UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

PROCEEDINGS OF A WORKSHOP ON CLATHRATES (GAS HYDRATES) IN THE NATIONAL PETROLEUM RESERVE IN ALASKA, JULY 16-17, 1979

MENLO PARK, CALIFORNIA

Edited by

Arthur L. Bowsher

OPEN-FILE REPORT NO. 81-1298

This report is preliminary and has not been reviewed for conformity with the U.S. Geological Survey editorial standards and stratigraphic nomenclature

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in the National Petroleum Reserve in Alaska",
July 16-17, 1979, Menlo Park, California
U.S. Geological Survey
Office of National Petroleum Reserve in Alaska

Open File Report No.

Purpose: The purpose of this report is to make available the results of the "Workshop on clathrates (gas hydrates) in the National Petroleum Reserve in Alaska," July 16-17, 1979, Menlo Park, California.

Scope: Written reports presented by participants of the workshop, relevant letters generated by this workshop and some "forms" created within ONPRA to aid in collecting information are an unusual assemblage but are presented in the proceedings because I feel they can be of use to others. The articles are arranged alphabetically because of the diverse aspects in style and subject matter. A comprehensive list of references was forwarded to Gas Research Institute to avoid duplication of bibliographic effort and because I have been unable to unscramble Russian references to the satisfaction of our editors.

The workshop on Clathrates in NPRA: The workshop was convened in Menlo Park on July 16-17, 1979, to review our knowledge of clathrates and to help develop background for ONPRA's program on clathrates. Speakers were invited to discuss clathrates or some aspect of the physical or chemical relations of clathrates. The letters of invitation, schedule of talks, list of attendees, and a list of workers interested in clathrates are inserted, although the procedure is unusual because these define the scope and objectives of the meetings.

Conclusions from the meeting: Conclusions of the discussions are: (a) very little is known about *in situ* clathrates, (b) our ability to identify *in situ* clathrates while drilling is poor, (c) the engineering of ONPRA wells is not conductive to the study of clathrates because of the large holes drilled, and (d) ONPRA could justify only limited investigations of clathrates. The attendees unanimously agreed that the next step to be taken by ONPRA should be to examine the wire-line logs and drilling records of NPRA wells to identify probable zones of natural occurring gas hydrates (clathrates). The atttendees stressed the need for more accurate data on natural thermoclines and additional compositional analyses of gases encountered in NPRA wells in order to more accurately define the P/T fields of natural clathrates of NPRA. Article 2 is an overview of results of the meeting.

ARTICLES FROM PARTICIPANTS

ARTICLE 1 (Callahan, J.)

Conservation Division
Office of the Area Geologist
Anchorage, Alaska 99510
P.O. Box 259

July 12, 1979

Memorandum

To: Arthur L. Bowsher, Chief, Exploration Strategy, ONPRA, U.S. Geological Survey, Menlo Park, California

From: James Callahan, Geologist, Conservation Division, Alaska Area

Subject: Workshop on clathrates (gas hydrates) in the National Petroleum Reserve in Alaska, July 16-17, 1979--Clathrates associated with coals.

I won't be able to attend your meeting on gas hydrates next week, as I have other committments.

I have been trying to run down the only reference to hydrates associated with coal that I've heard of, but haven't had much luck. Several years ago, the Bureau of Mines was trying to put together an engineering and economic model for an underground coal mine in northwest Alaska. One of their engineers, Bob Warfield, suggested the possibility of severe gas problems at depths near the base of permafrost, where the reduction of pressure as a result of mining might cause sudden, large inflows of methane released from the hydrate form. He indicated that this had been suspected in one or more underground mines at Svalbard. A recent report by the University of Alaska Mineral Industry Research Laboratory regarding mining in permafrost areas discussed conditions at the mines at Svalbard as well as in the Soviet Arctic rather thoroughly. The authors visited several of the Norwegian and Russian mines. The Norwegian mines are all within the permafrost zone (above a depth of about 300 meters). Gas generation in the Norwegian mines is about .5 cubic meters of gas/24 hr/ton of coal. The Russian Mines reach a depth of 650 meters, well below the base of permafrost. In these mines, gas generation amounts to as much as 17.5 to 20 cubic meters/24 hr/ton of coal. This difference could be the result of gas released from the hydrate state in the sub-permafrost zone. I talked to the MIRL people involved in the permafrost mining study. They did not have any information on hydrates associated with coal, nor could they recall any mention of hydrates in their discussions with the mine operators at Svalbard.

There is a large volume of literature on underground mining problems in the Soviet Arctic. None of the titles specifically refer to hydrates, but the titles do suggest there has been a good deal of research on gas problems, particularly at the Vorkuta mine in the Pechora basin, where the permafrost is 45 to 135 meters thick, with many unfrozen areas and a large ice content. I have someone trying to locate translations of some of these articles, but won't have time to acquire and review them prior to leaving for the field later this month.

I would be interested in participating in the proposed study, but need a little background information to know what I could contribute.

/signed/
James Callahan

ARTICLE 2 (Cox, J.)

August 22, 1979

Mr. Arthur L. Bowsher
Office of National Petroleum Reserve of Alaska
U.S. Department of Interior
345 Middlefield Road
Menlo Park, CA 94025

Dear Art:

I apologize for taking so long to follow-up on your Natural Gas Hydrates Workshop.

I have finally worked up the notes of the final discussion of the meeting you led.

During the final discussion session of the Natural Gas Hydrates Workshop that was organized and staged by the USGS in Menlo Park on July 16 & 17, several consensus of opinions were reached by the participants that may be useful to ONPRA.

> The ONPRA is in a unique position to conduct analytical field experiments to delineate the occurrence of natural gas hydrates in NPRA. In view of the character of the USGS and the purpose of ONPRA, a special effort within the overriding constraints that exist should be undertaken to conduct such studies. Inasmuch as the results would be of interest to a number of organizations aside from ONPRA, efforts should be made to coordinate any positive action taken with them. In this regard it was felt that natural gas hydrates either have or may have an impact on resource exploration, drilling operations, energy resources, environment, and safety.
>
> While the participants did not reach a consensus on a detailed course of action that should be undertaken by USGS, there was agreement in regard to the major points of a program which are as follows:
>
>> USGS should first make an assessment of all the existing data (information) available with regard to occurrence of natural gas hydrates in ONPRA, this consists of identifying what information is available from exploration and drilling activities that have been performed in the domain of ONPRA. This information should be integrated with laboratory experimental information to make a best estimate of hydrate occurrence in ONPRA based on existing information. The P-T-X data from laboratory studies on both Structure I and Structure II natural gas hydrates must be considered in this assessment. The P-T-X data of the Structure II hydrate are particularly important since it is stable at higher temperatures than Structure I. The proper gathering and studying of all this information should allow one to high grade areas within ONPRA for field studies.
>> The extent of the field studies will depend heavily upon the outcome of the analytical-assessment study and internal

constraints. What field experimental information should be gathered was poorly defined in the discussion and must be given detailed consideration in the analytical-assessment study.

The use of a pressure core barrel for sampling though, was one piece of information that was generally agreed to be needed. Other information that would be useful, if not essential, was discussed at the GRI Workshop on Natural Gas Hydrates in Denver on February 1, 1979. It was strongly emphasized that the field experiments should not be undertaken without having first conducted the analytical-assessment study.

If you have any questions regarding the above, please feel free to contact me. GRI is very interested in keeping abreast of developments that pertain to natural gas hydrates and I would appreciate it if you could keep me informed of your efforts there. If I can be of assistance, let me know.

Sincerely,

/signed/
John L. Cox
Gas Research Institute
Chicago, Illinois

cc: Ferol Fish
John Sharer

ARTICLE 3 (Davidson, D. W.)

Comments on Study of Natural Gas Hydrates (Clathrate Ices)

(For Workshop on Clathrates in the
National Petroleum Reserve in Alaska)

1. There is probably sufficient accumulated knowledge of the physical and thermodynamic properties of gas hydrates for adequate treatment of questions on hydrate stability conditions, the energy required for decomposition of hydrate, the pressure generated by decomposition of hydrate, and the like.

2. Pure methane forms a hydrate of von Stackelberg's (1954, Zeitschrift Elektrochem, v. 58, p. 25-162) structure I; small proportions of propane and isobutane promote the formation of structure II which generally has a wider range of stability, i.e., occurs over a greater range of depth. For example, for a mean surface temperature of -10^{o}C and pressure and thermal gradients of 10 kilopascals/m and 0.025^{o}C/m, the structure I methane hydrate is stable between depths of about 200 and 900m, while if the methane contains 1% propane, the corresponding structure II hydrate is stable between about 75 and 1110m. However, the structure II hydrate is relatively rich in propane (30 to 40% for conditions cited) and the quantity of structure II formed will be limited by depletion of propane in the gas unless the hydrate is (or was) in contact with a substantial pool of free gas.

3. Among the important questions to be answered by field studies are:

(a) In individual hydrate-bearing formations does hydrate coexist with liquid water (or ice at low temperatures) or free gas or are water and gas almost exclusively combined in hydrate, excess water or gas having migrated out of the zone of hydrate stability?

(b) Does the hydrate exist as structure I or structure II or as a mixture of these crystalline forms? The answer depends on the overall hydrocarbon composition, the temperature and pressure, and may also depend on the history of the hydrate deposit.

4. Most of physical properties (e.g., sound velocity, electrical resistivity) of natural gas hydrates (clathrate ices) are similar to those of ordinary hexagonal ice. The presence of hydrate may be recognized by ice-like features in seismic and logging records provided the temperature is known to be above 0^{o}C. At lower temperatures these fail to clearly distinguish between ice and hydrate.

5. There is apparently no record of successful recovery of a pressurized hydrate-bearing core from a land-based well. Despite the hazards, it would be useful to recover such cores, which could be depressurized and stored at low temperatures and subjected to exhaustive laboratory study by such techniques as X-ray diffraction, proton and carbon-13 nuclear magnetic resonance, infrared spectroscopy, and mass spectrometric examination of the gases evolved during controlled decomposition of the hydrate.

6. The regime for exploratory drilling through a hydrate zone should include frequent analysis of the decomposition gases.

/signed/
D. W. Davidson
National Research
Council of Canada
Ottawa K1A 0R9
(613) 993-2011

ARTICLE 4 (Folk, S.)

STEWART FOLK & COMPANY, INC.
2200 South Post Oak Road - Suite 700
Houston, Texas 77056
(713) 622-9700

January 12, 1979

MEMORANDUM

TO: A. L. Bowsher

FROM: S. H. Folk

RE: Gas Hydrates

I was glad to learn from your memo of January 3, that the Gas Research Institute is sponsoring a workshop on gas hydrates, and that you will participate in it.

Enclosed is preliminary draft of depth/temperature curves for gas hydrates, based on Fig. 3 of Baker, P. E., 1974, Experiments on hydrocarbon gas hydrates, in Kaplan, I. R., (editor), 1974, Natural Gases in Marine Sediments, Plenum Press, N. Y. and London. Art Grantz has a copy of the volume and called my attention to it last fall.

Information suggesting the existence of gas hydrates in the Prudhoe Bay area is discussed in enclosed copy of page 410 of the above cited volume.

/signed/
Stewart Folk

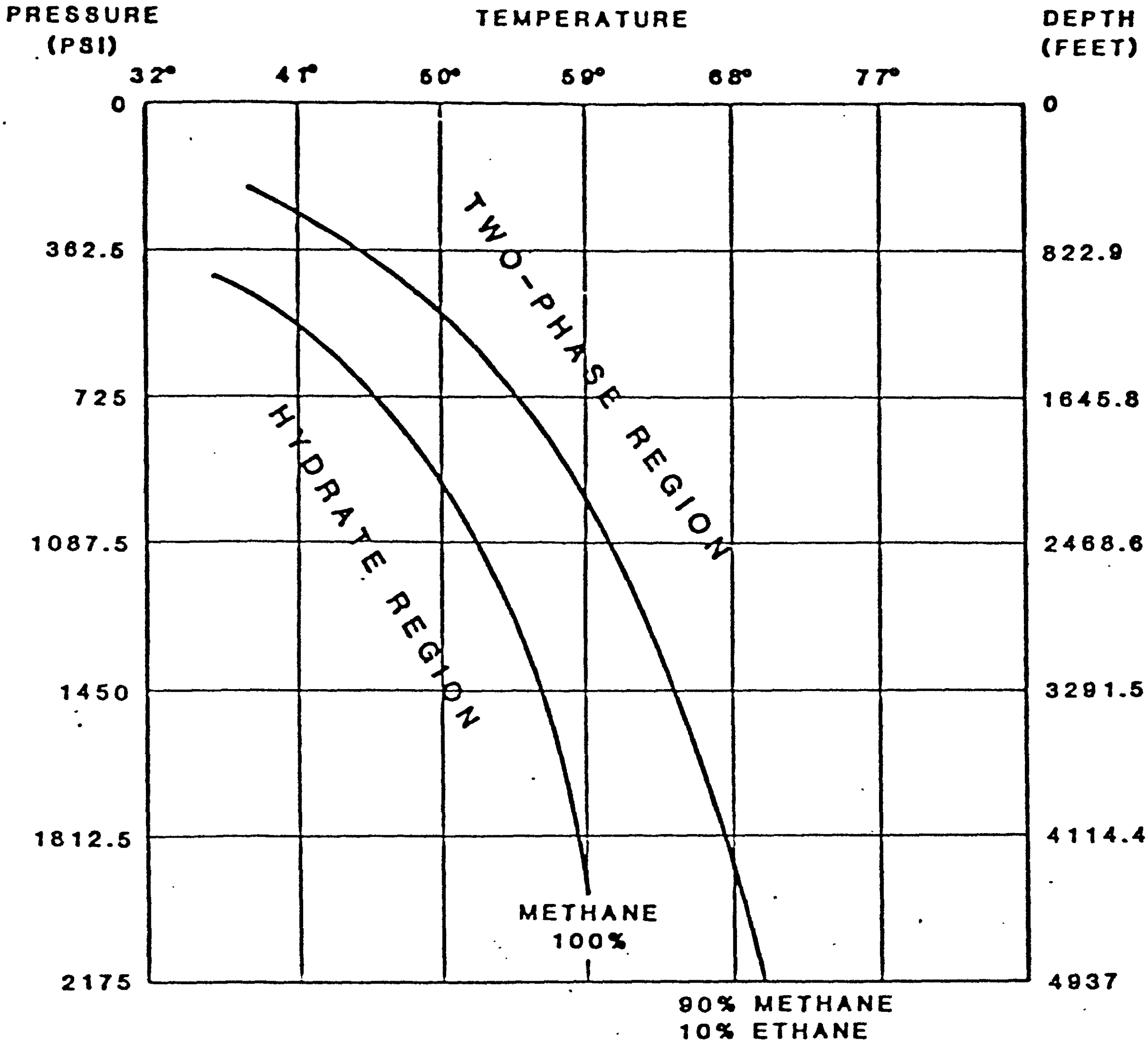
Enclosures

Baker (1974, p. 410):

"There have been no published reports of the occurrence of natural gas hydrates in the Arctic slope petroleum province of Alaska. Unpublished and unconfirmed information indicates that cores taken in the permafrost zone and recovered to the surface, still under conditions of reservoir temperature and pressure, contain much greater quantities of natural gas than would normally be expected under reservoir PT conditions, a fact strongly indicative of the presence of natural gas hydrates, in situ in the permafrost. Even beneath the permafrost zone conditions are still conducive for the occurrence of natural gas hydrates, and Katz (1971) has shown that at Prudhoe Bay, with 600 meters of permafrost, methane may be expected as a gas hydrate between 600 and 1035 meters, and a natural gas of 0.6 gravity would be in hydrate form between 600 and 1220 meters. The formation of hydrate would reduce the gas pressure if water does not move in to maintain reservoir pressure. One might therefore speculate that, in part, the low pressure in the 1140-1245 meter-deep reservoir discovered in Upper Cretaceous sandstones in Arco-West Sak River St. 1, in which the reservoir pressure was so low that the 18°-API gravity oil failed to flow to the surface Adams (1972) was the result of depletion of the gas cap through the formation of hydrates; it should be noted that gas hydrates can form from gases dissolved in liquids and do not require a free gas phase, and thus hydrates in crude oil or condensate reservoirs are possible Katz (1972). Both these Alaskan observations concerning the possible occurrence of natural gas hydrates require confirmation. However, in view of the demonstrated presence of natural gas hydrates in the U.S.S.R. under similar conditions, there seems little reason to doubt the presence of natural gas hydrates under suitable PT conditions in the shallower oil and gas reservoirs in the Arctic slope petroleum province of Alaska."

Baker, P. E., 1974, Experiments on hydrocarbon gas hydrates in unconsolidated sand; in Kaplan, I. R., 1974, ed., Natural gases in marine sediments: New York, Plenum, p. 227-234.

Katz, D. L., 1971, Depths to which frozen gas fields (gas hydrates) may be expected: Journal of Petroleum Technology vol. 23, p. 419-423.



DEPTH: TEMPERATURE CURVES FOR
GAS-HYDRATE EXISTENCE

[ASSUMING PRESSURE GRADIENT 0.44 PSI/FOOT
EQUIVALENT TO 20,000 PPM TOTAL DISSOLVED SOLIDS
IN FORMATION WATER]

ADAPTED FROM BAKER, P. E., 1974
S.H. FOLK JANUARY 1979

Figure 1

ARTICLE 5 (Franklin, L.)

HYDRATES

IN THE ARCTIC ISLANDS

The occurrence of hydrates in wells drilled in the polar regions has been recognized for some time and I am sure all present here have examined closely the various papers on the subject. I think the paper by Bily and Dick (1974) entitled "Naturally Occurring Gas Hydrates in the Mackenzie Delta" deals quite effectively with the subject and I am fundamentally in agreement with the authors' findings and their conclusions reached with respect to naturally occurring hydrates.

I am able to find nothing of great significance about our own Arctic experience, but possibly a description of some of the problems we have experienced, and the solutions we have sought, will help to stimulate discussion that could be productive.

Assuming reasonable pressure and temperature gradients based on field measurements (and I hereafter utilize pressure .435 PSI per foot and temperature gradients of 1°F per hundred feet in permafrost and 1.5°F per hundred feet below permafrost) it can be shown that hydrates are limited to certain specific depths as illustrated in the Bily and Dick paper (1974, Fig. 6). Our offshore experience in drilling from ice platforms has led us to examine further this pressure/depth relationship.

In the offshore areas, where no permafrost exists, and the sea-bed temperature is of the order of 29-30°F, a different pressure/temperature regime occurs.

By a simple mechanical overlay of the temperature/pressure contours in the near shore regions, one is able to develop a vertical section which illustrates where hydrates might be anticipated in the area close to the shoreline.

With a conventional shoreline section there will be an area in the shallow water near shore where no hydrates might be expected; the hydrate regime occurs onshore and offshore from this narrow band. A cross section can be developed in general accord with the bottom simulating reflector (BSR) phenomena observed in offshore seismic work along the north shore of Alaska (i.e. BSR observed at a water depth of 500' or deeper).

A review of the rather meagre information obtained in the reports from the early wells drilled in the Arctic Islands reveals that concern was not so much to recognize and evaluate hydrates, but rather to drill through the troublesome zone with a minimum of problems. In many instances elevated mud temperatures were utilized to preclude freezing in the hole in the event of pump breakdown or other requirement to leave the drill pipe in the hole for extended periods during the drilling of the permafrost section. For this reason, rapid evolution of gas from hydrate sections was common.

In much of the drilling around King Christian Island, Ellef Ringnes Island, and Amund Ringnes Island the presence of hydrates in the drilled section can be inferred from the reports, although in many instances no direct drilling problem resulted. I will site some examples of indications of hydrates gleaned from examination of the old records and conversations with field personnel who were present at the time. In 1971 KCI N-06 was drilled on King Christian Island. At this hole 20" casing was set at 524 feet followed by 13 3/8" casing at 1,600 feet and 9 5/8" casing set at 3,800 feet. Gas was observed early to be emanating from around the 20" casing although no drilling problem was recorded due to gas in the drilling mud. To eliminate the dangerous accumulation of gas in the cellar there was fabricated a metal cap which was attached to the casing bowl to gather the gas and lead it off to some safe point away from the rig where a continuous flare was operated as drilling proceeded. The procedure worked well and a flare from one feet to five feet in length persisted throughout the drilling. It has been indicated that the practice was so common to many wells of the early 70's that no record was maintained concerning the practice.

Another well drilled in Helicopter Bay on Ellef Ringnes Island in 1972 has records that indicate a shallow conductor was set (circa 50') and then a 17 1/2" hole was drilled to 1,330 feet. There was no indication of gas problem during the drilling although the records indicate that water was being added to the mud to cool it. Following the setting of casing at 1,330 feet drilling proceeded to 6,000 feet where a second string of casing was set. The records indicate that while driling at 8,411 feet with 76^{O}F mud a gas flow from between the inner casing and outer casing was observed. In this instance a valve on the surface had been left open and a fire resulted due to the gas flow. Inspection of the records indicates that the intensity of the gas flow reduced when drilling was interrupted to fight the fire. Following the installation of an appropriate valve to close the annulus at surface no further problem was reported.

More recent and better documented experience was gained while drilling at Hearne Point on Mellville Island this past winter. At this well 9 5/8" casing was set at 155 metres followed by 7" casing at 605 metres; drilling proceeded to a total depth of 1,676 metres.

While drilling below the 155 metre casing at a depth of 356 metres and using mud at 8^{O}C, a 22 percent gas reading was recorded. An attempt to drill stem test to determine the source of this gas resulted in the drill stem test tool being frozen in the hole and a prolonged fishing job was required for its recovery. Drilling thereafter proceeded to 605 metres with mud temperatures ranging up to 20^{O}C with no incidence of gas problems. A substantial well-kick was experienced at 895 metres. Drilling continued to 928 metres and a test of the bottom hole interval yielded a classical hydrate test result. Gas to surface was experienced very quickly; the flow died rapidly to a small flame with flow rate too small to measure; on shut-in the pressure built up slowly but steadily to a level higher than hydrostatic mud pressure. Drilling proceeded to 1,676 metres with experimental modifications in mud weight and mud temperature continuing. It was with some difficulty that hole stability was achieved to permit safe removal of the pipe for bit changes (principally by cooling the mud). At a depth of 1,676 metres while logging, the hole kicked and in the exercise of rapid recovery of logging tools the line jumped a sheave and logging tools were lost down the hole. During a prolonged fishing operation no substantial gas problem was experienced and logging tools were finally pushed to the bottom of the hole.

A series of drill stem tests in the interval 346 metres to 1,507 metres provided classical results of either tight formations or hydrates. Small flows, too small to measure were recorded with gas to surface in some instances and at other times no gas to surface. A second test of the interval 895 to 928 provided results again showing a hydrate section with gas to surface at a low rate and pressure build up equal to or greater than the hydrostatic head of the mud. Some effort was made to heat up the hole by heating the mud to stimulate flow from the hydrate sections but the effort proved unsuccessful. The counterflow heat exchange appeared to be too great to permit meaningful application of heat to the bottom part of the hole. Starting wth 110°F mud, the system quickly came to equilibrium 60°F in and 50°F out. No gas evolution was generated.

OFFSHORE DRILLING

The drilling of Arctic holes from an ice platform adds an additional dimension to the problem of dealing with hydrates and I would like to review incidents describing hydrate problems in the offshore.

JACKSON BAY

This hole was drilled in 200 feet of water in 1976. The hole was drilled to 1,084 feet where casing was set. When drilling was proceeding at 1,485 feet gas readings of 5 to 9 percent were recorded but no pressure was evident when the well was shut in. Mud temperature in tanks was 48°F. As drilling proceeded to 1,860 feet a well kick was experienced and shut in pressure of 200 PSI was recorded. Mud was weighted up from 10.5 to 14 lbs. per gallon by which time shut-in pressures of 300 PSI were recorded. Gas could be bled off easily and there appeared to be no volume to sustain flow. Drilling proceeded to 1,990 feet and mud was cooled to 34°F. It was with some difficulty that the hole was sufficiently stabilized to change the bit at this depth. Drilling proceeded to 2,530 feet in a careful manner with strong background gas at all times and evidence of gas intrusion into the hole when circulation was interrupted. When casing was set at 2,530 feet an extended period of circulation had to be conducted prior to cementing in order to stop gas flow in the casing annulus so that an effective cement job could be performed. During the setting of the cement 200 PSI pressure built up on the casing annulus, but it was bled off after initial cement set was achieved. During the drilling below casing to 4,000 feet strong background gas was observed; it was impossible to tell if it was of hydrate source coming up through the cement or if it was a high pressure/low volume gas associated with the new hole being opened.

At 4,000 feet, due to ice movement, it became necessary to move over and redrill the hole. The second hole was drilled with sea water using a rotating head to handle gas evolution. Casing was set at 1,200 feet and drilled out with sea water. Drilling proceeded with sea water to 1,715 feet where a 50 barrel kick was taken. As drilling proceeded to the 4,000 foot casing point with drilling mud, the gas flow after each connection resulted in the loss of about 5 barrels of mud. At 4,000 feet much difficulty was experienced in bringing the hole to a stable condition so that the drill pipe could be removed. Mud weight was raised to 14 lbs. and some 3 days of circulating were required before the hole was sufficiently stable to permit the running of casing. In the drilling that proceeded below the casing at 4,000 feet there was continuous background gas of 1 to 5 percent while drilling and gas of 10 to 12 percent on connections. It has not been determined if that gas was emanating from behind the casing or was associated with the lower section of the hole.

WHITEFISH

In 1979 at the Whitefish location in 278 metres of water 13 3/8" casing was set at 398 metres. Drilling proceeded to 650 metres depth with a drill mud of 36°F. At this depth the well became very violent and efforts to cool the mud proved unsuccessful in achieving the required stability. At a depth of 656 metres it was decided that the hole was too unstable to risk removing the riser to run the next string of casing and the decision was taken to set a bottom hole plug. A 100 metre bottom hole plug was set with cement and drilled off to 620 metres. At that point the hole was sufficiently stable that the riser could be pulled and 9 5/8" casing was run and cemented. Following drill-out of the casing and reaching the 656 metres again the well kicked. With secure casing cemented in place and seabed blowout preventors in place one drilled ahead confidently, accommodating the gas. After drilling had proceeded beyond the 900 metre depth no further significant gas problem is recorded.

CONCLUSION

On the basis of what we can gather from old reports, and from conversations with personnel having long experience in the Arctic Islands, supplemented by my own more limited recent experience and observations, I am confident that we can safely drill, test, produce and abandon wells having substantial hydrate sections. The offshore wells present more problems and the source of gas evolved is more difficult to ascertain; all gas to surface is observed in the riser and it is not easy to learn if it is from new hole or from behind casing.

We will be continuing our efforts to improve operational efficiency in the hydrate section, and we will be pleased to cooperate in efforts to utilize our drilling activity to obtain more information on hydrate phenomena if suitable financing of our incremental cost can be generated. At present there is little enthusiasm with our industrial participants to expend significant effort/funds on hydrate study when the rewards (if any) are so distant.

REFERENCES

Bily, C., and Dick, J. W. L., 1974, Naturally occurring gas hydrates in the Mackenzie Delta, N.W.T.: Bulletin Canadian Petroleum Geologists, vol. 22, no. 3, p. 340-352.

ARTICLE 6 (Goodman, M.)

HYDRATES: DRILLING AND COMPLETING WELLS IN THE NORTH AMERICAN ARCTIC

BY

MALCOLM A. GOODMAN

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(713) 521-9033

PRESENTATION AT USGS WORKSHOP ON GAS HYDRATES
JULY 16-17, 1979
MENLO PARK, CALIFORNIA

PRESENTATION AT USGS WORKSHOP ON GAS HYDRATES

JULY 16-17, 1979

MENLO PARK, CALIFORNIA

ARCTIC WELL COMPLETION PRACTICES

- PERMAFROST EXPERIENCE
  - DRILLING
  - THAW-SUBSIDENCE
  - FREEZEBACK-COLLAPSE
- HYDRATE EXPERIENCE
  - ALASKA
  - CANADA
  - USSR
- RECOMMENDATIONS FOR HYDRATE COMPLETIONS
  - DRILLING
  - CEMENTING AND CASING DESIGN
  - HYDRATE DETECTION

Figure 2

PORE PRESSURE REDUCTION IN THAWED PERMAFROST AT PRUDHOE BAY

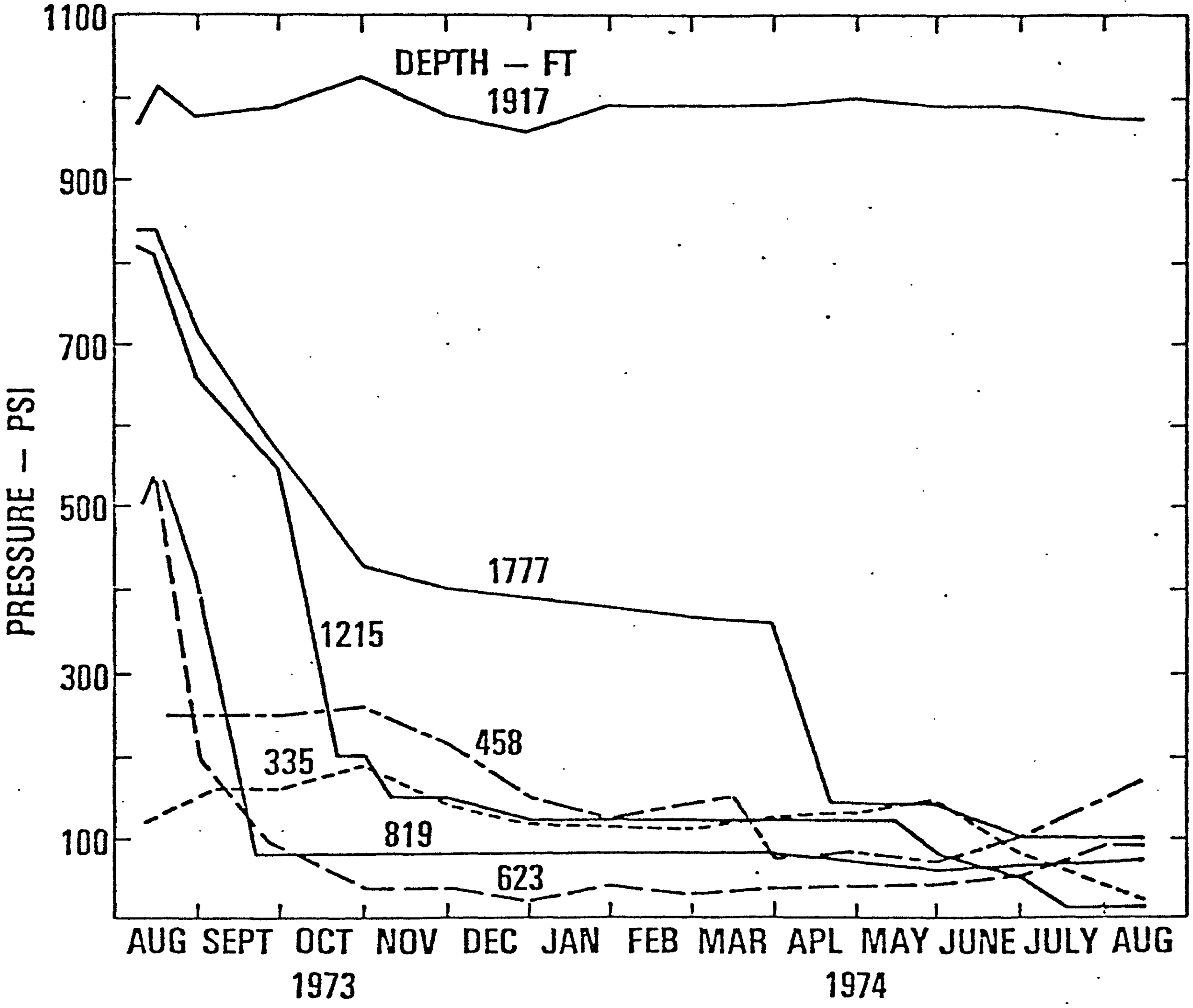


Figure3

PERMAFROST COMPACTION DUE TO PORE PRESSURE REDUCTION UPON THAW

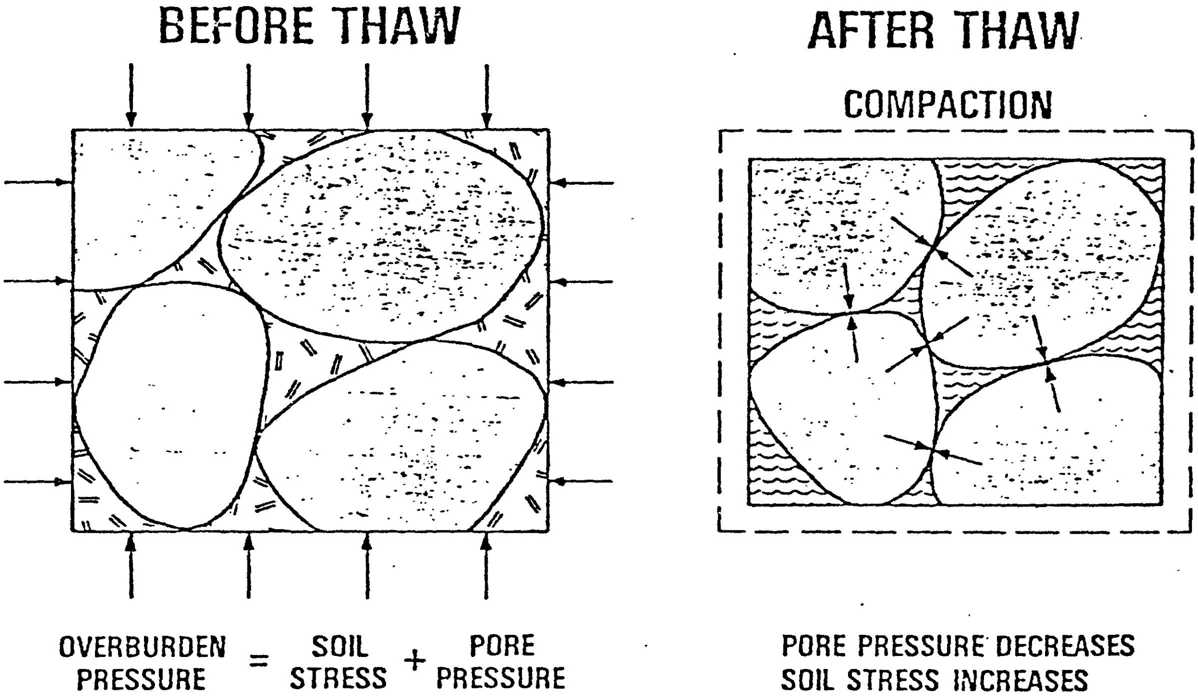


Figure 4

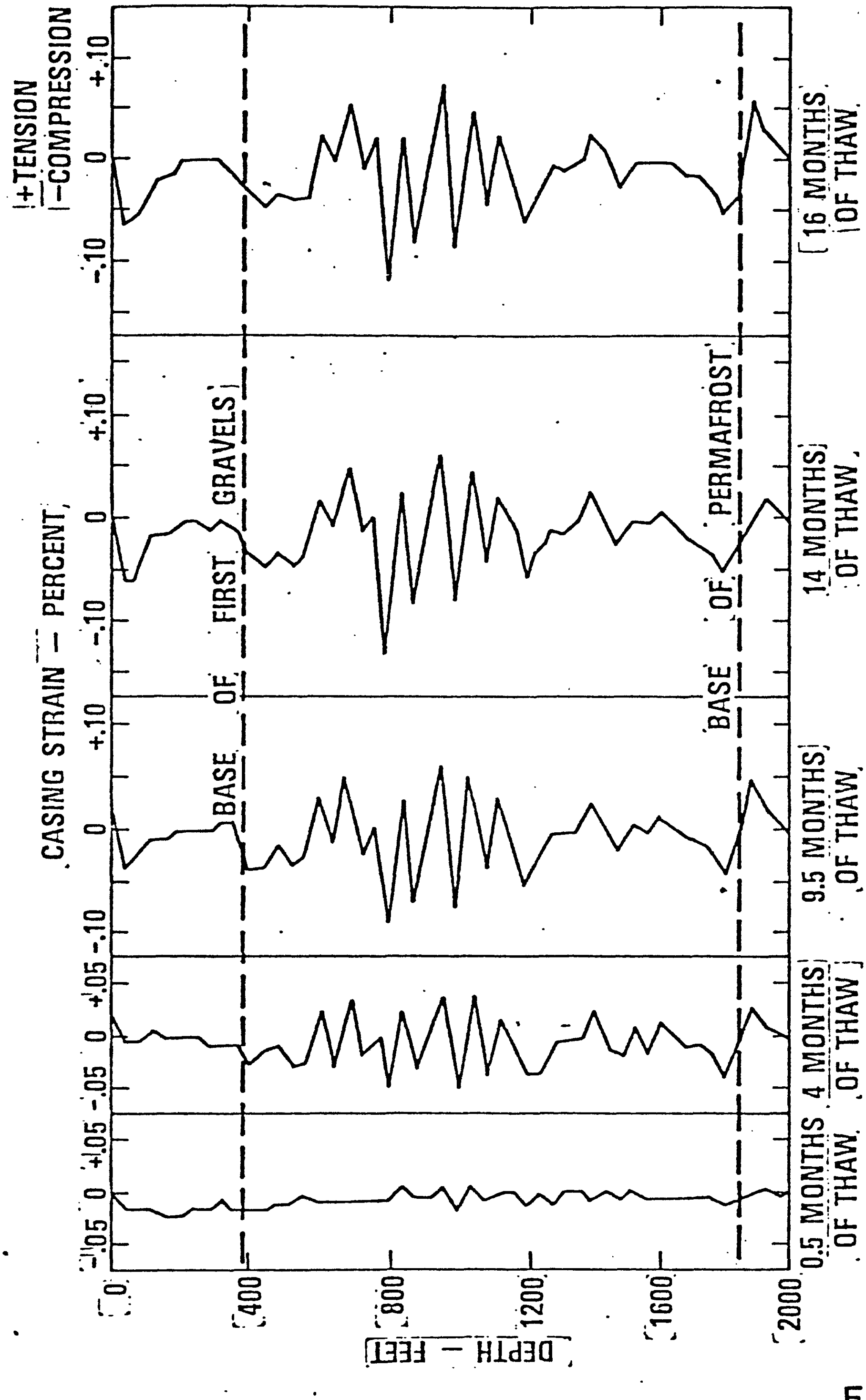

+TENSION
−COMPRESSION
CASING STRAIN — PERCENT
-.10
0
+.10
-.05
+.05
BASE OF FIRST GRAVELS
BASE OF PERMAFROST
16 MONTHS OF THAW
14 MONTHS OF THAW
9.5 MONTHS OF THAW
4 MONTHS OF THAW
0.5 MONTHS OF THAW
DEPTH — FEET
0
400
800
1200
1600
2000

Figure 5

PORE PRESSURE REDUCTION LOADING MECHANISM

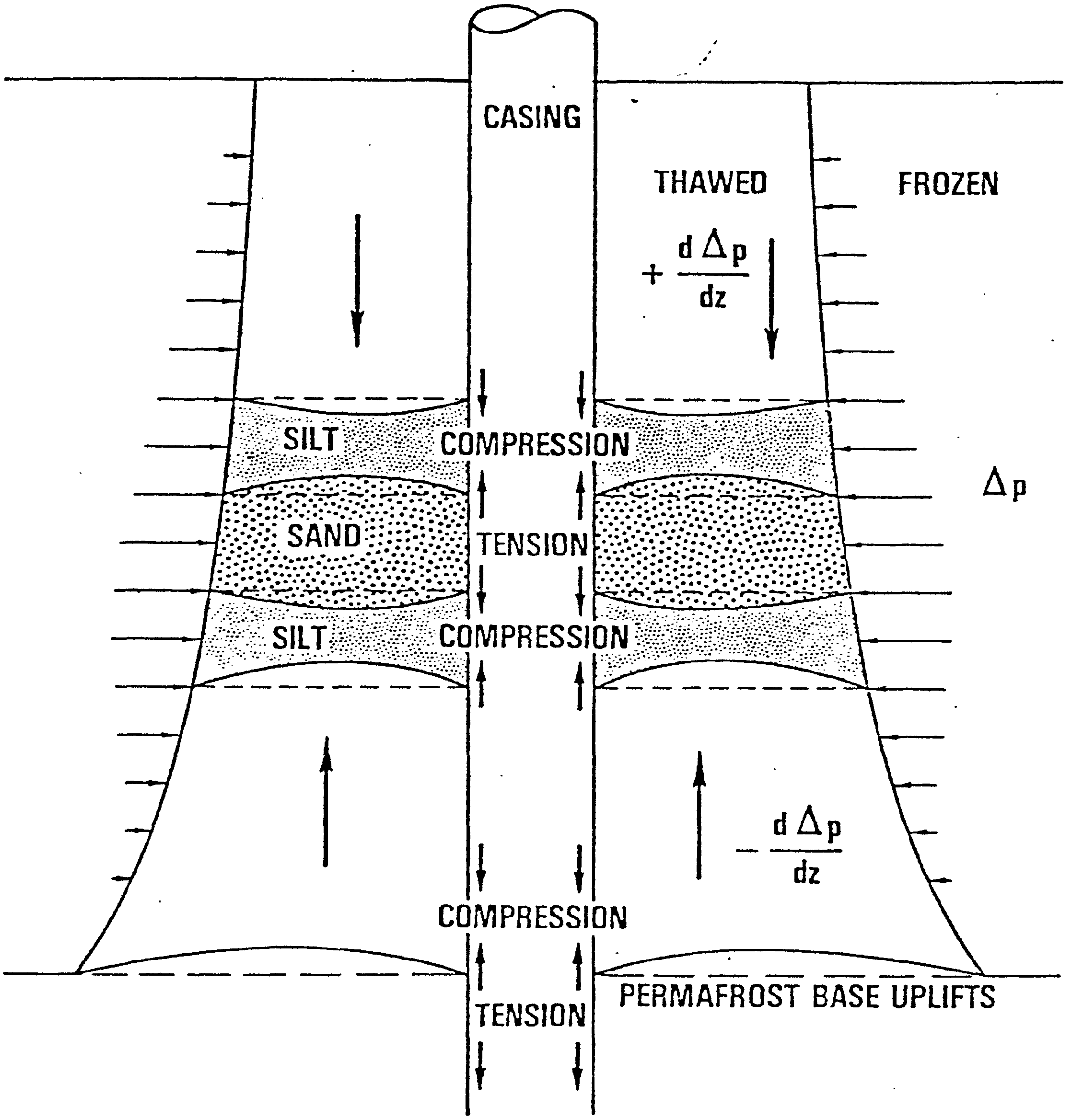
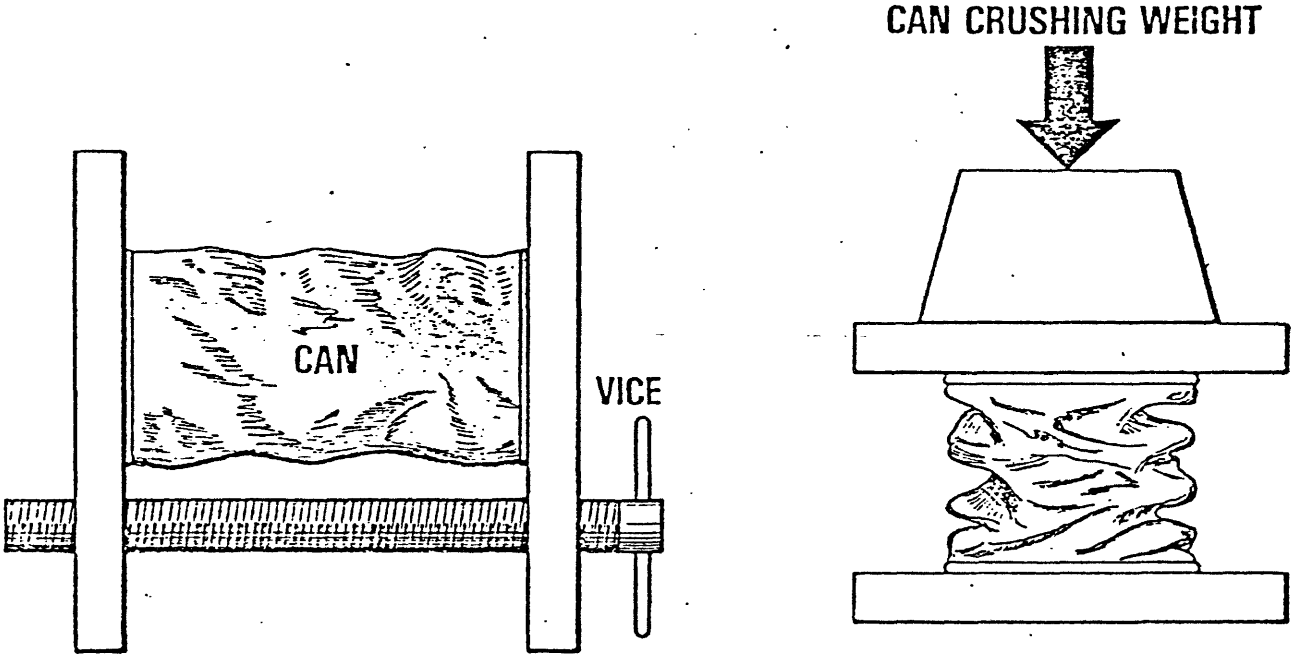


Figure 6

CAN CRUSHING ANALOGY



STRAIN INDUCED PROBLEM

STRESS INDUCED PROBLEM

Figure 7

SHRINK-FIT CONCEPT FOR EXTERNAL FREEZEBACK PRESSURE

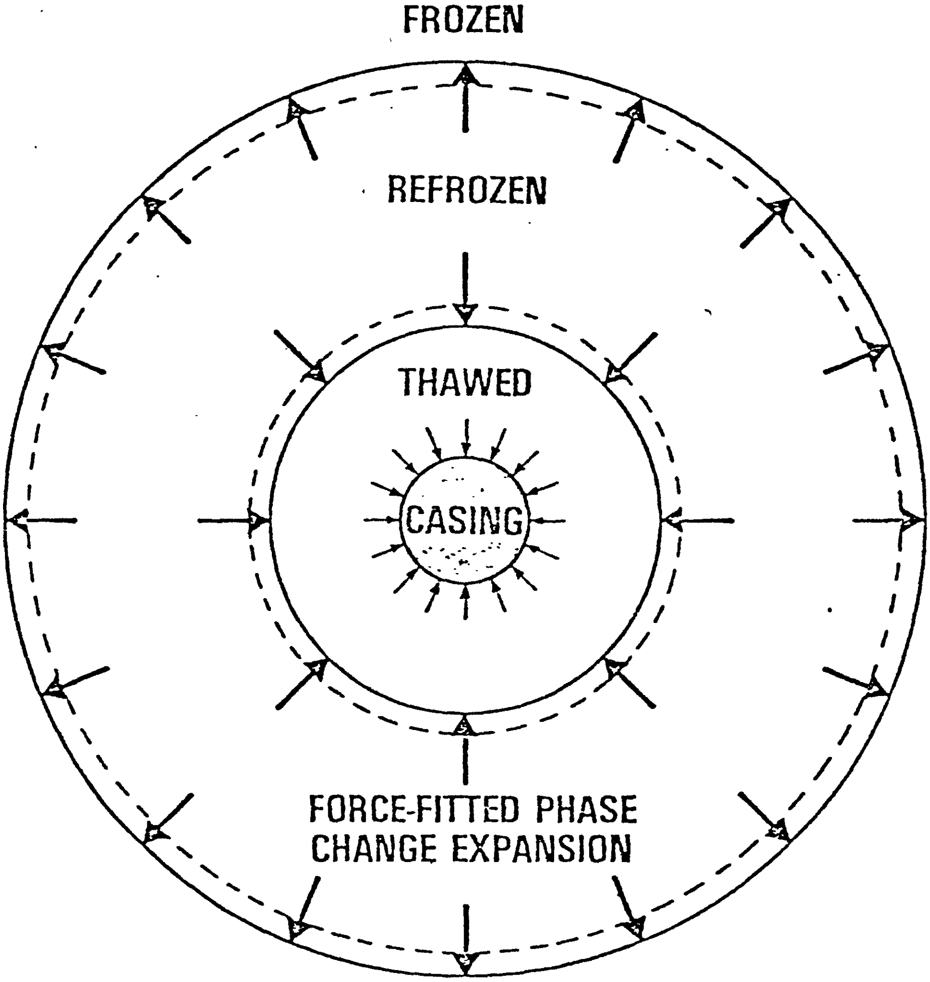
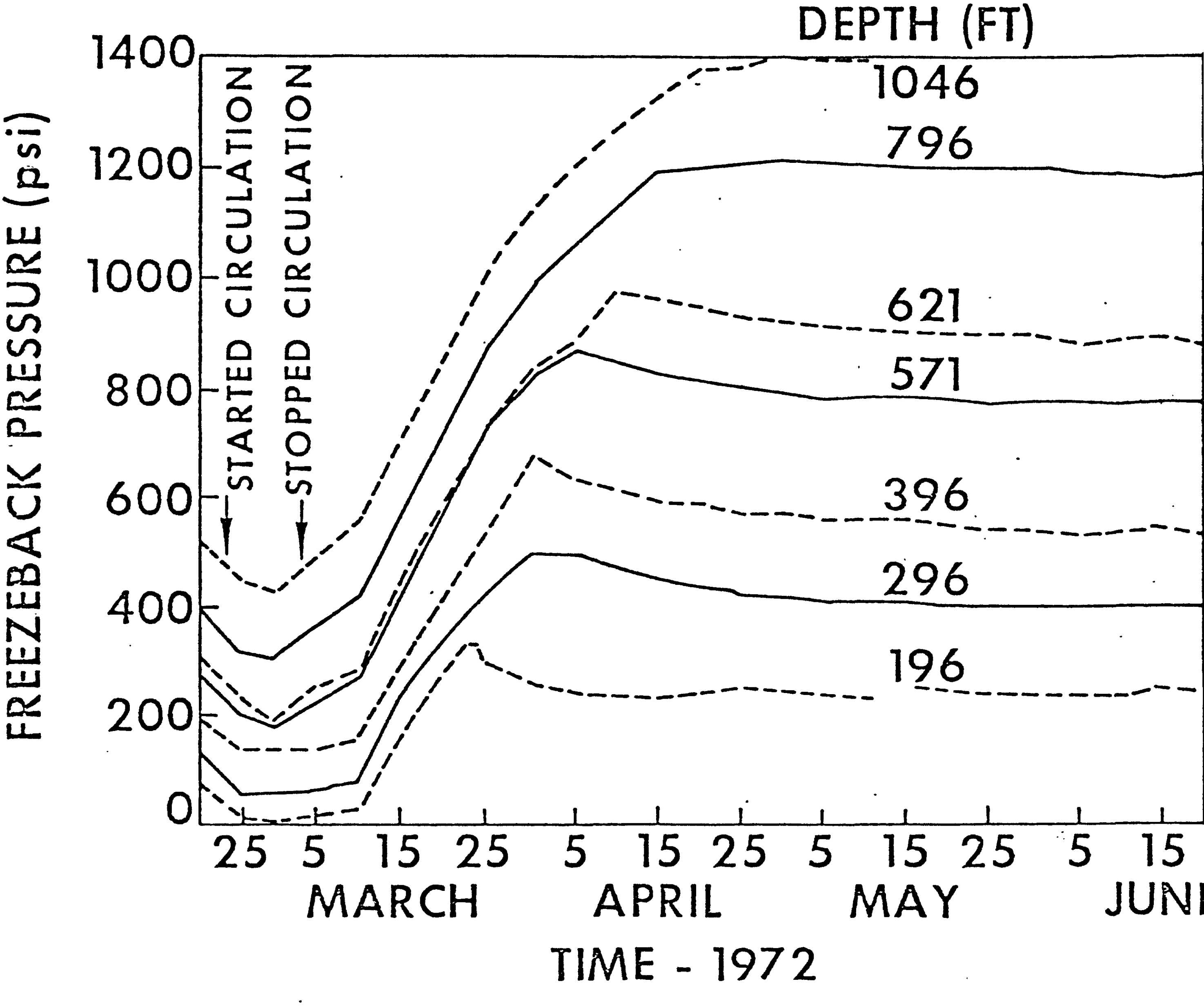


Figure 8



FREEZEBACK PRESSURE (psi)
1400
1200
1000
800
600
400
200
0
STARTED CIRCULATION
STOPPED CIRCULATION
DEPTH (FT)
1046
796
621
571
396
296
196
25
5
15
25
5
15
25
5
15
25
5
15
MARCH
APRIL
MAY
JUN
TIME - 1972

Figure 9

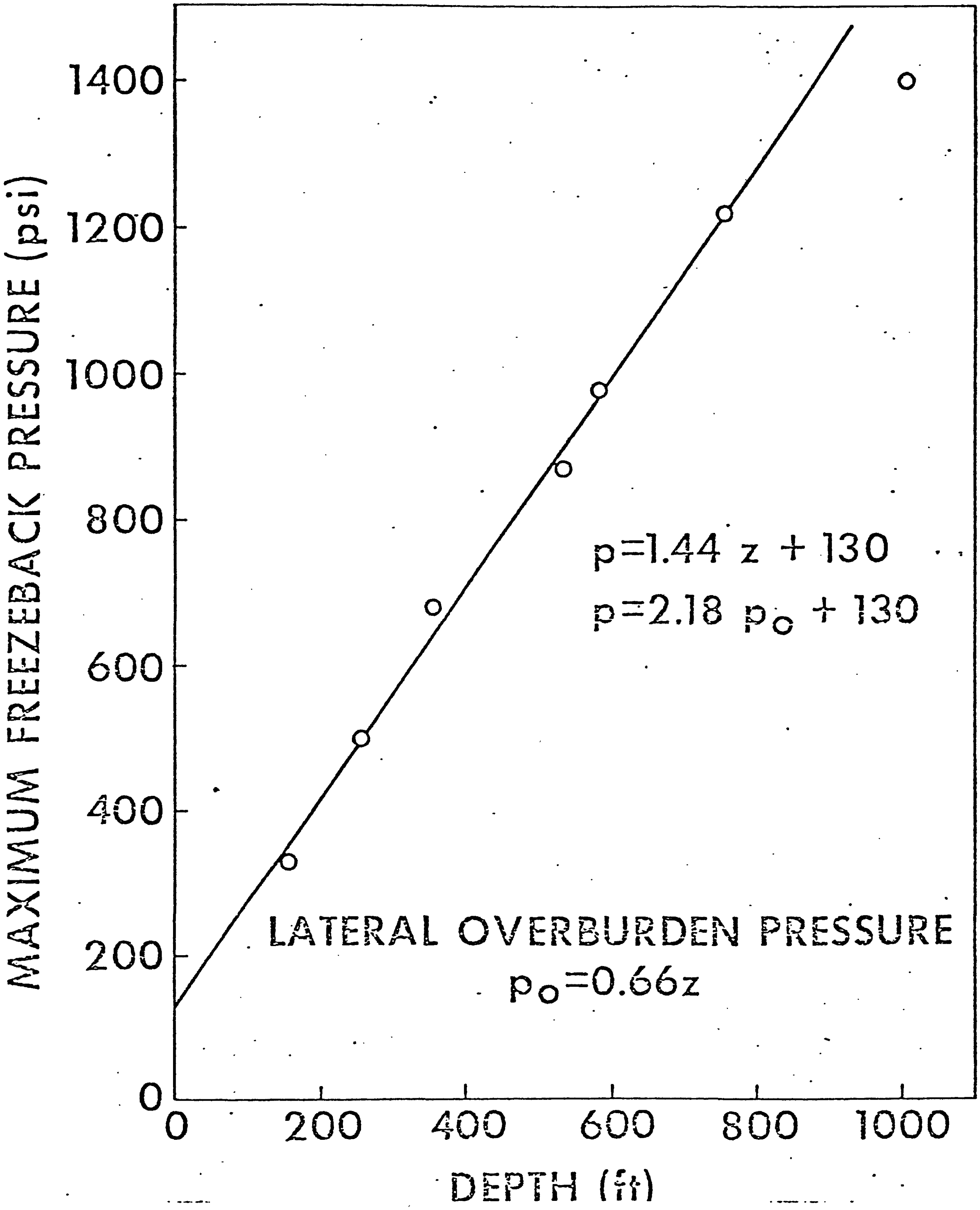

MAXIMUM FREEZEBACK PRESSURE (psi)
1400
1200
1000
800
600
400
200
0
p=1.44 z + 130
p=2.18 p$_o$ + 130
LATERAL OVERBURDEN PRESSURE
p$_o$=0.66z
0
200
400
600
800
1000
DEPTH (ft)

Figure 10

HYDRATES NEAR PRUDHOE BAY

SOHIO-BP ALASKA

- SHALLOW GAS
- NO HYDRATE EVIDENCE

MOBIL

- DEEP (2400 FEET) PERMAFROST
- NO HYDRATE EVIDENCE

ARCO-EXXON

- NO HYDRATE EVIDENCE AT PRUDHOE
- ONE HYDRATE OCCURRENCE WEST OF PRUDHOE
- HYDRATE CORE RETRIEVED
- CORE TESTED AND HYDRATES CONFIRMED

Figure 11

HYDRATES IN CANADA

- EVIDENCE INDICATES HYDRATE PRESENCE
- WELL CONTROL PROBLEMS ENCOUNTERED
    - GAS BUBBLING AT SURFACE
    - FIRES
- HYDRATE EXPERIENCE DURING DRILLING ONLY. NO PRODUCTION EXPERIENCE
- HIGH MUD WEIGHTS DO NOT PREVENT GAS INFLUX
- NO DIRECT EVIDENCE FROM CORES
- NO CASING FAILURE PROBLEMS
- MUD GAS INFLUX DECREASES AFTER HYDRATE INTERVAL PENETRATED
- AMBIENT COOLING OF MUD USED, BUT NO ARTIFICIAL REFRIGERATION
- MOSTLY METHANE WITH SOME PROPANE AND ETHANE
- OPEN-HOLE LOGS

Figure 12

RUSSIAN HYDRATE EXPERIENCE

- HYDRATE EVIDENCE
- INJECTION OF HYDRATE INHIBITORS
- CASING FAILURE AT MESSOYAKHA
  - PRESSURE TRANSDUCERS ON SHUT - IN WELL
  - 1100 PSI (98 FT) AND 3040 PSI (427 FT)
  - 11.3 PSI/FT AND 7.1 PSI/FT
  - CASING AND TRANSDUCER CABLES CRUSHED
  - FREEZEBACK OR HYDRATE ?

Figure 13

HYDRATE DRILLING RECOMMENDATIONS

- CHILL DRILLING FLUID FOR PROPER DOWNHOLE TEMPERATURES
- WEIGHT DRILLING FLUID TO OFFSET GAS CUT MUD
- USE HIGH CIRCULATION RATES TO MAINTAIN COOL TEMPERATURES AND CIRCULATE GAS OUT
- CONTROL PENETRATION RATE TO REDUCE GAS FROM CUTTINGS
- SELECT AND SIZE WELL CONTROL EQUIPMENT TO HANDLE HYDRATE GAS
- COLLECT AND SAMPLE MUD GAS TO DETERMINE HYDRATE INTERVAL
- MONITOR AND RECORD MUD INLET/OUTLET TEMPERATURES
- TEST PERMAFROST CASING SEAT PERIODICALLY TO EVALUATE THAW EFFECTS
- MONITOR CASING-CASING ANNULI FOR LEAKAGE
- CONTINUE TO USE COOL MUD AFTER CASING IS SET TO PREVENT PRESSURE BEHIND CASING

Figure 14

CEMENTING AND CASING DESIGN

- CIRCULATE MUD FREE OF GAS TO PREVENT PERMEATION OF CEMENT
- USE CEMENT WITH LOW HEAT OF HYDRATION
- SET HIGH STRENGTH CASING OPPOSITE HYDRATES
- TEST HYDRATE CASING SEAT FOR GAS INFLUX
- DO NOT RETRIEVE CONVENTIONAL CORES OR SIDEWALL CORES WITHOUT PROPER PRECAUTIONS
- PERFORM DRILL STEM TESTS ON HYDRATE ZONES AND NEIGHBORING FREE GAS ZONES

Figure 15

LOGGING AND HYDRATE DETECTION

- MONITOR MUD GAS LOG CONTINUOUSLY
- MONITOR SHAKER SCREEN
- RUN OPEN HOLE LOGS IMMEDIATELY AFTER HYDRATE ZONE PENETRATION
- OPEN HOLE LOGS SHOULD INCLUDE SONIC, RESISTIVITY, GAMMA RAY, DENSITY, NEUTRON POROSITY, SPONTANEOUS POTENTIAL, AND CALIPER

Figure 16

NEEDED WORK

- DRILLING MANUAL FOR HYDRATES
- SET LOGGING AND EVALUATION PROCEDURE
- RESEARCH IN CEMENT/HYDRATE INTERACTION TO EVALUATE EFFECT OF DECOMPOSITION ON CEMENT STRENGTH
- EFFECT OF SOIL TYPE ON HYDRATE EXISTENCE
- RESEARCH IN HYDRATE DECOMPOSITION LOADS FOR CASING DESIGN
- THERMAL SIMULATION STUDIES TO DETERMINE DECOMPOSITION RADII AND GAS INFLUX AS FUNCTION OF DRILLING CONDITIONS

Figure 17

ARTICLE 7 (Hall, G.)

National Petroleum Reserve in Alaska
2525 'C' Street - Suite 400
Anchorage, Alaska 99503

August 22, 1979

Memorandum

To: Arthur L. Bowsher, Chief, Exploration Strategy, Menlo Park

From: George H. Hall, Petroleum Engineer, ONPRA, Anchorage

Subject: Recognition of Hydrates by Use of Open Hole Logs of NPRA Wells

The reference material that was first available in an attempt to find and study published information on how Clathrates may be identified from conventional open hole well logs appeared straightforward and uncomplicated.

The basic concept for the determination and identification of the phenomenon appeared as is illustrated in the idealized log sketch that is attached and which indicates:

1. That the Clathrate (or Hydrate) sandstone interval is characterized by a larger resistivity kick than the adjoining gas saturated sandstone.

2. That the Clathrate (or Hydrate) sandstone interval is also characterized by a much smaller negative S.P. response than that of either the gas saturated sandstone or the water saturated sandstone.

3. That the Caliper log of the Clathrate (Hydrate) interval usually indicates an oversized hole.

In attempts to relate the above criteria to NPRA well logs, confident or conclusive interpretations were not reached.

Additional reference material indicated that coring and field testing may sometimes be necessary to establish the relationship of the permafrost and Clathrates to log response.

Also, in the instance of NPRA, it is difficult to effectively compromise the objectives of drilling deep exploratory tests and the precise evaluation of shallow permafrost and Clathrate intervals.

The utilization of very costly deep capacity drilling rigs and the complementing large and expensive pad and camp support as currently employed in NPRA do not comprise the most compatible equipment to conduct research oriented programs such as may be associated with the drilling of slim holes with refrigerated drilling fluids and rubber sleeve coring equipment that may be necessary to actually identify the presence of permafrost and clathrates.

As an example of minimum hole size, rate of penetration, and mud temperatures at Tunalik; a 42-inch conductor was set at 80 ft. on 10 November 1978, and within 13 hours an additional 500 ft. of 17½ hole was drilled, to be later opened to 36 inches for the setting of 30-inch at 516 ft.

After setting 30-inch casing at 516 ft., 1,034 ft. of 17½ hole was drilled in 22½ hours. The mud temperature was approximately 100°F.

Other Log Observations and notes from the Tunalik Test Well No. 1 Logs are as follows:

Depth	Resistivity	S.P.	Sonic (M/Sec./Ft.)	Notes
645	40	-20mv	120	Cutting gas could be affected by coal beds.
665	30	Nil	90	Absence of negative S.P. response may indicate permafrost or hydrates, reference was recalled that sonic times can be affected, but that the effect is unlikely to be seen unless the log is run so soon after drilling that the thawed zone extends only a few inches ...(R. Bateman). Other references indicate that cycle skipping had been noted where hydrate intervals had been exposed to warm drilling mud for several days. (D. W. Davidson-National Research Council of Canada). Logic is expressed that the "frozen effect" limits the penetration of mud filtrate thus reducing the negative S.P. - and also (that the neutron in corresponding instances has essentially the same characteristics as water saturated intervals in the hydrates as contrasted to the usual lesser Neutron response in gas saturated intervals than in most fluid saturated intervals...). All of which appears to indicate that some of the indications of hydrates are present, but the confidence of conclusive evidence is mixed.
695-	85	-15	160	Lithology Log indicates coal.
750-760	90	-27	90-120	Better than other S.P.'s but high resistivity

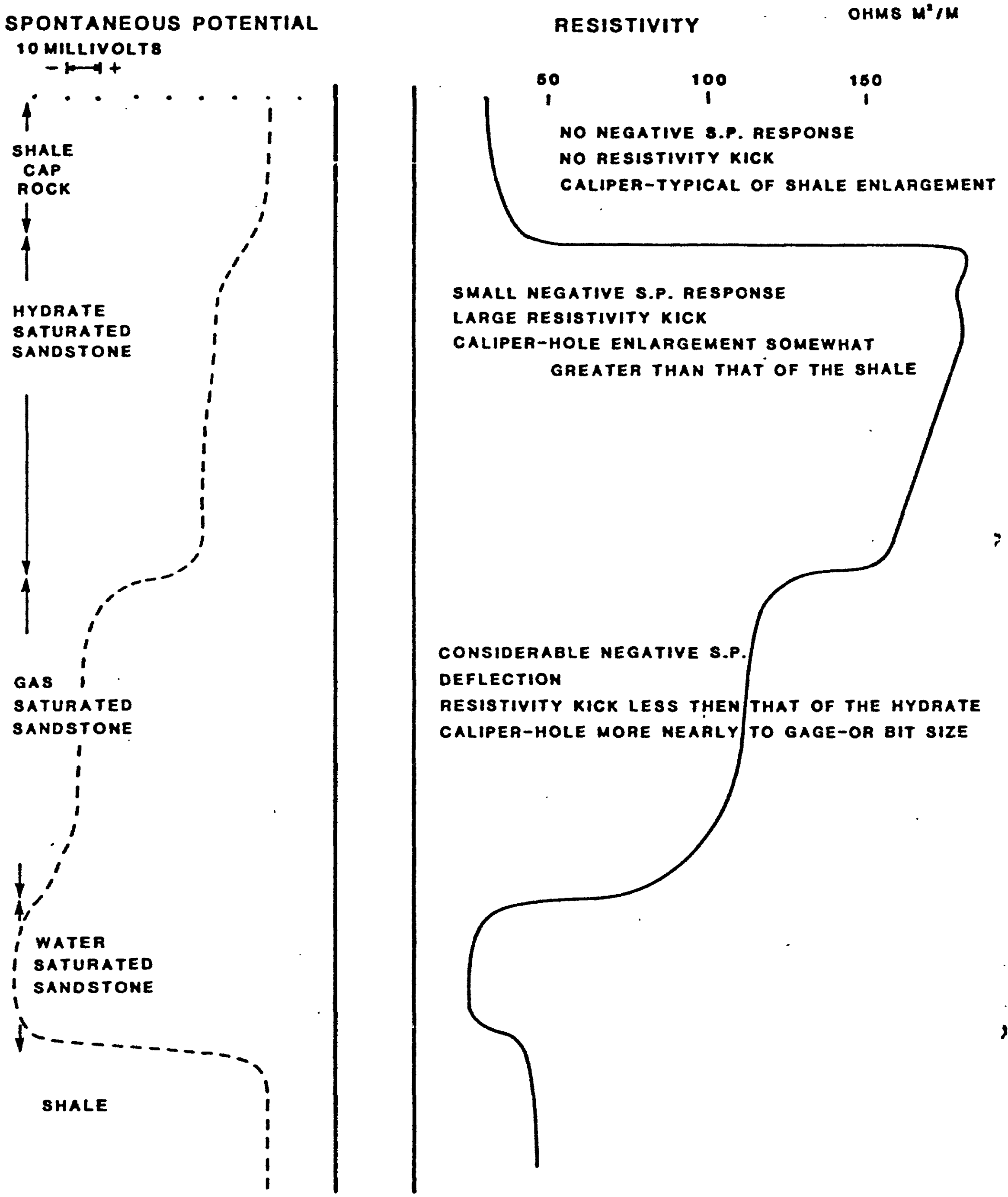
850	60	- 5	60	Possible thin interval between some coal.
1150	80-100	- 5	80	Possible thin interval - hydrate.
1340	55	-10	90	Possible thin interval with coal interference.
1410-1455	50	-10	60	Possible thin interval between coal seam, but depth is probably deeper than likely of hydrate according to temperature pressure assumptions.

Among tools and methods suggested by Dr. Goodman to improve quantitative interpretation is the application of Crystal Cable Velocity Surveys. An example illustrated that the tool indicated velocities of 7,500 to 13,000 ft./sec. in permafrost, compared to 5,000 to 6,500 ft./sec. in unfrozen sections.

Thus, the literature indicates that hydrate identification from open hole relationships has been accomplished in certain instances; however, determinations under routine drilling and logging operations appears to remain subject to considerable subjective judgement.

/signed/
George H. Hall

Attachment (1)



NO NEGATIVE S.P. RESPONSE
NO RESISTIVITY KICK
CALIPER-TYPICAL OF SHALE ENLARGEMENT

SMALL NEGATIVE S.P. RESPONSE
LARGE RESISTIVITY KICK
CALIPER-HOLE ENLARGEMENT SOMEWHAT GREATER THAN THAT OF THE SHALE

CONSIDERABLE NEGATIVE S.P. DEFLECTION
RESISTIVITY KICK LESS THEN THAT OF THE HYDRATE
CALIPER-HOLE MORE NEARLY TO GAGE-OR BIT SIZE

(AFTER MAKOGAN, YU.F.,1974, TRANSLATED BY CIESLEWICZ, W.J.,1978, P.125, FIG.101)

RUSSIAN HYDRATE STUDIES (G_e HALL, 1979)

Figure 18

ARTICLE 8 (Hoffman, E.)

February 22, 1979

Mr. Arthur Bowsher
NPRA
U.S. Geological Survey
345 Middlefield Road
Menlo Park, CA 94025

Dear Mr. Bowsher:

Enclosed is a draft of the notes from GRI's Hydrate Workshop. These notes have been recorded by Mr. Hoffman who also acted as secretary for this meeting. I would appreciate it very much if you could find time to review the draft he has prepared. I feel that your future input is vitally important, and ask that you be both critical and constructive in the review. We encourage you to indicate your comments, additions or deletions on the draft. Please feel free to exercise your own personality in doing this.

Once you have reviewed and commented on the draft, it should be returned to:

Mr. Ed Hoffman
P.O. Box 1352
Laramie, WY 82070

He will incorporate all of the reviews and comments into a final form. Since things have moved so well to date, I would hope that we can have the final ready for mailing by the end of March. This, of course, will depend upon the timeliness of your response.

Finally, I would like to take this opportunity to thank you for your contribution to this overall effort. The success of this endeavor was made possible through your participation and committment, and it is our feeling that the personal workshop was very successful.

Sincerely,

/signed/
John L. Cox
Manager
Basic Research

Enclosure

NOTES FROM GRI
GAS HYDRATE WORKSHOP

Sponsored by
Gas Research Institute
and
American Gas Association

Stapleton Plaza Hotel, Denver
February 1, 1979

John L. Cox, Presiding

The meeting opened with brief presentations by John Cox of GRI, George Claypool of the USGS, and Dendy Sloan of the Colorado School of Mines.

Dr. Cox encapsulated the background and purposes of the Gas Research Institute and the reasons for initiating the meeting on natural gas hydrates. The need for examining this and other unconventional resources was emphasized.

Dr. Claypool spoke of the geochemistry of organic matter in sediments, and the presence of methane occurring as hydrate in oceanic, deep sea sediments. A pressure-temperature diagram for hydrates was shown, along with the temperature profile occurring with depth. It was noted that traces of other compounds or minerals affected the stability of the hydrates.

The use of a "bottom simulating reflector" (BSR) was described. It provides a means of cutting across layers of sediment, and follows the temperature isotherm rather than pressure, which is a function of depth. A cross section of the volume of sediment is obtained in which methane hydrate could be stable. However, it was noted that methane occurrence is fairly rare and is only localized where the hydrate would be stable.

A pressure-composition diagram for the methane-water system was shown, which illustrated the phase changes that would occur in the formation of the hydrate. An error was indicated in the diagram.

No direct physical evidence has been uncovered for the existence of hydrates in marine sediments. Rather, the evidence has so far been indirect (the P-T requirements). Deep-sea drilling, however, may now be available whereby a pressure core barrel can be used to take a sample. Tests haven't yet been made where hydrates might be present. The Scripps Institute is managing the deep sea drilling project (DSDP) funded by the National Science Foundation (George Brett of NSF is in charge).

Dr. Sloan sketched the history of the discovery and studies of gas hydrates. The chronology is as follows:

A BRIEF HISTORY OF HYDRATE THERMODYNAMICS DEVELOPMENT

1823-	Faraday discovers chlorine hydrates
1890's-	French scientists study hydrates
1931-	Hammerschmidt finds hydrates plug pipelines
1941-	Wilcox, Carson, & Katz present K value charts
1946-	Deaton & Frost (USBM) do definite gas study
1950's-	Stackelberg, Muller, Claussen, Pauling & Marsch determine structures
1959-	Vander Waals & Platteeuw - Statistical mechanics model
1960's-	Kobayashi & co-workers put parameters in S.M. model
1960's-	Robinson & co-workers study hydrates
1970-	Russian discovery of gas hydrate fields
1970-	Katz predicts hydrates field depths

1971-	Stoll, Ewing, and Bryan find hydrates in ocean sediments
1972-	Parrish & Prausnitz - SM parameters & 3 component mixtures
1972-present	Kobayashi & co-workers measure water content of gas in equilibrium with hydrates
1972-75-	Katz, Hand, & co-workers form hydrates without gas
1976-	Katz & Holder study H_{I}-H_{II} equilibria and liquid denuding
1976-present	Sloan, Parrish and co-workers determine u and h for SM model
Present-	Bishnoi and co-workers study kinetics of hydrate formation

A phase diagram was shown on which the GPA charts for water content are based. The water content of the gas (in lbs. per million cubic feet) forms one coordinate, temperature the other. The two-phase regions were divided into Gas-Ice (G-I), Gas-Liquid (G-L), and Gas-Hydrate (G-H), with three phase equilibria loci denoted by I-G-H, I-G-L, and H-G-L. The GPA charts are formed from a series of instant pressure lines in the G-L region which are extrapoled from the G-L region across the H-G-L equilibrium into the H-G region. It was noted that these lines should curve in the H-G region, bending toward the I-G-H equilibrium curve.

It was observed that adding propane, etc., will shift the boundaries for the formation of the hydrates.

As to the behavior in the gas-hydrate region, Dr. Kobayashi noted (and Dr. Sloan concurred) that the original measurements failed to detect the pressure of metastable liquid water in the gas-hydrate regions.

THERMODYNAMICS AND KINETICS
of
HYDRATE FORMATION

The meeting discussion commenced with the query as to whether the thermodynamics is at a stage to predict hydrate formation in actual practice. The rejoinder was a qualified "no", mainly due to the pressure of brines. The exact condition would be difficult to duplicate in the laboratory. Other factors, moreover, affect the thermodynamics. One such is the porosity of the formation. Additives, of course, alter the conditions for formation and existence, and relate to the economics for natural gas recovery from hydrates.

A thermodynamic model now exists whereby, given temperature and composition, it is possible to calculate the pressure where hydrates form. It applies to known multicomponent systems, and extension can be made to inhibitors. The model is semi-theoretical, or semi-empirical, depending on one's preference of terms, and points up to the need for more experimental data so that further generalization may be made.

Roger Fishnoi of the University of Calgary has done perhaps the principle work on the kinetics of hydrates. This work was funded by the National

Research Council and started out as an environmental problem. More specifically, there was the concern about blowouts of oil and gas wells in the Arctic, and if hydrates would form under these conditions. No information was available at that time on the kinetics, which led to a study of methane hydration rates.

In the United States, it was mentioned that the Office of Saline Water supported work on hydrates, which included the kinetics of hydrate formation. This work undoubtedly related to the formation of hydrates with light hydrocarbons (e.g., propane) as a means of producing fresh water. Work was conducted at Syracuse University under Berdun. Work on desalination with hydrates was also investigated at Kansas State University and the University of Oklahoma.

DIRECTIONS OF RESEARCH UNDERWAY

As to ongoing research on hydrates per se, GRI is not presently supporting any work on gas hydrates, though some support in thermodynamics is in effect. GRI has one project related to the assessment of hydrates as a potential gas resource, and whether it should be so included. It is in the Planning division of GRI under Ken Darrow.

NSF is supporting experimental work by Riki Kobayashi at Rice University and by Dendy Sloan at the Colorado School of Mines. There is not likely to be work supported elsewhere. Thus, these are the only two programs underway.

Dendy Sloan has a proposal submitted to NSF which would involve the study of methanol and other additives. Exxon is contributing to Riki Kobayashi in support of studies on H_2S and propane hydrates, the use of methanol, and glycol inhibitors for C_3-C_4 mixtures. A coordination of this work is anticipated, with the suggestion that Dendy Sloan might also be supported by industry.

It was commented that much or most of the previous work on hydrates has been process oriented. That is, the objective has been to control or eliminate the formation of hydrates in gas processing. This is embodied by Hammerschmidt's rule, the determination of how much methanol need to be added to inhibit hydrate formation.

The work is now moving into the incompressible region, that is, into the brine phase. This introduces, more pertinently, the matter of how best to recover natural gas from the hydrate form, and the need for information which will assist in the determination.

ANTICIPATED RESEARCH EFFORTS

Among the basic data needed are the thermal properties of hydrates and the environment in which they are found. In addition to this are the transport properties, which relate to the flow of heat and the flow of mass.

Beyond this are the kinetic properties, notably the rate of which hydrates are formed and are decomposed. A distinguishing difference noted repeatedly by those who have worked with hydrates experimentally is that hydrates are much easier to decompose than to form. Thus, for example, the reforming of water-gas systems at temperatures and pressures where hydrates are known to exist is not necessarily a conclusive test.

Further data is needed on the effect of inhibitors or additives, and the interaction of polar and nonpolar molecules. Though the hydrate phase is apparently well taken care of, the other phases require further investigation, i.e. the fluid phases.

OCCURRENCES AND SOURCES

The question was asked if the natural occurrence of hydrate was limited to the permafrost regions and to ocean sediments. The antarctic regions are a still unexplored area as far as drilling, and other regions should not be excluded. While hydrates occur in producing from certain formations, it is from the cooling due to throttling or pressure drop durig flow (the Joule-Thomson effect and latent heat effects with phase change).

It was commented that there was something else in the arctic regions besides temperature which causes hydrates.

As to the worldwide distribution of organic matter which would be the source of natural gas for hydrate formation, ordinary rock contains about a half a percent organic matter. This organic matter undergoes coalification under the appropriate conditions of temperature and pressure and converts to gas (and liquids). That generated in fine grain sediments is largely lost to the atmosphere, etc.

The total organic material present in rock is many orders of magnitude greater than the known fossil fuel reserves. The coalification, liquefacation, and gasification processes, however, are much slower than the rate at which fossil fuels are being used up.

The carbonaceous solids, gases and liquids which are produced mostly remain diffused throughout the rock or are lost to the atmosphere. However, in instances, the material migrates and collects in pools or formation. These concentrations are the oil and gas strata that are economically producible.

The distinction was made between biogenic and abiogenic carbonaceous material. Biogenic is from a microbic source, abiogenic is not from a microbic source. A further distinction is carbonaceous material formed by the process of maturation, e.g., coalification. The North Slope gas is biogenic, for instance.

The biogenic material has as its source both plant and animal matter, chiefly of microscope origin. Hydrates occur in both the Paleozoic and the Devonian. The Russian deposits are Paleozoic.

The most likely occurrences of commercially attractive gas hydrates in sedimentary basins are the Arctic slope of Alaska, the Mackenzie delta and Arctic Archipelago of Canada, the northern portion of the West Siberian basin and the Vilyuy basin of the U.S.S.R. (Brian Hitchin, "Occurrence of Natural Gas Hydrates in Sedimentary Basins", in I. R. Kaplan, Ed., 1974, Natural Gases in Marine Sediments: Plenum, New York.) These regions are characterized by thick layers of permafrost. According to the article, natural gas hydrates have only been well documented in the Messoyakha field in the West Siberian basin.

There is evidence of hydrates on the North Slope, however. Exxon and Arco have used a pressure core barrel for testing, and have recovered some hydrates.

No drilling program for clathrates has been conducted in the Antarctic; only a few experimental holes. The temperature profile is such that hydrates could exist down to 6,000 ft. Air hydrates, incidentally, have been found in Antarctic glaciers. No kind of estimate is available on the extent of antarctic reserves.

Apart from the land regions, large deposits of natural gas hydrates are a possibility in oceanic sediments. This prospect has been noted in several articles which have appeared. The evidence almost entirely has been indirect and is based in considerable part on work by the USGA in establishing the "bottom hole reflector", and awaits further resolutions.

Mapping of the offshore arctic indicates a hydrate area of 7,500 square kilometers. This is the result of seismic work--studies that are easier to obtain offshore than onshore.

THE PROCESSES OF HYDRATE FORMATION AND DECOMPOSITION

During hydrate formation or decomposition, component migration occurs along the crystal boundaries. These processes of diffusion depend upon the fracture of the crystal structure but have not been studied in detail, e.g., with isotope migration.

The gas gets into the hydrate by physical entrapment. This in fact is the source for the term "clathrate", which means "crablike". The process may be viewed as one of physical reaction rather than chemical reaction. The kinetics is that of getting into the structure or "cage" rather than swapping electrons. It was mentioned that there are two structures, having cavities of different sizes.

An interesting phenomenon observed in the formation of hydrates is in the preparation of the water. If distilled water is first frozen and then thawed, the induction period for hydrate formation is reduced.

The processes of diffusion are evidentally related to the existence of hydrate deposits. As the permafrost boundary moved downward through the zone of hydrate susceptibility, hydrates were created. A regression is now occurring as the permafrost boundary moves upward. A sort of zone melting (and recrystallization) occurs with these changes, a phenomenon observed for oceanic sediments. It would be helpful if these hypothesized processes for hydrate formation could be firmly established and verified.

RESERVES (magnitude)

The question was asked of whether there were any reliable estimates of hydrate reserves. The response was that extensive coring and logging will have to be conducted, the same as for oil and gas.

The Russians believe that there may be 1018 cubic meters of natural gas occurring as hydrates, whereas the conventional reserves are 10^{13} cubic meters. This raised the further comment of whether the figures relate to an occurrence (gas in place) or to economically recoverable reserves. At one time the Russians predicted that there were 100 trillion cubic feet (cubic meters?) recoverable by known technology. This figure is not published anymore.

Hydrates occur at the well bore surface (sand face) due to cooling effects from pressure reduction in flow during production. This may be the cause behind the moderate figures first reported by the Russians, and the reason these figures were discounted.

A geological map of hydrate occurrence which appears in a recent issue of Pravda indicates some 10 trillion cubic meters of gas in the form of hydrates in the Soviet Union. Mention was made that even China is covered by 23% permafrost, mostly in Tibet and the mountainous regions.

The total estimated reserves of gas in the McKenzie Delta have been increased by 15% due to the occurrence of hydrates. These increases are based in thin zones and stringers, however. The exact figures of the estimate for the McKenzie Delta have not been published.

SEISMIC EXPLORATION

It may be possible to devise seismic tests for hydrate reserves. The oceanic sediments could be calibrated from drill holes (it is theoretically possible to gain the data from only two holes). Anomalies in seismic velocities in the arctic sediments presumably would suggest hydrates, though there are other effects to be considered.

A phenomenon used as an indicator of hydrates, particularly in marine sediments, is the seismic behavior of a zone called the "bottom simulating reflector" or BSR.

The nature or characteristics of the bottom simulating reflector (BSR) are described in USGS Circular 733. It is a zone below the ocean floor which reflects seismic waves. It mimics or simulates the bathymetry of the ocean floor, yet lies some 200-600 meters below the floor. It occurs only where the sea is deeper than 400-600 meters and extends beneath the deepest waters traversed.

The BSR is most strongly developed beneath bathymetrics highs, and may be absent beneath lows. Observations of the seismic behavior suggest that the BSR is produced by a zone of free gas in the sediments immediately below an impervious cap. Furthermore, since the zone lies at the approximate pressure-temperature condition for natural gas hydrates, it is postulated that the gas is trapped beneath an impermeable cap of sediment which is cemented with hydrates.

In the interpretation of seismic data, it was noted that pseudo anticlines may appear where a little gas can cause a large acoustic impedence.

DRILLING IN HYDRATE ZONES

There is no concerted effort to find gas hydrate fields as such since they could not be produced anyway--at least at present. Hydrates in lateral association with free gas could be significant. The gas below or above the hydrates would maintain pressure. The ratio of free gas to hydrate is an unknown.

In wells drilled in the Canadian Arctic, downhole temperatures were not measured since the temperatures were below the instrument range. However, the drilling mud return (which was at 50-60°F) provided an indication. Puffs of gas were inferred to come from hydrate decomposition. By chilling the mud (the permafrost layer would act as refrigerant), the hydrate decomposition would be controlled. Otherwise, high casing pressures could result (to 15,000 psia). Moreover this pressure would not bleed off into the formation, presumably due to the lack of permeability of the hydrate in place.

In drilling, a closer check on hydrates should be initiated. For tubing collapse is a possibility. Imcompressible phases and gases are apparently formed rather than a refreezing of the permafrost.

The log of the drilling mud behavior may be used to detect hydrates encountered. Ordinarily, if a gas-bearing formation is encountered, the mud weight (density) may be increased to check the gas in place. Hydrates, however, are in part carried up with the mud and give off puffs of gas as (thermal) decompositives occur. Decomposition in the bore may be prevented by chilling the drilling mud.

TESTING FOR HYDRATES

Equipment and techniques now exist for reliably indicating hydrates in place. These include:

1. Mud logs
2. Temperature logs (down to 12-15°F)
3. Drill hole logs
   Resistivity, sonic, etc.

The last-mentioned are only satisfactory below the permafrost, since permafrost would give similar indications.

In the permafrost the best evidence is pressure and the performance of low- vs. high-temperature mud. That is, the use of high-temperature mud will cause a marked pressure rise if hydrates are encountered.

Pan Arctic is drilling to 6,000 ft. in the Canadian Arctic. It is now routine to run a gas log on the drilling mud (so much gas per unit time coming off mud, a relative figure).

PRESSURE CORE SAMPLING

Direct evidence for the existence of hydrates may be obtained by the taking of a core using a pressure core barrel. It is applicable to either in-shore or off-shore drilling practice.

In offshore drilling, the comment was made that pressure core operation would be the easiest part. It was noted that in sampling the control of the temperature is more important than the control of the pressure. While there is a time lag of perhaps 30-40 minutes in recovery of the sample, the decomposition will be minimal, particularly if the sample is pulled up through chilled drilling mud. Furthermore, the permafrost itself tends to refrigerate. In fact, the low temperature gradient in the drill hole precools the core barrel, which would offset some of the difficulties ordinarily expected. In fact, subcooling might occur--that is, the permafrost is colder than the formation.

Cores taken from the permafrost layer have the unfavorable habit of thawing and leaving a bucketful of mush. An air drill was proposed as an alternate means of taking a hydrate sample.

OTHER HYDRATE PROPERTIES

The question was raised whether there might be any unusual physical properties of hydrates that could be built into a downhole tool. These might include NMR (nuclear magnetic resonance) properties, spectroscopic properties, presence of high energy hydrogen, etc. No specific response was given except that techniques already in use are probably sufficient if properly applied. These include core data (permeability and porosity), microbiology, and well logs: electric, SP, seismic, etc., plus a mud log. The question remains, however, of behavior in the permafrost layer and how to determine the concentration of hydrate (or gas) in the layer. A neutron log was suggested as a possibility in that it will measure hydrogen atoms.

R & D DRILLING PROGRAM

There are two types of drilling programs, each conducted differently from the other. One is for the gathering of seismic data, the other is for commercial purposes. Either or both can be directed toward obtaining information on the occurrence of hydrates.

If an R & D program of drilling and sampling is to be initiated, it would be necessary to start planning at least a year ahead. The logistics are formidable in the arctic region. For instance, Pan Arctic is drilling in 1600-1700 ft. of water from an ice platform. While the drilling itself may last only a few weeks at each site, there is the matter of preparation of the site.

It was thought necessary to lay out a drilling program some 18 months before actual drilling commenced. In drilling from the ice, the question is compounded by the fact that some years the ice is not suitable. Thus, some years it is possible to drill off Prudhoe Bay, other years it is not.

The comment was made that it is better to add research to an ongoing drilling program than the other way around. Furthermore, no research would probably be allowed on an operations hole. For in operations, the engineering is geared to 10,000 or 20,000 feet or whatever the depth, rather than to 2,000 feet or wherever the hydrates may exist.

While some wells can be logged as a standard procedure, other programs will have to be made specific to the objectives. The first 2,000 feet are not ordinarily logged, since most wells are drilled to 8,000-9,000 feet or more.

A specific hole may be the answer. Thus in the course of the Pan Arctic drilling program, several rigs are used. A smaller rig could be deployed for a shallow hole. In this manner, R & D could be tied into ongoing operations if sufficient advance planning was made.

The possibility of a joint R & D effort was brought up, one which might involve the U.S. government, the Canadian government, and industry--if not cost impacted.

The Department of Energy (DOE) has nothing in the present budget for R & D in drilling for fossil fuel extraction. The 1980 budget has been formed, and 1981 nearly so. The earliest date would be 1982.

As to other sources of funding, GRI has budgeted monies available for 1979, but none for 1980. The items might be put back in the budget for 1981.

The question was raised as to what organization or firms have the personnel and testing facilities for assisting in such an R & D program. The USGS is apparently winding down its efforts in this direction unless renewed funding comes about. Geochem Research Inc., for example, has the experience in interpreting logs, etc. There are very few experienced in taking pressure core samples.

It was suggested the GRI (or others) might develop a program to gather information on the sea floor--from the first few hundred feet down to perhaps 1000 feet below the floor. Even if there are not immediate production possibilities, this information will utimately be needed.

The Russians routinely look for hydrates in the exploration of oil and gas. It is part of their drilling program, and the interpretation of resistivity and gamma logs is extended to hydrates. The west should do the same.

ADDITIVES - METHANOL vs GLYCOL

Any discussion of hydrate recovery methods usually starts off with the use of methanol and glycol, additives which are used to control hydrate formation in natural gas processing.

The effect of adding methanol to pure components is established. Application to actual hydrate systems encountered in the field is not resolved since the composition of the phases is not generally known, particularly if brines are present.

Enthalpic changes have been measured for the addition of methanol. The latent heat changes are not much different than for ice. The effect is endothermic causing a lowering of the temperature of the mixture.

Glycol is generally considered more effective than methanol in controlling hydrate formation in natural gas processing. Extended to hydrate decomposition, it is expected that glycol would be more effective. The amount of additive left in the formation, however, could be prohibitive. Usage could be effective in startup operations, however. Moreover, the aqueous solutions formed could be circulated--though the high requirements for solvent separation would be out of the question.

When methanol injection is used to control hydrate formation in natural gas processing, about 50% of the methanol is recovered in the liquid phase. The other 50% remains in the gas. With glycol the recovery is considerably better.

In a paper by Bily and Dick of Imperial Oil Ltd., Calgary, Alberta, mention was made of attempts to stimulate a hydrate zone with methanol. Productivity was not increased. C. Bily and J. W. L. Dick, "Naturally Occurring Gas Hydrates in the Mackenzie Delta, N.W.T.," Bulletin of Canadian Petroleum Geology, 22 (3), 340-352 (Sept., 1974). This same paper provides illustrations of logs obtained of the hydrate-bearing zones, and distinguishes between gas, hydrate, and water. The logs obtained were caliper, gamma, SP, LAT 8, sonic, and total mud gas.

PROPOSED PRODUCTION METHODS FROM HYDRATE ZONES

The type of hydrate system encountered will influence the method of recovery. Five possibilities were listed:

1. All hydrate
2. Excess gas
3. Excess water
4. Excess ice
5. Free gas and ice

Each will have a different effect on heat loss in hydrate decomposition and recovery.

Several methods were considered for hydrate decomposition in place. These include the following:

1. Hot gases (from combustion)
2. Hot water (or cold water)
3. Steam
4. Methanol or glycol

Each has its pros and cons. In first discussing the matter, a mode of injection and circulation will be assumed a priori.

Hot gases may be furnished from combustion of the resultant gases from hydrate decomposition, assuming an initial induction period to establish a flame front. Or hot combustion gases may be directed down the hole, assuming heat losses are controllable. An obvious difficulty is the dilution of the natural gas with inert combustion products (nitrogen and carbon dioxide).

Water (or brine) may be injected into the formation. The hotter the water, of course, the less required. A lower limit of 35°F is anticipated. Thus, formation water or above-ground water both merit consideration as sources, with or without the addition of heat.

Steam may be considered as a special case of water injection. It reduces the amount required by its extra heat content. At the same time the additional cost and trouble of steam-generating facilities are introduced. A part of the gaseous product would be diverted to supply the heat required.

The density of water is greater than the density of methane hydrate--or the specific volume of the water is less. Therefore, on melting a void space would be created which contains compressed gas. As production ensues, the formation will display a different permeability to the gas than to the water (or brine, as the case may be). Thus the relative permeability to the gas may by 100 times greater than to the water. In fact, the water may hardly move. There are other factors which enter, however, such as wetting and surface tension and the solubility of gas in water--which is slight.

The injection of an oil would be another means of adding heat to the hydrate zone.

The possibility of providing combustion in a gas zone below the hydrate zone was brought up as a means of producing from the hydrate.

The point was made that reducing the pressure would lower the freezing point of the hydrate, thus giving some degree of control. This conceivably is a way around artificially supplying heat.

The best place, initially, might be to concentrate efforts where the geology would assist recovery. Specifically, this would involve a free gas zone below the hydrate zone, with excess gas available. Decomposition would occur upward from the gas zone and would preclude the use of methanol or glycol.

With pulldown of the gas, the pressure at the interface is lowered. At the same time, the warmer gas from below (due to the natural temperature gradient) approaches the hydrate zone. Both contribute to the decomposition of the hydrate at the interface. Presumably the rate of water encroachment would be very slow.

The underground or in situ recovery of gas from hydrates should be environmentally acceptable, whereas mining--even if feasible--would be less so.

FRACTURE OR RUBBLIZATION

The need for fracturing or rubblizing the hydrate bearing formation was considered as an adjunct of production. Hydrate formations have little or no natural permeability, and means are required to create flow channels in order to have contact with the recovery agent.

Fracture was not regarded as a promising method of creating permeability. For explosive methods the heat of explosion would liberate water which would be expected to refreeze unless temperatures could be sustained by the introduction of circulating water or gases. Hydraulic methods might be more satisfactory, with the fracture sustained by sand particles.

CONTROLLED STUDIES
of
RECOVERY METHODS

Discussion was initiated on means by which gas recovery from hydrates could be studied on a laboratory or pilot plant scale. The principal difficulty to begin with is in the forming of the hydrates in a porous medium. There has apparently been a small amount of work in this direction (e.g., at Columbia University, using water and methane, with pressure and cooling).

The Institute of Gas Technology (IGI) has conducted experiments on how to determine if a core of hydrate has been formed. It was noted that hydrates tend to occlude water, and it was commented that unconsolidated vs. consolidated sands may be a factor. Furthermore, as others observed, hydrates are formed in a vertical direction.

The difficulty of forming hydrates in the laboratory may indicate that a natural site will have to be selected for recovery experiments. The North Slope region was suggested as a possible site area.

INFORMATION RETRIEVAL

Tom Wander of the American Gas Association has prepared a bibliography of hydrate-related articles, mostly covering the last 10 years. The bibliography is available on request. There were two patents noted in the literature on gas recovery from hydrates. One utilized propane, the other an electrical current.

A wholesale translation of Russian articles was brought up as a means of gathering information, with the possibility of GRI financing the translations. On the other hand, the comment was put forth that Russian information--or misinformation--has been a source of trouble. More useful are the studies conducted in this country. Some of the difficulty may be that the theoretical portions of the Russian work are not easily readable, another is the lack of identification of the information presented. Much U.S information comes back at us from Russian articles without citation, though Russia is now a member of the International Copyright Agreement (since 1974).

The query was made as to what work the Russians might already have done in research and development. John Cieslewicz's translation of Makogen's book (Hydrates of Natural Gas, Geoexplorer's Inc., Denver, CO) shows the Russian work as mostly qualitative, with quantitative results suspect. No data was presented on kinetics. Moreover, as indicated, the Russian work many times only presents data from U.S. studies, usually without bothering to give units.

The possibility of contacting Russian authorities was brought up. It was mentioned that John Cieslewicz of the Colorado School of Mines, who is facile with the language, had no success in contacting Russians working in the fields. However, Makogen was slated to come to a Permafrost Conference (and was contacted by Don Davidson of the National Research Council). He did not show up.

The prospect was then mentioned of sponsorship of some sort of international meeting (by GRI). For example, a session on hydrates could be conducted at the forthcoming International Petroleum Conference, to be held in Budapest.

With regard to previous wells drilled, various libraries of well logs exist in cities in major production areas about the United States and Canada. In this connection there are logging societies also at these same cities, e.g., Denver, Calgary, etc. In Canada, specifically, the Materials Production Laboratory at Calgary has a library of well logs. (Chuck Bily at Imperial Oil, Calgary, has more information on this source).

Canada has a program for examining shallow gas wells. The presence or absence of hydrate bearing formations may be indicated in the course of this program. Of 300 wells examined in northern Canada, hydrate were found in 12 wells. Of these, 11 are in the McKenzie Delta. There is strong indication of hydrates in wells in the Arctic islands.

Hydrates were indicated below the permafrost, not in the permafrost itself. This, however, is in part due to the fact that well logs cannot differentiate gas hydrate from the permafrost. Below the permafrost, the well log will differentiate the presence of hydrates.

YIELDS AND NET ENERGY ANALYSIS

The gas content of hydrate formations varies widely. For this reason, any analysis for gas yield and net energy yield is necessarily site specific, though limiting generalizations may be made.

It was stressed that a study of gas output vs. energy input is needed. In this way, perhaps, the optimum recovery method could be pre-determined. Also, a determination could be made of whether it is indeed worthwhile to recover hydrates from a net energy standpoint.

In particular, it was found that no overall calculations have yet been made on the net energy yield for the field recovery of natural gas from hydrate deposits. While a net energy analysis is required at the process development level for new projects funded by the government, such is not necessary at the R & D level. Nevertheless, it would be highly instructive for viewing the potential of hydrates. Though the heat of fusion may be compared with the heat of combustion, etc., the application to an actual reservoir in terms of heat leak, formation properties, actual gas yield, etc., is something else.

Ideally, for the $CH_4.7H_2O$ hydrate as an example, the heat of combustion represented by the methane is about 230 k cal/g-mole whereas the heat required for decomposition is some 15-30 k cal/g-mole. There is thus an intrinsic gain of around 170-200 k/cal/g-mole, theoretically. This of course does not allow for the thermal losses to the surroundings, etc.

In terms of English units, the formula $CH_4.7H_2O$ represents one lb-mole of methane per 142 lb of hydrate, giving a theoretical heating value of about 2,700 Btu/lb. This is not much lower than some low-grade coals encountered. Inasmuch as it may be economical to gasify these coals (in situ), it may also be feasible to thermally decompose hydrates--especially since hydrate decomposition is at a very low temperature compared to coal conversion.

From another standpoint, the equivalent volume of methane produced from the hydrate $CH_4.7H_2O$ would be approximately 188 SCF of methane per cubic foot of hydrate (or water, assuming the solid and liquid phase densities approximately equal).

If this amount of gas was compressed at 60°F to a volume of one cubic foot, the resulting pressure would be over 5,000 psi. If the volume of water released remained, the pressure would increase dramatically above this, even allowing for some solubility of the methane. Thus, the pressure that could be produced from the decomposition or melting of the methane hydrate in a closed system can be formidable if the water is retained in the system. This is sufficient cause for apprehension in drilling through hydrate zones.

Therefore, pressure-volume energy effects, as well as purely thermal effects, should probably be considered in the net energy analysis of gas recovery from hydrates.

POSITION STATEMENT

There so far seems to be no anti-hydrate philosophy, or at least it is thought that gas hydates have not been written off and still represent a resource of as yet largely undetermined potential. There remains, however, the demonstration of how the gas could be best produced--and, if so, what would be the gain.

PARTICIPANTS

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Ken Darrow - Gas Research Institute, Chicago, Illinois
Jim Ely - Shell Development Co., Houston, Texas
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ARTICLE 9 (Kharaka, Y., Sloan, C. E., and Carothers, W. W.)

CHEMICAL COMPOSITION OF FORMATION WATERS FROM THE NORTH SLOPE OF ALASKA--IMPLICATIONS FOR THE FORMATION OF CLATHRATES

by Yousif K. Kharaka, Charles E. Sloan* and William W. Carothers
U.S. Geological Survey, Menlo Park, CA and *Anchorage, AK

ABSTRACT

Chemical composition of water is a factor in determining the conditions (temperature, pressure) for the formation of clathrates. The temperature for the formation of methane hydrate at 1,000 psia pressure, for example, is lowered by 2°F and 5°F if the salinity of water is increased from 0 to 35,000 (seawater) and 100,000 mg/L dissolved solids, respectively. The temperature for the formation of methane hydrate at the above pressure, on the other hand, is increased by 2°F and 3°F if 10 percent and 20 percent CO_2 gas is added to methane, respectively; this temperature is increased by 4°F and 10°F if 1 percent and 5 percent H_2S gas is added to the methane.

Chemical analysis of surface water (lakes, rivers, streams and springs) from the North Slope of Alaska show that the water is fresh with salinities that are generally less than about 500 mg/L dissolved solids. Information on the chemical composition of formation waters from the North Slope of Alaska, on the other hand, is sparse. Chemical analyses of water obtained from various formation tests are available for a number of test wells at NPRA. In many wells, these analyses do not give the chemical composition of formation water because of mixing and contamination with drilling fluids. The reported salinity of water from these tests ranges from about 1,000 to 27,000 mg/L dissolved solids.

Detailed chemical analyses of three formation-water samples from South Barrow gas field and two from Prudhoe Bay oil field, Alaska, show that the salinity of water is remarkedly similar ranging from 19,000 to 22,000 mg/L dissolved solids for the samples from South Barrow and 17,000 to 22,000 mg/L dissolved solids from Prudhoe Bay. The samples from South Barrow were obtained from well numbers 5, 7 and 11 from depths ranging from about 2,200 to 2,500 ft. The samples from Prudhoe Bay were obtained from well numbers 1-13 and 3-8 that produce from Sadlerochit Group from depths ranging from about 8,800 to 9,000 ft.

The chemical data indicate that the salinity of formation water of interest in the formation of clathrates at NPRA (depth from below permafrost to about 5,000 ft.) may range from about 1,000 to 35,000 mg/L dissolved solids. These data also indicate that most of these waters will have salinities that range from about 10,000 to 20,000 mg/L dissolved solids. The most probable range of salinities will lower the temperature for the formation of methane hydrates at NPRA by a maximum of 2°F from that of pure water-methane at the same pressure (depth).

The concentration of H_2S in formation waters from South Barrow and Prudhoe Bay are below detection limit (0.1 mg/L). This and the absence of H_2S in the reported gas analyses indicate that H_2S gas probably will not affect the conditions for the formation of methane hydrates. The CO_2 content

of separator gas from Prudhoe Bay field is very high averaging about 15 percent. The reported CO_2 content of gas from test and producing wells at NPRA, on the other hand, is less than 2 percent which will increase the temperature for the formation of methane hydrate by less than 1°F.

ARTICLE 10 (Kienzle, J. K.)

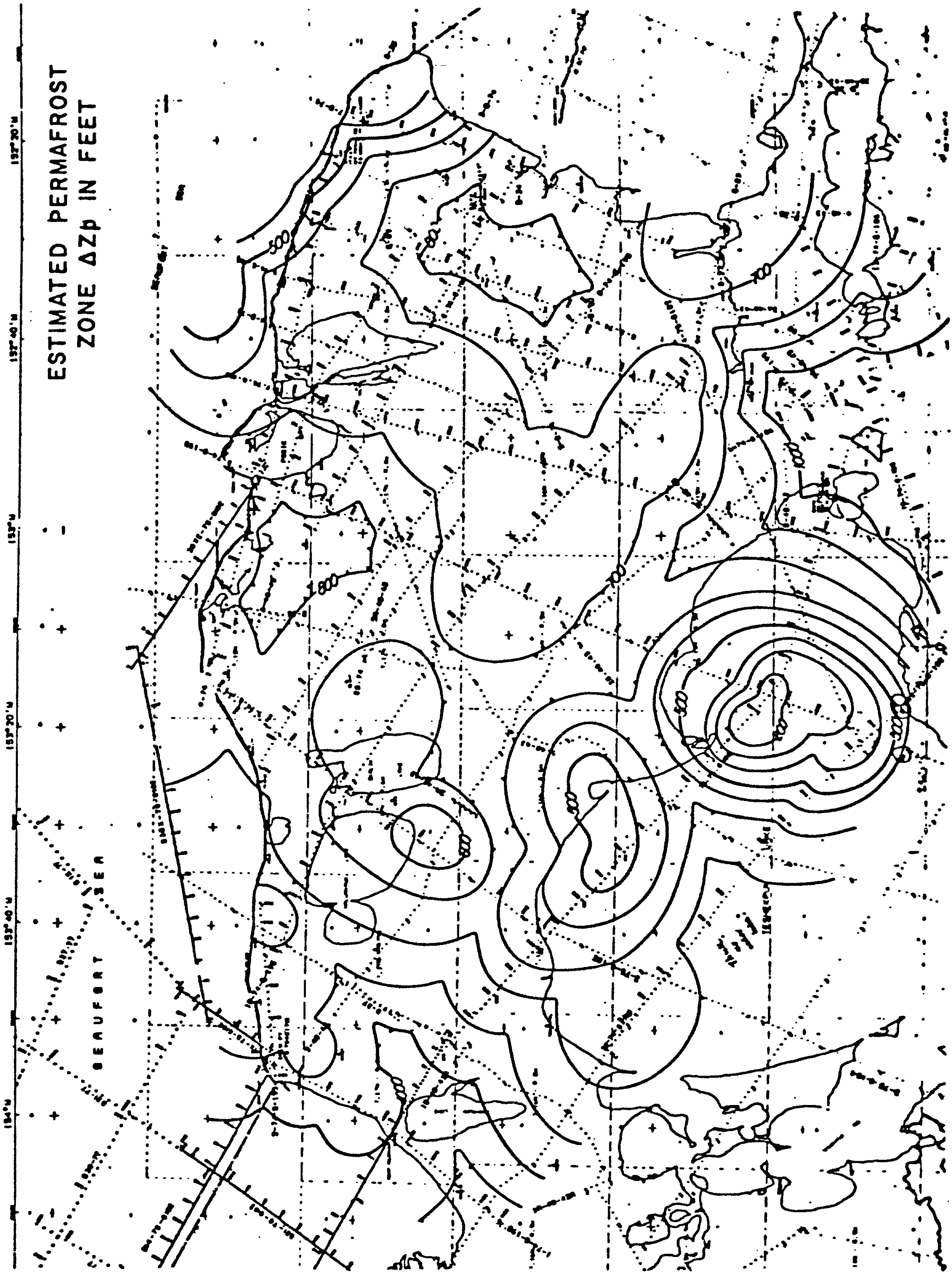
Seismic Technology and Permafrost

By J. K. Kienzle
U.S. Geological Survey
Menlo Park, California

Abstract

It has been known for many years that permafrost has an effect on seismic data. The problem has been recognizing the effect and trying to remove it so that the true subsurface structure can be determined. The permafrost effect is most obvious on seismic data over lakes where the permafrost thickness can decrease from over 1,000 feet to less than 100 feet. This creates a shallow low velocity zone under the lake which results in a time sag in all reflections below the low velocity zone. Regional changes in the thickness also occurs but this is very difficult to determine from the seismic data.

Calhoon Consulting Company has completed a study for NPRA in which they claim they can map the depth of the permafrost, (see Figure 19). This map is incorrectly called a permafrost thickness map; being in fact an isopach map of the high velocity zone. Permafrost thickness may or may not correspond to the high velocity zone depending on factors such as salinity, rock type and pore pressure. The Calhoon method uses root mean square (RMS) velocities to compute the depth of the high velocity zone. A plot of the RMS velocity vs. time is used to pick the minimum or stationary point (see figure two). Using the time to this point and an assumption about the velocity in the high velocity zone and below it the depth of the high velocity zone can be calculated. Although the method is good the map must be considered preliminary because of limited input data and an erroneous assumption that the high velocity zone has a constant velocity of 8,500 feet per second.



ESTIMATED PERMAFROST ZONE ΔZp IN FEET

Figure 19

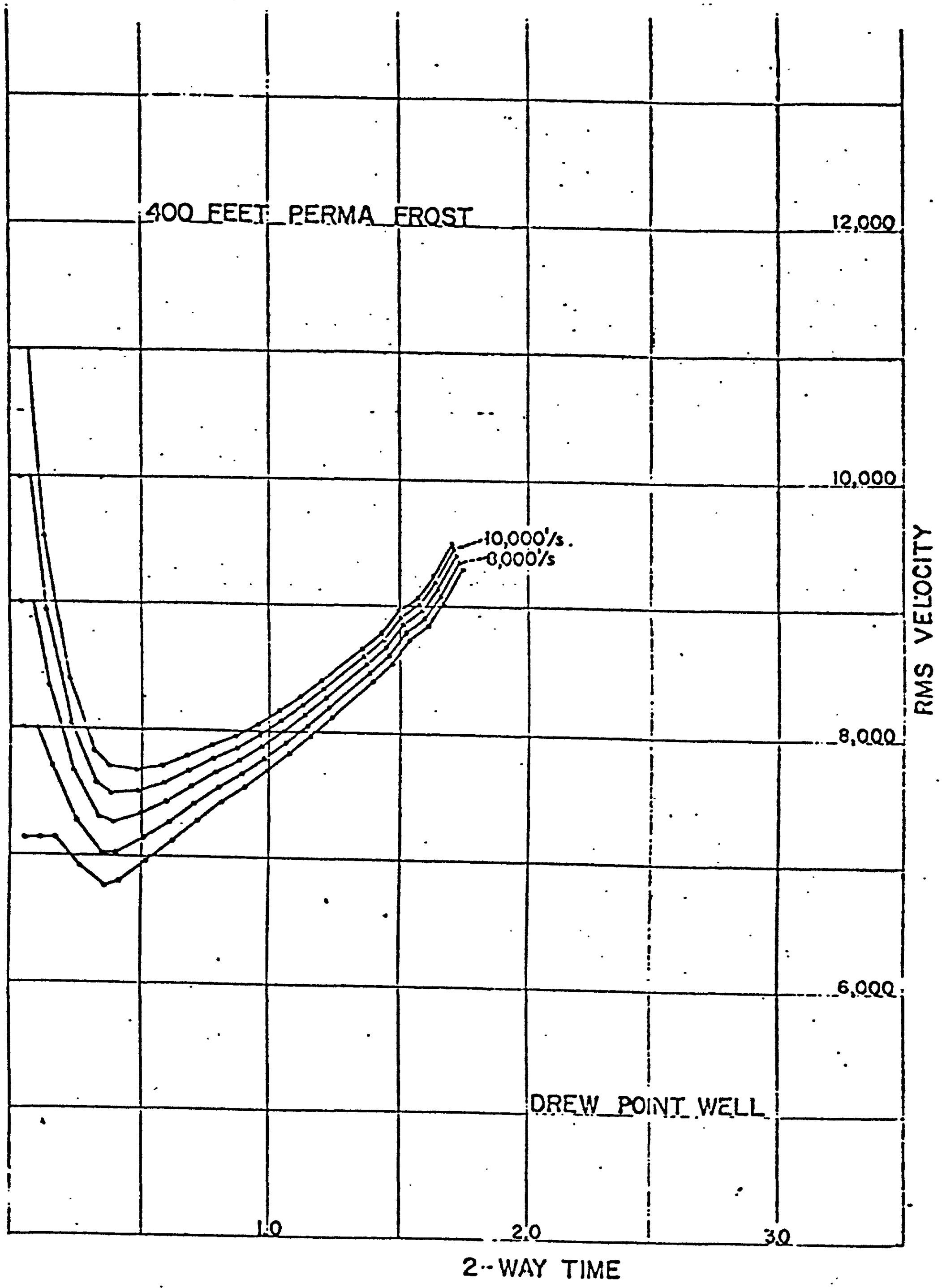

400 FEET PERMA FROST
12,000
10,000
8,000
6,000
RMS VELOCITY
10,000'/s.
8,000'/s
DREW POINT WELL
1.0
2.0
3.0
2-WAY TIME

Figure 20

ARTICLE 11 (Kobayashi, Riki)

A Talk About the Information Obtainable from Gas Hydrate Cores Applicable to the Determination of Gas in Place of Gas Hydrate Fields & Other Related Topics

Presented at
Workshop in Clathrates in NPRA
Menlo Park, California
July 16-17, 1979

by

Riki Kobayashi
Rice University

The intent of my discussion is not to answer questions but to provoke them. I have therefore chosen to collect a few of my thoughts and simply set them before you with the hopes that we can reexamine them together. For example, I find that establishing natural gas reserves in hydrate fields presupposes a production mechanism. Since the technology of producing hydrate fields are not well established, it follows that in general, we cannot establish reserves at this time. Nevertheless, relating the conditions under which natural hydrates occur can provide information needed to lay the ground work to establish gas in place and possible production methods is an important endeavor.

The Formation & Melting of Hydrates under Constant Volume-Constant Total Mass Constraints

For a number of years we have been forming and melting hydrates in the laboratory under the constraints of constant volume and constant total mass. These exercises are performed in a constant volume cell provided with stirring in the form of two steel balls which roll along the length of the cylindrical cell containing the charge of gas and known small amounts of liquid water.

The temperature drift of the bath is programmed and recorded in an outline digital computer. The resulting system pressures are transmitted through a transducer and likewise stored in the computer for later extraction.

The initial pressure and temperature of the system is in the upper right hand corner of Figure 21. In the first traverse, the maximum degree of super-cooling is required to precipitate hydrates. Once the phase change has been completed, the hydrate-gas mixture is heated slowly to establish the decomposition curve. The decomposition takes place over a range of temperature and hence, pressure. When decomposition of the bulk of hydrates has been completed, the curve rejoins the cool-down curve yielding a decomposition temperature reproduceable to a fraction of a degree. Evidently hydrate (micro crystals) survive to greater temperatures however. For, if one proceeds to cool down again, after the bulk hydrates have been destroyed, the degree of super-cooling or metastability experienced for bulk hydrate formation is very much a function of the extent to which the microscope hydrate crystals have been preserved, or the maximum temperature to which the cell and its contents have been allowed to heat up beyond the bulk hydrate decomposition temperature. Furthermore, at least to a certain extent, not precisely known, the upper portions of the path along curves S_1, S_2, and S3 ^{L} are reversable. One can heat up along the upper portion of curves S_1, S_2, and S_3 and retrace the cooling path just taken. The points of no return are not yet known. It appears that we have activation energies for the occurrence of mass hydration which is history dependent.

The curves demonstrate the hydrate formation and decomposition curves, even when conducted slowly, as low as 0.1^{o}C/hour, follow paths prescribed by the immediate prior history of the process. Kinetic studies using the technique discussed are projected for future experiments.

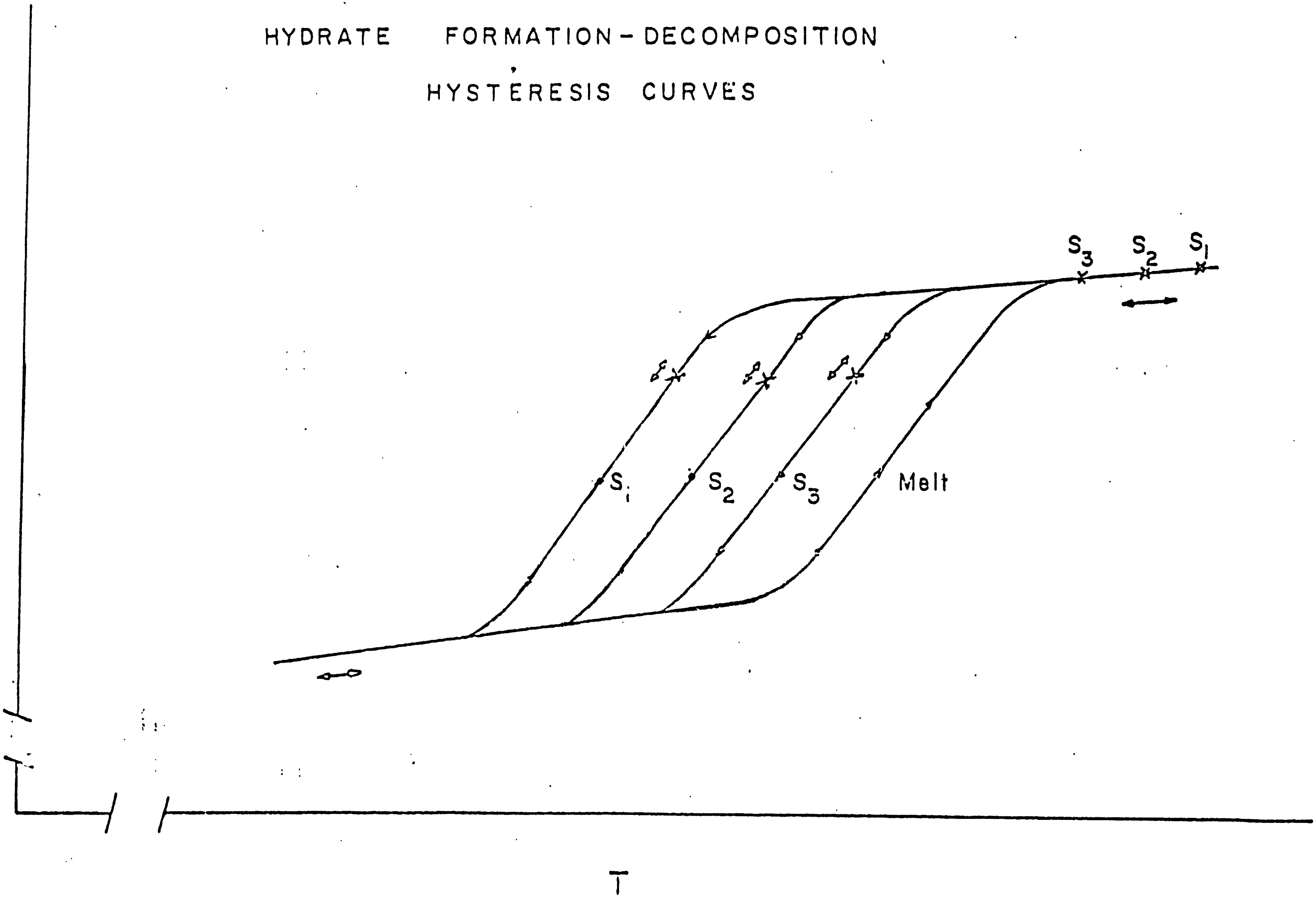

HYDRATE FORMATION - DECOMPOSITION HYSTERESIS CURVES

Figure 21

Some Reservoir Compositional Implications of the Van der Waals-Plateeuw Model for Gas Hydrate Equilibria

If it is supposed that large amounts of water (or brine) accompanied by much smaller amounts of gas provided the source of the gas which has been hydrated, then some interesting cursory hypotheses or questions can be set forth.

For example, in view of the validity of the absorption theory, concentration gradients in the reservoir should be evident and, therefore, anticipated. The heavier components would be trapped near the "leading edge" of the reservoir and the lighter components trapped in participation with the heavier components (structure II). Further away from the leading edge we may have only structure I hydrate, and perhaps a mixture in between if the pressure is sufficiently high.

During the decomposition of hydrates, Carson and Katz (1942) and Wilcox, Carson, and Katz (1941) noted that the hydrates of mixtures of methane and propane yielded gases of increased densities as the decomposition proceeded. Hence, they postulated that hydrates were solid solutions and developed empirical K-values to predict initial hydrate formation conditions. Therefore, care should be taken in decomposing cores to collect all of the gas and homogenize it to obtain the average composition.

In essence, the entire reservoir is probably a "fingerprint of geochemical history" and a very good one at that!

Information Obtainable from Hydrate Cores: Some Similarities & Differences from Conventional Cores

In classical oil and gas fields, the recovery and examination of a core is one of the most critical and important operations in the drilling of exploratory wells. Comparable operations in establishing hydrate fields are at least as important and may be even more important because technology for the production of such fields are largely undeveloped. The data obtained from classical cores include:

(1) permeability,
(2) porosity,
(3) fluid saturation, and
(4) the various fluid-water contacts,

In the case of the virgin hydrate cores, which must be taken at controlled temperatures under pressure, comparable measurements are largely meaningless since solid hydrate or both solid hydrate and ice coexist. It is true that the all important hydrate-brine contact can be established from the cores if the brine is not allowed to freeze. Or if frozen, can one thaw the brine but not the hydrate to determine connate brine?

Extremely good temperature and pressure control of the hydrates may allow us to distinguish between H_2O of hydration and connate brine! However, a number of important measurements on the solid hydrated core can be envisioned. If the core could be kept under controlled temperature and pressure conditions, a number of studies could be made on it. If the core could be refrigerated thoroughly by means of a refrigerant coil running through its center, a number of experiments could be performed. These include measurements of electrical resistivity, thermal conductivity, heat capacity, and compressibility. Additionally, pulsed NMR experiments might be used to differentiate between protons bound to carbon and protons bound to oxygen. By carefully measuring the heat of fusion of the core one could obtain a valuable thermal parameter.

After thawing the aqueous solids carefully, conventional measurements listed above on the cores would be in order.

Consideration of Some Cursory Hypotheses on the Formation of a Hydrated Gas Field

If the porous medium is fully filled with the hydrate phase the theoretical hydrate numbers indicate that (1) either a substantial amount of water migrated to a compressed gas phase, or (2) a substantial amount of hydrocarbon was transported to the hydrate--brine interface by a carrier, e.g. the motion of large volumes of brine past the interface, or (3) a substantial quantity of hydrocarbons diffused through the major phase, e.g. the brine to the solid hydrate--brine interface, or (4) some combination of these mechanisms.

One is led to speculate whether a careful analysis of the cores would delineate which of these mechanisms, if any, are plausible or could be ruled out from a careful analysis of the cores. Will our knowledge that hydrate formation from brine represents a desalination process allow us to include or exclude one possible mechanism for hydrate formation? Or given a gas reservoir, did water vapor migrate to the gas as the reservoir cooled or increased in pressure? Or does the diffusion process operating over geologic time obliterate these concentration gradients? Perhaps coring and analysis of hydrated fields would yield answers to some of these questions.

The Melting of Hydrates in Porous Media: A Fluid-Surface Heat and Mass Transfer Problem

The melting of hydrates in porous media is clearly a fluid-surface heat-mass transfer problem. The intervention of the porous media of low thermal conductivity and low permeability renders the problem much more difficult than from a fully fusable solid. The ease of melting the hydrates will be very much a function of the core parameters as measured classically. In addition, parameters such as the effective thermal conductivity, heat capacity and diffusivity are needed. The flow of fluids past the hydrate most probably will be in the laminar region, decreasing the heat and mass transfer rates appreciably. The roughness factor of the core would affect the region of laminarity. However, we cannot ignore the possibility of finding out how to increase interfacial heat and mass transfer.

One of the most challenging problems will be to keep the gas/liquid saturation ratio, Fig. 22, favorable for the flow of gas in view of the large amount of heat transfer medium needed (probably a water-rich liquid medium) to heat up the porous media, decompose the hydrates, and the large amount of water of decomposition produced.

Conclusion

Establishing the nature and extent of hydrated gas fields presents many formidable problems. The determination of the gas reserves in such fields cannot be made independently of the techniques and technology required to produce such fields. Accordingly, foresight should be exercised in securing and analyzing the cores to help in the development of production techniques as well as to establish the extent of gas in place as hydrates.

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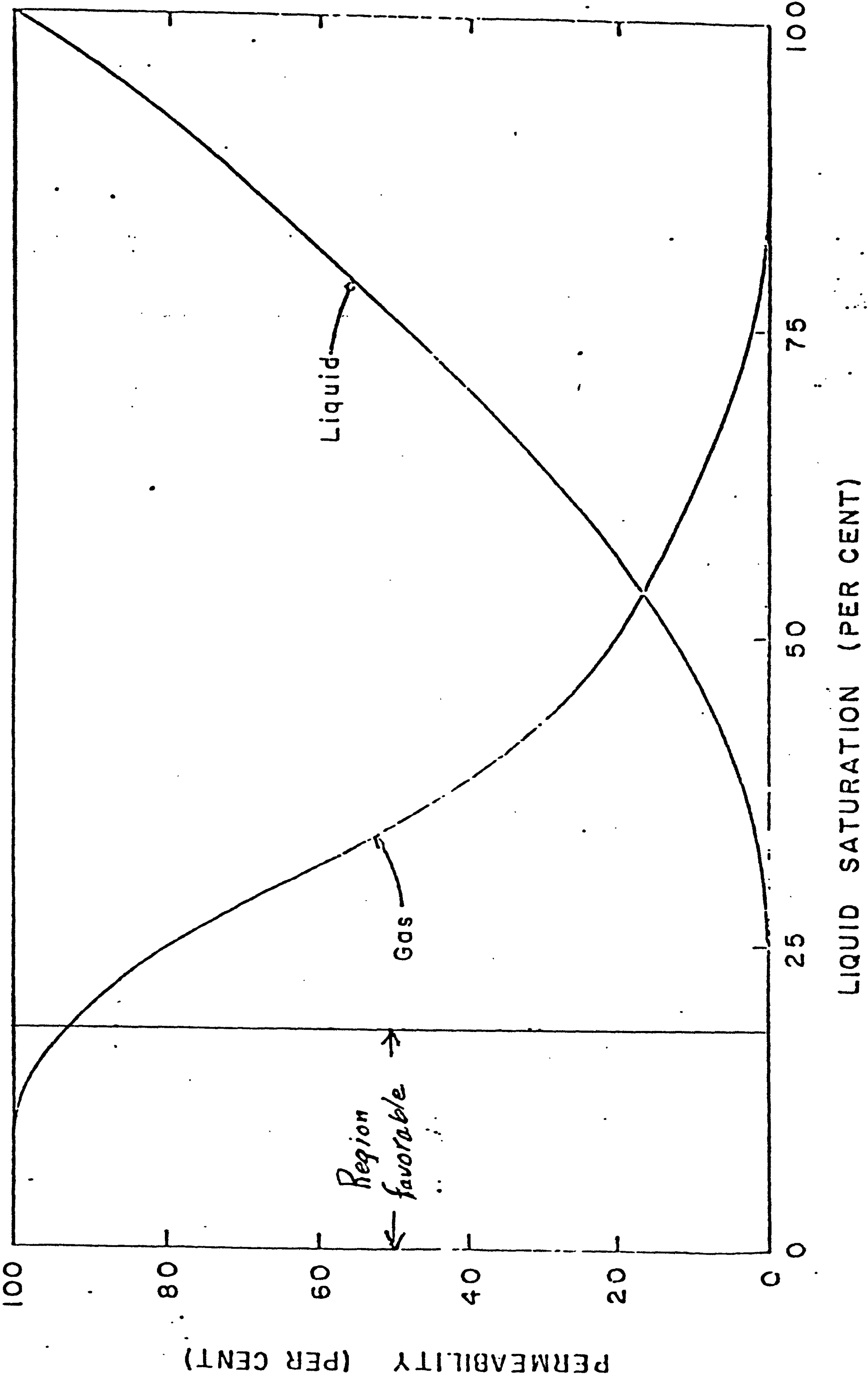
Wilcox, W., Carson, D. B., and Katz, D. L., "Natural Gas Hydrates," I.E.C. 33, 662 (1941).


PERMEABILITY (PER CENT)
100
80
60
40
20
0
LIQUID SATURATION (PER CENT)
0
25
50
75
100
Liquid
Gas
Region favorable

Figure, 22

ARTICLE 12 (Lantz, R.)

An Examination of Reservoir Conditions of the Barrow Gas Fields in Relation to Gas Hydrate Formation

Robert J. Lantz
U.S. Geological Survey
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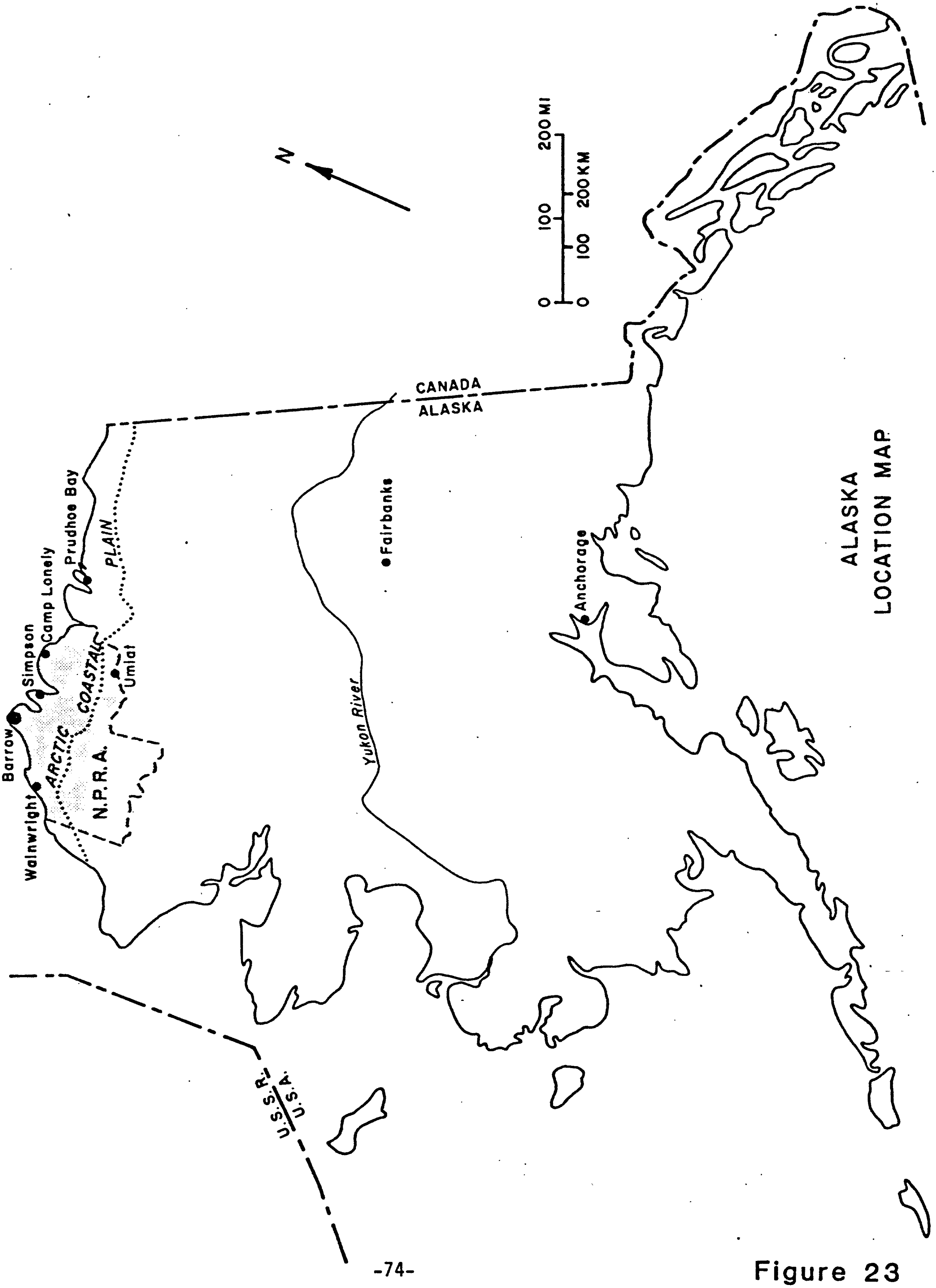
The Barrow gas fields are the most northerly producing fields in the United States. The two fields are situated on the northern extension of the Arctic. Coastal Plain near Point Barrow (Figure 23) within what was formerly called Naval Petroleum Reserve No. 4 (Figure 24). NPR-4 was transferred to the Department of the Interior in mid-year 1977, and renamed the National Petroleum Reserve in Alaska. Responsibility for the Barrow gas fields came with the transfer.

It has been suggested that the producing reservoir of the Barrow gas fields contains gas hydrates. The South Barrow field now has a reservoir pressure considerably less than the initial pressure, so the chances that South Barrow field contains clathrates at the present time is less than when the field was newly-discovered. Fortunately, the Geological Survey instituted the first thorough testing program ever carried out in the 30-year history of the South Barrow field so we now have more accurate information than was previously available, and can pretty well reconstruct initial conditions at South Barrow and see if they were favorable for the formation of gas hydrates. The East Barrow field has produced only small volumes of gas during drill stem tests and production tests, and, therefore,is still essentially at initial conditions.

It should be stated at the outset that the results of our testing programs in both fields resulted in calculated flow efficiencies and interference test responses that eliminated the possibility of gas hydrates being importantly present in the Barrow gas reservoir. In the discussion of the reservoir parameters of the fields, the values are rounded approximations. The accuracy of some of the instruments is in the order of ±5%, and many measurements are averaged values.

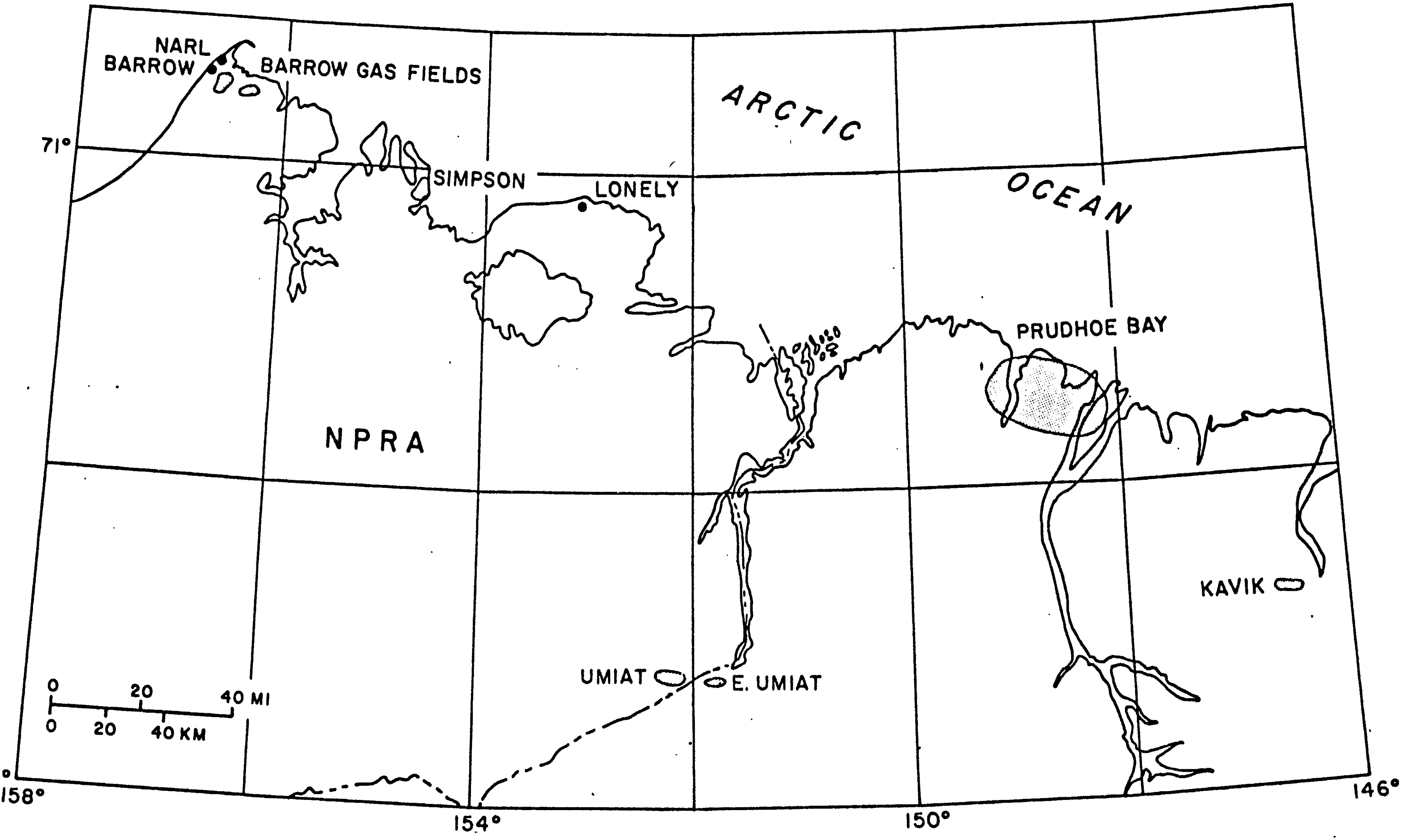
The South Barrow gas field, the oldest actively producing field in Alaska, was discovered in April 1949, by Barrow test well No. 2, drilled under the old Navy "Pet-4" exploration program. The well was located on a seismic structure near the Native village of Barrow, and also not far distant from the exploration Base Camp. Barrow No. 2 was completed as a producing well and gas was piped into the Base Camp as a more economic alternative to liquid fuel brought in by barge. Congress, in 1962, directed that gas should be furnished also to the village of Barrow, and the South Barrow field was slowly developed to its present size, consisting of 6 producing wells.

The East Barrow field was "discovered" in May 1974, by the Barrow No. 12, an unsuccessful well drilled on a near-by seismic structure. Navy followed the unsuccessful No. 12 with an additional test, the Barrow No. 14, successfully completed in March 1977, shortly before the transfer to Interior. The Geological Survey drilled two additional wells in East Barrow, the No. 17 and No. 19. The East Barrow field is scheduled to begin production



ALASKA LOCATION MAP

Figure 23



KNOWN PRODUCTIVE AREAS OF THE NORTH SLOPE

Figure 24

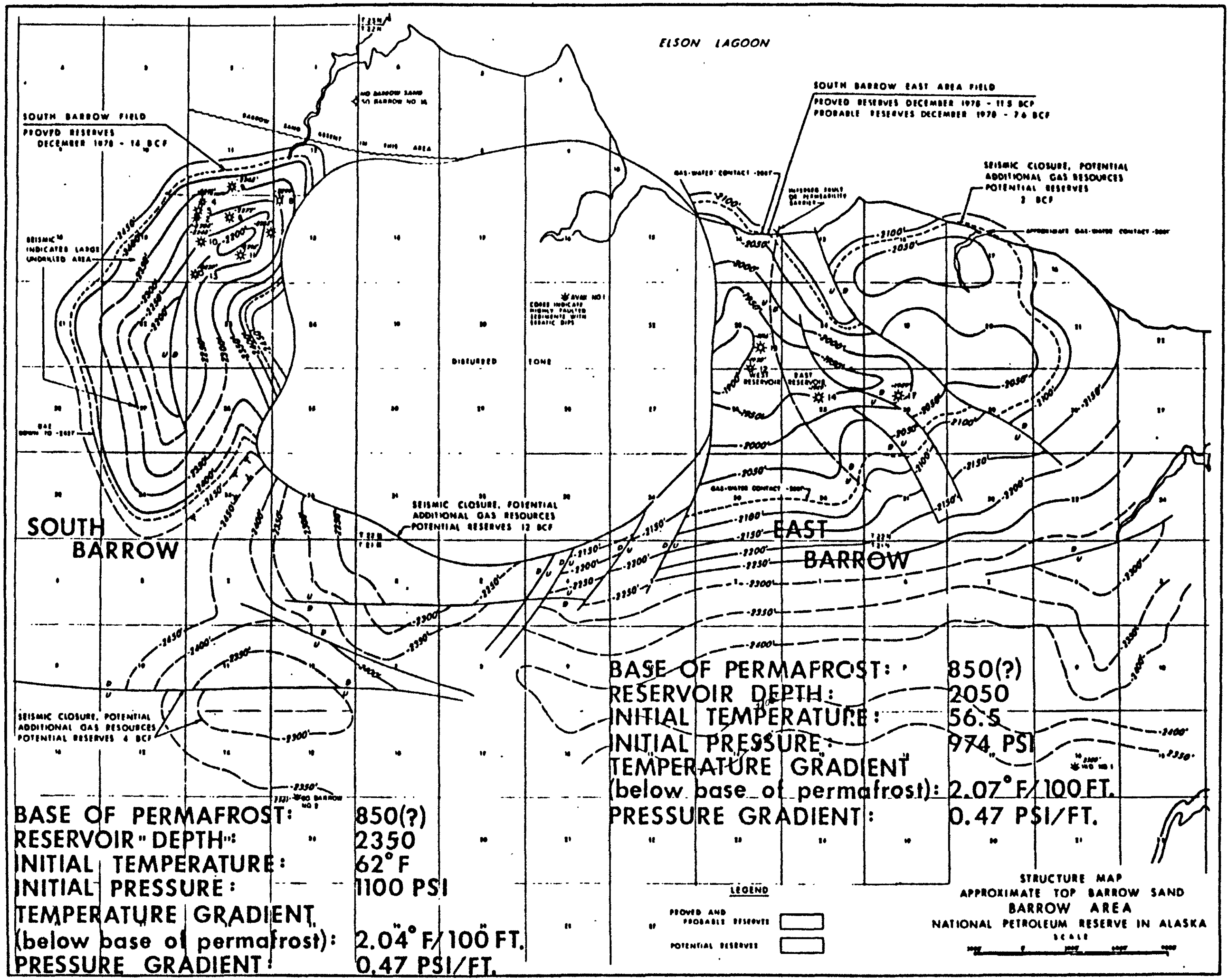
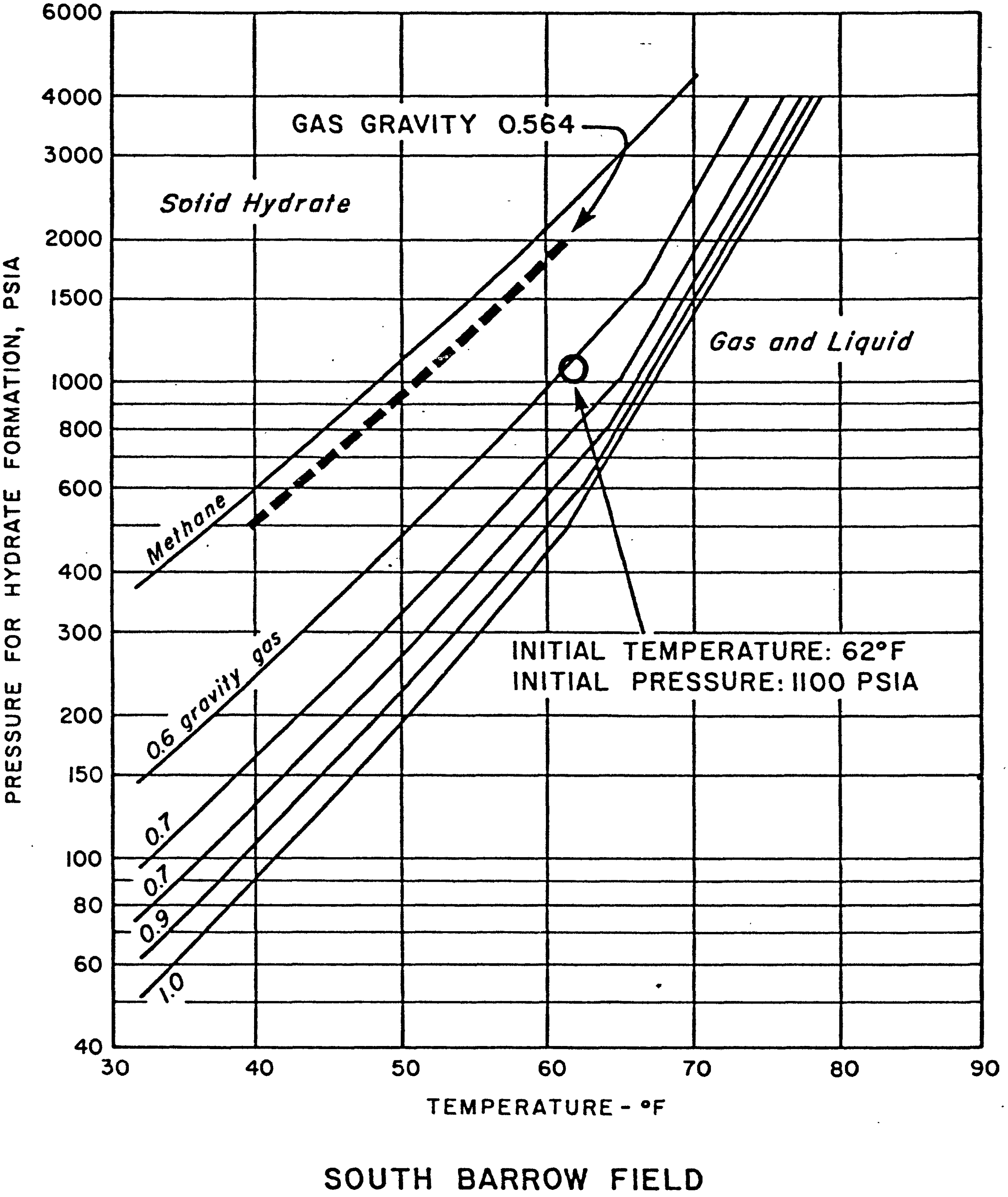

ELSON LAGOON
SOUTH BARROW FIELD
PROVED RESERVES DECEMBER 1978 - 14 BCF
SOUTH BARROW EAST AREA FIELD
PROVED RESERVES DECEMBER 1978 - 11.5 BCF
PROBABLE RESERVES DECEMBER 1978 - 7.6 BCF
SEISMIC CLOSURE, POTENTIAL ADDITIONAL GAS RESOURCES POTENTIAL RESERVES 2 BCF
SEISMIC CLOSURE, POTENTIAL ADDITIONAL GAS RESOURCES POTENTIAL RESERVES 12 BCF
SEISMIC CLOSURE, POTENTIAL ADDITIONAL GAS RESOURCES POTENTIAL RESERVES 4 BCF
SEISMIC INDICATES LARGE UNDRILLED AREA
GAS-WATER CONTACT
DISTURBED ZONE
WEST RESERVOIR
EAST RESERVOIR
SOUTH BARROW
EAST BARROW
BASE OF PERMAFROST: 850(?)
RESERVOIR DEPTH: 2350
INITIAL TEMPERATURE: 62° F
INITIAL PRESSURE: 1100 PSI
TEMPERATURE GRADIENT (below base of permafrost): 2.04° F/100 FT.
PRESSURE GRADIENT: 0.47 PSI/FT.
BASE OF PERMAFROST: 850(?)
RESERVOIR DEPTH: 2050
INITIAL TEMPERATURE: 56.5
INITIAL PRESSURE: 974 PSI
TEMPERATURE GRADIENT (below base of permafrost): 2.07° F/100 FT.
PRESSURE GRADIENT: 0.47 PSI/FT.
LEGEND
PROVED AND PROBABLE RESERVES
POTENTIAL RESERVES
STRUCTURE MAP
APPROXIMATE TOP BARROW SAND
BARROW AREA
NATIONAL PETROLEUM RESERVE IN ALASKA
SCALE
MAP No 2

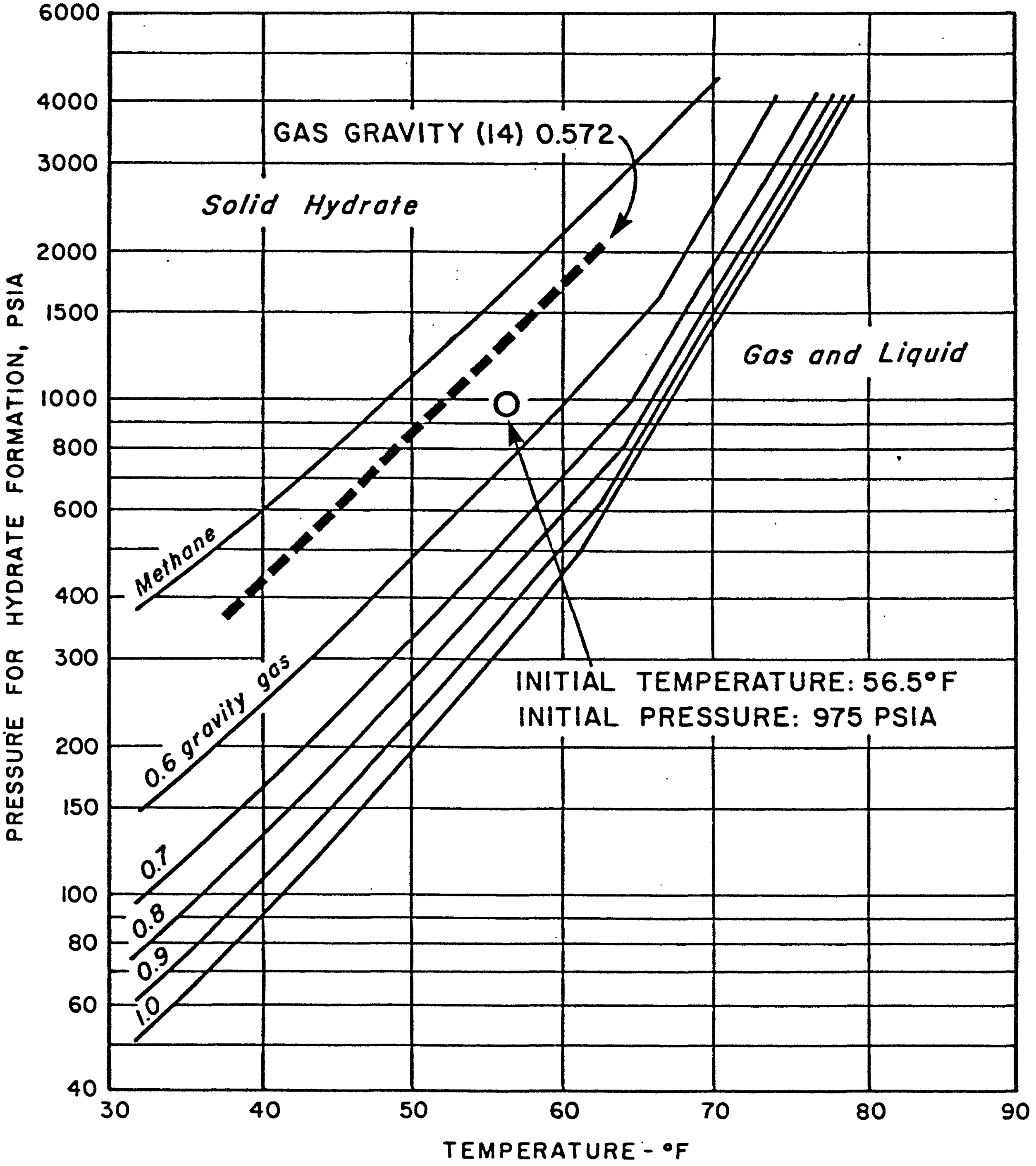
Figure 25



SOUTH BARROW FIELD

Conditions for formation of gas hydrates when water is present.

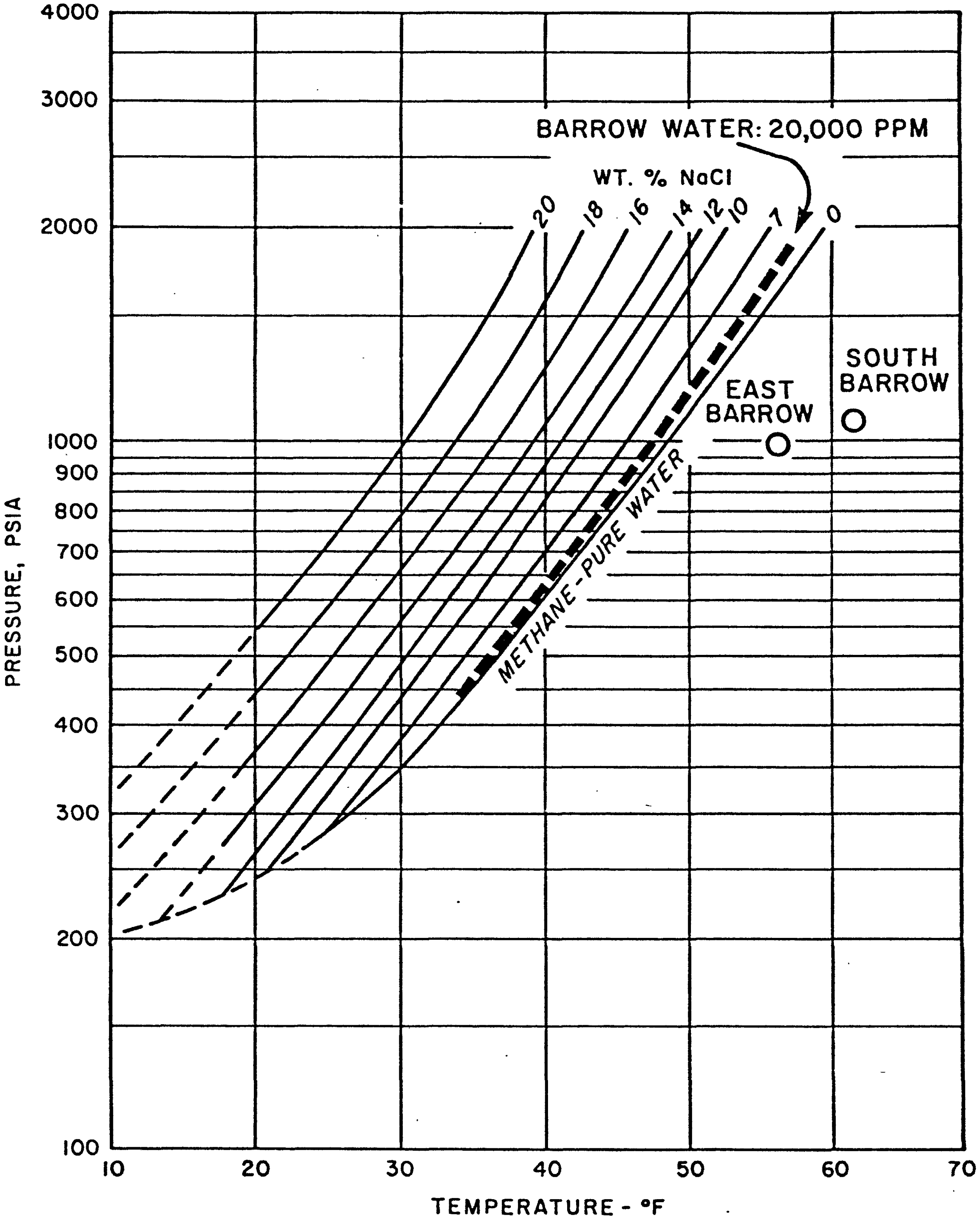
Figure 26



EAST BARROW FIELD

Conditions for formation of gas hydrates when water is present.

Figure 27



Effect of salt solution on hydrate formation.[6]

Figure 28

this coming winter, helping to supply gas to the North Slope community.

The South and East Barrow accumulations are structurally controlled (see Figure 25) and produce from a sandstone of Middle Jurassic age, imaginatively dubbed the "Barrow sand." The lower part of the sand, appropriately termed the "lower Barrow sand" is the primary reservoir of both fields, being more massive, porous, and less lenticular than the upper part of the sandy section, which, of course, is called the "upper Barrow sand." The "lower Barrow sand" has an average porosity and permeability of about 18% and 24 Md. The sand is thought to be about 20 feet in average thickness across the South Barrow field, although only three wells penetrated and logged the complete sand thickness and two wells did not even reach the primary reservoir. The initial pressure of the South Barrow field is generally regarded as being a little above 1,100 PSI. The temperature of the reservoir has been reliably measured at about 62 degrees F. The average depth of the reservoir is about 2350 feet. The initial gravity of the gas was 0.564. Figure 26 shows a plot of the initial pressure, temperature and gas gravity of the South Barrow field.

The wells in the East Barrow field are more recent and we have more accurate information here than in the older area. The "lower Barrow sand" has been completely penetrated by all the wells in the field. Extensive core analyses, electric log calculations, drill stem tests and properly instrumented draw-down and pressure build-up tests have accurately measured the reservoir parameters of the East Barrow area. The average porosity and permeability of the primary reservoir are about 22% and 25 Md. The sand averages about 18 feet thick in the wells drilled to date.

The East Barrow reservoir is still essentially at original conditions, having been produced only for relatively short testing periods. The initial reservoir pressure is approximately 975 PSI, the temperature near 56.5 degrees F. The average depth of the reservoir is about 2050 feet. The gravity of the gas produced while testing the Barrow No. 17 averaged 0.570 gravity; Barrow No. 14 averaged 0.572. Figure 27 shows the same temperature, pressure, gas-gravity relationships seen before with pertinent data from the East Barrow field superimposed.

Water salinity affects the formation of gas hydrates. Water produced from both fields has a salinity of approximately 20,000 PPM NaCl equivalent, or about 2% NaCl by weight. Figure 28 shows data from the South and East Barrow fields properly located to show pressure, temperature and salinity values.

The depth to the base of the permafrost in the South and East Barrow fields is not known accurately. A small, consistent "kick" on the gas-detection logs appears as a first gas occurrence below shallow beds obviously above the base of the permafrost. Assuming the permafrost is impermeable, the consistent first occurrence of gas may be trapped close to the base of the permafrost. If the above series of assumptions are true, the base of the permafrost is located at about 850 feet below the surface, and the temperature gradient in the thin section of rocks below the permafrost and above the metamorphic basement calculates to be about 2^{O}F per 100 feet.

ARTICLE 13 (Lawver, L.)

GEOTHERMAL GRADIENTS ON THE NORTH SLOPE

by
Lawrence A. Lawver

U.S. Geological Survey, Menlo Park, California

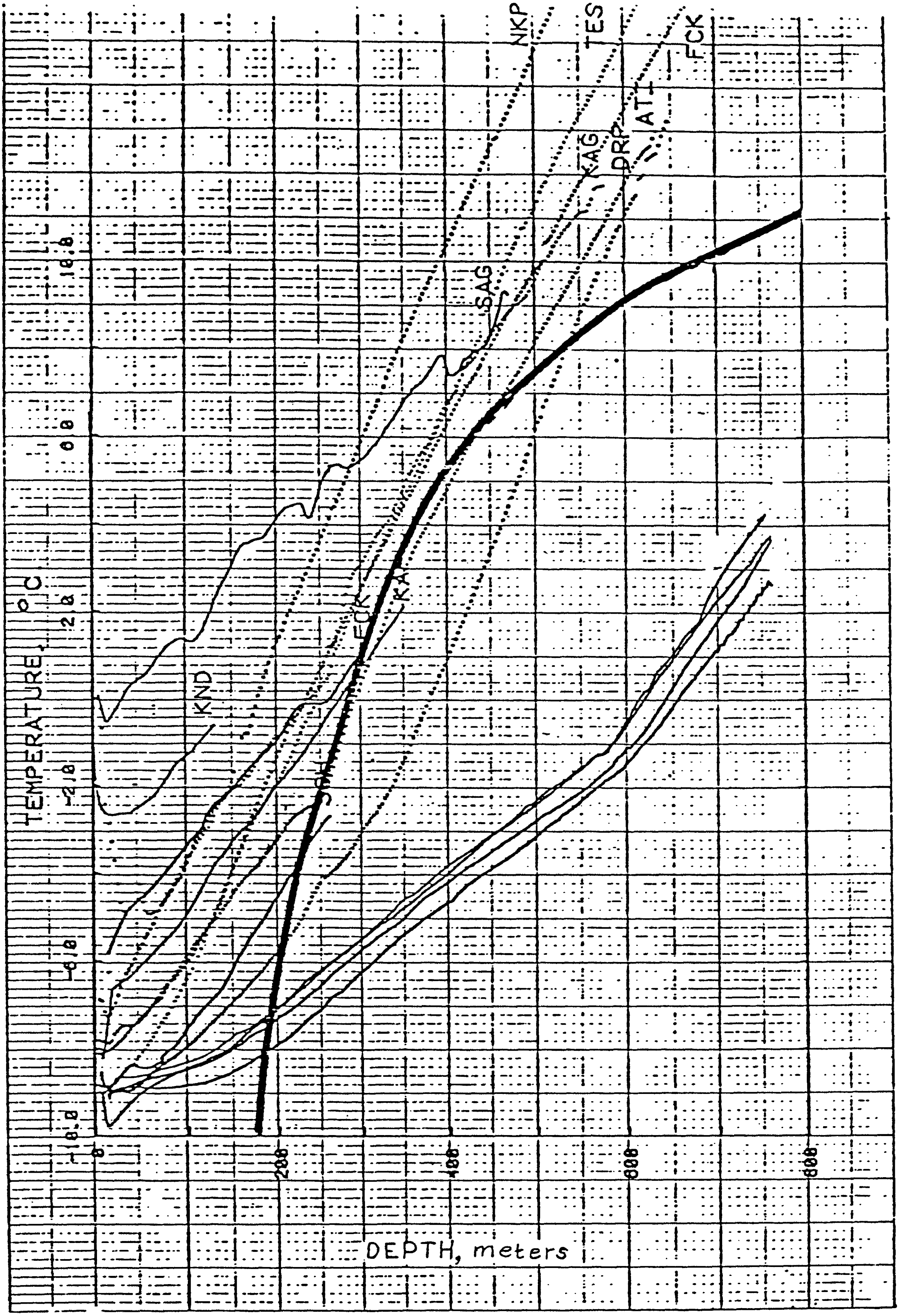
Important factors influencing the formation of hydrates, methane trapped in a frozen water structure, are the temperature and pressure at a given point. Secondary factors are the presence of propane and ethane gases and the brine content of the water structure. Temperature versus depth conditions at Prudhoe Bay indicate a potential stable hydrate zone between 180 meters and 1000 meters. Tests made at NW Eileen failed to find hydrates below 760 meters indicating that either the hydrate stability curve used (which assumed no propane or ethane content and no brine content) gave too large a depth range or that there were no hydrocarbon source beds favorable to a hydrate state between 760 meters and 1000 meters.

Of the seven wells in the NPRA in which thermal gradients were measured (North Kalikpik, NKP; East Teshepuk, TES; Fish Creek, FCK; Kagura, KAG; South Harrison Bay, SOH; Drew Point, DRP; and Atigaru, ATI), NKP, TES, FCK, and KAG are all well above the hydrate stability curve and would indicate that it is doubtful any hydrates would be found at those locations. DRP coincides with the stability curve shown while SOH could only be measured to 260 meters but would apparently intersect the curve at 240 meters. ATI is the only NPRA hole that shows a large zone of potential hydrate stability. Using the curves given, hydrates are potentially stable between 210 and 530 meters at the Atigaru site.

If the thermal gradient curves from the Prudhoe Bay region are applicable to the NW Eileen hole and other conditions are favorable to hydrate formation, then the zone of actual hydrate occurrence would indicate either the presence of brine depressing the methane hydrate stability curve or perhaps the theoretical stability curve is not applicable under these field conditions. An appreciable lowering of the stability curve by the presence of brine or by another mechanism would leave all the NPRA thermal gradient profiles outside the range of hydrate stability. Thermal gradients collected by Max Brewer and Art Lachenbruch at the Barrow wells during the early 1950's tend to lie within the potential methane hydrate stability region but only based on the extrapolation of relatively shallow data. Data from the old Simpson wells vary from being tangent to the stability curve (Simpson 28) to lying just below the curve (Simpson 13).

Data from wells to the south of Prudhoe Bay include Umiat, Echooka, and a Lawrence Livermore Lab site at Confusion Creek. These areas all show sufficiently high thermal gradients to suggest it is unlikely hydrocarbons would be present as hydrates. Except for the NPRA hole at East Teshepuk which already shows long-term thermal stability, all other ONPRA wells should be relogged for thermal gradients and all new wells will hopefully be preserved for thermal gradient measurements.

The data presented were collected by Tom Moses, Art Lachenbruch, Max Brewer, Lawrence Lawver and other members of the Geothermal Studies group of the USGS.



Comparison of typical temperature profiles near Prudhoe Bay with preliminary profiles from NPRA (see text for symbols). Heavy curve represents the boundary of the hydrate stability field (see text).

Figure 29

ARTICLE 14 (Lawver, L. A., Moses, T. H., Jr., and Lachenbruch, A. H.)

A PRELIMINARY MAP OF PERMAFROST DEPTH AT NPRA

by

L. A. Lawver, T. H. Moses, Jr., and A. H. Lachenbruch

Note added in proof: This paper has been withdrawn because errors in the extrapolation procedure render the map misleading. An up-to-date correct version based upon more recent data is in preparation.

Arthur H. Lachenbruch

ARTICLE 15 (Milton, D. J.)

The Future Supply of Nature-made Petroleum and Gas Technical Reports

An International Conference Sponsored by
The United Nations Institute for
Training and Research (UNITAR)
and
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As
The First UNITAR Conference on Energy and the Future
and
The Second IIASA Conference on Energy Resources
5-16 July 1976
Schloss Laxenburg, Laxenburg, Austria

J. Barnea and M. Grenon
Scientific Secretaries

R.F. Meyer
Editor

(1977)

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CHAPTER 53

METHANE HYDRATE IN THE SEA FLOOR--A SIGNIFICANT RESOURCE?

Daniel J. Milton [1]

INTRODUCTION

About 30 years ago it was noted that beneath the thicker zones of permafrost in Arctic regions, temperatures are low enough and pressures high enough to fall in the field of stability of the hydrate of natural gas, an ice-like clathrate compound with an ideal formula $(CH_4, C_2H_6, \text{etc.}) \cdot 5\text{-}3/4\ H_2O$. In 1970, well logging and formation tests in the Messoyakha gas field in Western Siberia indicated some tens of billions $(10^9)m^3$ of gas frozen in the hydrate form, the extraction of which on an economic basis remains problematic (Makogen, Trebin et al., 1971; Makogen, Tsarev, and Cherskiy, 1972). More recently, gas hydrates have been discovered in the Mackenzie Delta, Northwest Territories (Bily and Dick, 1974), and one must assume that they are widespread in the Arctic.

Sokolov in 1966 was apparently the first to point out that temperatures and pressures over much of the sea bottom fall in the stability field of natural gas hydrate, and Stoll, Ewing, and Bryan (1971) first presented observations suggesting its actual presence in sea floor sediments. The possible occurrence of submarine hydrate deposits is being actively investigated, particularly by Trofimuk, Cherskiy, Tsarev, and Makogen in the Soviet Union (Trofimuk et al., 1973; Mokogen et al., 1973) and several investigators in the United States associated with the Deep Sea Drilling Project (see especially Kaplan, 1974). In December 1975, Trofimuk, Cherskiy, and Tsarev published a calculation showing that over $10^{18}m^3$ of methane are frozen in the submarine zone of hydrate formation. Because previous estimates put the quantity of natural gas in the entire lithosphere and hydrosphere of the earth at one-sixth this amount, evaluation of the evidence is clearly of importance.

GAS HYDRATE IN RECOVERED SUBMARINE CORES

Perhaps the only person who may have been favored with the actual sight of naturally formed gas hydrate was A. G. Yefremova, who saw in large cavities in sediment cores lifted from the bottom of the Black Sea microcrystalline aggregates resembling hoarfrost that disappeared before her eyes (Yefremova and Zhizhchenko, 1974). In a number of sediment cores taken during the Deep Sea Drilling Project, gas evolved, sometimes for several hours, after the cores were lifted on deck. The gas pressures generated were on occasion sufficient to extrude cores from the barrel or rupture sealed containers. The quantity of gas evolved and the slow rate of evolution have been interpreted as indicating decomposition of gas hydrate, although the solid was never actually seen. Formation of ice on exposed cores in conjunction with gas discharge, mentioned by Stoll et al., supports this possibility. Dissociation of hydrate, which requires 13,000 cal/mol of CH_4 in methane hydrate, would cool the system much more than release of gas from aqueous solution, which requires only 4,600 cal/mol, or than Joule-Thompson cooling of gas on expansion.

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[1] U.S. Geological Survey, Reston, Virginia 22092, U.S.A.

INDICATIONS OF HYDRATE FROM SEISMIC SURVEYING AND DEEP SEA DRILLING

Information on sea floor sediments in situ comes largely from seismic exploration. Arguments for indications of gas hydrate are persuasive, but when examined closely are far from simple or self-evident. The most striking phenomenon is the bottom-simulating reflection. The reflector (known as the "BSR") parallels the water-sediment interface and lies several hundred metres lower. Where stratification is conformable with the interface, the BSR is difficult to detect, but elsewhere it appears transecting bedding reflections. A BSR was apparently first noted on the Blake-Bahama outer ridge of the North Atlantic Ocean (Markl et al., 1970; Ewing and Hollister, 1972), and one has since been reported from the Bering Sea and elsewhere in the North Pacific (Scholl and Creager, 1973) and the Beaufort Sea in the Arctic Ocean (Grantz, et al., 1976).

The only physical surface that would be expected to cross-cut bedding but parallel the bottom is an isotherm; it is therefore logical to conclude that the BSR represents a temperature-controlled phase change or diagenetic effect. Roughly the BSRs lie at depths that correspond to the univariant equilibrium gas + water = hydrate. But when one attempts to be more precise, a number of problems are encountered. The P-T conditions of the equilibrium depend on the composition of the gas phase. For the two localities which have been drilled (Blake-Bahama outer ridge and Bering Sea), the gas released from the cores has been analyzed and found to be essentially pure methane or methane with a few percent of carbon dioxide, which changes equilibrium conditions only slightly. In the Beaufort Sea, however, offshore from the Alaska North Slope gas fields, higher gravity gases could well be present, and would raise the temperature and pressure of the univariant equilibrium. Pressures at depth can be calculated fairly straightforwardly, but temperatures, except for a few downhole measurements, must be estimated from the heat flow at the top of the sediment layer and from assumptions as to the conductivities below (which are indeed not independent of whether a hydrate occupies the pores). Finally, conversion of seismic reflection times to depth requires a knowledge of the velocity profile (which again depends on whether a hydrate is present).

Two DSDP holes were drilled to investigate the BSR on the Blake-Bahama outer ridge, site 102 on the crest of the ridge in 3,426 m of water and site of 104 on the flank in 3,811 m (Hollister et al., 1972). The reflection occurred at 0.62 sec at site 102 and 0.61 sec at site 104, although Markl et al., indicate a deepening by about 0.1 sec as the water depth increases along the axis of the ridge from 2,500 to 4,500 m. The indicated depth is reasonable for the hydrate equilibrium (thermal data are lacking), as is the apparent deepening down the ridge axis. Drilling in hole 102 underwent marked slowing of penetration at about 620 m and hard drilling continued to the total depth of 661 m. The break occurred in hemipelagic muds and does not correspond to any marked lithologic change although there is a general downward increase in siderite nodules and lenses in that part of the section. Hole 104 unfortunately was terminated at 617 m, but after encountering 15 cm of very hard ankerite in either a layer or nodule at 615 m. The DSDP team correlate the drilling breaks with the BSR which, as the break falls no higher than middle Miocene at site 104 and at the Miocene-Pliocene boundary at site 102, would thus transgress stratification as it is seen to do on the seismic records. The entire section in these holes was gassy; voids in the core produced by gas expansion were noted in the log (including cores at 634 to 636 m and 659 to 661 m at site 102, below the presumed BSR). If the BSR is at 615 to 620 m, it means seismic velocities in the section above averge 2.0 km/sec rather than the 1.6 km/sec normal for the upper few hundred metres of deep sea sediments. Such high velocities have been independently confirmed by sonobuoy measurements in the area (Bryan, 1974). Stoll et al. (1971) proposed that the anomalous velocity occurs in a frozen hydrate zone above the BSR and they demonstrated experimentally that crystallization of hydrates in sediments does indeed increase the acoustic velocity.

Beneath the flat seabed of the Umnak Plateau of the Bering Sea at about 1,900 m depth the time interval between the bottom reflection and the BSR is constant within ± 3 1/2 percent (J. Howell, personal communication). The apparent depth to the BSR as seen on the record published by Scholl and Creager (1973) appears, however, to decrease markedly as the water deepens to 3,100 m; this behavior is opposite to what would be expected for the hydrate equilibrium surface. If a velocity profile of 1.7 km/sec in the top 400 m and 2.62 km/sec below is taken, the BSR lies at 600 to 610 m beneath the bottom. These velocities are based on measurements on cores (the properties of which would change if hydrates thawed during the lift) but are also supported by sunobuoy velocities, which appear to be the same in nearby areas where the BSR is present and where it is not (Howell, personal communication).

Three DSDP drill holes in the Bering Sea (Creager, Scholl, et al., 1973) penetrated to the probable depth of the BSR, revealing a transition from diatom ooze or highly diatomaceous deposits downward to mudstone or claystone nearly barren of siliceous microfossils. In two holes the change occurs within a few metres; in one it is transitional through about 100 m of section. The horizon is time-transgressive, and because it is unlikely that pelagic diatom ooze would transgressively bury a gently sloping bottom, it is assumed to be a diagenetic boundary. 1/ The bulk density and acoustic velocity on cores are much greater in the lower unit and the contrast could cause the reflection event.

Downhole temperatures were measured at DSDP site 184 (water depth 1,910 m) where the BSR appears to be at 600 m depth (Erickson, 1973). The bottom water temperature was 2°C; the temperature measured 174m, 16.25°C, and at 342 m, 18.5°C, but technical difficulties during the operation led Erickson to question the latter measurement. Thermal cnductivities of cores from the bottom to 600 m subbottom measured on shipboard were rather constant at about 2.16 mcal/cm sec °C. From this conductivity and the thermal gradient to 174 m, Erickson calculated a heat flow of 1.77 ucal/cm^2 sec, a reasonable value for a marginal basin behind an active island arc. Extrapolating this gradient to 600 m subbottom gives a temperature of 49°C, far too high for methane hydrate to exist at the prevalent pressure. On the other hand, if the measurement at 342 m is accepted and the gradient between 174 and 342 m is extrapolated, it gives 23.6°C at the BSR, which is not far from the 18°C expected for a methane + water = hydrate equilibrium. The measured conductivities are reasonable for sea floor sediments. The conductivity in a frozen water-saturated sediment can be calculated by the formula:

$$K_f/K_t = (K_i/K_w) = 4$$

1/see p. 94

involving the conductivities of the frozen and thawed material, ice and water, as indicated by the subscripts and, the volume faction of pore space (Gold and Lachenbruch, 1973). The conductivity of a clathrate ice has never been measured, but a reasonable guess would be 13 percent less than that of ordinary ice, corresponding to the lower relative density of the empty

No! The conductivity is less than a liquid-saturated sediment (Stoll, Ewing, and Bryan, 1979 and (obscure siberian publ.), 1974).

clathrate lattice. Water content and density measurements on cores from site 184 indicate = 0.73, so that:

$$K_f/Kt = (3.5)\ 0.73 = 2.5.$$

This does not account for the sixfold increase in thermal gradient (which would require an impossible porosity) but it goes far enough in the right direction that the correctness of the measurement at 342 m and the presence of a hydrate zone below some level approximately 175 m are attractive possibilities.

Various suggestions for the nature of the actual reflector at the BSR have been advanced. At the Blake-Bahama outer ridge, the normal densification of sediments with depth would put the velocity below the BSR at just about the abnormal (hydrate-enhanced?) velocity above, so there would be little velocity contrast to generate a reflection. Bryan (1974) suggests that the contrast is between a high velocity hydrated section above the equilibrium isotherm and a thin low velocity zone rich in free gas trapped beneath the hydrate zone. An alternative hypothesis for this locality was suggested by Ewing and Hollister (1972): that the equilibrium isotherm is at slightly greater depth and the reflector is a thin high velocity hydrate-rich zone produced at the base of the zone of stability as gas migrated upward and was trapped by freezing. This however, would not explain anomalous velocities higher in the section, the original reason for postulating the presence of hydrate.

Claypool and Kaplan (1974) suggest that at both localities the reflection comes from a horizon of lithologic change produced by diagenesis but related in an indirect way to the hydrate equilibrium boundary. They interpret the subreflector unit at both localities as having been lithified by the dissolution of carbonate and silica from microfossils and reprecipitation as cement. These processes depend on the pH of the pore water, which depends on the concentrations of CH_4 and CO_2, which in turn depend on various processes of bacterial action. Claypool and Kaplan suggest two ways in which the hydrate equilibrium may be involved: first, bubbles of free gas trapped beneath a hydrate layer could create open spaces in the sediment in which precipitation takes place; or second, CO_2 in the hydrate zone could be locked up in the hydrate and unavailable for reaction. The latter hypothesis may perhaps be taken as representative of a host of possible effects on pore water chemistry of reaction with hydrates.

Recently a BSR has been found in the Beaufort Sea on the continental slope north of Alaska, recognizable on about 60 percent of seismic lines run (Grantz et al., 1976). The BSR appears to be 100 to 300 m beneath the bottom. It extends shoreward from the limit of survey in water more than

2,500 m deep to a disappearance at a water depth of 400 to 600 m. It is most strongly developed beneath bathymetric highs and is weak or absent beneath bathymetric lows. In a few places where it is particularly well developed beneath highs, the underlying reflectors appear on time sections to be bowed downward. The investigators conclude that a hydrate zone has formed pseudo-anticlinal traps beneath which free gas has accumulated in sufficient quantity to create an interval of anomalously low seismic velocity. In the Arctic Ocean where low water temperatures allow the zone of hydrate formation to extend to shallower water, the seaward deepening of the BSR beneath the bottom should be apparent, if it indeed represents the base of the zone of hydrate formation. No drilling has been done in this area; higher gravity gas of thermocatalytic origin similar to that in the nearby onshore gas fields could well be involved.

NECESSARY CONDITIONS FOR THE ACCUMULATION OF HYDRATE

For a gas hydrate to exist, not only must the temperature and pressure fall within the range of stability of the hydrate, but the content of gas in the system must exceed the limit of solubility in the coexistent water. This point has not always been properly appreciated. The solubility of methane in water in equilibrium with free gas (represented by the surface L-V+L in Fig. 30) increases with pressure (at constant temperature) and decreases with temperature (at constant pressure) to a minimum at $70^{o}C$ or $80^{o}C$, above which it increases. The solubility as temperature or pressure approach the univariant equilibrium L-V-H can be determined by extrapolation of standard experimental measurements, such as those of Culberson and McKetta (1951), with minor corrections if the anomalous decrease in solubility with decreasing temperature just before univariant curve reported by Makogon (1974) is correct. The question is the solubility in equilibrium with hydrate, represented by the surface L-H+L. Makogon (1974) in his book[1] reports that the solubility undergoes an immediate and drastic decrease at the univariant curve, for example from about 90 to about 18 mmol/kg at $10^{o}C$ and 72 atm, a phenomenon which he ascribes to a change in the structure of liquid water. Thereafter the solubility slowly increases with pressure. His findings, which have been accepted explicitly by Claypool and Kaplan (based on an earlier report by Makogon et al., 1972) and implicitly by Trofimuk et al. (1973), make almost inevitable the accumulation of hydrate in sea floor sediments at the level where water suddenly loses its ability to contain dissolved methane. However, such a discontinuity in the solubility of a component in a phase violates thermodynamic principles. The boundaries L-V+L and L-H+L must intersect at the univariant equilibrium. A change in the properties of water could only lead to an anomalous curvature in either of these boundaries, and

---

A proper treatment should work with activities, not solubilities, but this should serve as a guide.

[1] I have not had the opportunity to read the original report of the experiment (Makogon, Koblova, and Khalikov, 1971).

it is difficult to see why such behavior, if it does occur, should occur at temperatures and pressures that correspond to the methane hydrate univariant equilibrium. The solubility on the divariant surface L-H+L must decrease with increasing pressure because formation of the hydrate results in a decrease in volume. The volume change for the reaction may be calculated from the volume

$$CH_{4(liq)} + nH_2O\ (liq)\ \text{--}\ CH_4.nH_2O\ (hyd)$$

of hydrate per mol water, the partial molal volume of methane in aqueous solution, and the mol volume of liquid water:

$$V = nV_{(hyd)} - V_{CH_4(liq)} - nV_{H_2O}$$

$$V = 22.68n - 35.0 - 18.02n.$$

The occupancy of vacancies in the clathrate structure increases with pressure, so that n decreases from about 7.25 at the quadruple point to nearly the ideal 5.75 above 1,000 bars. V thus increases from $V = -1.22$ to $V = -8.09$, indicating that the pressure effect on solubility will be negative, and greater at greater pressures, as indicated by the curvature of lines L-H+L on the isothermal sections of Fig. 30.

An experiment by Hemmingsen (1975) yielded results conflicting with Makogon's. He placed a beaker of water in a CH_4-filled pressure chamber and measured the flux of CH_4 into a Teflon tube completely immersed in the water and brought to the outside via a capillary tube. The flux of CH_4 through the Teflon barrier at 5°C increased by a factor of three as a linear function of the gas pressure as the gas pressure was increased from 20 to 68 atm. The gas flux is directly related to the fugacity of the gas in solution. Since the fugacity for real gases in aqueous solution at constant composition increases only about 15 percent to 100 atm (Enns et al., 1965), the experiment may be taken as indicating an approximately linear increase in solubility with pressure not only to the univariant equilibrium but beyond this point in the metastable liquid. In the presence of hydrates (which formed spontaneously only when the pressure was raised to about 70 atm) the gas flux remained unchanged at pressures between 52 and 82 atm at the same flux as for hydrate-free water at the three phase equilibrium pressure of 44 atm. If the fugacity of methane in solution in equilibrium with its hydrate depends only on the temperature, as this experiment would seem to suggest, then solubility along the L-H+L boundary would have the value at the univariant equilibrium reduced in accordance with the pressure effect on Henry's law constant. The solubility of methane in sea water in a frozen zone of bottom sediment at 2°C would thus decrease from about 70 mmol/kg at a water depth of 350 m, the minimum for hydrate stability, to about 40 mmol/kg at a water depth of 4,000 m (Fig. 31). Actually, as there is no reason why the fugacity on the phase boundary should be perfectly constant, this extrapolation should not be taken as more than an indication of the general magnitude of the solubility. Along the base of the hydrated zone in the sediment column from shallow to deep water the solubility increases along the univariant curve from 70 to about 200 mmol/kg below 700 m of sediment and 4,000 m of sea water. In any vertical section through the hydrated zone, the concentration of dissolved methane in water in equilibrium with the hydrate will decrease from bottom to top, with the steepness of the gradient greatest under the deepest water. This is indicated in Fig. 53-2, which also shows the solubility in equilibrium with free gas at greater depths.

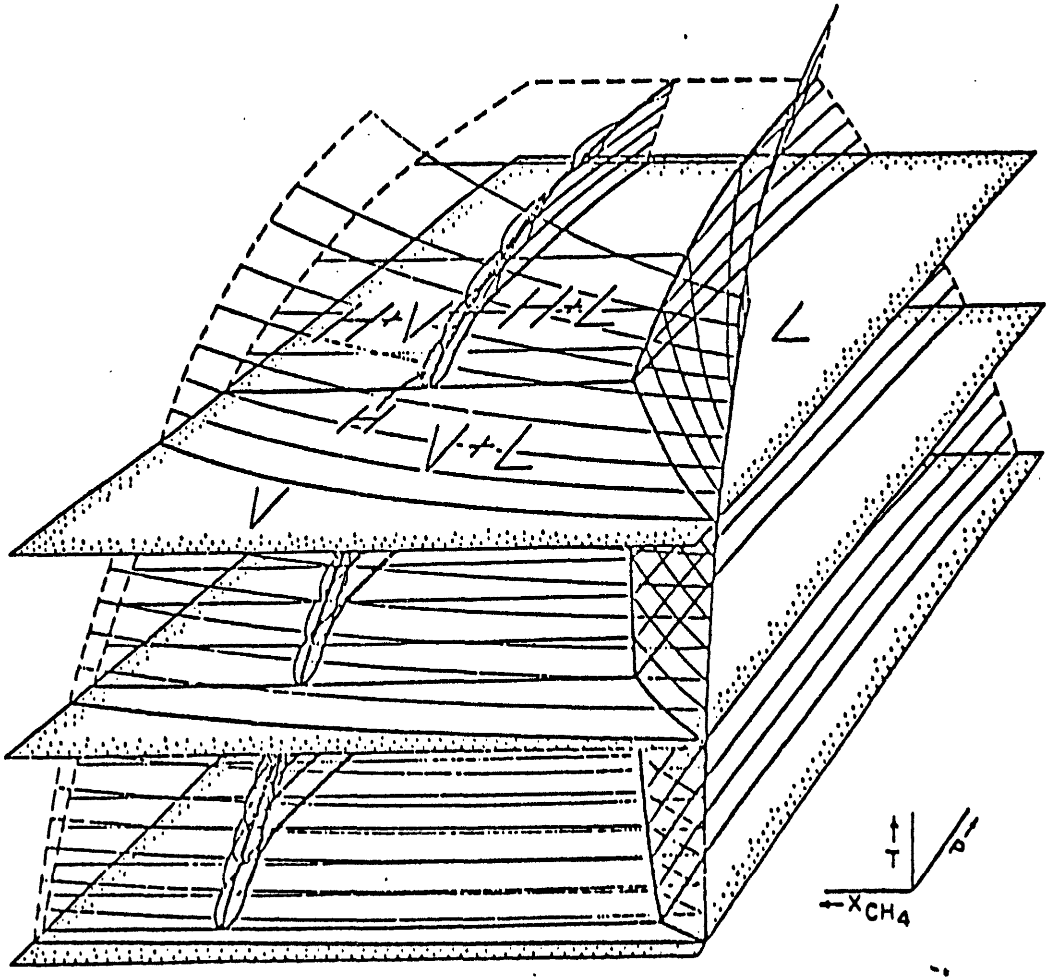

Figure ~~53-1~~.--Schematic phase diagram for a part of the CH_4-H_2O system, showing univariant curves (heavy lines) and traces of divariant surfaces in isothermal planes (light lines)

Figure 30

Is the concentration of biogenic methane in interstitial water likely to reach the minimum value for hydrate formation? Hammond (1974) found about 20 mmol/kg methane (no more accurately than a factor of two) in DSDP cores from the Carioco Trench off Venezuela, where high productivity of the water and anoxic bottom conditions favor methane genesis and high bottom water temperatures exclude formation of hydrate. Claypool and Kaplan estimate from the δC^{13} data on deep sea cores that only 20 to 30 mmol/kg of methane form biologically. If these values prevail, there is no reason to expect hydrates to form from biogenic methane. Our knowledge of sea floor biogeochemistry, however, is far too incomplete to place a limit on methane concentrations in sediments.

Consider a column of sediment with methane being generated throughout. Leakage to sea water or destruction by methane-consuming bacteria at the shallowest levels (Barnes et al., 1976) will keep the concentration at the water-sediment interface near zero, so methane will diffuse upward through the pore water. As the concentrations increase, at some level the solubility limit is reached. This may occur within the zone of hydrate stability, more likely in the upper part where the solubility is lowest, rather than at the base as predicted from the Makogon model. Or it may occur first at a greater depth, producing free gas that would bubble upward, extending the interval of saturation until hydration occurs at the limiting isotherm. When hydrate forms, six or seven molecules of H_2O are frozen for every molecule of CH_4. But since there are a thousand molecules of H_2O for every two or three of CH_4, the effect on the permeability is negligible. The concentration gradient in the pore water in the presence of hydrate will be that along the hydrate-liquid equlibrium curve, which would be steeper than that in the unfrozen section below and less steep than in an unfrozen section above (dashed line in Fig. 32). If the initial concentration gradient through the column was at a steady state for diffusive equilibrium, then the effect of hydrate formation paradoxially may be to facilitate transport of methane through the hydrated zone. Accumulation of hydrate to the extent where it would destroy the connectivity of the pore water system or extension of the depth interval of hydrate formation depends not only on the equilibrium conditions, which are functions of temperature, pressure, and composition, but on such factors as the rate of methane genesis, the kinetics of the hydrate reaction, the permeability of the pore water system, and particularly on local irregularities and perturbations in these factors. Theoretically, the problem can be solved, but practically not until more is learned about conditions and processes in sea floor sediments, both by actual exploration and by laboratory investigation of simple models.

CONCLUSIONS

The "zone of hydrate formation" is better considered a zone of potential hydrate formation. We do not know enough to state whether in any particular environment it will or will not occur. It is perhaps slightly easier to explain why hydrate should fail to accumulate, even in sediments with fairly active methane genesis, than to explain why it should accumulate. Nevertheless, it appears that hydrate does exist in submarine sediments. The best evidence is the behavior of cores outgassing slowly and endothermically after recovery. The correspondence of the location and configuration of the bottom simulating reflector with the expected base of the zone of hydrate

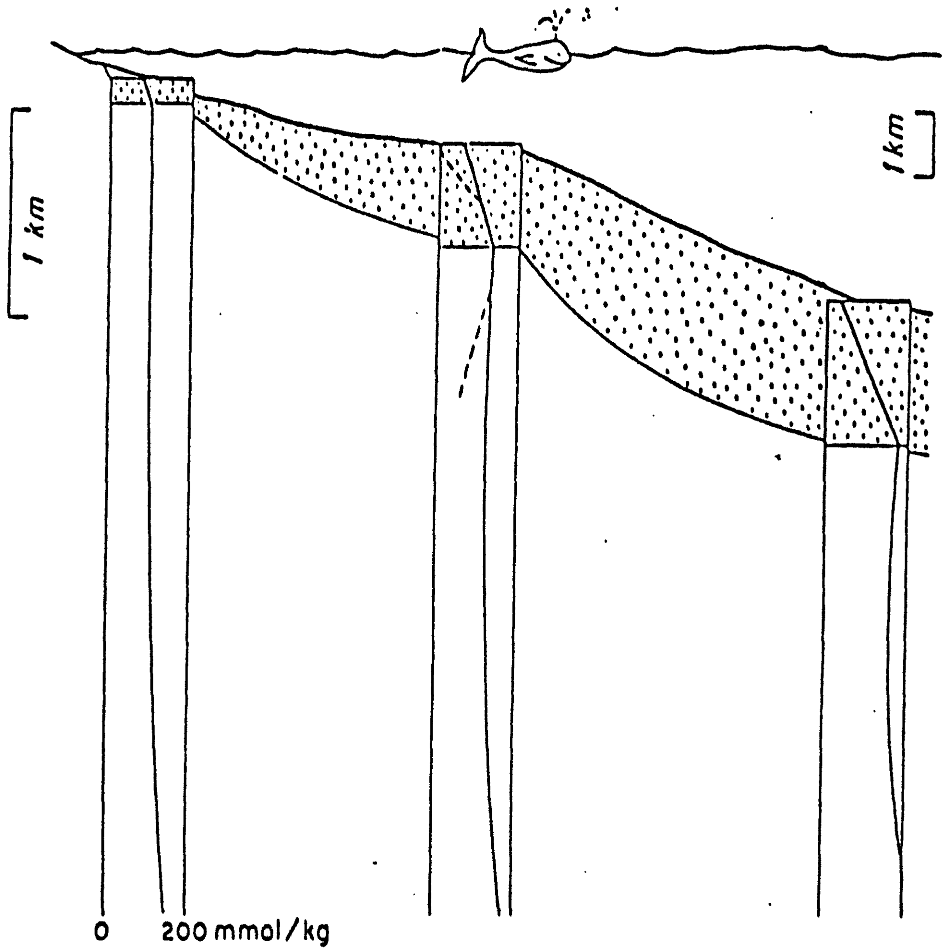

Figure 53-2.--Profiles of methane concentration is pore water in the potential hydrate zone (stippled) and below for average geothermal and ocean temperature gradients. Solid lines indicate solubility limit; dashed line gives an example of possible concentrations consistent with the existence of hydrate close above and free gas close below the equilibrium depth. Note difference in scales in water and subbottom depths.

Figure 31

formation is highly suggestive, but drilling at the two best known localities has not provided definitive evidence for the presence of hydrate.

Recovery of cores at bottom pressure is an obvious desideratum and may be necessary before the BSR is accepted as an indicator of hydrate. Attempts have been made but without success (Creager et al., 1973). Measurements in situ in deep sea drill holes of such properties as thermal conductivity or acoustic velocity (which have been measured successfully during shallow coring) or even gas fugacities would be valuable in understanding subbottom conditions.

Outstanding problems in the chemistry of hydrates critical to understanding their occurrence in nature concern not only the incompletely mapped phase space, as discussed above, but despite much work that has been done already (Makogon, 1974), aspects of the kinetics of hydration and decomposition.

Commercial recovery of gas from submarine hydrate itself would seem a very difficult task. A hydrate zone, however, could have direct economic importance as a trap for natural gas, perhaps of thermocatalytic rather than biogenic origin, migrating from greater depths. Nonrecognition of a hydrate zone, or false identification where one does not exist, during the exploration of an offshore gas field would be hazardous to both the success and safety of a drilling program. Finally, a stage of clathrate freezing may have figured in the history of apparently ordinary gas fields and sedimentary sequences with geologic consequences that remain to be investigated.

Hein, Scholl, Barron, Jones, and Miller (1978) interpret the Bering Sea BSR as an isothermal surface at which Opal-A transforms to Opal-CT. If so, it may have nothing to do with hydrates.

White (1979) has bright spots on seismic sections from the Gulf of Oman that he rather persuasively argues are gas trapped by hydrate layers.

Grow, et al., (1979) have diapirs at the base of the Continental Slope off the Carolina coast with BSR; they interpret as due to hydrates.

Tucholke, Bryan, and Ewing (1977) discuss the Blake Outer Ridge and BSR's of New Jersey as hydrate horizons.

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ARTICLE 16 (Moore, D.)

Gruy Management Service Co.
2501 Cedar Springs Road
Dallas, Texas 75201

May 8, 1979

Mr. Max C. Brewer
Chief, Operations NPRA
2525 "C" Street - Suite 400
Anchorage, Alaska 99503

Re: Presence of Gas Hydrates
South and East Barrow Fields

Dear Max:

In accordance with your letter of April 24, 1979, I have reviewed Mr. Thomas Payne's memorandum of March 24, 1979, and the data available in the Dallas and Houston offices of H. J. Gruy and Associates, Inc. and Gruy Management Service Co. Based on review of this data, I have prepared the following commentary relative to the possible presence of gas hydrates in the Barrow Sand and the Triassic (Sag River) "Sand".

A. General Comments on Hydrates

Based on review of the data in Chapter 5, Handbook of Natural Gas Engineering,[1] the primary factors that affect hydrate formation, and those that must be considered in determining hydrate conditions, are pressure, temperature, and gas composition. A generalization can be made that, for a given temperature, the hydrate pressure decreases as the specific gravity of the gas increases. Also, the nitrogen content of the gas has a very large effect on hydrate conditions. This is demonstrated graphically in Figure 5-41 of reference 1.

An initial attempt was made to determine the hydrate condition of the gases based strictly on specific gravity. However, due to varying gas compositions, I elected to calculate the hydrate conditions utilizing equilibrium constants from Figures 5-42 through 5-46 of reference 1. Except in the case of the Barrow 1 gas, which has 12% nitrogen, the hydrate conditions determined by the generalized curves and those determined by equilibrium constants agree fairly well. I feel that the equilibrium determined hydrate points are the most accurate.

B. "Barrow Sand"

1. South Barrow Field

Based on the data in Table 1, which was taken from the 1976 study,[2] there appears to be little chance the gas existed in a hydrate condition at original conditions. This is fully discussed in the report[2] along with the likelihood that hydrates did form during drawdown early in the productive history. This is shown graphically in Figure 5 of the report.[2]

TABLE 1

TABULATION OF RESERVOIR & FLUID PROPERTIES SOUTH BARROW FIELD

1. Depth of producing zones(s) RKB: 2200'-2400' (2)
2. p_i = 1102 psia @ -2250' (2)
3. Gas composition, fraction (2)

   C_1 - 0.9796
   C_2 - 0.0095
   C_3 - 0.0015
   C_4 - 0.0002
   N_2 - 0.0080
   H_e - 0.0002
   CO_2 - 0.0010

   1.0000

4. Gas gravity = 0.564 (2)
5. $T_R = 62^{\circ}$ F. @ 2375 (4)
6. Gas hydrate pressure @ 62° F. (1)

   p = 2000± psia (specific gravity)

   p = 1912± psia (equilibrium constants)

Table 1

2. East Barrow Gas Field

I did not utilize the figure in Mr. Payne's memorandum[3] which reflected hydrate conditions. Since his curves were apparently based on a binary gas system of 90% methane and 10% ethane, I did not feel that this gas composition was representative of that actually present in the "Barrow Sand" of the E. Barrow Field. Table 2 shows the compositional analyses of the gas produced from Barrow Wells 14 and 19. These compositional analyses were taken from the East Barrow field study[4]. The compositional analyses of the gas from these two wells reflect the extremes of samples collected from the East Barrow wells.

One of the primary problems encountered in trying to determine the probability of hydrates in this field is the lack of a measured bottom hole temperature. In dealing with a gas at these pressures, a small change in reservoir temperature makes a significant difference in whether or not hydrates exist. Therefore, an accurate estimate of the reservoir temperature had to be made.

Figure 33 is a visual presentation of the temperature data on Table 8 of the 1976 study[2]. This figure also includes the temperature recorded in Barrow No. 13 when the Sperry Sun bottom hole pressure test was conducted. (Since the conditions for running this test are known, this temperature point is felt to be the most accurate of those recorded thus far.) Unfortunately, the scatter of the data points does not allow projection of the data to determine the geothermal gradient in the area. The gradient must be determined by another means.

It has been estimated that the base of the permafrost is between 800 feet and 1200 feet.[2] If the depth-temperature point taken in Barrow No. 13 is honored, a geothermal gradient of 1.9°/100' would exist if the permafrost base was 800 feet.

If the permafrost base is 1200 feet, a geothermal gradient of 2.5°/100 exists. This assumes that the base of the permafrost is at a temperature of 32°F. Using an average top of the L. Barrow "Sand" in the East Barrow Field of 2,020', the reservoir temperature must be between 53° and 55°F.

Utilizing the lowest probable reservoir temperature of 53°, the hydrate pressure determined for the Barrow 14 and Barrow 19 gases by equilibrium constants are 1122 psia and 1457 psia respectively. Since the original reservoir pressure was determined to be 1008 psia[3], the gas would not be in hydrated state.

Table 2 reflects that the hydrate pressure for the Barrow 14 and Barrow 19 gases determined from specific gravity correlation would be below the original reservoir pressure. The accuracy of these hydrate pressures are particularly suspect since analysis of the well tests conducted on Barrow No. 19 in May 1978, indicated a flow efficiency of 75% or greater and flow rates in excess of 3,600 MCFPD. If the gas was in a hydrate state, this would hardly have been possible. This is not to be interpreted to mean that hydrate do not form at the sandface during drawdown. As in the case of S. Barrow, any appreciable drawdown should result in the formation of hydrates at the sandface. This is shown on Figure 33 which

TABLE 2

TABULATION OF
RESERVOIR & FLUID PROPERTIES
EAST BARROW FIELD

Lower Barrow Sand

1. Depth to producing zone RKB: 2020-2057 (6)

2. p_i = 1008 psia @ -2000' (4)

3. Gas composition, fraction (4)

		19	14
C_1	-	0.8730	0.9711
C_2	-	0.0037	0.0057
C_3	-	0.0006	0.0003
C_4	-	0.0012	0.0015
C_5	-	0.0007	0.0015
C_6	-	0.0000	0.0007
N_2	-	0.1200	0.0187
CO_2	-	0.0008	0.0005
		1.0000	1.0000

4. Gas gravity

   a. Barrow 19 = 0.609

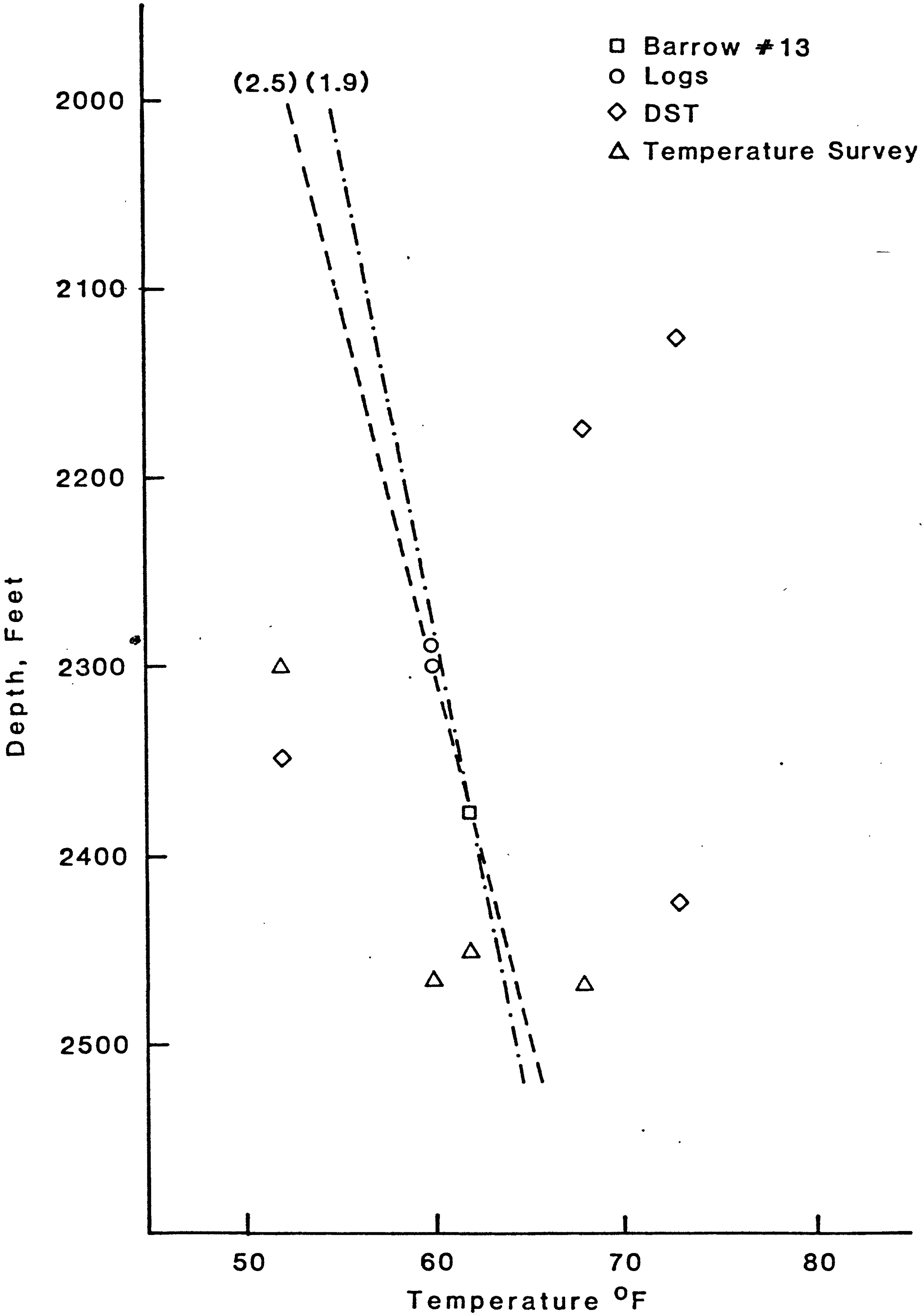
   b. Barrow 14 = 0.572

5. T_R @ 2020' RKB = 53° F. (Figure 1 @ 2.5°/100' gradient)

6. Gas hydrate pressure, psia @ 53° F.

	Barrow 19	Barrow 14
Equilibirum constants (1)	1457	1122
Specific gravity (1)	767	900

Table 2



DEPTH-TEMPERATURE DATA

Figure 32

is taken from Figure 5-48 of reference 1. It is also believed that Figure 33 is overly pessimistic. If care is taken to minimize the drawdown during production, formation of hydrates should not be a significant problem and adequate flow rates can be attained. This was demonstrated during the tests of Barrow No. 19.

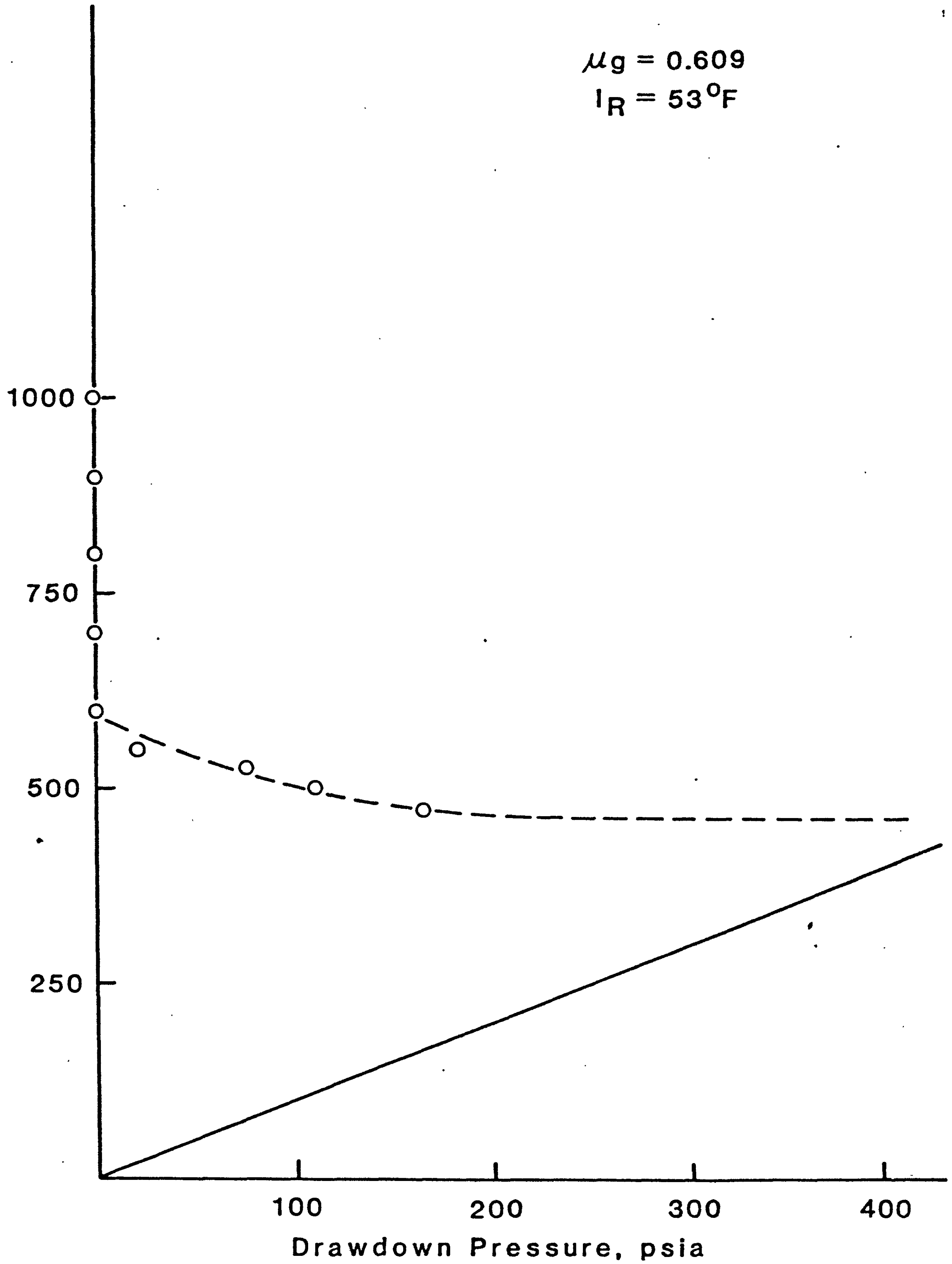
C. Triassic "Sand" (Sag River)

The probability of hydrates in this zone is hard to define due to the scarcity of data. There is one fluid study[5] which indicates that the Sag River is a saturated oil reservoir with a saturation pressure of 847 psig. However, the fluid study was carried out at 51°F and Figure 33 indicates that the Sag River reservoir temperature at 2250'± should be 59°F. Standing's correlation indicates a saturation pressure of 760 psia at 59°F. Since the reservoir pressure appears to be greater than 1000 psia, based on drill stem test data, there is probably a gas-cap present in this zone. This can also be inferred from the fact that gas was produced from the Sag River in Barrow No. 19. This well is slightly updip from Barrow No. 12 which produced oil.

Mr. Payne states that the low pressure in the Sag River may be due to hydrates. This is somewhat hard to support since drill stem tests in Barrow No. 17 and Barrow No. 19 recorded shut in pressures of 1007 psig at 2187' and 995 psig at 2111' respectively. These pressures are only maximum recorded pressures after final shut in times of 240 and 367 minutes and have not been extrapolated to equilibrium pressure. These pressures would appear to be more in line with "Barrow Sand" pressures than the 889 psig recorded in the Sag River of Barrow 12 when the subsurface fluid samples were collected on April 11, 1974. If these pressures are representative of the Sag River original bottom hole pressure, and the fluid study data[5] is correct, the Sag River would be an undersaturated oil reservoir with no gas-cap. Therefore, without additional data, I cannot conclusively state that there is a gas-cap in the Sag River. However, the 100% gas recovery in Barrow 12 lends a great deal of evidence to the presence of a gas-cap in this zone.

The composition of the gas-cap in equilibrium with the reservoir is unknown. Also, to attempt to calculate the composition would be a waste of time with the data available. It can instead be reasonably assumed that the gas-cap would have a gravity somewhat close to that liberated from the oil under differential depletion during the fluid study.[5] During the first pressure step shown on page 5 of the study[5] this gas gravity is 0.606. If this is a representative value of the gas-cap gas gravity, the hydrate pressure would be approximately 925 psia. However, without knowing the nitrogen content, this hydrate pressure is suspect since nitrogen would increase the hydrate pressure. The presence of some nitrogen in the gas-cap gas is probable since the well head gas sample collected from Barrow 12 contained 7.88% nitrogen.[5] This gas sample was obtained at the same time as the subsurface fluid samples.

Mr. Payne suggests that the dissolved gas in the Sag River oil could have been removed by the formation of hydrates. This is hard to visualize since there is actually no free gas phase present in the saturated oil at initial



DRAWDOWN PRESSURE FOR HYDRATE FORMATION

Figure 33

reservoir conditions. All light hydrocarbons, such as methane are part of the mole composition of the liquid as shown on page 8 of reference 5. Since the reservoir fluid is saturated, all excess gas has migrated to the probable gas-cap through gravity segration.

Based on the foregoing, it must be concluded that:

1. The "Barrow Sand gas" in the South and East Barrow Fields is not in a hydrate state at initial reservoir temperature and pressure.

2. Hydrates will form at the formation face, and in the immediate area of the well bore, if appreciable drawdown occurs during production. This problem is reduced as the reservoir pressure declines.

3. There is a probable gas-cap in the Sag River zone of the East Barrow Field. Due to lack of data on composition of the gas-cap gas, the hydrate pressure cannot be accurately determined. Production of gas from Barrow 19 indicates that the gas is not in a hydrate state.

I hope the commentary in this letter fulfills the request stated in your letter of April 24, 1979.

Your very truly,

/signed/
Don W. Moore

Enclosures

cc: Mr. Bob Lantz
USGS, Seattle
Mr. John Ross
H. J. Gruy & Associates, Inc., Houston

TABLE 3

CALCULATION OF HYDRATE PRESSURE USING EQUILIBRIUM CONSTANTS

S. Barrow Field @ 62° F.

Component	Mole %	K @ 2000 psia	y/K	K @ 1500 psia	y/K
Methane	0.9796	1.01	0.9699	1.05	0.9329
Ethane	0.0095	0.47	0.0202	0.55	0.0173
Propane	0.0015	0.103	0.0146	0.12	0.0125
Butane	0.0002	0.072	0.0028	0.085	0.0023
Nitrogen	0.0080	---	---	---	---
Helium	0.0002	---	---	---	---
CO_2	0.0010	---	---	---	---
	1.0000		1.0075		0.9650

p Hydrate = 1912 psia

E. Barrow Field @ 53° F.

Component	Mole %	K @ 1000 psia	y/K	K @ 1500 psia	y/K
Methane	0.9711	1.090	0.8909	0.9800	0.9909
Ethane	0.0057	0.233	0.0245	0.1670	0.0341
Propane	0.0003	0.043	0.0070	0.0355	0.0084
Butane	0.0015	0.024	0.0625	0.0150	0.0100
Pentane	0.0015	---	---	---	---
Hexane	0.0007	---	---	---	---
Nitrogen	0.0187	---	---	---	---
CO_2	0.0005	0.7500	0.0007	0.6500	0.0008
			0.9856		1.0442

p Hydrate = 1122 psia for Barrow 14 gas

Component	Mole %	K @ 1000 psia	y/K	K @ 1500 psia	y/K
Methane	0.8730	1.090	0.8009	0.9800	0.8908
Ethane	0.0037	0.233	0.0159	0.1670	0.0221
Propane	0.0006	0.043	0.0139	0.0355	0.0169
Butane	0.0012	0.024	0.0500	0.0150	0.0800
Pentane	0.0007	---	---	---	---
Nitrogen	0.1200	---	---	---	---
CO_2	0.0008	0.750	0.0011	0.6500	0.0012
			0.8818		1.011

p Hydrate = 1457 psia for Barrow 19 gas

Table 3

TABLE 4

TABULATION OF RESERVOIR & FLUID PROPERTIES EAST BARROW FIELD

Triassic (Sag River)

1. Depth to producing zone RKB: 2198'-2277'
2. p_i = 1170 psia @ 2315' (DST No. 4 in Barrow 17)

   Pressure is very questionable.
3. R_{si} = 117 ft.^{3}/bbl. @ 30 psig & 74° F. (5)
4. °API = 25.3 (5)
5. T_R = 59° @ 2250' (from Figure 1)
6. P_b = 847 psig @ 51° F. (5)

   P_b = 760 psia @ 59° F. (Standing)*
7. μ_{o_1} = 45 cp @ T_R & dead oil (Beal & Frick)*

   μ_{o_b} = 21 cp @ 74° F. & 117 ft.^{3}/bbl. (Chew & Connally)*

   μ_{o_b} = 48.89 cp @ 847 psig & 51° F. (5)

*Estimate based on correlation charts.

Table 4

REFERENCES

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2/ Reservoir Engineering and Geologic Study of the S. Barrow Gas Field, H. J. Gruy and Associates, Inc., October 7, 1976.

3/ Memorandum, "Possible Gas Hydrate Effect on Recovery of Oil and Gas from Reservoirs in East Barrow Field," Thomas G. Payne, March 27, 1979.

4/ Reservoir Engineering and Geologic Study of the E. Barrow Field (Preliminary Copy), H. J. Gruy and Associates, Inc., December 20, 1978.

5/ Reservoir Fluid Study, Barrow No. 12 Well, Core Laboratories, Inc., November 5, 1974.

6/ Memorandum, "Standard" Information on E. Barrow Gas Field, Bob Lantz, June 6, 1978.

ARTICLE 17 (Payne, T.)

2801 Dundee Court
Fort Collins, Colorado 80525

March 27, 1979

Memorandum

To: Arthur L. Bowsher

From: Thomas G. Payne

Subject: Possible gas hydrate effect on recovery of oil and gas from reservoirs in East Barrow field

Attached are sketches that illustrate the possible importance of gas hydrates in exploring the Barrow area. Stewart Folk's memo of January 12, 1979, started me thinking on this subject.

The attached graph shows the depth-time curves for the hydrate zone and the transition zone, based on 90% methane and 10% ethane (Baker, 1974). Superimposed on the hydrate curves are depth-temperature lines, based on a geothermal gradient of 2°F/100'. Each line represents a given depth to the base of the permafrost as shown on the left side.

The graph and cross section (Figure 34 and 35) suggest the possibility that the formation of gas hydrates may have reduced the oil drive in the Sag River(?) sandstone in the East Barrow field and may also have reduced the flow rate of gas in the "Barrow sand". Please note that the presentation is intended only as a demonstration since I do not know the depth to the base of the permafrost and the geothermal gradient in this area. I merely assumed values for demonstration.

The cross section extends eastward from the disturbed zone through East Barrow field to Scott Point on the coast, a distance of about 7 miles. A-A' on the graph is a depth-temperature profile of the Sag River(?) sandstone along the line of cross section. B-B' is a similar profile for the Barrow gas sand. Note that, by my assumptions, both reservoirs bracket the hydrate, transition, and no hydrate zones. The profile above the cross section shows the assumed eastward rise of the permafrost.

Low pressure in the Sag River(?) oil sand in East Barrow field could be explained by the formation of gas hydrates resulting in (1) depletion of the gas cap, if any, (2) removal of dissolved gas from the oil (Katz, 1972), and (3) immobilization of part or all of the water. This condition would have reduced or eliminated gas cap drive, solution gas drive, and water drive. According to the assumptions East Barrow field is mostly in the hydrate zone in the Sag River. Presumably the adverse effects would decrease going downdip eastward across the transition zone to Scott Point, where hydrates should be absent.

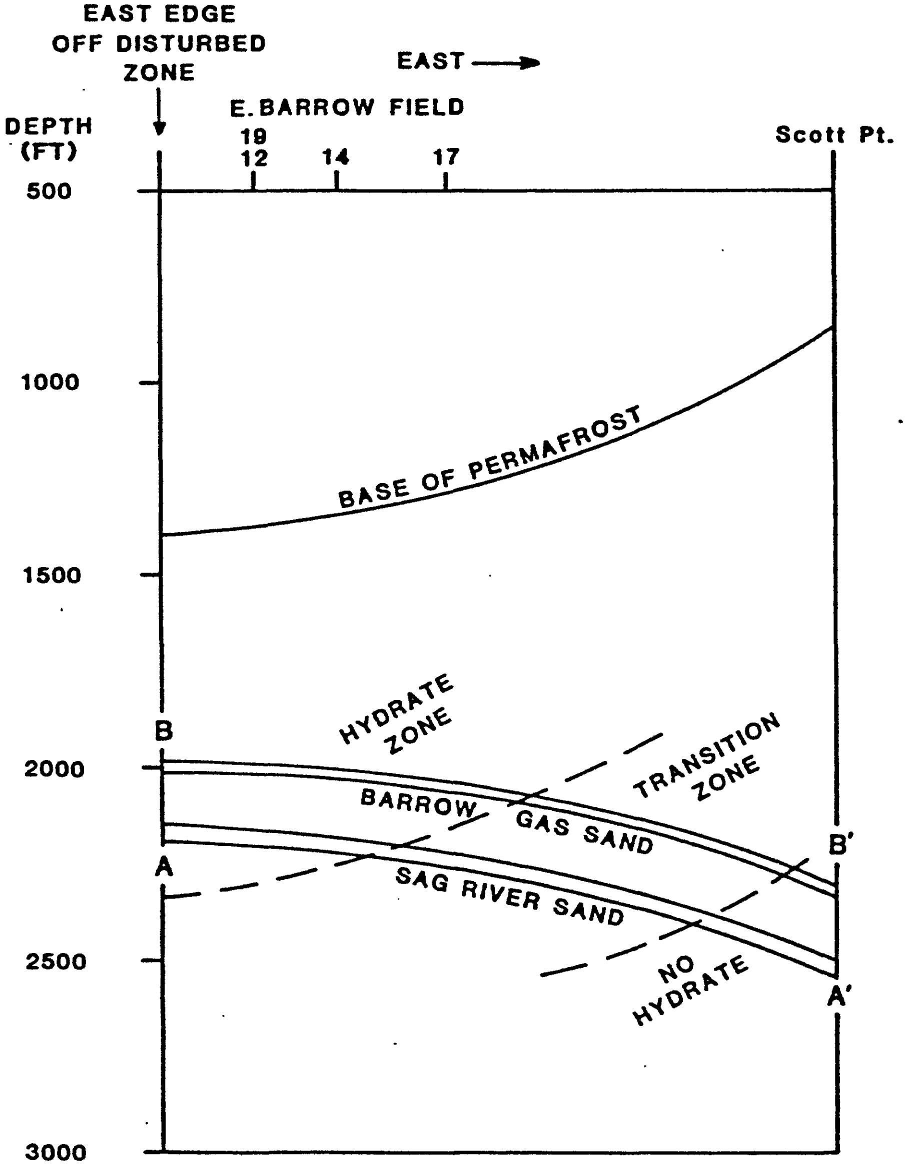
The above reasoning applies also to the "Barrow gas sand" (B-B'), which in the field area falls entirely in the hydrate zone as shown by the cross section (Figure 35). Part of the gas in the field is tied up in hydrates, which reduces the available pore space and flow rate.

A geothermal gradient less than 2°F/100' would shift the traverse lines A-A' and B-B' to the left and thereby bring more of the area into the hydrate zone. Or a lower gradient would lessen the depth to the base of the permafrost required to maintain the traverse lines in their present position.

In my opinion the Sag River Sandstone in the greater Barrow area is very favorable from the standpoint of hydrocarbon source. The huge drainage area extends a long distance to the east, north and south, and includes the subcrop belt, where the Sag River is covered by "pebble shale unit" in a trend extending northwestward across the Simpson Peninsula and westward in the offshore area. The Kingak shale and possibly the Shublik could also have served as a source. If reservoir properties are favorable, a large oil accumulation should have occurred. The Sag River(?) oil in East Barrow field could be an immobilized manifestation of a very large oil field.

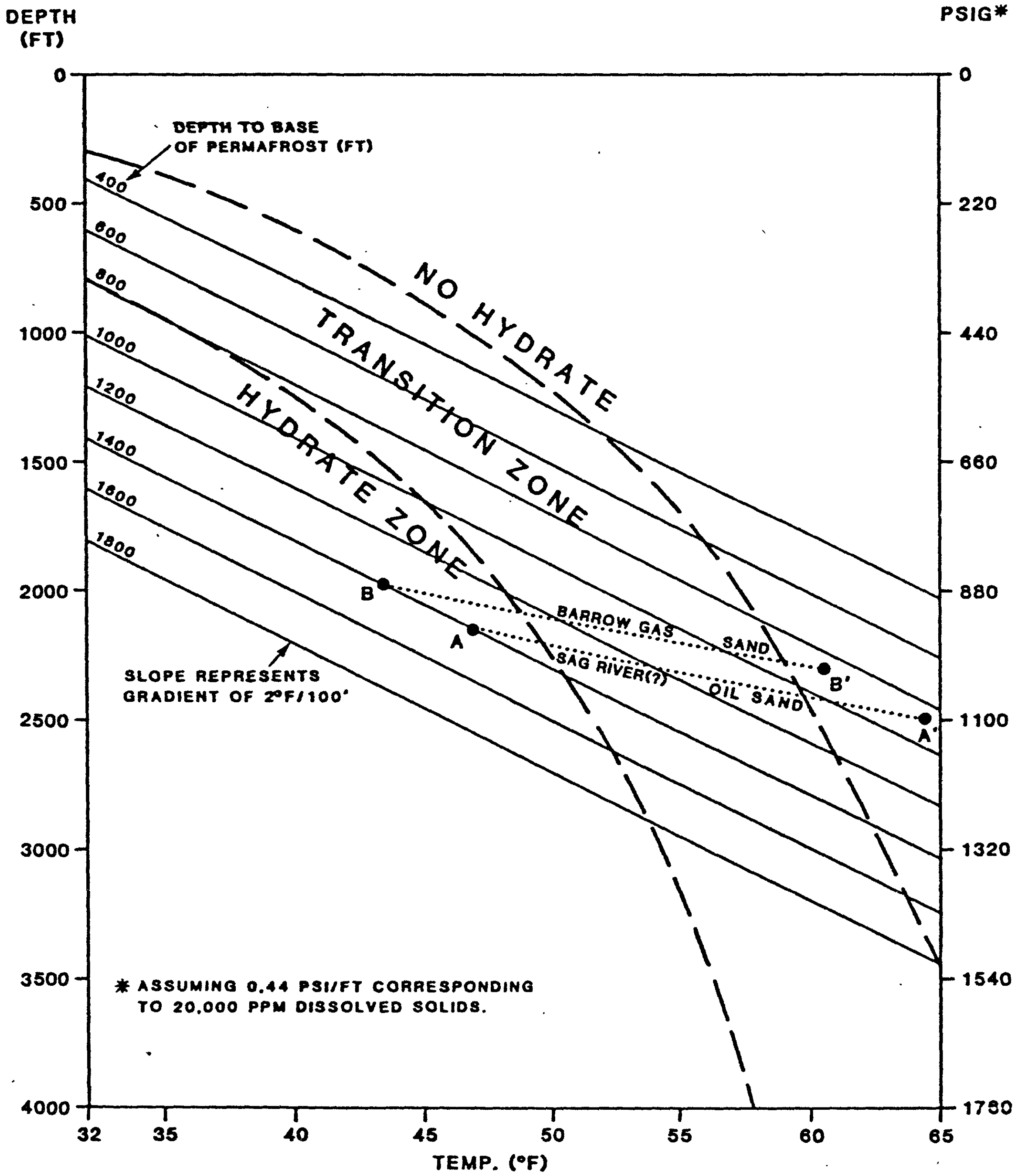
I recommend that temperature and permafrost depth data be assembled and that maps be prepared showing the distribution of the hydrate, transition and non-hydrate zones by reservoirs. If the thermal picture fits the immobilization concept here described, consideration should be given to testing the Sag River just outside of the transition zone to investigate the possible presence of a large oil accumulation.

By the same reasoning the lack of drive in Nanushuk sands of the Simpson area could be explained by the presence of gas hydrate, including both the eastern or Simpson seeps trend and the western area that embraces the Simpson oil field, Simpson #1, and Admiralty seeps.



CROSS SECTION MODEL BASED ON
ASSUMED GEOTHERMAL GRADIENT OF 2°F/100'

Figure 34



DEPTH-TEMPERATURE RELATIONSHIPS FOR INTERPRETING PRESENCE OF GAS HYDRATES IN RESERVOIRS

Figure 35

ARTICLE 18 (Pratt, R. M.)

GAS HYDRATE EVALUATION AND RECOMMENDATIONS
NATIONAL PETROLEUM RESERVE - ALASKA

Prepared for:

HUSKY OIL NPR OPERATIONS, INC.

Prepared by:

R. M. Pratt

TC - 7916
27 February 1979

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ILLUSTRATIONS

ABSTRACT

Gas hydrates are ice-like crystalline solids formed by the incorporation of hydrocarbon gas into water structures. They are stable at depths of between 500 and 3500 feet and up to temperatures of 50° or 55° F. They incorporate up to 200 times the gas volume in one volume of solid and, therefore, could be excellent potential reservoirs. On NPR-A the most favorable areas to look for hydrate are:

1. THE BARROW AREA - where known gas is shallow and close to the hydrate stability field.
2. THE TUNALIK AREA - where abundant shallow coal is a good source of gas in the permafrost zone; and
3. NEAR THE COLVILLE DELTA - where recent sedimentation supports deep permafrost and gas rich shallow sediments.

Recommended exploration techniques include:

1. Slim hole drilling with oil based cold muds to keep the hole frozen.
2. Careful gas analysis of the mud in the shallow section during drilling.
3. Careful detailed logging with resistivity and sonic tools starting at the surface.
4. Crystal cable velocity measurements in the holes to seismically define the permafrost.
5. Drill stem tests and methanol treatment near the lower stability depths to see if gas flow from hydrate can be initiated.

GAS HYDRATE EVALUATION
NATIONAL PETROLEUM RESERVE - ALASKA

I. INTRODUCTION

Gas hydrates have been known as chemical-physical substances since 1810 when first described by Sir Humphrey Davy (Miller, 1973; Bily and Dick, 1974). Numerous chemical and physical investigations have defined the crystal structure and temperature - pressure stability zones for various hydrates and their molecular structure is known. The first references to natural hydrates in relation to the petroleum industry were in connection with natural gas pipe lines, because gas hydrates adversely clog the lines. Extensive engineering investigations (Katz, 1959; Deaton and Frost, 1949) have reviewed and dealt with the problem of hydrates in pipe line transmission. Essentially the problem is now solved by drying natural gas before shipping. To date, the major concern of gas hydrate formation in NPR-A has been in connection with the production at Barrow gas field. Periodically it is necessary to shut down the producing wells and flush them with methanol to remove the hydrate.

The possibility of naturally occurring gas hydrates with potential economic value was not realized until the early 1970's with references in both the Russian and American literature (Makogon and others, 1971; Bily and Dick, 1974; Katz, 1971). We must assume considerable industrial thought on the possibility of gas hydrates with the development of Prudhoe Bay and northern Canadian gas provinces. In particular, a paper presented by D. L. Katz (1971) at the 1970 meeting of the Society of Petroleum Engineers created a flurry of interest in industrial circles. About the same time, the possibility of natural gas hydrates in deep-sea sediments was postulated to explain anomalous shallow seismic reflectors (Stall and others, 1971). These few scientific references and ideas have been expanded in popular press reports of both the United States and Russia. Some articles suggest that vast fields of gas hydrate, sufficient to solve our gas needs for many years, occur under the permafrost and in deep-sea sediments (Hodgson, 1978); Chersky and Makogon, 1970).

Gas hydrates occurring in the natural state seem to be generally accepted by informed workers. Their occurrence has been documented in both the Canadian Arctic (Bily and Dick, 1974) and in the Deep-Sea (Tuchalke and others, 1977). However, documented occurrence and major producible reserves are two entirely different things. In the Arctic, gas hydrates are probably stable to temperatures of 50° or 55° F at depths of 3000 to 3500 feet but they are much more prone to occur intermingled with permafrost or immediately beneath the permafrost. Gas hydrates are an ice like solid - they occur in association with perma-frost; therefore, their detection and evaluation are intrinsically tied to the detection and evaluation of permafrost. In NPR-A the detection of gas hydrates, both seismically and in well bores, should be tied to a careful study of the permafrost zone and this entails careful evaluation of shallow data.

II. DEFINITION

Natural gas hydrates are a special form of chemical substances known as clathrate. In a clathrate compound there is a crystal lattice containing cages or voids that can incorporate guest molecules (i. e., methane). In hydrates, the framework consists of water molecules and, therefore, hydrates can be considered as forms of ice that are only stable when gas molecules are present in the cages. About 18 types of gas will form hydrates including N_2, O_2, CO_2, etc. as well as hydrocarbon gas from methane up through isobutane. The lattice work of water molecules is held together by hydrogen bonds and is supported by the gas molecules in the cages. Two separate molecular configurations are known, giving a 1:20 gas-water ratio for small gas molecules and a 1:24 or 1:28 ratio for large gas molecules, although reported values differ somewhat (Holder and others, 1976). From a practical point of view, natural gas hydrates have about 90% of the cages filled with guest molecules and the gas is dominantly methane. The significant fact is that 170 to 200 volumes of gaseous methane can be held in 1 volume of hydrate depending on the reference and filling of the voids.

III. FORMATION AND STABILITY

The formation of natural gas hydrates depends on:

1. Available methane (or other gas mixture)
2. Available water
3. Temperature below critical value on a temperature-pressure stability curve
4. Pressure above critical value on the curve
5. Gas concentration above the solubility of gas in water

Stability curves have been worked out for numerous combinations of gas (Parrish and Prausnitz, 1972) as shown in the accompanying diagrams (Figure 30). An often overlooked factor is that concentrations of gas must be above their natural solubility in water - this probably greatly restricts the natural extent of hydrates, especially in deep-sea sediments.

As shown on the diagrams, hydrates can occur in combination with permafrost at moderate depths or above the freezing point for permafrost at slightly greater depth. They are restricted at the surface by low pressure limits and at depth by geothermal temperature limits. Any practical exploration should probably look for concentrations of hydrate in connection with permafrost or immediately below the permafrost - ideally, where proven natural gas occurrences can be followed updip into deep permafrost.

Various ideas are postulated in regard to the formation of extensive gas hydrate bodies; however, extensive reserves are as yet unproven.

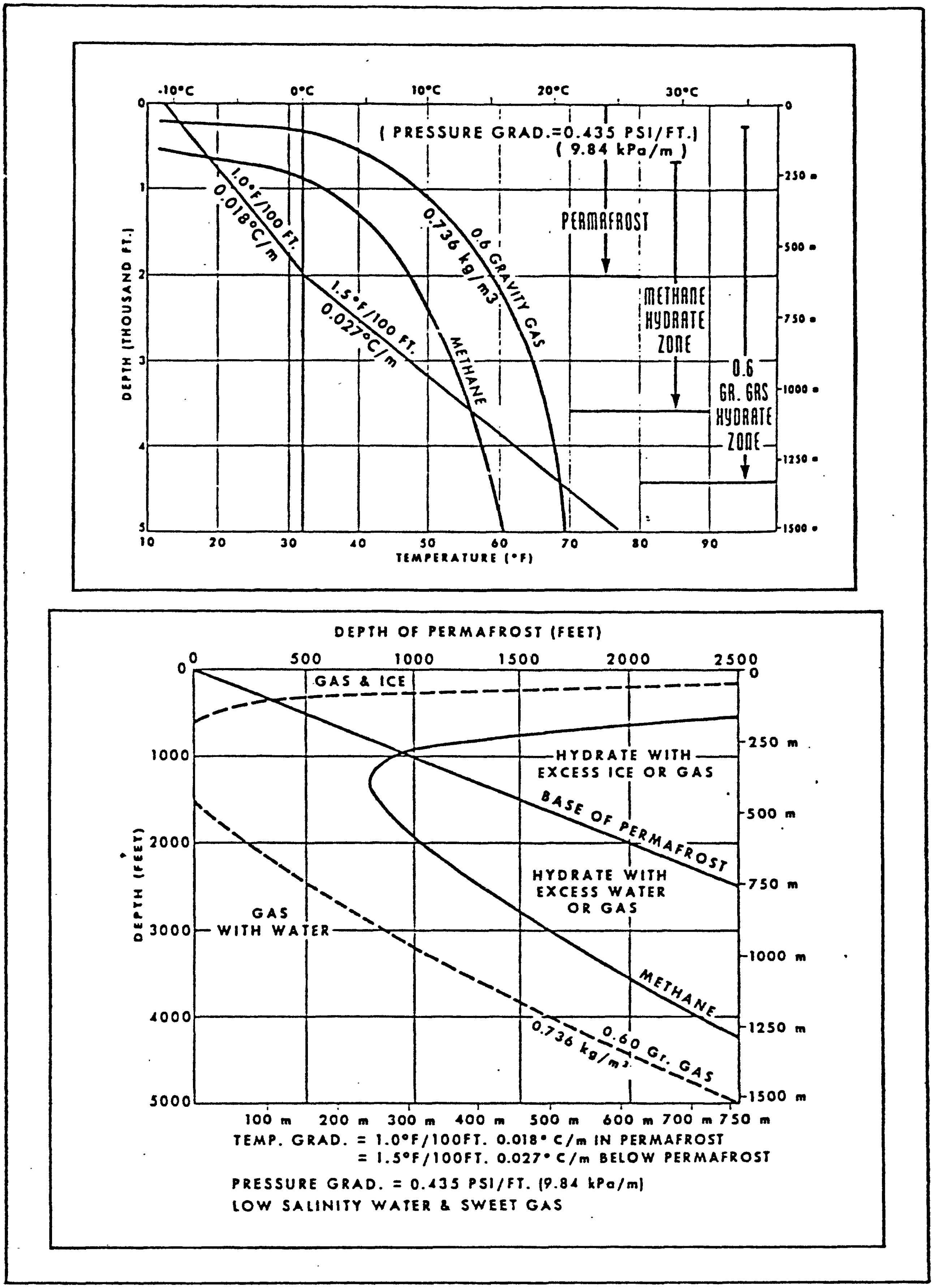
1. The gas hydrate could be part of a shallow gas reservoir before cooling and permafrost development, i. e., hydrate developed by "freezing" a pre-existing gas field.

2. Hydrate bodies could form by concentrating gas, i. e., by stabilizing a continuing gas flux by solidification in the frozen zone.

3. Hydrate might concentrate by entrapment beneath the permafrost layer by virtue of the impermeability of the permafrost.

4. Hydrates may be left behind as concentrated deposits upon recession and melting of the permafrost. This idea occurs in several Russian references.

5. Hydrates may be concentrated in coal seams and peat by virtue of being stabilized by freezing as the gas is evolved rather than bleeding off to the surface.



DEPTH-TEMPERATURE STABILITY ZONE FOR NATURAL GAS HYDRATE IN RELATION TO THE BASE OF THE PERMAFROST (UPPER) AND PHASE COMPONENTS IN AN IDEAL RESERVOIR (from BILY and DICK, 1974, p. 345).

Figure 36

IV. MODES OF OCCURRENCE

Much of the literature on gas hydrates concerns factors and occurrences other than potential fuel reserves. Most of the factors listed below have adverse effects in gas production:

1. Natural gas reservoir potential at shallow depth - the primary consideration in this evaluation.
2. Hydrate formation in gas transmission lines causing blockage of the lines and well bores in cold areas. This is a real problem delt with extensively in gas engineering handbooks (Katz, 1959; Deaton and Frost, 1949).
3. Reflectors at shallow depth in deep-sea sediments off the continental slope and rise (Tucholke and others, 1977; Grantz and others, 1973).
4. Possible factor in denudation of gas from oil reservoirs at shallow depths. Gas can combine with water within an oil pool and thus remove the light hydrocarbon fraction by crystal formation (Verma and others, 1975).
5. Factor in permeability blockage and gas flow inhibition in sandstone reservoirs - hydrate is a solid not a fluid - and, therefore, does not flow.
6. Hydrates can form with ice below the freezing point of water and thus take gas out of natural gas reservoirs within the permafrost zone. They occur within glacial ice.
7. Hydrates can form above the freezing point of water thus extending

the adverse effect of permafrost.

8. Gas expansion from hydrates are potentially dangerous in coring operations because the 170 to 200 times expansion upon retrieval at the surface can occur with explosive force.

9. Gas liberated from hydrate zones during drilling could potentially blow out because of the expansion.

10. It has been postulated that hydrates may have an important effect on the diagenesis and mechanical properties of sediment, particularly in the deep-sea where much of the methane may concentrate in particular zones.

11. The phase transformation of hydrates, particularly expansion into gas layers, may have a marked mechanical triggering effect in sediments in relation to mud slides, disruption of bedding, etc., particularly on continental slopes. The transformation also releases water which can cause increased pore pressure.

12. It has been postulated that much of the hydrocarbon on earth could be locked up as hydrate in deep-sea sediments since the deep-sea is generally within the temperature - pressure stability zone for hydrate and covers more than 50% of the earth's surface.

V. DOCUMENTATION OF NATURAL OCCURRENCES

A critical evaluation of the literature reveals one documented visual report of gas hydrate in deep-sea sediment and two documented reports from oil field drilling - one Canadian and one Russian.

In the deep-sea occurrence, A. G. Yefremova claims to have actually observed hydrate in gas filled cavities in a sediment core from a 2000 meter depth in the Black Sea (Yefremova and Zhizhchenko, 1974). The hydrate crystals were in cavities and disappeared before her eyes on the deck of the ship. Hydrate in the Black Sea seems reasonable because the bottom is anerobic (lifeless) and amenable to the preservation of hydrocarbons. Normal oceanic sediments are highly oxidized and reworked extensively by bottom feeding animals. Concentrations of gas above the solubility point of methane in sea water should not normally occur in deep-sea sediments.

Cores taken in the Deep Sea Drilling Program often evolve small amounts of methane which is postulated to have been in hydrate form, but equally likely developed from bacterial action in the warm core on the deck of the ship. At any rate, none of the drill holes had serious problems with gas and two holes drilled specifically to test the hydrate reflecting layer encountered chert and indurated sediment instead of gas or hydrate (Hollister and Ewing, 1972; Leg 11 Deep Sea Drilling Project).

The Canadian occurrence is in the Mackenzie Delta, Imperial Oil exploratory wells Mallik L-38 and Ivik J-26, and is reported by Bily and Dick (1974). Several reviews and popular summaries make reference to the report and even republished the figures but add nothing to the basic facts. Essentially, the two wells encountered gas hydrates beneath the permafrost at depths of 3000 to 3600 feet. The zones were detected by sharp gas increases on the mud log during drilling and the very slight pressure increase during the shut in on a drill stem test. No hydrate was actually recorded at the surface but the drilling record and drill stem test comparison between the suspected hydrate zone and established free gas reservoir zones leaves little doubt about the validity of the interpretation.

The documented Russian occurrence is by Makogon and others (1971) in the Messoyakha natural gas field in the northeastern part of Western Siberia. In this case, a producing field was deliberately evaluated and studied to determine the temperature - pressure zone where hydrate might be stable. The average stratal pressure was determined as 78 kg/cm^2 and temperatures range from 8° to 12° C. At a pressure of 78 kg/cm^2 the temperature of hydrate formation proved to be 10° C, thus the field is divided into an upper potential hydrate zone and a lower free gas zone. The presence of hydrate was demonstrated by injecting methanol into critical strata at the equilibrium boundary. The methanol catalytically broke down the hydrate and the liberated gas greatly increased the productivity of the extraction zone. Using the increased gas flow data, calculations suggest that the overall gas reserves from gas present as hydrates are 54% higher than reserves based on the assumption of free gas filled reservoir. There is still some question as to how much gas was actually released from the hydrate phase by the methanol and how much increase was from the hydrofracing effect of pumping into the free gas reservoir. As in the case of the Canadian report on the Mackenzie, this Russian report is variously quoted in the Russian literature.

VI. DETECTION OF HYDRATES

The critical problem in exploration for gas hydrate reserves is how to detect them. Gas hydrates are a solid - a form of ice - and, therefore, many of the parameters applicable to measurements in permafrost should be usable with hydrates. These are included in:

1. Geophysical measurements
2. Well bore logging techniques
3. Temperature measurements and models

Geophysical prospecting in permafrost areas has long been complicated by the anomalous velocities of the ice. Anomalies vary from place to place and are not uniformly detectable by velocity analysis. Considering the problems and uncertainty in the detection of conventional permafrost, it is doubtful if included hydrates can be detected by seismic means. Velocities in deep-sea sediments have been experimentally shown to increase from 1.97 km/sec. to 2.55 km/sec. in zones where hydrates are stable (Stoll and others, 1971). The interval velocity of gassy (hydrate) layers in the sediments is generally about 2.2 km/sec.

In well bores the following observations are most pertinent (Bily and Dick, 1974):

1. A sharp gas kick is pronounced on the mud log because hydrated gas is released by the drilling action - this is the best positive indication of hydrate in the permafrost or hydrate stability zone.

2. Oversized caliber occurs because of spalling from decomposition (gas expansion) of hydrates next to the well bore.

3. Sonic logs increase in velocity. This could be diagnostic but is not substantially different from that in permafrost.

4. Relatively high resistivity occurs. In particular, the long normal tends to separate out from the short normal which reflects a melting zone next to the bore hole.

5. Relatively low SP deflection.

6. Only slow, straight-line pressure increase during the shut in phase of a drill stem test. This is because hydrates release gas slowly and block effective reservoir permeability. DST character was considered diagnostic of hydrate zones in the Canadian example.

7. In the Mackenzie test (Bily and Dick, 1974) there was no improvement in the DST recovery with methanol treatment. This is in contrast to the Russian test (Makogon and others, 1971) and is probably because the test was well up in the T-P zone of stability rather than at the top of a producing gaseous gas zone.

8. Reduction of permeability by gas hydrate formation is possible if gas is tested or enters the well bore and mixes with water under critical T-P conditions. Impermeation has been demonstrated experimentally by passing gas and water through samples in a cold pressure chamber. After a while, the gas flow stops completely (Evrenos, 1971).

9. Under laboratory conditions gas hydrate in minute amounts is detectable by X-ray diffractions, but must be within the T-P stability zone to remain crystalline.

10. Temperature measurements of the well should indicate the zone of hydrate stability under given T-P conditions. Valid temperatures can only be obtained after the well has cooled and do not necessarily indicate hydrate - only the stability zone of potential hydrate.

VII. POSSIBLE METHODS OF PRODUCTION

Once gas hydrate reserves are established then a method of production must be devised. The main choices are:

1. Reduction of pressure in the stratum.
2. Warming of the deposit.
3. Introduction into the stratum of catalyzers facilitating decomposition of the hydrate. Methanol greatly increased production in the Russian example (Makogon, 1971), but failed to stimulate the well in the Canadian example (Bily and Dick, 1974).

Essentially, well formed gas hydrate is an ice-rock layer and it is difficult to see how it can be effectively produced. Hydrate is not stable at surface pressures; therefore, any consideration of conventional mining techniques is probably out of the question. However, it might transform to a gas with explosive chain reaction into a low pressure chamber or hole once the hole is established.

VIII. POSSIBLE RESERVES

Reserves of natural gas in the form of gas hydrate have been postulated for both:

1. the far north, and
2. the deep-sea.

At the present time, reserve possibilities are discussed in connection with alternative energy resources and extreme statements are sometimes related in the news media. An example: The National Geographic in a recent article headlines: "Soviets Predict 300-Century Supply"; mostly from hydrate related gas in Siberia (Hodgson, 1978, p. 65).

In the deep-sea basins, pressure from the hydrostatic depth and temperature are within the stability range of hydrate and it is postulated that any organic matter releasing gas (methane) into bottom sediments would be a source. Hydrate would accumulate as a stable solid in the bottom sediment and thus the deep-sea sediments form a hydrocarbon sink (Milton, 1976). Cores from the Deep Sea Drilling Program and anomalous seismic horizons (Tucholke and others, 1977; Trofimuk and others, 1973) suggest the presence of limited amounts of hydrate in localized areas, particularly at the base of the continental slope. Art Grantz (1976) suggests that much of the deep-Beaufort-Sea has a layer of hydrate and gas accumulation.

In reality, the deep-sea drilling program has failed to encounter any significant quantities of gas - beyond organics that can only be detected under laboratory condition; the deep-sea sediments are mostly oxidized and organics are completely recycled by bottom organisms. The most critical factor is the solubility of methane in sea water, because there has to be excess free gas to form hydrates. Documented de facto evidence of hydrate layers in deep-sea sediments is lacking.

Gas hydrate layers in permafrost areas are not documented. The two cases discussed where hydrate is thought to be demonstrated are very limited and connected with existing gas prone areas and, in Russia, a producing shallow field. None of the shallow or deep wells drilled on the North Slope ever had gas problems from depths where hydrate might be expected. If there is indeed a widespread layer of free gas immediately beneath a hydrate zone in permafrost regions, one would suspect some sort of record of gas complications with water or oil test drilling programs. The presence of a layer of gas hydrate of regional nature trapped at the base or within the permafrost zone. has yet to be demonstrated.

IX. HYDRATES IN NPR-A

A review of the existing available reports and hard data from NPR-A reveals one reference to a hydrate reserve layer on NPR-A. This is in a paper by Katz (1971) in which a diagrammatic layer of hydrate is shown under perma-frost, thickest along the coast and thinning to the south. Permafrost depths are given for Cape Simpson and Barrow (and other points in Alaska and Russia). From the depth of permafrost the potential methane and .6 gravity gas layers are calculated, however, the reference for permafrost depth is not given (it is probably from Brewer, 1958). Another potential source of hydrate in NPR-A is in connection with coal seams, which occur extensively near the surface in the western part of the Reserve.

Adverse effects of hydrate formation have been considered in connection with the gas development at Barrow; it is thought that shallow sands over the field at Barrow might be plugged with hydrate. However, it is significant that the producing zone at Barrow is just beneath the stability depths for gas hydrate.

Log records of recently drilled wells have no indication of hydrates nor gas beneath the permafrost. In fact, one of the major problems in interpretation is trying to pick the base of the permafrost. It is difficult to detect any anomalous zones of hydrate within the permafrost when the permafrost itself is poorly understood and sonic and resistivity logs are characteristically incomplete above the first casing point.

Permafrost is defined as permanently frozen ground at a temperature below 0^o C (freezing). In actual circumstances, brine layers and rock that are not actually frozen but below 0^o C are considered to be in the permafrost layer. Permafrost is detected seismically by high, erratic near surface velocity and in well logs by high sonic and resistivity spikes. There has been much discussion and thought about permafrost problems in NPR-A but many of the problems are not completely resolved because permafrost is not precisely indicated by any single tool. Gas hydrates most certainly occur under proper conditions of pressure and temperature; however, they are most likely within the permafrost zone. In other words, when and if gas occurs within the permafrost it would occur as gas hydrate. Conversely, most permafrost at stable depth (pressure) for hydrate probably has a fraction of hydrate. The big problem is separating gas hydrate from permafrost with our present exploration methodology.

X. RECOMMENDATIONS FOR STUDY

As stated in the last section, the detection and definition of gas hydrate is intricately tied to a study of permafrost. With present drilling methods, permafrost is not evaluated because surface casing is too large and log suites are not run to the surface. In the seismic program, parameters are defined for deep reflectors and often not even recorded in the permafrost (hydrate) zone.

To alleviate the deficiencies in the shallow exploration program, the following might be considered:

1. Slim hole drilling through the permafrost and hydrate zone with care to log all gas in the mud from near the surface and care in running near surface well logs. In particular, dual scale sonic and resistivity logs should be run so that values are completely readable near the surface. At deep exploratory well sites, the hole could subsequently be reamed and surface casing set.

2. Special core barrels are available that retain pressure. Cores should be taken through suspected hydrate zones, particularly through coal seams. Anomalous amounts of gas can be measured from the cores or, if possible, X-ray diffraction equipment should be set up in the mud logger's unit to identify included hydrate.

3. Shallow high resolution velocity measurements should be made at available wells. This is done in Canada with a crystal cable set up. Until the base of the permafrost can realistically be described by seismic signature, there is little chance of differentiating hydrate layers.

4. Shallow high resolution sparker programs might be useful to define near surface layering, particularly in near shore areas and on lakes. High resolution sparker work defines the anomalous layers in the deep-sea.

5. Much care is needed to fully evaluate the existing and/or future wells at Barrow. Gas at Barrow is very close to the hydrate stability zone. Drill stem tests should be made up hole from the producing gas sand to see if a flat recovery curve develops (as in the Canadian situation); injection of methanol at about the lower stability zone for hydrate might develop more flow (as in the Russian situation).

6. Schlumberger now has a multiple spot pressure testing sond. This might be useful because formation pressure is low in zones of hydrate formation.

In conclusion, detection and evaluation of hydrates is intimately tied to the detection and evaluation of permafrost. In practice, this is a matter of careful work with the shallow hydrate bearing section using existing exploration tools and methods.

XI. SUMMARY AND CONCLUSIONS

Natural gas hydrates are ice-like crystalline solids formed by the incorporation of light hydrocarbon gas into water structures. The general chemical expression is:

$$CH_4 \text{ (vapor)} + 6\ H_2O \text{ (liquid)} \longrightarrow CH_4 .6\ H_2O \text{ (solid)}$$

They are stable under temperature less than about 55° F and depths of 500 to 3500 feet, depending on the geothermal gradient, the depth of permafrost and the composition of the gas. They are not stable at land surface pressure. A large body of experimental evidence has established the physical-chemistry of hydrates and there is little doubt that they can form under natural conditions in permafrost zones and in the deep-sea. The most reasonable occurrences are probably in association with coal seams or as layers and inclusions within the permafrost. In one documented occurrence in Russia hydrates probably are an upper phase in a producing gas field that intersects the T-P zone of solid stability. In this case, hydrates would disassociate and release gas as the field pressure was depleted and thus add to the reserves of the gas field.

No documented occurrences of hydrates in NPR-A could be found, although there are documented problems with hydrate formation in gas lines at So. Barrow. By virtue of being a solid and unstable at surface pressure, it is difficult to envision practical, economic recovery of hydrate bodies without considerable technological innovation. Drill stem tests in hydrate zones in Canada and laboratory experiments suggest that hydrates are a great inhibitor of permeability and are probably far more of a detriment to production than an asset.

In NPR-A the most reasonable area to explore for hydrates is in the So.

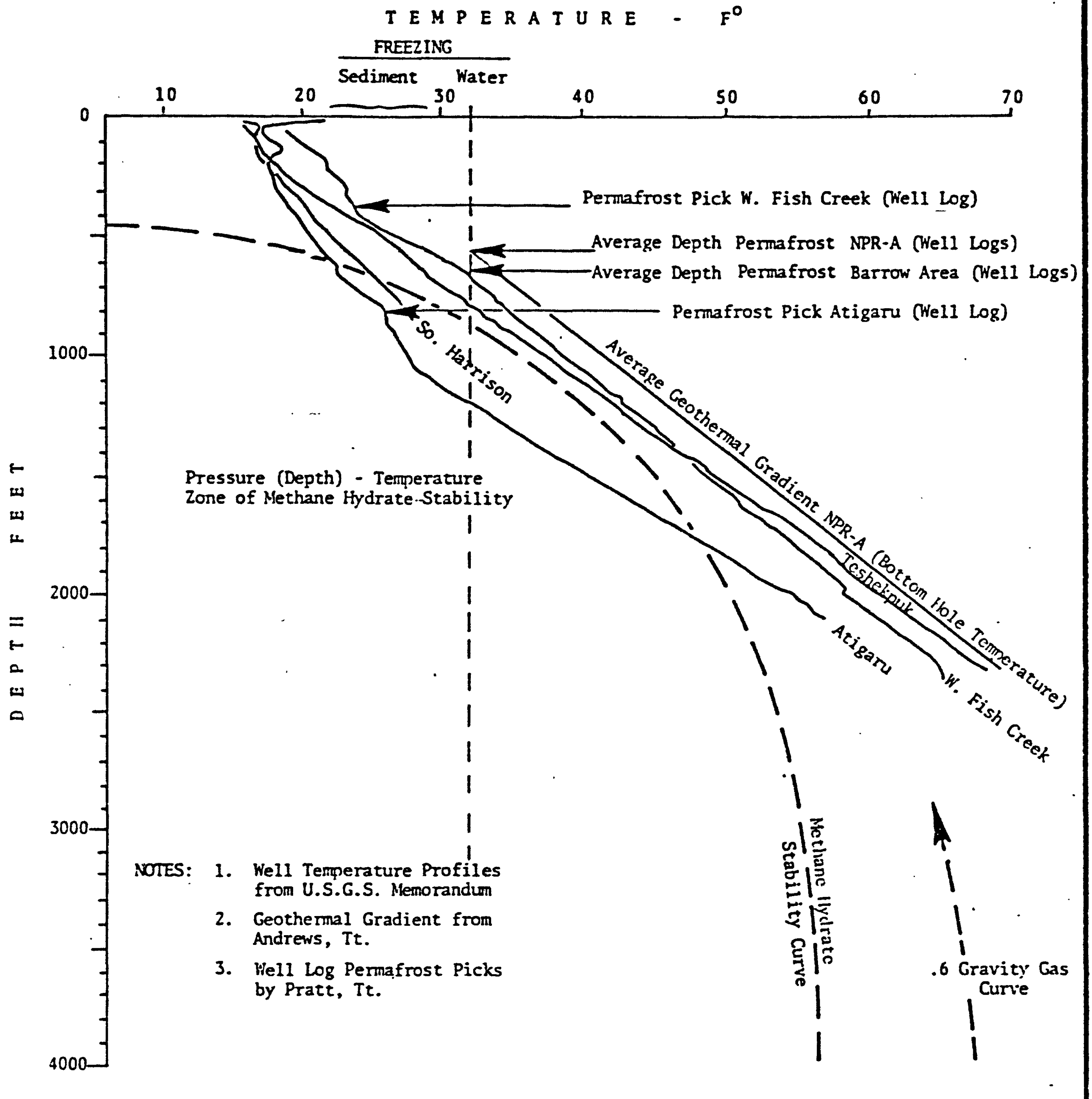
Barrow area where known gas reservoirs are probably very close to the stability limit of hydrate. Definition of hydrate is very similar to the detection and definition of permafrost layers - the two cannot really be separated by existing seismic and well logging techniques.

Geothermal temperature gradient curves have been measured in four wells from actual post drilling probes and generally from averaging bottom hole temperatures (Figure 37). The best estimate of permafrost depths in existing wells (Table 5) when related to the hydrate stability curve and geothermal gradient (Figure 37) gives an indication of the most favorable areas to explore for hydrate on the Reserve.

It is recommended that great care be given to shallow logging programs in existing and proposed wells, particularly with regard to sonic and resistivity measurements near the surface. It may be necessary to initially slim hole drill with cold oil base mud in the upper part of the well to get reliable log data. In addition, shallow, high resolution seismic velocity data may help to define hydrates as well as the permafrost zone.

The three most favorable areas to explore for hydrates on NPR-A are:

1. The South Barrow area because known gas reservoirs are shallow.
2. The Tunalik area because of the tremendous thickness of nonmarine coal near the surface; and
3. The Colville Delta area because of deep probable permafrost and high gas evolution in deltaic sediments.



NOTES:
1. Well Temperature Profiles from U.S.G.S. Memorandum
2. Geothermal Gradient from Andrews, Tt.
3. Well Log Permafrost Picks by Pratt, Tt.

In the above temperature-depth plot, the methane stability curve is from Figure 1 and geothermal gradients from measured values as given. In actuality, the zone of crystalline ice formation is below freezing and indicated by the change of slope on the temperature curves. Note that the vertical flat part of the West Fish and Atigaru curves correspond to the permafrost pick from the well logs (Table 1). In reality, the average Geothermal Gradient Line should start at sediment freezing rather than water freezing point and the methane stability curve should be slightly higher because of some heavier gas mixture. The area between the methane stability curve and the temperature gradient curves is the zone of potential hydrate stability.

RELATION OF METHANE HYDRATE STABILITY CURVE
TO TEMPERATURE AND PERMAFROST DEPTH, NPR-A.

Figure 37

WELL	DEPTH (as defined on Resistivity and Sonic logs)
So. Barrow 4	673
So. Barrow 3	820
So. Barrow 2	630
So. Barrow 12	640
So. Barrow 16	620
So. Barrow 14	760
So. Barrow 17	610
So. Barrow 19	680
So. Barrow 13	590
Iko Bay	420
AVERAGE BARROW AREA	644

WELL	DEPTH (as defined on Resistivity and Sonic logs)
Simpson	890
So. Harrison	340
Atigaru	810
Halkett	810
No. Kalikpik	430
West Fish Creek	390
Fish Creek	575
No. Simpson	510
Ikpikpuk	155
Drew Point	490
W. T. Foran	380
Kaolak	680
Meade	490
E. Oumalik	340
Oumalik	410
Umiat 11	480
*Tunalik	<100
*So. Meade	<500
*So. Simpson	<500
*Kugrua	<500
AVERAGE NPR-A	562

* Logs Incomplete

The gas hydrate zone and permafrost are not distinguishable with existing data. The methane hydrate stability depth at soil freezing temperatures is about 750 to 800 feet (see Figures 1 and 2); therefore, only areas with comparable depths of permafrost can be expected to have significant hydrate. The permafrost data is presented in tabular form because it is variable (as picked by the writer) and could not be reasonably contoured.

TABLE . DEPTH OF PERMAFROST IN SELECTED WELLS, NPR-A, AS DEFINED ON RESISTIVITY AND SONIC LOGS.

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ARTICLE 19 (Sloan, E. D.)

HYDRATE EQUILIBRIUM STUDIES

E. D. Sloan

I. Introduction
   A. History of Natural Gas Hydrates
   B. Crystal Structures

II. Hydrate Dissociation Conditions
   A. P-T Relationships in 3 Phase Region
   B. P-T-C Relationships in 2 Phase Region
   C. Composition and Structure
   D. Effect of Inhibitors on Dissociation
   E. Pressures Generated by Dissociation
   F. The First Law of Thermo and Dissociation

III. Questions to be Resolved by Sampling
   A. Structure
   B. Composition
   C. Phases Present

Introduction Summary of Hydrate Equilibrium Studies

for

Workshop on Clathratic (Gas Hydrates)
in The National Petroleum Reserve in Alaska
July 16-17, 1979, Menlo Park, California

by

E. D. Sloan
CPR Department Colorado School of Mines
Golden, Colorado 80401

The history of natural gas hydrates is marked by five significant events as follows: (1) hydrate discovery by Davy in 1810, (2) hydrate discovery in natural gas pipelines in 1931, (3) the determination of microscopic prediction method in 1941, (4) the determination of crystal structure in the 1950's which lead to a microscopic prediction method in the 1960's, and (5) the recent determination of what appears to be significant deposits of gas hydrates in permafrost regions and in ocean sediments.

All natural gas hydrates crystal structures are either labeled structure I (body centered cubic) or structure II (diamond lattice). When significant amounts of propane are present, the formation of structure II naturally occurs; however this hydrate structure denudes the natural gas of propane, leaving behind methane and ethane which form structure I. The structure of the hydrate is very important because structure II may have field depth as much as 50% greater than that of structure I.

If there is no free water present in the hydrate-gas mixture, the dissociation will be appreciably different than if there are three phases present. The effect of several inhibitors, e.g. salts and methanol, on hydrate dissociation may be predicted, however, all large scale dissociation will require some heat input in addition to changes in pressure and temperature in order to fulfill the first law of thermodynamics requirement. The amount of heat to be added is a function of the structure present. Pressures generated by dissociation are likely to be large; at $0^{\circ}C$ if 1 m^3 of methane hydrate were dissociated in a 1 m^3 container, pressures of 130 atm could be generated.

The core sampling program should be designed so as to obtain as much of the following information as possible: (1) the structures present, (2) the composition of the gas, both free and in hydrate form, and (3) the number and type of phases present.

ARTICLE 20 (Tailleur, I. L., and Bowsher, A. L.)

Office of National Petroleum Reserve in Alaska
345 Middlefield Road
Menlo Park, California 94025

July 18, 1979

Memorandum

To: Arthur L. Bowsher

From: Irvin L. Tailleur

Subject: Abstract for Tunalik clathrate

Requested abstract is attached for your edit and inclusion in preprints. A couple more sentences and a vu-graf Xerox of the logs should prepare the subject for dissection by the group.

I notice that I. Kaplan edited one volume on clathrates, but I haven't seen his name on participant lists. Is he not going to make it?

That might have been the opportunity to discuss the special sulfur studies he thought might be relevantly initiated by ONPRA.

/signed/
Irvin L. Tailleur

Attachment

Abstract for Clathrate Meeting Hydrates in Tunalik No. 1, ONPRA

by

I. L. Tailleur and A. L. Bowsher

We have inferred that the gas logs from the upper kilometer of Tunalik Test Well in the northwestern Reserve reflect coal gas locked in clathrates to at least 350 m depths. Whereas cutting gas detection correlates strongly with other log indicators of coal, coal did not yield methane to the drilling fluid above about 500 m, a reasonable limit to methane-hydrate stability. We offer this inference for dissection and, given validity, as a potential for specialized clathrate studies and for unmeasured energy resources.

ARTICLE 21 (Tailleur, I. L., and Bowsher, A. L.)

Potential fuel resource of coal-gas clathrate in northwestern Alaska

by

I. L. Tailleur and A. L. Bowsher

The unmeasured potential of widespread coal deposits in northwestern Alaska has been noted for some time (Tailleur and Brosge', 1975; Martin and Callahan, 1978) and the resource potential of natural gas in the solid form of clathrate is being considered in the current exploration of the National Petroleum Reserve. The drilling of Tunalik well, to assess the hydrocarbon prospectiveness of the deep section of rocks in the northwest limit of the Reserve, indicates that the generation of methane from coal and the several-fold volumetric concentration of organic gases on solidifying with water, at near-freezing temperatures and near-surface rock pressures, create another resource of unknown potential.

The pertinent parts of logs from the Tunalik well generalized in figure 1 show methane being released to the drilling fluid in relatively large amounts on penetration of coal layers below the base of permafrost (0°C) in contrast to the release in nondetectable amounts from coal layers in the probably frozen zone above. That the difference reflects the presence of clathrate and not some other factor is inferred with considerable assurance from the absence of significant difference between amounts of gas evolved on pulverization of the drill cuttings from correlative intervals.

The known behavior of gas locked up in solid hydrate readily accounts for the measured responses from the disturbance by drilling. Methane evolves from the pores of the actually small amount of rock cut into the elevated conditions of the drilling fluid while remaining locked up in ice in unexposed pore space in the walls of the borehole until energy for transformation conducts to it. Reduced or absent porosity and permeability on account of the clathrate cement inhibits the flow of any free methane that might have generated in excess of the capacity for hydration. In contrast, methane produced into spore space related to coals at subhydration depths escapes to the borehole on penetration of permeable rock. Cuttings with clathrate, though carried quickly to the surface and analysis by 90°F drilling mud, need show gas-retentivity little different than cuttings from depths where the thermal gradient precludes clathrate.

We cannot, of course, speculate on the volumes or viabilities of this probable store of fossil energy. Neither can we recommend assured methods for the requisite determinations. We do think, though, that this is an additional potential resource and, given energy demands that have already made small amounts of coal gas competitive, worth note and consideration.

The log display also bears importantly on attempts to assess the potential coal resources in northern Alaska. The indications of coal on the lithology and resistivity logs resembles the evidence of coal in the Kaolak and Meade test wells. The apparent amounts of coal in those old wells made up about 60 percent of the base for calculating a 100-billion-ton reserve (Barnes, 1967) and projected to the extraordinary figure of nearly 3 trillion tons of hypothetical resource (Tailleur and Brosge', 1975).

Several-fold greater thicknesses of coal measured by cuttings than by the gamma-ray, sonic or density logs of Tunalik well verifies the suspicion that the 10 percent coal in the Kaolak and Meade cuttings exaggerated the amount of coal actually present in the subsurface. The proportion of coal beds in Tunalik aggregates about 4 percent (Gary Stricker, personal commun., 1978), the same order of coal concentrations as in the geologically analogous Mesa Verde Group of the western conterminous states.

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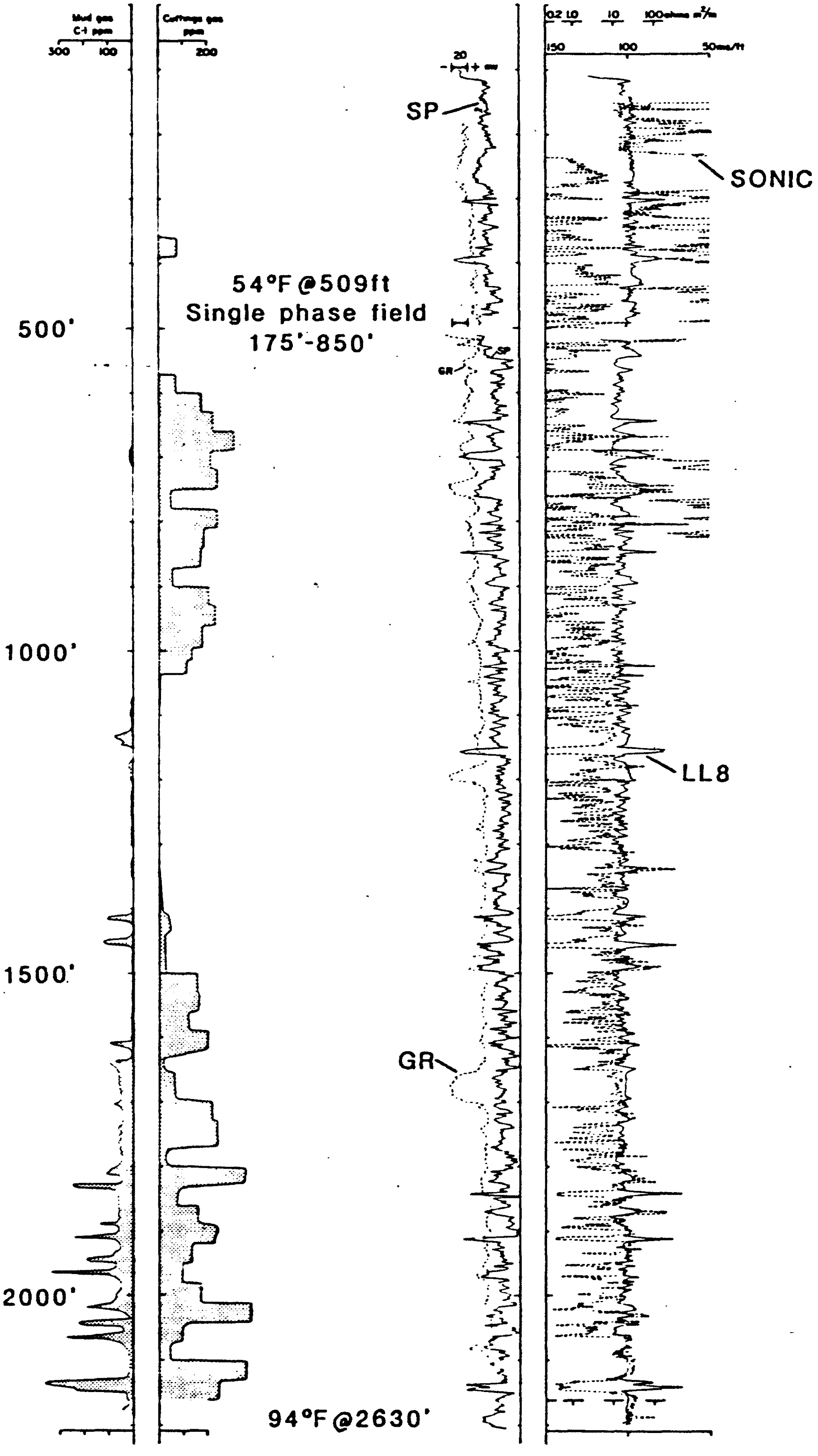
Tailleur, I. L., and Brosge', W. P., 1976, Coal resources of northern Alaska may be the nation's largest, in Rao, P. D., and Wolff, E. N., eds., Focus on Alaska's Coal '75 (Conference, Fairbanks, Oct. 1975): Alaska Univ. Mineral Industry Research Lab. Report 37, p. 219-229.



HUSKY OIL NPR OPER. INC.
TUNALIK NO. 1
T. 10N., R. 36W., SEC. 20 SE 1/4, U.M.
KB ELEV. 110 FT

Figure 38

STUDIES OF CLATHRATES BY ONPRA SINCE THE WORKSHOP OF JULY 16-17, 1979

The editor initially planned to include a comprehensive bibliography of Clathrates (gas hydrates) as a part of the proceedings. A preliminary bibliography was prepared, recorded on a word processor disk, and several copies were printed for editing. After many months, the editing was incomplete and there was no hope of completing the editing for use of the bibliography in these proceedings. The editor was unable to get assistance in editing the numerous references to Articles by Russian authors. The press of operations in ONPRA forced the editor to assign a low priority to the editing.

Decision was made recently to send the bibliography to Gas Research Institute because Dr. John Cox and Dr. E. Hoffman were preparing abstracts of papers on clathrates for publication by Gas Research Institute, and because the open filing of the proceedings was being delayed in deference to editing of the bibliography. It is hoped GRI will publish a list of these references. Although the editing of the bibliography was not completed, preliminary copies of the unedited version have been furnished to interested workers who requested it.

The editor attended a meeting in Houston, Texas, on June 26, 1980, that was coordinated by Enertech Engineering and Research Co. under Gas Research Institute Contract No. 5014-321-0245. The purpose of the meeting, attended by Canadian and American representatives of industry and government, was to consider (a) recommendations for hydrate field testing (Task I-1.5.2A), and (b) review activities on hydrates by industry/government (Task I-3.1), (Goodman, M., 1980, Insitu gas hydrates; Evaluation of Past experience, Quarterly Report, October 15: Chicago, Illinois, Gas Research Institute).

The investigation of insitu gas hydrates in selected NPRA wells by Enertech Engineering and Research Co. under contract 14-08-0001-19148 continues. Strongest emphasis of this study is given to wells drilled within NPRA during the winter of 1980-1981.

Proceedings of the gas hydrates workshop, Denver, Colorado, February 1, 1979, sponsored by Gas Research Institute, 10 West 35th Street, Chicago, Illinois, have been distributed.

A very interesting article "Gas from natural gas hydrates" was published in the July-August 1979, Vol. 7, no. 10 issue of Gas Energy Review (American Gas Association, 1515 Wilson Boulevard, Arlington, Virginia).

Los Alamos Scientific Laboratory (P.O. Box 1663, Los Alamos, New Mexico, 87545) issued "Methane hydrate as an energy Resource? A Review with recommended Future Research (Informal Report, LA-8368-MS, June 1980) and Alternative Gas workshop (Conference, LA-8155-C, March 1980).

Kvenvolden, K. A., and McMenamin, M. A., 1980, made available, "Hydrates of Matural gas: A review of their geologic occurrence," in U.S. Geological Survey Circular 825.

Gas Research Institute issued, "Update on Natural gas hydrates" by E. J. Hoffman on March 1980.

Los Alamos Scientific Laboratory issued also, "Nethane hydrate resource assessment program (Progress Report, LA-8568-PR, April-June 1980)."

Quarterly reports under Gas Research Institute Contract 5014-321-0245 discuss on "Insitu gas hydrates", July 15, 1980, and "Evaluation of Past experience", October 15, 1980.

Investigations of *in situ* gas hydrates ~~in~~ wells of the North Slope on Alaska and the National Petroleum Reserve Alaska by the Gas Research Institute and the Office of National Petroleum Reserve Alaska are continuing. Reports of these studies will be made public as soon as they are available.

Report of the Potential Gas Agency "Potential Supply of Natural Gas in the United States (as of December 31, 1980) Potential Gas Resources from Nonconventional Sources, Gas Hydrates, p. 76-89, Potential Gas Agency, Colorado School of Mines, Golden, Colorado (1981), 119 p.

Office of National Petroleum Reserve in Alaska
345 Middlefield Road
Menlo Park, California 94025

April 19, 1979

Memorandum

To:

From: Arthur L. Bowsher, Chief, Exploration Strategy, ONPRA, U.S. Geological Survey, Menlo Park, California

Subject: Workshop on clathrates (gas hydrates) in the National Petroleum Reserve in Alaska, July 16-17, 1979

ONPRA will conduct a workshop on clathrates (gas hydrates) in U.S. Geological Survey Bldg. 3 (Topography), Facility A, on July 16-17, 1979. The purpose of the workshop is to develop a plan for the study of clathrates in NPRA as part of the FY '80 and FY '81 exploration program. We will, accordingly, review knowledge of physical and chemical properties of clathrates and of their distribution in nature as a basis for designing such a plan. It appears probable that ONPRA will be authorized to continue the exploration drilling in FY '80. No plan to study clathrates has been budgeted for FY '80. However, after a study plan is prepared, effort will be made to accomplish as much of such a plan as feasible in FY '80. It is important to develop an overall plan of study as soon as possible. The study is needed to determine the significance of clathrates in NPRA to engineering, to resource assessment, and as a possible source of energy.

We respectfully request you to make the presentation listed on the attached schedule of the meeting. Your expertise will help to characterize clathrates as a basis for our planning the study. Please notify me of your willingness to participate. You are requested to furnish this office summary statements that may be distributed as background reference material to other participants prior to the meeting. Any reports or summaries furnished us at the time of the meeting will be distributed by us. It is planned also to produce a report as a record of the meeting.

The Gas Research Institute, Chicago, Illinois, has been informed of the workshop and invited to attend. Some participants of the GRI Gas Hydrate Workshop in Denver, February 1, 1979, are invited to participate in the ONPRA workshop.

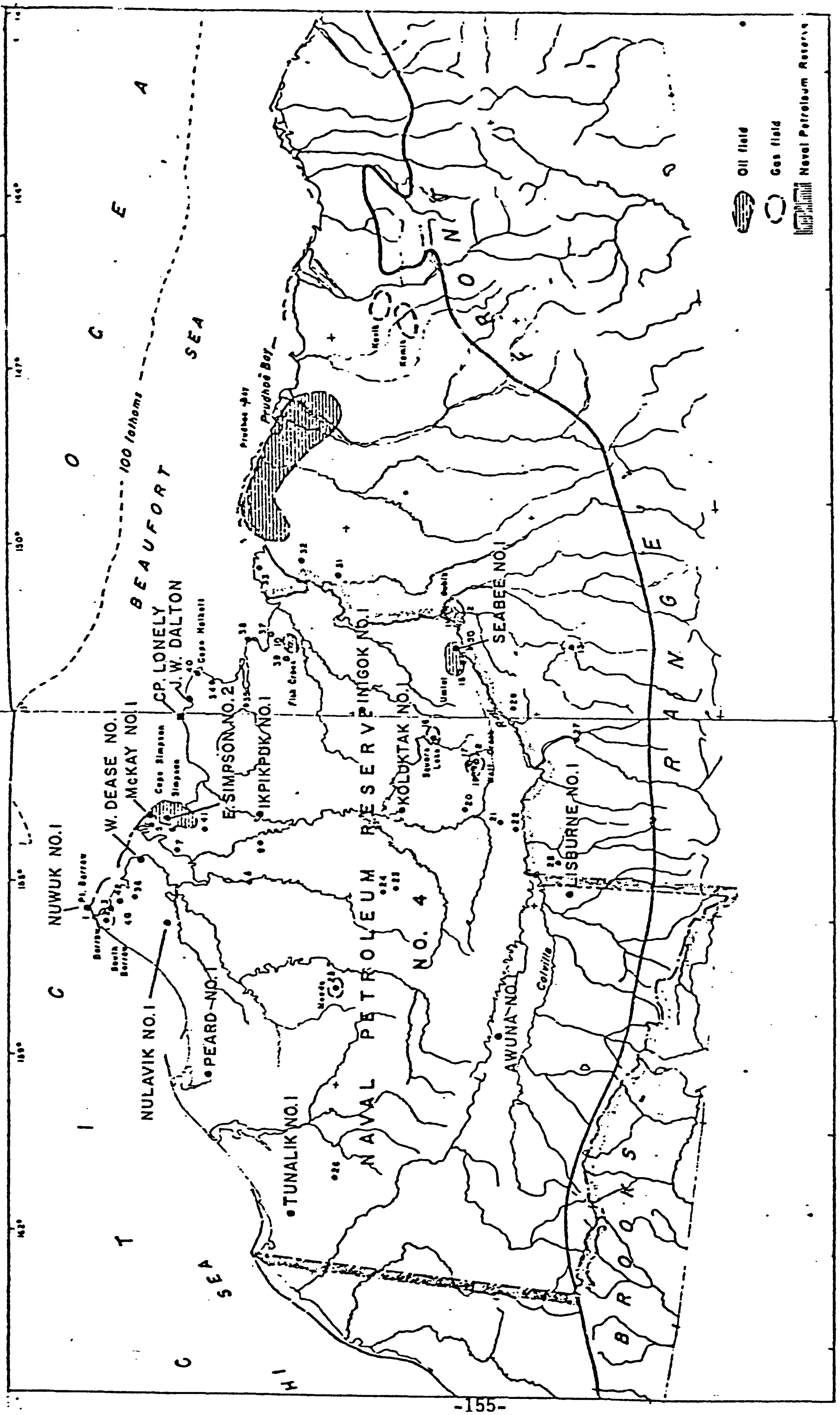
A map of NPRA showing the location of operational camps and possible drilling sites for FY '79-80 is attached.

Suggestions for improvement of the agenda of the meeting are welcomed.

/signed/
Arthur L. Bowsher
Chief, Exploration Strategy
ONPRA

Attachments

cc:
Brewer, ONPRA, Anchorage
Carothers, Water Resources, Menlo Park
Cox, John, Gas Research Inst., Chicago, Ill.
Callahan, J., Conservation, Anchorage
Dalby, Husky Oil, Houston, Texas
Davidson, D. W., Nat'l. Sci. & Eng. Research Council, Ontario, Canada (Ottawa)
Franklin, Lindsay, Pan-Arctic Oils, Calgary, Alberta, Canada
Gryc, G., ONPRA, Menlo Park
Hall, George, ONPRA, Anchorage
Hewitt, S., Husky Oil, Anchorage
Hilderbrand, M. A., Exxon Production & Res. Co., Houston, Texas
Kharaka, Y., Water Resources, Menlo Park
Kienzle, Jack, ONPRA, Menlo Park
Kobayashi, R., Rice Univ., Houston, Texas
Lachenbruch, OES, Menlo Park
Lantz, USGS, Seattle, Wash.
McCarthy, J., Husky Oil, Houston, Texas
McIver, R. D., Geochem
Milton, USGS, Reston, VA
Pessell, Alaska Dept. of Natural Resources, Anchorage, Alaska
C. Sloan, ONPRA, Anchorage
D. Sloan, Colo. School of Mines, Golden, Colo.
Tailleur, ONPRA, Menlo Park
A. Grantz, Br. of Alaskan Geology, Menlo Park
R. Carter, ONPRA, Menlo Park
M. Goodman, Enertech Engr. and Research Co., Houston, Texas



POSSIBLE DRILLING AND OPERATION SITES
ONPRA FY'79-80

Figure 39

Office of National Petroleum Reserve in Alaska
345 Middlefield Road
Menlo Park, California 94025

WORKSHOP ON CLATHRATES IN NPRA

July 16-17, 1979

Welcome! We extend our thanks to you for attending. This workshop is convened to solve problems. An assessment of the hydrocarbon resources of NPRA is being conducted by the U.S. Geological Survey. The exploration program in the Reserve that is the responsibility of ONPRA is to assist in the assessment. At present no facet of the program gives serious concern to clathrates.

The subject of clathrates is like the scattered pieces of a formidable jig-saw puzzle. Therefore, we are concerned about an important question.

> "Are clathrates of significance in an assessment of hydrocarbon resources???"

If the answer is "yes", we go on to:

> "What clathrates are present in NPRA, how do we recognize them, and how do we estimate the volume of reserves?"

It is for this purpose that we are meeting. You can help us review clathrates and decide what needs to be done in this area of study, if anything, by ONPRA.

Many of you were asked to present a part of the program. The time allotted to you is a maximum, if we are to accomplish our task. It is desirable that you leave time for discussion. However, discussion is scheduled for 4:15 p.m. today, and 2:00 p.m. tomorrow, except if speakers should have time within their allotted period. A question sheet is furnished. Please write questions on it to be deferred to a discussion period. Perhaps someone will consider the question in their presentation. Our time may, therefore, be used more effectively.

The panel discussions starting at 2:00 p.m. tomorrow will be recorded on tape for as accurate a record as possible of all conclusions and questions that develop.

Please fill out the attendance sheet.

Thank you for attending.

Workshop on Clathrates in ONPRA
Menlo Park, California
July 16-17, 1979

July 16, 1979 (Monday)

9:00-9:15 am	Welcome - George Gryc
9:15-9:30 am	Introduction - Art Bowsher
9:30-10:15 am	Temperature distribution and permafrost - Art Lachenbruch and Max Brewer
10:15-10:30 am	Break
10:30-11:00 am	Hydrates in Barrow gas fields - Robert Lantz
11:00-11:30 am	Drilling and permafrost - Sam Hewitt and J. McCarthy [1]
11:30 am-1:00 pm	Lunch
1:30-2:15 pm	Formation water and salinity - C. Sloan and Yousif Kharaka
2:15-3:15 pm	Hydrate phases and gas/water equilibrium with gas hydrates - R. Kobayashi and D. Sloan
3:15-3:30 pm	Break
3:30-4:15 pm	Hydrates in nature - D. Milton
4:15-4:45 pm	Discussion - Art Bowsher

July 17, 1979 (Tuesday)

8:30-8:45 am	Hydrates in Tunalik No. 1, ONPRA - Irv Tailleur
8:45-9:15 am	Coal and hydrates - James Callahan [1]
9:15-9:45 am	Seismic technology and permafrost - Jack Kienzle
9:45-10:30 am	Hydrates in the Arctic Islands - L. Franklin
10:30-10:45 am	Break
10:45-11:15 am	Hydrates-drilling and completing wells in N.A. Arctic - M. Goodman
11:15-11:45 am	Electric logging for hydrates - George Hall
11:45 am - 1:30 pm	Lunch
1:30-2:00 pm	Pressure coring - R. McIver
2:00-3:15 pm	Panel discussion - R&D to recognize clathrates in drilling programs - A. Bowsher and M. Brewer
3:15-3:30 pm	Break
3:30-5:00 pm	Design of a field program to study clathrates in NPRA - A. Bowsher and M. Brewer

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[1] Not presented; unable to attend meeting.

Attendees
Workshop in Clathrates in NPRA
Menlo Park, California
July 16-17, 1979

Bowsher, Arthur L., Chief, Exploration Strategy, ONPRA, USGS, 345 Middlefield Rd., Menlo Park, CA 94025, phone 415-323-8111, ext. 2917.

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Milton, Daniel, USGS, 12201 Sunrise Valley Drive, Reston, VA 22092, phone 703-860-6503.

Pessell, Garnett H., Div. Geological and Geophysical Surveys, Alaska Dept. of Natural Resources, 3001 Porcupine Drive, Anchorage, AK 99504, phone 907-277-6615.

Sloan, Charles E., Water Resources Div., 218 E Street, Anchorage, AK 99501, phone 907-277-5526.

Sloan, D., CPR Dept., Colorado School of Mines, Golden, CO 80401, phone 303-279-0300, ext. 2723.

Tailleur, I. L., ONPRA, USGS, 345 Middlefield Rd., Menlo Park, CA 94025, phone 415-323-8111, ext. 2139.

Office of National Petroleum Reserve in Alaska
345 Middlefield Road
Menlo Park, California 94025

August 14, 1979

Memorandum

To: Distribution

From: Arthur L. Bowsher, Chief, Exploration Strategy

Subject: Open-File of Proceedings of "Workshop on Clathrates in NPRA"

The abstracts or short papers that you furnished for "The Workshop on Clathrates in NPRA" in Menlo Park on July 16-17 are to be assembled with a review of the meeting and a bibliography of clathrates. These will be submitted as a unit for Open-File by the U.S. Geological Survey. Attached is a list of papers to be included. Please notify me if this copy is satisfactory or furnish me a revised edition on or before October 31, 1979. Please furnish any illustrations you wish to accompany your article.

I have been delayed in summarizing the workshop and will be a time yet in assembling the unit. However, it will be done.

Please accept my heartfelt thanks for your contribution to the workshop. It was most educational to me and I hope to each of you. It has helped ONPRA to better evaluate the course of study of clathrates necessary in our program.

/signed/
Arthur L. Bowsher
Chief, Exploration Strategy, ONPRA

Attachments

cc:
Lawver
Moore
Franklin
Goodman
Milton
Hall
Tailleur
Kharaka
Sloan
Callahan
Davidson
Folk
Hoffman
Judge
Lachenbruch
Payne
Kobayashi

Well ____

Location ____

1. Gas flow through the annulus into the cellar (did) (did not) occur during drilling.

2. Volume of mud gas (did) (did not) respond significantly to circulation or lack of circulation of drilling mud. (Gas hydrates in formations decompose because of heat introduced by drilling mud circulation. Hydrates may occur in pockets or in isolated layers as opposed to the traditional concept of a gas reservoir).

3. Gas (did) (did not) cut mud at time of running and/or cementing surface casing.

4. Assuming gas-cut mud at the surface casing point, increase in mud weight (did) (did not) control gas in mud. (Gas hydrates respond to mud temperature, but increase in mud weight achieves very little control).

5. Cementing of surface casing (was) (was not) adversely affected by gas influx.

6. Average "mud-in" temperature was (greater) (less) than 45o F while drilling between depths 600 to 4,000 feet.

7. Unusual drilling problems (were) (were not) encountered from 0 to 6,000 feet.

8. Sloughing and washouts (did) (did not) occur 0 to 6,000 feet. If so, in what intervals?

9. Unusual behavior of drill cuttings (did) (did not) occur on the shaker screen.

10. Significant water influx (did) (did not) occur during drilling.

Please cross out non-applicable terms. If answer is unknown, circle number at lead of statement.

Remarks (other abnormal gas behavior 600-4,000 feet):

Date ____________________ Signature ________________________

Please return to: Arthur L. Bowsher
ONPRA, U.S. Geological Survey, MS 87
345 Middlefield Road
Menlo Park, California 94025

Instructions for Well Temperature Data Sheet

The U.S. Geological Survey is conducting experiments in simulating well tempertures prior to drilling. If the predicted temperatures match the actual temperatures then this could be of great use in future planning of wells. The attached data sheets, that you fill out, will provide us with the actual mud temperatures (and other relevant data) which will enable us to test the validity of the computer simulated temperatures. Unlike other data sheets, this one is dependent primarily on changes in circulating conditions and the time at which they occur, and depth is secondary. Specific instructions for recording on the data sheet are as follows:

1. Data should be recorded at the time when a change occurs in any of the following parameters; mud weight (± 0.3 lbs/gal.), inlet mud temperature (± 3°F), flow rate (pump pressure ± 500 psi), and most significantly when drilling and/or circulating stops and begins (this is not to include average connection time, rather, for example: trips, wiper trips, surveys or rig repairs over 2 hours, E-logging, cementing/casing, testing, etc.). These rig/drilling changes should be time dependent and the depth should be secondary; but record the depth at the time of (other) changes at the nearest 10 foot interval. Or if none of the above mentioned parameters change in a 100 foot interval at which time data should be recorded. (As mentioned above the study is time dependent and depth is secondary; however, record depth at all recording points and record parameters at the next 100 foot interval if no significant change has occurred).

2. Specific operations should be identified in the remarks column; e.g. drilling, coring,, shut-in, surveying, logging, cementing, etc.

3. The mud logger is the sole source for mud temperatures, so be sure to keep the sensors and recording instruments calibrated on a regular schedule.

4. Circulation rate may be obtained from the "Geolograph" or "Totco" recorder in the dog house after a tower change if you do not have a pump pressure gauge in the unit.

5. Attached is an example sheet of a theoretical well.

Thank you

/signed/
David C. Blanchard