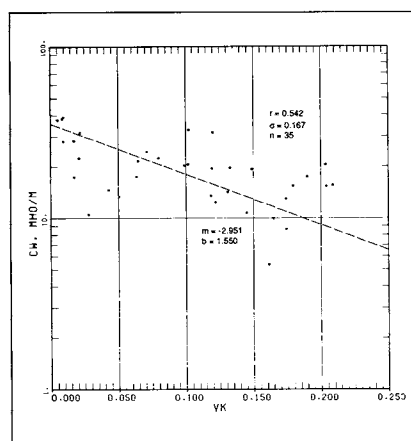


Fig. 11—Formation-water conductivity as related to kerogen volume for 35 core samples from CSW Nos. 1A, 4A, and 5.

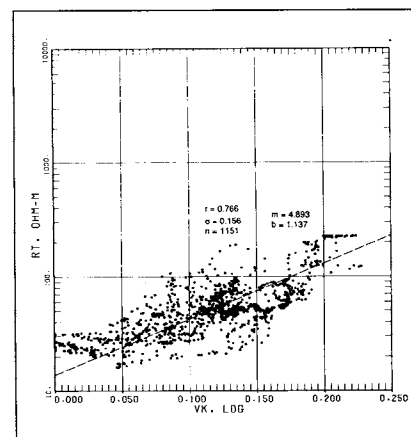


Fig. 12— R_t as related to V_k calculated from logs in the cored intervals of CSW Nos. 1A, 4A, and 5.

SPE 15212 presented at the 1986 SPE Unconventional Gas Technology Symposium, Louisville, KY, May 18–21.

2. Campbell, R.L.: "A Devonian Shale-Specific Formation Evaluation Log," *GRI Eastern Devonian Shale Technology Review* (Oct. 1987).
3. McBane, R.A., Campbell, R.L., and Truman, R.B.: "Comparison of Diagnostic Tools for Selecting Completion Intervals in Devonian Shale Wells," *JPT* (Feb. 1988) 187–96.
4. Guidry, F.K. *et al.*: "Devonian Shale Formation Evaluation Model Based on Logs, New Core Analysis Methods, and Production Tests," *Proc.*, SPWLA Annual Logging Symposium (1990) paper NN.
5. Luffel, D.L. and Guidry, F.K.: "Reservoir Rock Properties of Devonian Shale From Core and Log Analysis," paper 8910 presented at the 1989 Soc. of Core Analysts Annual Symposium, New Orleans, Aug. 2–3.
6. Luffel, D.L. and Guidry, F.K.: "New Core Analysis Methods for Measuring Rock Properties of Devonian Shale," *JPT* (Nov. 1992) 1184–90.
7. Heseldin, G.M.: "A Method of Averaging Capillary Pressure Curves," *Proc.*, SPWLA Annual Logging Symposium (1974) paper E.
8. Alger, R.P., Luffel, D.L., and Truman, R.B.: "New Unified Method of Integrating Core Capillary Pressure Data With Well Logs," *SPEFE* (June 1989) 145–52.
9. "Geochemical Report, GRI-CSW No. 2 Well, Calhoun County, West Virginia," GRI Devonian Shale Program, Chicago (March 1, 1988).
10. Curtis, J.B.: "Report of Geochemical Analyses, E.J. Evans No. 91, Breathitt County, Kentucky," GRI Devonian Shale Program, Chicago (Oct. 19, 1988).
11. Curtis, J.B.: "Report of Geochemical Analyses, Peake Energy No. 753, Jackson County, West Virginia," GRI Devonian Shale Program, Chicago (Oct. 19, 1988).
12. Curtis, J.B.: "Report on Geochemical Analyses, E.J. Evans No. 91, Breathitt County, Kentucky, and Peake Energy No. 753, Jackson County, West Virginia," GRI Devonian Shale Program, Chicago (Feb. 8, 1989).
13. Peters, K.E.: "Guidelines for Evaluating Petroleum Source Rock Using Programmed Pyrolysis," *AAPG Bulletin* (March 1986) 70, No. 3, 318–29.

SI Metric Conversion Factors

$$\begin{aligned} ^\circ\text{API} &= 141.5 / (131.5 + ^\circ\text{API}) = \text{g/cm}^3 \\ \text{ft} \times 3.048^* &= \text{m} \\ ^\circ\text{F} &= (^\circ\text{F} - 32) / 1.8 = ^\circ\text{C} \\ \text{psi} \times 6.894757 &= \text{kPa} \end{aligned}$$

*Conversion factor is exact.

Provenance

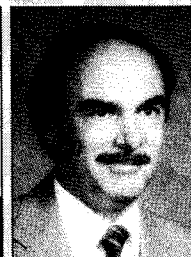
Original SPE manuscript, *Evaluation of Devonian Shale With New Core and Log Analysis Methods*, received for review Oct. 31, 1990. Revised manuscript received Feb. 20, 1992. Paper accepted for publication April 14, 1992. Paper (SPE 21297) first presented at the 1990 SPE Eastern Regional Meeting held in Columbus, OH, Oct. 31–Nov. 2.

JPT

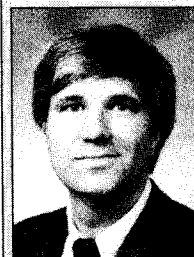
Authors



Luffel



Guidry



Curtis

Donald L. Luffel has been an interpretation specialist at ResTech Houston Inc. for 6 years. He previously worked at Exxon Co. U.S.A. for 37 years in research and operations in reservoir engineering and formation evaluation, primarily

in early evaluation of new reservoirs. Luffel was a member of the 1980–83 Editorial Review Committee and technical program committees for the 1975 and 1977 Annual Meetings. He holds a BS degree in chemical engineering from the U. of Kansas. **Francis K. Guidry**, ResTech Houston vice president, performs formation evaluation services on single wells and multiwell field studies and is manager of a GRI Devonian Shale Project. He was a 1985–86 member of the Editorial Review Committee. Guidry holds a BS degree in electrical engineering from the U. of Southwestern Louisiana. **John B. Curtis** is an associate professor in the Dept. of Geology & Geological Engineering and director, Potential Gas Agency/Inst. for Energy Resource Studies at the Colorado School of Mines, Golden. His research interests include petroleum geochemistry, formation evaluation of fractured reservoirs, and assessment of hydrocarbon resources. Before joining the Colorado School of Mines, Curtis worked at Texaco Inc., Columbia Gas, and Exlog/Brown & Root Laboratories. He holds BA and MS degrees from Miami U. and a PhD degree from Ohio State U., all in geology.