3426.1/B-6934/DT/84/01/03/0

Distribution: w/o enclosure
File: ✓ (B-6934)
WMEG r/f
NMSS r/f
REBrowning
MJBell
JTGreeves
DTiktinsky & r/f
SNeuder
HJMiller
JOBunting
MRKnapp
PSJustus
PDR
LPDR (B,S,N)

JAN 10 1984

Mr. Earle Amey
U.S. Bureau of Mines
Division of Minerals, Health and
Safety Technology
2401 E. Street, N.W.
Washington, D.C 20241

Dear Mr. Amey:

Attached for review by the Methane Control group of the Bureau of Mines (BOM) under the interagency agreement (NRC-02-80-075) between the BOM and the Nuclear Regulatory Commission are the following documents:

1) Report entitled Methane Gas production testing in the vicinity of the candidate Repository Site.

2) Report covering the possibility of a methane accumulation under the Reference Repository Location Hanford Site.

3) Consultant report from Roger King, BOM

The NRC's concern about methane is the potential safety hazard associated with the methane, not the origin of the gas, etc. What we want to know is whether the quantity of methane present at BWIP is a sufficient hazard to justify NRC raising it as a potential problem or whether the occurence should just be noted as not of major concern.

Please note that Roger King of the BOM has advised BWIP and in the review of these documents a conflict of interest must be avoided.

We would want a written report of the review by February 10, 1984.

If you have any problems or questions about this request, please call me at (301) 427-4131.

Sincerely,

Original Signed By:

David H. Tiktinsky
Engineering Branch
Division of Waste Management

WM Record File B-6934
WM Project 10, 11, 16
Docket No.
PDR ✓
LPDR B, N, S
Distribution:
(Return to WM, 623-SS)

cc: H. Nicholls (BOM)
M. Logsdon (NRC)
B. Wright (NRC)

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828

Internal Letter

Rockwell International

Date August 26, 1982

No.

TO: (Name, Organization, Internal Address)
R. A. Deju

FROM: (Name, Organization, Internal Address, Phone)
G. S. Hunt

Subject: Study 4 Letter Report

Ref: (a) Letter, July 27, 1982, R. A. Deju to J. H. Anttonen, "Studies to be Undertaken for Exploratory Shaft Siting Decisions"

(b) Letter, August 13, 1982, R. A. Deju to J. H. Anttonen, "Criteria Used to Support Exploratory Shaft Siting Decisions"

References (a) and (b) outline the logic and description of tasks to be performed in making Exploratory Shaft siting decisions. As part of this decision process, a series of studies were identified to be completed. This transmittal is in fulfillment of Study 4 (Gas Production Testing of RRL-2 Breccia) as identified in the above references.

Attachment 1 lists the results of gas analyses at the RRL-2 and DC-16 sites and addresses possible origins.

If there are any questions, feel free to contact me.

G. S. Hunt, Manager
Site Department

GSH/REG/bac

Att.

cc: S. M. Baker
R. J. Bielefeld
R. W. Bryce
J. D. Davis
H. B. Dietz
R. E. Gephart
R. J. Gimera
D. L. Graham
S. M. Price
W. H. Price
F. A. Spane
S. R. Strait
Drill & Test Field Files
Rec. Ret. (2)

METHANE GAS PRODUCTION TESTING IN THE VICINITY OF THE CANDIDATE REPOSITORY SITE

Data

Gas data available for the candidate repository site area are listed in Table 1. The data are from boreholes RRL-2 and DC-16. No data from borehole RRL-2 are available for the Saddle Mountains Formation. However, limited gas data for the Saddle Mountains Formation from borehole DC-16 are available. Boreholes DC-16 and RRL-2 are approximately 1 mile apart.

The data from borehole DC-16 indicate that CH_4 occurs at many intervals throughout the Wanapum Formation. Gas data are not yet available for the Wanapum Formation from RRL-2 because of malfunctions of the pump equipment used to sample the gas. However, the positive delta (δ) 13 values for total dissolved inorganic carbon observed and the low concentrations of $SO_4^=$ for groundwater samples suggest that CH_4 is likely present in at least the Roza Member of the Wanapum Formation in RRL-2. Future testing will be directed to confirm this.

Methane gas discovered in the Grande Ronde Formation (Umtanum flow top and Umtanum fracture zone near the base of the Umtanum entablature) in borehole RRL-2 was the first confirmed methane gas occurrence observed in the Grande Ronde Formation within the Hanford Site. Molal concentrations of gas dissolved in groundwater are given in Table 1. The Umtanum flow top and the fracture zone near the base of the Umtanum entablature appear to have comparable production rates and concentrations of dissolved methane gas. Production rates are 11 ft^3 CH_4/hour and 8 ft^3 CH_4/hour at a groundwater flow rate of 1.6 gallon per minute respectively.

Potentials for Origin

Methane gas may be generated by either biologic metabolisis (biogenic gas) or by thermocatalytic processes (the destruction and recombination of organic matter by elevated temperatures). These two means of methane gas generation can be distinguished on the basis of delta 13 composition of the dissolved inorganic carbon (DIC) in the groundwater from which the gas exsolves and by the isotopic composition (delta ^{13}C) of the methane gas itself. However, a more definitive definition of the origin of the gas requires, in addition, the consideration of isotopic composition of the hydrogen component of the methane gas, and quantitatively measured reflectances of the vitrinite component of associated organic matter. Additional genetic inferences can commonly be derived from analysis of helium and argon, if associated with the methane gas.

Biogenic methane is formed in terrestrial environments only under certain conditions. These conditions are:

- o reducing environment (negative Eh)
- o low sulfate concentration (less than about 25 mg/l)
- o temperatures in the range of 0-70°C

By comparison, thermogenic gas requires obtainment of temperatures commonly greater than 100°C for its generation. Biogenically generated

TABLE 1. Summary of Methane and Related Data for RRL Area Boreholes.

Borehole	Stratigraphic Unit	Sampling Interval	Methane		$\delta^{13}C$ (‰)		$\frac{C_1}{\Sigma C_1-C_5}$ **	Sulfate
		Feet Below Ground Surface	Mole % of total Gas	Concentration µmoles/mole H_2O	DIC*	CH_4	(Dryness)	mg/l
RRL-2	Priest Rapids	1574-1714						1.6
RRL-2	Roza	1735-1772			+8.5			2.0
RRL-2	Lower Frenchman Springs	2244-2644			-0.3			21.0
RRL-2	Sentinel Bluffs	2719-2913						1.4
RRL-2	Umtanum Flowtop	3576-3781	97.8	800		-37.8	0.998	1.7
RRL-2	Umtanum Fracture Zone	3781-3827	96.7	630				
DC-16	Rattlesnake Ridge	668-835			-11.1			22.1
DC-16	Selah	928-1021	0.1		-14.3			4.4
DC-16	Mabton	1395-1568	9.9		-11.8			4.6
DC-16	Priest Rapids/Roza	1569-1828	92.0		+9.4			2.0
DC-16	Frenchman Springs #1	1892-2000	94.0		+10.7			1.2
DC-16	Frenchman Springs #2	2125-2156	69.0		- 2.7			1.9
DC-16	Frenchman Springs #3	2201-2261	96.2			-52.9	1.00	6.5
DC-16	Frenchman Springs #4	2266-2371	91.0	410		-51.8	0.999	6.0

* Dissolved Inorganic Carbon

** C_1 = total CH_4 concentration; C_1-C_5 = summation of all hydrocarbon gas concentrations methane gas is generally very dry, that is, it is relatively pure methane, with very little heavier hydrocarbon gases such as ethane, pentane, butane, etc. present. Methane gas generated by thermocatagenic processes generally contains a relatively greater proportion of heavier hydrocarbon gases compared to biogenically generated gas.

Delta ^{13}C values represent the isotopic ratio of $^{13}C/ ^{12}C$ expressed as per mil (parts per thousand). Natural gas becomes isotopically heavier, as a general rule with increasing age and depth of generation, as carbon-carbon bonds are broken at an increasingly rapid rate by thermal catagenesis. Oil is generally associated with hydrocarbon gases having methane delta values in the range of -40 to -35. Increasing time and temperature ultimately results in the cracking of liquid hydrocarbons to produce "wet" (ethane, butane, pentane, etc.) gas plus condensate. Biogenic gas is relatively enriched in ^{12}C compared to thermogenic gas. Biogenic gas commonly forms as a result of metabolic processes associated with anerobic bacteria in environments of low sulfate concentration, by reduction of CO_2. Bicarbonate is reduced to methane, resulting in the relative enrichment of the DIC in groundwater in ^{13}C and depletion in ^{13}C of the methane gas generated (less negative or more positive delta ^{13}C and greater negative delta ^{13}C values respectively). Such isotopic fractionation, as a result of thermo-catagenic or biogenic processes permits, by comparison with isotopic compositions with gases of known origin, methane gas origins to be ascertained. Delta ^{13}C signatures of the DIC and methane associated with the groundwater are distinctively different for biogenically generated gas compared to thermogenetically generated gas. Thermogenically associated gas shows no significant increase in delta ^{13}C DIC as is seen with biogenically associated gas. In addition the delta $^{13}C_{CH_4}$ of thermogenic gas is usually much heavier than it is for biogenic gas.

Because of secondary fractionation mechanisms, the upper limit of biogenic gas delta $^{13}C_{CH_4}$ concentrations is not well established. For this reason, other determinations such as the hydrogen isotopic composition of the methane, the ^{14}C content of the methane and dissolved carbonate in the groundwater, various dissolved chemical species and vitrinite analyses are required to better determine the gas origin.

Methane Gas Occurrence

Methane gas has been observed from an extensive area within the Cold Creek syncline. Boreholes in which methane gas has been detected from basalts and interbeds shallower than the Grande Ronde Basalt include DB-15, DC-12, DC-15, DC-16 and the McGee Well. Most gas at these sites appears to occur from between the Mabton interbed and the middle to lower Frenchman Springs flows. North of the Umtanum Ridge-Gable Mountain anticline, all gas occurrences sampled to date in the basalts are nitrogen.

The methane gas from groundwaters within the Saddle Mountains and Wanapum Basalts across the Hanford Site appear to be biogenic in origin based on their delta ^{13}C and delta deuterium compositions. Also, where gas occurs, the environment is reducing, $SO_4^{=}$ content of groundwater is low, and the temperature is well within the activity range of methanogenic bacteria. These environmental conditions are also apparently present in analogous zones within the RRL area (Table 1). The gas collected in borehole DC-16 from the Frenchman Springs #3 and #4 flows has a negative delta ^{13}C value (≃52‰).

The gas data from the Umtanum flow top at RRL-2 is somewhat unique, compared to gas from other Hanford boreholes analyzed to date, because it is the only measured occurrence of methane in the Grande Ronde Basalt across the Hanford Site. In other boreholes penetrating the Grande Ronde (that have been sampled for methane gas) either no gas was present or the gas present was greater than 90% nitrogen.

In borehole DC-12, located about 8 miles southeast of RRL-2, no gas samples were collected. However, $\delta^{13}C$ value of the dissolved inorganic carbon are very positive, indicating that methane gas may also be present in the Grande Ronde at that location. From this inference, the potential exists that groundwater from the western part of the Cold Creek syncline contain relatively greater quantities of methane gas than does the eastern part of the Cold Creek syncline.

The methane present in RRL-2 (Umtanum flow top) has an isotopic composition significantly different from methane found in the shallower basalts. The $\delta^{13}C$ value (-37.8) of the methane in this part of the Grande Ronde suggests that the methane may be associated with some organic matter that has undergone coalification. Such methane may be the result of either biogenic or thermocatalytic processes or a combination of the two. The fact that this gas was also dry suggests that if thermal activity was the source, it is at an early stage of thermogenesis.

Because of the limited carbon isotopic data at hand, and the lack of hydrogen isotopic data for the methane gas, absence of vitrinite reflectance data for the Grande Ronde intervals penetrated in the candidate repository area, and absence of argon isotopic data, no firm conclusions can yet be reached concerning the gas origin and its potential for exsolution from Grande Ronde groundwater at significant rates and volumes.

Recommendations for Future Studies

In order to obtain a firm basis for assessing the hazard and resource potential of the methane gas discovered in the candidate host-rock horizon in the western end of the Cold Creek Syncline, the following recommendations are made:

- o Continue methane gas analytical work.

- o Carbon and hydrogen isotopic analyses should be made for gas sampled not only from RRL-2 and DC-16, but from other site characterization wells. A better distribution and larger data base is needed for definitive interpretation of the gas data.

- o Chip samples and cores from other site characterization wells should be examined for organic matter suitable for vitrinite reflectance analysis.

- Efforts should continue in our obtaining of argon isotopic gas data from the site characterization wells.

- Comparisons of the gas observed in the Grande Ronde Basalt in the RRL area, with gas from one or several of the wells of the old Rattlesnake Hills gas field, should be made. If the gas in the two locations is of similar origin, the Rattlesnake Hills gas field data could provide BWIP with insights to potential gas production rates and pressures.