Methane Hydrate Production from Alaskan Permafrost

Hydrate Reservoir Characterization and Modeling

Topical Report

October 1, 2001 to January 31, 2005

by

Donn McGuire (Anadarko Petroleum Corp.)

Steve Runyon (Anadarko Petroleum Corp.)

Richard Sigal (Anadarko Petroleum Corp.)

Bill Liddell (Anadarko Petroleum Corp.)

Thomas Williams (Maurer Technology Inc.)

George Moridis (Lawrence Berkeley National Laboratory)

February 2005

DE-FC26-01NT41331 (Tasks 17, 18, 19)

Anadarko Petroleum Corp. 1201 Lake Robbins Drive The Woodlands, TX 77380

Maurer Technology Inc. 13135 South Dairy Ashford, Suite 800 Sugar Land, TX 77478

Lawrence Berkeley National Laboratory 1 Cyclotron Road Berkeley, CA 94720

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Abstract

Natural-gas hydrates have been encountered beneath the permafrost and considered a nuisance by the oil and gas industry for years. Engineers working in Russia, Canada and the USA have documented numerous drilling problems, including kicks and uncontrolled gas releases, in arctic regions. Information has been generated in laboratory studies pertaining to the extent, volume, chemistry and phase behavior of gas hydrates. Scientists studying hydrate potential agree that the potential is great – on the North Slope of Alaska alone, it has been estimated at 590 TCF. However, little information has been obtained on physical samples taken from actual rock containing hydrates.

This gas-hydrate project is in the final stages of a cost-shared partnership between Maurer Technology, Noble Corporation, Anadarko Petroleum, and the U.S. Department of Energy's Methane Hydrate R&D program. The purpose of the project is to build on previous and ongoing R&D in the area of onshore hydrate deposition to identify, quantify and predict production potential for hydrates located on the North Slope of Alaska.

Hot Ice No. 1 was planned to test the Ugnu and West Sak sequences for gas hydrates and a concomitant free gas accumulation on Anadarko's 100% working interest acreage in section 30 of Township 9N, Range 8E of the Harrison Bay quadrangle of the North Slope of Alaska. The Ugnu and West Sak intervals are favorably positioned in the hydrate-stability zone over an area extending from Anadarko's acreage westward to the vicinity of the aforementioned gas-hydrate occurrences. This suggests that a large, north-to-south trending gas-hydrate accumulation may exist in that area. The presence of gas shows in the Ugnu and West Sak reservoirs in wells situated eastward and down dip of the Hot Ice location indicate that a free-gas accumulation may be trapped by gas hydrates.

The Hot Ice No. 1 well was designed to core from the surface to the base of the West Sak interval using the revolutionary and new Arctic Drilling Platform in search of gas hydrate and free gas accumulations at depths of approximately 1200 to 2500 ft MD. A secondary objective was the gas-charged sands of the uppermost Campanian interval at approximately 3000 ft.

Summary results of geophysical analysis of the well are presented in this report.

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1. Introduction

A special project conducted by Maurer Technology, Noble Corporation, Anadarko Petroleum, and the U.S. Department of Energy was undertaken to plan, design and implement a program that will safely and economically drill/core and produce natural gas from arctic hydrates. The project team documented planning, operations and lessons learned to assist in future hydrate research and field operations to make an objective technical and economic assessment of this promising natural gas reservoir potential.

Hot Ice No. 1 was planned to test the Ugnu and West Sak sequences for gas hydrates and a concomitant free-gas accumulation on Anadarko's 100% working interest acreage in section 30 of Township 9N, Range 8E of the Harrison Bay quadrangle of the North Slope of Alaska. To the west and updip of the Hot Ice location, occurrences of gas hydrates have been noted in wells of the Tarn and Meltwater fields and was at least partially responsible for the blowout in the Arco-Cirque #1 well in February 1992. The Ugnu and West Sak intervals are favorably positioned in the hydrate-stability zone over an area extending from Anadarko's acreage westward to the vicinity of the aforementioned gas hydrate occurrences. This suggested that a large, north-to-south trending gas-hydrate accumulation may exist in that area. The presence of gas shows in the Ugnu and West Sak reservoirs in wells situated eastward and down dip of the Hot Ice location indicate that a free-gas accumulation may be trapped by gas hydrates.

Hot Ice No. 1 was designed to be cored from surface to the base of the West Sak interval using the revolutionary Arctic Drilling Platform (Kadaster and Millheim, 2004) in search of gas-hydrate and free-gas accumulations at depths of approximately 1200 to 2500 ft MD. A secondary objective was the gas-charged sands of the uppermost Campanian interval at approximately 3000 ft. Total depth of the well was originally planned as 3500 ft MD.

In this area, sedimentary rock section situated from just below the recent alluvium to the planned total depth of 3500 ft in the Cretaceous Campanian is entirely within the Brookian Megasequence. These Brookian strata, which comprise a portion of the Late Cretaceous and Early Tertiary marine and deltaic complex that was derived from the southern sourced, Brookian Range origin, prograded north and northeastward across the greater Kuparuk-Prudhoe Bay area. The Ugnu and West Sak sequences represent the lowermost sandstone units of the fluvial-deltaic, coal bearing sandstone, conglomerate and shelf-shale deposits of the Sagavanirktok Formation.

The West Sak interval is Late Cretaceous in age and is composed of very fine to fine grained sandstones and silty sandstones interbedded with siltstones and mudstones. They represent a transition from inner shelf deposition for the lower member to shallow marine or delta front deposition for the upper member.

The Ugnu sequence straddles the Cretaceous/Tertiary boundary. Its lower portion consists of fine to medium grained, well sorted sands interbedded with siltstones and mudstones progressively coarsening upwards to medium-coarse grained delta front sands and fluvial gravels and conglomerates interbedded with siltstones and mudstones in the upper portion. Both the Ugnu and West Sak deposits are interbedded with coal seams and coalified wood fragments. The sands, gravels and conglomerates are unconsolidated to moderately indurated at depth, and porosity is a function of compaction with depth since no significant cements or diagenesis are evident. Porosity versus depth relationships, derived from cores and sidewall

data of wells in the Kuparuk field area, indicate that typical porosities for sands of the Ugnu and West Sak intervals at the Hot Ice location should be in the range of 30-40% for measured depths of 1200-2500 ft. Permeabilities of hundreds of millidarcys to darcys in range should be expected.

Gas available for entrapment in the prospective gas hydrate and free gas accumulations is sourced from hydrocarbons spilled from the underlying Prudhoe Bay Field reservoirs that have migrated up faults and charged the overlying shallow, clastic reservoirs. In addition, biogenic gas, generated from microbial breakdown of spilled oil emplaced in the fresh-water-bearing shallow horizons, is also thought to make a significant contribution to the gas volume. Primary exploration risk factors include vertical seal capacity and continuity of the mudstone seals, updip presence and continuity of gas hydrates for trapping free-gas accumulations and reservoir continuity.

Several alternative locations on Anadarko's 100% working interest acreage were considered. The location in section 30 of T9N, R8E was preferred for several reasons. First, it is the highest structural position on Anadarko's acreage and therefore affords the best chance for encountering dry gas, which is better suited to the formation of gas hydrates with high gas concentration. Second, most of the Ugnu and West Sak reservoir facies are positioned in the Hydrate Stability Zone, providing maximum exposure to the formation of gas hydrates. Last, it provides the closest proximity to a known occurrence of gas hydrate in the Arco-Cirque #1 well.

2. Experimental

2.1 Task Statements

This Topical Report presents results for Task 17, 18 and 19 from the hydrate project. Results for other tasks are described in companion Topical Reports and the Final Report. The complete Statement of Work for these tasks is presented below.

2.1.1 Task 17.0 – Reservoir Characterization of the Core

The project team will characterize the hydrate reservoir, based on analyses of fluids, geology, engineering, logs, geophysics, and rock physics. All these data will be included in a well simulator. The team shall determine the percentage of gas contained in the hydrate zone that can be recovered from the reservoir, and the potential production rates. Core studies will be conducted to accurately predict reservoir producibility potential.

2.1.2 Task 18.0 – Reservoir Modeling

The project team will use information developed in reservoir characterization efforts to quantify Lawrence Berkeley National Laboratory's hydrate simulator. LBNL's advanced simulator system is based on EOSHYDR2, a new module for the TOUGH2 general-purpose simulator for multi-component, multiphase fluid and heat flow and transport in the subsurface environment. Reservoir simulation during this phase of the project will focus on considering production schemes, both short and long term, for hydrate production on the North Slope based on all the reservoir characterization data obtained. Depressurization, injection and thermal methods are some of the production processes to be considered with the simulation.

2.1.3 Task 19.0 – Quantify the Model

This task will be conducted in parallel with Tasks 17 and 18. The reservoir model used will need to be continuously refined as well test data are acquired. This effort is an ongoing task required for making projections. Models will be enhanced iteratively to incorporate dynamic production data during the well test period.

3. Results and Discussion

3.1 Summary Results for Tasks 17, 18 and 19

3.1.1 Task 17.0 – Reservoir Characterization of the Core

The project team characterized the reservoir, based on analyses of fluids, geology, engineering, logs, geophysics, and rock physics. All these data were included in a report and provided to Lawrence Berkeley National Laboratory for incorporation into the well simulator. LBNL's simulation is summarized in **Appendix B**.

3.1.2 Task 18.0 – Reservoir Modeling

The team used information developed in reservoir characterization efforts to quantify Lawrence Berkeley National Laboratory's hydrate simulator. LBNL's advanced simulator system is based on EOSHYDR2, a new module for the TOUGH2 general-purpose simulator for multi-component, multiphase fluid and heat flow and transport in the subsurface environment. Reservoir simulation during this phase of the project will focus on considering production schemes, both short and long term, for hydrate production on the North Slope based on all the reservoir characterization data obtained. Depressurization, injection and thermal methods are some of the production processes to be considered with the simulation. LBNL's simulation is summarized in **Appendix B**.

3.1.3 Task 19.0 – Quantify the Model

This task was conducted in parallel with Tasks 17 and 18. The reservoir model used will need to be continuously refined as well test data are acquired. This effort is required for making projections. Because there was no direct evidence of hydrate occurrence at the site, hydrate-related data provided by Anadarko were based on reasonable extrapolations from known permafrost hydrate accumulations in the North Slope of Alaska and in Northern Canada.

3.2 Geological Investigation

Geological investigation of the methane hydrate potential of the "top set" area of the North Slope of Alaska, particularly as it related to Anadarko's acreage position, began in June 2002. A tentative deadline for a presentation to the Department of Energy (DOE) had already been established for late August/early September of that year. A partial literature search had yielded information on hydrate formation, USGS reports, the Russian combination hydrate/free-gas field and model, and various papers related to engineering topics on hydrates. Subsequent searches for geologic-oriented material yielded information on oil and gas development, regional geology of the North Slope area, stratigraphy, lithology, field studies, etc. Substantial time and effort were given to review all pertinent geologic data that had been generated by Anadarko's Alaska Exploration project such as montages, cross sections, maps, etc. as they related to oil and gas field studies, regional geologic studies of hydrocarbon source history and potential, sequence stratigraphy, tectonic events and subsurface structure determined from well control and seismic interpretation.

Several USGS reports documenting the presence of hydrates over the Prudhoe Bay field contained an extensive data base that was used by the project geophysicist to map the top, base and thickness of the Hydrate Stability Zone (HSZ) and the permafrost cover over the area of interest. These maps established the depth range over which hydrates could be expected to be encountered in the area. To determine the prospective geologic succession for hydrates and to understand stratigraphy, depositional environments, lithology, reservoir guality and source potential of those sediments, over 20 horizons were correlated over the area using reducedscale logs of more than 100 wells. Unit zonation was based on previous work initiated by the USGS. All oil and gas shows, producing zones, test results and hydrate indications gleaned from mud logs, scout tickets and published data were plotted on the logs. This time-intensive undertaking revealed that the prospective stratigraphic interval within the vertical limits of the HSZ was late Cretaceous to Tertiary, fluvial-deltaic sediments of the Sagavanirktok Formation. Hydrates previously identified by the USGS at Prudhoe Bay occur in the sand beds of this major sequence. A prerequisite for the development of methane hydrate is the presence of highquality reservoir formations, which is met by the slightly compacted, highly porous and permeable sands of the Sagavanirktok.

Once the stratigraphic framework was established, a structure map was generated utilizing well control on the Top of the West Sak sequence (a unit of the Sagavanirktok Formation). This map depicts an east dipping, north to south striking monocline with a dip rate of approximately 100 ft/mile. The structural configuration of these beds explains why the permafrost and HSZ become thinner in a westerly direction and become nonprospective west of the Meltwater and Tarn Fields. Successive units of the Sagavanirktok Formation are exposed at the surface and eroded. Reservoir quality of the rock units underlying these beds is insufficient to accommodate the presence of a thick permafrost layer or the formation of hydrates.

At this stage of the investigation, enough background work had been generated to understand the hydrate model developed by the USGS in the Prudhoe Bay area and its relationship to Anadarko's acreage position. The model depicted in the USGS cross section A-A' (see Section 3.3.2) shows gas migrating up dip in a westerly direction along sandstone beds of Paleocene to Eocene age (units A-E of zones 12-16). As these progressively younger to older sand units cross into the temperature and pressure regime of the HSZ, gas is transformed into methane hydrate. The hydrates in turn, provide the up-dip seal and trap a substantial free gas accumulation. Methane in this system originated from hydrocarbons spilled from the underlying Prudhoe Bay and Kuparuk River field reservoirs that migrated up faults and charged the overlying shallow clastic reservoirs. Biogenic gas, generated from the microbial breakdown of the spilled oil emplaced in fresh water-bearing shallow horizons, is thought to make a significant contribution to the gas volume, as well.

To document the work to this point, a base map was generated illustrating the acreage position of Anadarko and the rest of the oil industry, all of the pertinent well control, field outlines, a subsurface controlled structure map on the top of the West Sak interval and colored coded wells with text to display the USGS's hydrate model in map view (see Section 3.3.1). From inspection of this map, an eight-section block of Anadarko acreage located in T10N R11E appeared favorably positioned south and in close proximity to the Prudhoe Bay/Kuparuk River hydrate/free-gas accumulation detailed by the USGS. However, this area was a poor candidate

for hydrate potential as illustrated in cross section B-B'. The primary drawback was the lack of continuity of the hydrates units A-E from the established area to this acreage block, based on detailed subsurface correlations. Furthermore, several gas shows purported to be indicative of the presence of hydrates by the USGS were questionable because the gas shows appeared to be related to thick coal seams within the sandstone intervals. This area was downgraded for hydrate potential and the investigation moved to the large Anadarko acreage block located just east of the Meltwater and Tarn fields.

Evaluation of this area revealed a high likelihood for an accumulation of gas hydrate and a concomitant free gas trapped within the very porous and permeable fluvial deltaic conglomerates, gravels, sandstones and siltstones of the Ugnu and West Sak intervals of the lowermost portion of the Sagavanirktok Formation. In this general area, the Ugnu and West Sak sequences are favorably position within the HSZ at depths of approximately 1200 to 2300 ft measured depth. The hydrate/free gas accumulation and hydrocarbon source model developed by the USGS in the Prudhoe Bay/Kapurak River area was the analog model for the play type employed in this case. Verbal communication and reports by the USGS indicated that hydrates in the Ugnu and West Sak intervals are present in wells of the Meltwater and Tarn fields and contributed to the blow-out that occurred in the Arco-Cirgue #1 well in 1992. These fields and the Cirgue well are situated in a north/south trend along structural strike, about four miles west and up dip of the westernmost edge of Anadarko's acreage position. Further east and down dip from this area are several wells that experienced mud log gas shows in the West Sak interval indicating that free gas was present in this system of reservoir sands and available for transformation into hydrates updip in the HSZ. The project team believed that this north/south trend of hydrate occurrences was evidence that a hydrate accumulation that could possibly extend eastward over Anadarko's acreage block. This methane resource could also be augmented by free gas stratigraphically trapped by hydrates which would act as a seal to prevent methane from escaping up dip. The Hot Ice No. 1 location was chosen to maximize structural elevation and proximity to the north to south hydrate trend established up dip and west of Anadarko's acreage position.

A presentation for project approval was made to Anadarko management followed by a similar review by the DOE. The geological exhibits prepared for those reviews were also delivered to the DOE as part of Phase II deliverables (see next section).

Post-review work was centered on writing reports, preparing exhibits for the Hot Ice No. 1 location forecast and evaluating procedures for logging the well with hydrates present. Prospect/play write-ups, a shallow gas hazard report, a stratigraphic column, forms, annotated type logs and mud logs exhibits, maps, etc. were prepared. Well evaluation was reviewed with input from team members and Schlumberger personnel and a logging program was formulated, approved and implemented.

The Hot Ice No. 1 well was cored and logged in March 2003 to a depth of 1400 ft. Casing was set before drilling/coring activities were curtailed due to the arrival of warm weather. Evaluation of the Ugnu interval revealed that the reservoir quality was excellent, but no hydrates were evident. All pertinent exhibits were updated and sent with a set of logs and a list of log tops to the DOE in April 2003.

During May to July of 2003, effort was shifted to a more regional examination of the shallow Brookian section. An additional 50 wells were added to the study. These wells were correlated and horizon tops were added to the data base. A study of the Ugnu and West Sak viscous oil accumulation and production program was undertaken. The literature search was expanded and a montage and several cross-sections created. These exhibits indicated that Anadarko had an acreage position in a trend with opportunity for viscous oil recovery. Unfortunately, curtailments of manpower prevented completion of these phases of the project.

Field operations continued in January 2004 with the resumption of coring in Hot Ice No. 1. Team geophysicists prepared the logging program, oversaw logging operations, evaluated the new section cores, and prepared final exhibits and reports. These exhibits are presented in the next section.

3.3 Geological Exhibits

3.3.1 Base Map with Structural Contours (see Appendix A-1)

This exhibit is the primary reference map for Anadarko's geological investigation for gas hydrates on the North Slope of Alaska. It depicts the following:

- 1. Anadarko's acreage position with prospective Hot Ice locations spotted.
- 2. Wells displayed on the map are those with available shallow log data that could be used for this study.
- 3. Color coding on well control depicts the presence of free gas as red, gas hydrates in green or the presence of neither as blue (based on data presented in USGS open file reports or from our own investigations). The text indicates the presence of free gas, gas hydrates or both by Z-zonation and alphabetically designated units based on USGS cross-section presented in this report as cross-section A-A' and USGS open file reports.
- 4. Cross-section lines A-A' (USGS cross-section), B-B', C-C', D-D' and NW–SW lithologic section are annotated.
- 5. Revised structure map on Top of the West Sak sequence (basal Ugnu shale) at a contour interval of 200 ft. Structural strike is generally north and south with monoclinal east dip. Structural contours and faults are a digitized and slightly edited version of maps for Milne Point and West Sak units that are exhibits of public record available from the AOGCC. The detail apparent in the contouring and the presence of faults indicate that the maps are probably both seismic and subsurface controlled and generated by the operator Conoco/Phillips. The horizon mapped by the operator matched the team's picks for the Top of the West Sak interval exactly with only very little editing needed around some of the faults. Because of the high degree of small scale faulting present on the original AOGCC exhibits, only about 60% of the faults were digitized for this map. A similar map publicized by the AOGCC and generated by the operator depicts an even greater density of faulting presence in the underlying Kuparuk reservoirs. Many authors have surmised that (and there is evidence to support the contention) the high density of faulting present in the geologic sedimentary section over the Prudhoe Bay/Kuparuk area of the Barrow Arch is the avenue by which hydrocarbons (both gas and oil) spilled from the underlying Prudhoe Bay and Kuparuk field reservoirs have sourced the overlying shallow horizons.

Hot Ice No. 1 well encountered the top of the West Sak sequence at 1463 ft MD (-1249 ft SS) only 1 ft higher than anticipated. The structural difference at this horizon between the Hot Ice No. 1 location and the Cirque #2 well (located about 4 miles west and updip structurally) is 389 ft, confirming that the rate of dip is approximately 100 ft/mile to the east. A local structural nose with 300 ft or so of elevation compared to the regional dip rate is evident where the proposed Hot Ice No. 3 location is spotted.

3.3.2 Cross-Section A-A' (see Appendix A-2)

This display is a 10-well cross-section extending offshore from the Reindeer Is. Stratigraphic Test Well #1 on the east to the Arco-Cirque #2 well on the west in section 17, T9N-R7E (see reference base map). The presence of free gas intervals (red), gas hydrate zones (green), various Z-zonations and lettered units, top and base of the hydrate stability zone (HSZ) and base of ice-bearing permafrost zone (IBPF) are a product of the USGS. This cross-section depicts the model for gas-hydrate accumulation present in the Kuparuk/Prudhoe Bay field area as defined by the USGS. With structural dip to the east, down-dip free gas bearing horizons become gas hydrates as they enter the updip HSZ. A by-product of the gas hydrate occurrence is the down-dip free gas accumulation, apparently trapped by the up-dip gas hydrates acting as seals to the further migration of the gas.

This cross-section helps explain why Anadarko Petroleum's 100% acreage in the Cirque field area will not be prospective for the hydrate bearing units A-E present in the Kuparuk/Prudhoe Bay area as illustrated on this exhibit. Anadarko's 100% acreage proximal to the Arco-Cirque #2 well, is situated west and structurally up-dip of the hydrate bearing intervals depicted on this cross-section (units A-E). These units are exiting the HSZ in this area and are not prospective for hydrate accumulations on Anadarko's acreage position. Instead, the stratigraphically lower Ugnu and West Sak intervals (purple or lavender zones on this cross-section) will fall within the HSZ and become prospective for gas hydrates.

The log on the right side of the cross-section is an enlarged version of one of the wells on the cross-section. It is useful for characterizing log responses in permafrost, gas hydrates and free gas zones. Classic responses for permafrost and gas hydrates include high resistivity and fast travel times in highly porous reservoirs. Resistivity and acoustic logs are recording the presence of ice. Gas hydrates in permafrost can only be differentiated by the presence of gas usually identified from the mud log. Relatively lower resistivity values and slower travel times within porous reservoirs indicate the presence of free gas. The acoustic signal responds, in this case, to the presence of porosity in the reservoir or gas that is not locked up in ice.

3.3.3 Cross-Section B-B' (Eileen St. Area) (see Appendix A-3)

Cross-section B-B' ties cross-section A-A' at wells W. Kuparuk St. 40613 and K.R.U. 1D-08 and then continues southward encircling Anadarko's 100% acreage in T10N-R11E. The top of the HSZ, the base of the temperature derived and log derived HSZ, and the base of the ice bearing permafrost zone are indicated. These are based on data available from the USGS or extrapolated indirectly from mapping of that same data. The various Z-zonations are based on USGS correlations. Mudlog gas shows are displayed in solid pink or red with blue text while coal related gas shows are shown adjacent to the depth column on the logs as red bar stripes with accompanying red text. Oil shows are displayed as tan strips with tan text.

Anadarko considers this area unfavorable for formation of gas hydrates due to the following risks:

- 1. Poor lateral continuity of gas-hydrate bearing sands
- 2. Gas hydrate occurrence poorly defined from log response
- 3. Only one potentially hydrate bearing interval identified
- 4. High risk of hydrate zone on Anadarko land occurring in permafrost and thereby limiting potential testing
- 5. Lack of multiple free gas bearing zones down-dip as model predicts to establish multiple hydrate bearing zones
- 6. Presence of coal seams and concomitant coal gas coincident with identified hydrate zones problematic
- 7. Limited running room for future development on Anadarko acreage

3.3.4 Reservoirs in the HSZ (see Appendix A-4)

Gas hydrates have been identified in the reservoirs of the Ugnu and West Sak intervals in the Tarn, Cirque and Meltwater fields. Because these hydrate occurrences fall within the permafrost zones, they cannot be tested. Anadarko's proposed location, situated just a few hundred feet structurally down-dip of these fields, positions these potential hydrate intervals below the permafrost enabling production testing should gas hydrates be encountered. The schematic on the left side of this exhibit depicts the east dipping Ugnu and West Sak reservoir package fully positioned within the HSZ on Anadarko acreage affording good to excellent reservoir quality for potential gas hydrates accumulations in close proximity to recognized gas hydrate occurrences.

The stratigraphic chart on the right of the exhibit illustrates the West Sak and lower portion of the Ugnu as late Cretaceous in age and the upper portion of the Ugnu as earliest Paleocene. These units comprise the uppermost Prince Creek or lowermost Sagavanirktok sequences.

3.3.5 Amstrat Cross-Section D-D' (see Appendix A-5)

Illustrated boundaries on this American Stratigraphic Company (Amstrat) exhibit include the top and base of the HSZ, the base of the IBPF (ice bearing permafrost), and the top and base of the West Sak and Ugnu intervals. Amstrat color-coding consists of shale and claystone as gray or brown, coal as black, siltstone as orange, sandstone as yellow and gravel and/or conglomerate as white.

The West Sak and Ugnu sequence represents, overall, a progradational, fluvio-deltaic system from its base to the top. Pro-delta, fine-grained sandstone and siltstone interbedded with claystone become progressively coarser grained as the sediments transition upwards into the deltaic environment and finally terminate in a non-marine, fluvial setting. Excellent reservoir quality deltaic sands are characteristic of the upper West Sak to lower Ugnu interval and nonmarine fluvial sands, gravels and conglomerates represent the remaining portion of reservoir quality sediments for the Ugnu sequence. Conventional core data indicate that these unconsolidated sediments are situated at depths too shallow to have been affected by cementation. Hence, porosity is a function of compaction with depth. At the Hot Ice No. 1 proposed location, the West Sak and Ugnu reservoirs were predicted to occur at depths of approximately 800 ft to 2300 ft, and porosity was expected to range from 35% to greater than 40% with concomitant permeabilities of hundreds of millidarcys to darcys in magnitude.

In the Tarn, Cirque and Meltwater fields, gas hydrates have characteristically occurred stratigraphically in the uppermost portion of the West Sak and lowermost portion of the Ugnu intervals. This is the interval that was expected to be most prospective for gas hydrates at the Hot Ice No. 1 proposed location as well. An inspection of the lithologies for that interval on the Amstrat logs displayed on this section, reveals that a preponderance of coarser grained clastics prevail providing excellent reservoir conditions for the formation of gas hydrates.

An interim version of the post-drill lithology log for Hot Ice No. 1 was added to this section to compare core lithology to lithology interpreted from drilled cuttings by Amstrat for nearby wells. The results to date show that the top and base of the Ugnu and West Sak sequences and the base of the permafrost were predicted accurately. The top and base of the Ugnu was 820 ft and 1358 ft, respectively, and the top and base of the West Sak was 1463 ft and 2300 ft, respectively. The base of the permafrost was 1263 ft.

Overall, lithology and depositional environments evident in the core were as expected. The West Sak interval exhibited a lack of variability with gradational transitions between sand and mudstone units. The grain size column of the lithology log indicates that grain size progressively coarsens upward from the base of the core to the top with the West Sak interval dominated by a finer fraction compared to the overlying Ugnu. The occurrence of layers of shell fragments and whole bivalve shells support deposition on a marine shelf environment. On the other hand the Ugnu interval (especially the upper two-thirds) is dominated by coarser grained clastics, is highly variable in character, contains an abundance of coal, woody fragments, rootlet traces, and carbonaceous material plus the presence of conglomeratic beds just above the top of the Ugnu attest to a very shallow marginal marine to fluvial depositional environment.

Reservoir quality in the sandstone units was exceptional as predicted. Porosity and permeability information derived from testing core plugs for the Ugnu is annotated on the lithology log. It reveals that core porosity over 40% was not unusual with mid to high 30's being the norm. Permeability was measured in the darcy range, extending to as high as 16 darcys in one sample. Core plugged data for the underlying West Sak interval is not completed at this time but the pervasive invasion affects present on the resisitivity logs over sand zones attest to very good reservoir quality. The CMR log indicates a very high effective porosity (low bound water) in these sands and concomitant permeability that exceeded 1 darcy and ranged to over 10 darcys in places.

The 115 ft sand unit at the base of the Ugnu (1242-1357 ft) and the 77 ft sand interval at the top of the West Sak sequence (1463-1540 ft) are thought to be marine deposited sands. In a regional sense, these two time periods are dominated by sand deposition and these stratigraphic units can be correlated over the prospect area. They were predicted to be present at this location and offered the highest potential for hydrate occurrence because they were the same stratigraphic units that have been reported to contained methane hydrate in wells of the Meltwater and Tarn fields and the Cirque #1 well. Although methane was detected in the upper West Sak sand as expected, no gas hydrates were found in the core of the Hot Ice No. 1 well in these zones.

3.3.6 Gross Sand in HSZ (see Appendix A-6)

Gross sand thickness within the hydrate stability zone (HSZ) was derived using a 45 API gamma ray cutoff. The amount of reservoir section available for formation of gas hydrates is approximately 300-700 ft near the Hot Ice locations. An eastward thickening HSZ provides more section available for reservoir quality sediments based on the gamma ray cutoff so a thicker gross sand isopach is apparent. Actual net (gross sand) to gross HSZ interval is similar for both areas.

3.3.7 Cross-Section C-C' (see Appendix A-7)

Displayed on this exhibit are logs of various wells situated closest to Anadarko's Hot Ice locations. Various boundaries that comprise the HSZ, permafrost and stratigraphic intervals are depicted. Confirmed occurrences of free gas and gas hydrates are annotated in dark red and green respectively while extrapolated, possible or potential free gas or hydrate bearing intervals are portrayed in lighter shades.

The Tarn and Cirque field gas hydrate occurrences are situated stratigraphically in reservoirs of the upper and lower portions respectively of the West Sak and Ugnu intervals. Reservoir units that contain gas hydrates appear to be continuous in the area so these intervals have been extrapolated to the West Sak # 20 well and the Hot Ice No. 3 proposed location to demonstrate their prospectivity as possible or potential gas hydrate bearing units. While gas hydrates were not recognized to any large extent from logs or during drilling in either the West Sak #13 or #20 wells, which directly offset Anadarko's 100% acreage and the Hot Ice locations, this doesn't preclude their presence. Both of these wells were drilled in the late 1970's to early 80's and drilling practices (such as the use of warm drilling fluids, fast drilling rates and enlarged boreholes) were not conducive to detecting the presence of gas hydrates. The low magnitude, lazy mud log show of gas in prospective intervals of the West Sak #20 well may be liberated methane from unrecognized gas hydrates that are situated in permafrost.

The following summarizes potential at the Hot Ice locations:

- 1. Potentially greater lateral continuity of gas hydrate bearing sands (upper West Sak and lower Ugnu deltaic sands)
- 2. Confirmed thick presence of hydrates in offsetting Cirque and Tarn wells
- 3. Multiple potential hydrate bearing intervals identified (multiple free gas bearing zones downdip and hydrate zones updip)
- 4. Limited coals and lazy gas show in offsetting West Sak 20 well were encouraging
- 5. Greater probability of hydrate zone on Anadarko land occurring at or below permafrost allowing for potential testing
- 6. Large future development potential on Anadarko acreage

Post-drill updating of this cross section includes the addition of logs for the K.R.U. Tarn 2N-349 well and Hot Ice No. 1. Zones that were annotated as prospective for hydrates in Hot Ice No. 1 have been deleted since no hydrates were encountered. The presence of free gas in the uppermost sand of the West Sak interval has been appropriately annotated. The HSZ zone base was recalculated using information obtained from a water sample extracted from the core

at the base of the permafrost. The updated base of the HSZ is 2026 ft instead of the 2300 ft as shown on this cross section.

3.3.8 Gas Hydrate Potential Map (see Appendix A-8)

This exhibit illustrates the potential areal extent of gas hydrates (green) and concomitant free gas (red) accumulations that may exist as delineated by investigations conducted by the USGS and Anadarko Petroleum in this general area. Western and eastern boundaries of the potential gas hydrate accumulation in the Tarn/Cirque/Meltwater area are roughly defined as the entry and exit point of the West Sak and Ugnu interval in the HSZ. The southern boundary is established by the absence of indications of free gas or gas hydrates in wells of that area. To the north the potential is undefined. USGS has documented the presence of gas hydrates in some wells situated to the north of the dashed line that indicates a loosely defined border in that direction.

Post-drill assessment reduced the areal extent of the "Probable Gas Hydrate" realm by limiting the eastern boundary to a position just west and up dip of the Hot Ice No. 1 location where no hydrates were encountered. The absence of gas hydrates in the Hot Ice No. 1 wellbore does not preclude the possibility that hydrates could still be present in nearby areas. A few 8½-inch wellbores in an area of this size do not represent a significant sampling. The situation of the NW Eileen State wells should be considered. Hydrates were identified in one well but were not recognized for whatever reason in the adjacent twin well. Therefore, the cross-hatched area labeled "Possible Gas Hydrate" signifies an area where there is still some potential for hydrates to occur even though hydrates were not found at Hot Ice No. 1. Since gas was encountered in the uppermost sandstone unit of the West Sak interval, the Hot Ice No. 1 well is situated in an overlap area where a free gas or gas hydrate accumulation or a combination of both is possible.

4. Conclusions

Hot Ice No. 1 was designed to be cored from surface to the base of the West Sak interval using the revolutionary Arctic Drilling Platform in search of gas-hydrate and free-gas accumulations at depths of approximately 1200 to 2500 ft MD. A secondary objective was the gas-charged sands of the uppermost Campanian interval at approximately 3000 ft. Gas available for entrapment in the prospective gas hydrate and free gas accumulations is sourced from hydrocarbons spilled from the underlying Prudhoe Bay Field reservoirs that have migrated up faults and charged the overlying shallow, clastic reservoirs.

Geological investigation of the methane hydrate potential of the "top set" area of the North Slope of Alaska, particularly as it related to Anadarko's acreage position, began in June 2002. A partial literature search had yielded information on hydrate formation, USGS reports, the Russian combination hydrate/free-gas field and model, and various papers related to engineering topics on hydrates. Subsequent searches for geologic-oriented material yielded information on oil and gas development, regional geology of the North Slope area, stratigraphy, lithology, field studies, etc.

The Hot Ice No. 1 well was cored and logged in March 2003 to a depth of 1400 ft. Casing was set before drilling/coring activities were curtailed due to the arrival of warm weather. Evaluation of the Ugnu interval revealed that the reservoir quality was excellent, but no hydrates were evident. During May to July of 2003, effort was shifted to a more regional examination of the shallow Brookian section. An additional 50 wells were added to the study.

Field operations continued in January 2004 with the resumption of coring in Hot Ice No. 1. Team geophysicists prepared the logging program, oversaw logging operations, evaluated the new section cores, and prepared final exhibits and reports. A series of geological exhibits was prepared (see **Appendix A**):

- A-1. Base Map with Structural Contours (primary reference map for investigation of gas hydrates on North Slope)
- A-2. Cross-Section A-A' (cross section including 10 wells in the region)
- A-3. Cross-Section B-B' (cross section tying A-A' and continuing southward)
- A-4. Reservoirs in the Hydrate Stability Zone (HSZ)
- A-5. Amstrat Cross-Section D-D' (based on American Stratigraphic Company format; showing top/base of HSZ, base of ice-bearing permafrost, top/base of West Sak and Ugnu intervals)
- A-6. Gross Sand in HSZ (gross sand thickness derived based on 45° API gamma-ray cutoff)
- A-7. Cross-Section C-C' (logs of several wells closest to Hot Ice)
- A-8. Gas Hydrate Potential Map

Reservoir quality in the sandstone units was exceptional as predicted. Porosity and permeability information derived from testing core plugs for the Ugnu is annotated on the lithology log. It reveals that core porosities of over 40% were not unusual with mid to high 30's

the norm. Permeability was measured in the darcy range, extending to as high as 16 darcys in one sample.

The 115-ft sand unit at the base of the Ugnu (1242-1357 ft) and the 77-ft sand interval at the top of the West Sak sequence (1463-1540 ft) are thought to be marine-deposited sands. In a regional sense, these two time periods are dominated by sand deposition and these stratigraphic units can be correlated over the prospect area. They were predicted to be present at this location and offered the highest potential for hydrate occurrence because they were the same stratigraphic units that have been reported to contained methane hydrate in wells of the Meltwater and Tarn fields and the Cirque #1 well. Although methane was detected in the upper West Sak sand as expected, no gas hydrates were found in the core of the Hot Ice No. 1 well in these zones.

Figure 1 illustrates the potential areal extent of gas hydrates (green) and concomitant free gas (red) accumulations that may exist as delineated by investigations conducted by the USGS and Anadarko in this general area. Western and eastern boundaries of the potential gas hydrate accumulation in the Tarn/Cirque/Meltwater area are roughly defined as the entry and exit point of the West Sak and Ugnu interval in the HSZ. The southern boundary is established by the absence of indications of free gas or gas hydrates in wells of that area. To the north the potential is undefined. USGS has documented the presence of gas hydrates in some wells situated to the north of the dashed line that indicates a loosely defined border in that direction.



Figure 1. Gas Hydrate Potential Map near Hot Ice (see Appendix A-8)

Post-drill assessment reduced the areal extent of the "Probable Gas Hydrate" realm by limiting the eastern boundary to a position just west and up dip of the Hot Ice No. 1 location where no

hydrates were encountered. The absence of gas hydrates in the Hot Ice No. 1 wellbore does not preclude the possibility that hydrates could still be present in nearby areas. A few 8½-inch wellbores in an area of this size do not represent a significant sampling. The region labeled "Possible Gas Hydrate" signifies an area where there is still potential for hydrates to occur even though hydrates were not found at Hot Ice No. 1. Since gas was encountered in the uppermost sandstone unit of the West Sak interval, the Hot Ice No. 1 well is situated in an overlap area where a free gas or gas hydrate accumulation or a combination of both is possible.

5. References

Ali G. Kadaster, and Keith K. Millheim, 2004: "Onshore Mobile Platform: A Modular Platform for Drilling and Production Operations in Remote and Environmentally Sensitive Areas," IADC/SPE paper 18740, presented at IADC/SPE 2004 Annual Meeting in Dallas, Texas, March.

Appendix A. Geological Exhibits

- A-1. Base Map with Structural Contours
- A-2. Cross-Section A-A'
- A-3. Cross-Section B-B'
- A-4. Reservoirs in the Hydrate Stability Zone (HSZ)
- A-5. Amstrat Cross-Section D-D'
- A-6. Gross Sand in HSZ
- A-7. Cross-Section C-C'
- A-8. Gas Hydrate Potential Map





Appendix A-2. USGS Cross-Section A-A' Prudhoe Bay / Kuparuk River Field Area With Hydrate Type Log



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Areal Extent Ugnu/West Sak Gas Hydrate Occurrence Tarn/Cirque/Meltwater Area







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	LARAMIDE OROGENY
MILNE PT. W. SAK	HUE : 180 - 900'
	SCHRADER BLUFF : 0 - 2250' SEABEE : 0 - 1200'
	NANUSHUK : 0 - 10,200'
	TOROK : 3000 - 18000'
	HR2.30-135
PT. MOINTYRE KUPARUK R. PTTHOMSON MILNE PT	KUPARUK : 0 - 690'
KUPARUK R.	MILUVEACH : 0 - 540'
DELTA	
	KINGAK : 0 - 3300'
PRUDHOE BAY	SAG RIVER : 0 - 120'
PRUDHOE	SHUBLIK : 0 - 300'
	IVISHAK : 0 - 640' ECHOOKA : 0 - 870'
PRUDHOE BAY	LISBURNE : 0 - 3600'
	ENDICOTT : 0 - 2010'

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HOT ICE PROJECT

Detailed Amstrat descriptions and Core Log of West Sak and Ugnu sands & conglomerates demonstrating continuity of potential hydrate bearing reservoir section in vicinity of Hot Ice hydrate test well

Appendix A-5. Amstrat Cross-Section D-D'

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Meltwater

20000 Ft/In

Appendix B: Numerical Simulation Studies Related to the Hot Ice No. 1 Well

By: George J. Moridis Lawrence Berkeley National Laboratory, Berkeley, CA, USA

September 9, 2004

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1. Introduction

A Maurer/Anadarko team led a project focusing on the evaluation of gas production from onshore natural hydrate deposits associated with permafrost in the North Slope of Alaska. Lawrence Berkeley National Laboratory (LBNL), funded by the National Energy Technology Laboratory of DOE, conducted a modeling study in support of the planned field activities of the Maurer/Anadarko team.

2. Objectives

Objectives of the LBNL study were to investigate by means of numerical simulation the following subjects that were important tasks in the Maurer/Anadarko project:

- 1. Hydrate preservation during core recovery
- 2. Gas production potential from hydrate accumulations representing geologic and reservoir conditions expected at the planned drilling site

Numerical studies were conducted using the EOSHYDR2 model (Moridis, 2003), which is a member of the TOUGH2 family of codes (Pruess et al., 1999) for multi-component, multiphase fluid and heat flow and transport in the subsurface. In this report we discuss the conditions of the simulated scenarios and the corresponding results. In the hydrate preservation component of this study, we identify important parameters controlling hydrate dissociation during core recovery from gas hydrate present in typical permafrost accumulations. In the gas production component of the study, we explore different dissociation-driven gas production strategies (thermal stimulation and depressurization), determine the relative importance of the hydrate and reservoir conditions on production volumes, and evaluate the impact of various operational and production parameters.

Based on simulation results, conclusions are reached and recommendations are made for this and other related hydrate field studies. In addition, we provide a short section addressing the discrepancy (and possible explanations) between predictions and actual field conditions at the site of the Hot Ice No. 1 field test (conducted in the winter seasons of 2003 and 2004).

3. Hydrate Preservation During Core Recovery

The subject is of particular importance because no representative (undisturbed) sample of natural gas hydrates has ever been recovered. The overwhelming majority of the available information on hydrate behavior has been derived from laboratory studies. A representative natural sample can provide answers to questions regarding the occurrence, properties and behavior of hydrates in natural systems, and address the issue of suitability of synthetic hydrate samples (pure and in porous media) as adequate analogs.

Recovering undisturbed hydrate-bearing samples is difficult because hydrates occur under a high pressure and low temperature regime, and are unstable at the pressure and temperature conditions at the surface of the earth. Under atmospheric conditions, methane hydrates (the most common representative of permafrost-associated natural hydrates, and the first target for gas production) are only stable at temperatures below -80°C. Thus, exposure of the relatively warm core (occurring at temperatures ranging between -5°C to 13°C below permafrost deposits)

to continuously decreasing pressures during recovery (as the core ascends in the wellbore) prior to storage under controlled pressure and temperature conditions induces significant changes in the recovered sample.

Pressure is the major factor affecting hydrate preservation because its effect on the core is practically instantaneous. The effect of temperature is expected to be secondary because conduction (the main heat transport mechanism during core recovery) is a slow process compared to the expected rate of core ascent, and may not be a significant issue at the surface prior to storage because of the very low temperatures in the arctic North Slope during the winter (the operational window of the field operations of the project).

3.1 System Description

For this study, the hydrate-bearing core is assumed to reach the surface in 15 minutes from its initial position (at a depth of 740 m). An additional 15 minutes are needed from the moment the sample reaches the surface to its storage under stable (controlled) conditions in pressurized vessels.

We investigate the effect of important operational parameters (i.e., core diameter and drilling mud temperature) on overall hydrate preservation. We also study the importance of initial sample conditions (permeability, temperature, and hydrate saturation) on final hydrate recovery.

System properties and specifics of the simulations are listed in detail below.

3.1.1 Core Properties

Core diameter: D = 2.5 in, and 3.345 in

Core length: L = 10 ft (of which only 5 ft were simulated because of symmetry)

Steel sleeve thickness: 1/8 in

Distance between core and steel sleeve: 0.00025 m

3.1.2 Reservoir Properties and Initial Conditions

Depth to bottom of hydrate zone: Z = 740 m Hydrate pressure: P = 1051 psig (7.3439x10⁶ Pa), i.e., hydrostatic pressure Hydrate temperature: T = 9°C, and 4°C Hydrate saturation: S_H = 85%, and 50% Porous medium permeability: k = 10 mD, 100 mD, and 1000 mD Porosity: $\phi = 0.30$ Relative permeability and capillary pressure parameters: *Consistent with a sand*

3.1.3 Operational Parameters

Mud temperature: $T_m = 0^{\circ}C$, and $-5^{\circ}C$ Time for core to reach surface: 15 minutes Time to bring core to stability after arrival at the surface: 15 minutes

3.1.4 Grid of the Domain

Cylindrical system (r, z)

Discretization in r: uniform $\Delta r = 2 \text{ mm}$

Discretization in z: non-uniform, with min $\Delta z = 2$ mm and max $\Delta z = 10$ mm

3.1.5 Important Assumptions

- 1. Uniform and isotropic porous medium
- The core top and bottom are exposed to a linearly decreasing hydrostatic pressure and mud temperature T_m is constant while the core is raised to the surface (740 m in 15 min). Core is then exposed to a constant atmospheric pressure and T_m during another 15 min of study/observation.
- 3. Hydrate dissociation follows a kinetic model. This is a valid assumption, given the fact that depressurization in this case is a gradual process (and is intrinsically less aggressive than thermal stimulation using hot water).

3.2 Simulation Results in the Core Preservation Study

3.2.1 Simulations of the D = 2.5" Core and for T = 9°C

3.2.1.1 Temperature distribution, 100 mD case

Figures 1 through 6 show temperature distribution of the 100-mD core in the symmetric 1.5 mlong core at t=5 min, 10 min, 15 min, 20 min, 25 min and 30 min. In this simulation set, $S_H = 85\%$, $T_m = 0^{\circ}C$ and $T = 9^{\circ}C$.

The temperature distribution appears quite uniform in z except at the end of the core, while significant radial variations (i.e., in the r direction) are observed. Temperature of the hydrate-impregnated core continuously declines during the 30-min simulation period. This is due to the strongly endothermic dissociation of hydrates, which absorb heat from their immediate vicinity and result in temperatures below freezing. The temperature decline follows movement of the dissociation front, i.e., from the periphery (exposed to declining pressures and subject to dissociation through depressurization) toward the center of the cylindrical core. Note that the temperature distribution is not a good indicator of the dissociation profile because, under the conditions of core recovery, depressurization is the main dissociation mechanism, but interacts heavily with the thermal regime of the system.

3.2.1.2 Pressure distribution, 100 mD case

Figures 7 through 12 show the pressure distribution (in Pa) of the 100 mD core corresponding to the temperature distribution discussed in Section 3.2.1.1. These figures indicate a remarkable radial uniformity of pressure, i.e., the opposite of the temperature distribution. Pressure declines rapidly as time advances, but is practically constant along r at a given z, with the exception of a narrow band in the immediate vicinity of the gap between the core and the sleeve (where rapid pressure decline is observed). These results are consistent with exposure to lower boundary pressures during the core recovery. As expected, maximum pressure is

observed at the bottom of the simulated half core (i.e., at the symmetry plane of the core). This indicates that minimum depressurization (and, consequently, maximum hydrate preservation) is expected at the midpoint of the core. Additionally, this is a good indication that better recovery may be achieved with longer cores, although the advantage may not be significant in the 100 mD case because of the very low pressure gradient (see Figure 12).

3.2.1.3 Pressure distribution, 10 mD case

Figures 13 through 18 show the pressure distribution when the medium permeability is 10 mD, and all other conditions are the same as in the case discussed in Section 3.2.1. The effect of lower permeability is reflected by curvature of the isobars, indicating lack of uniformity in both r and z. Pressure gradients are steeper both in z and in r. Additionally, pressures are generally higher than those of the 100 mD case at the same time due to the resistance to flow brought about by the lower permeability. As expected, the highest pressures are observed at the center (in r) and midpoint (in z) of the cores.

3.2.1.4 Effect of permeability on hydrate preservation

Figure 19 shows the remaining hydrate (as a fraction of the original hydrate saturation or mass) in the core when k = 10 mD, 100 mD, 1000 mD. These results correspond to $S_H = 0.85\%$, D = 2.5", $T_m = 0$ °C and T = 9°C.

This figure indicates that higher hydrate recovery will be attained in lower permeability cores. This result also indicates that depressurization is the main dissociation mechanism during core recovery. Additionally, Figure 19 shows that hydrate preservation declines rapidly with time. The clear implication is that hydrate preservation can be maximized if the core is pressurized as early as possible.

3.2.1.5 Effect of mud temperature on hydrate preservation

Figure 20 shows the remaining hydrate (as a fraction of the original hydrate saturation or mass) in the core when k = 10 mD, 100 mD, 1000 mD. These results correspond to $S_H = 0.85\%$, D = 2.5", $T_m = -5^{\circ}C$ and T= 9°C. Thus, the only difference between these results and those in Section 3.2.1.4 is mud temperature.

Figure 20 shows that colder mud results in substantially (and consistently) higher hydrate recovery. This is caused by higher dissociation pressures that correspond to the lower temperatures. Thus, colder hydrates will remain stable at a lower pressure. As in the case of the $T_m = 0$ °C mud, hydrate recovery increases with a decreasing permeability. The implication of this observation is that the coldest possible mud should be used for hydrate core recovery. It is important, however, that the mud should not contain large amounts of salts or alcohols (often used for low-temperature drilling) because these substances are hydrate inhibitors and tend to promote dissociation.

3.2.1.6 Effect of hydrate saturation on recovery

Figure 21 shows effects of saturation on hydrate preservation. The 100-mD core was assumed to have a $S_H = 50\%$. For reference, Figure 21 includes recovery curves for a) $S_H = 85\%$, $T_m = -5^{\circ}C$, and b) $S_H = 85\%$, $T_m = 0^{\circ}C$.

As expected, higher initial hydrate saturation leads to higher eventual hydrate preservation in the cores. What is remarkable (and rather unexpected) is that the effect of hydrate saturation appears to be less important than that of mud temperature.

3.2.2 Simulations of the D = 3.345" Core

In response to updated information on the specifics of the coring operation and the site geology (following discussions with Anadarko on 6/7/02), a second set of core preservation runs was made. These simulation sets were based on more realistic scenarios, and assumed a mud temperature of 0°C and permeability of 1000 mD. Effects of core diameter (varying from 2.5 in to 3.345 in) and of initial formation temperature (9°C and 4°C) were studied.

3.2.2.1 Pressure distribution, 1000 mD case

Figures 22 through 27 show pressure distribution of the 1000-mD core in the symmetric 1.5 mlong core at t=5 min, 10 min, 15 min, 20 min, 25 min and 30 min. In this simulation set, $S_H = 85\%$, $T_m = 0^{\circ}C$ and $T = 4^{\circ}C$.

Patterns observed here are very similar of those in Figures 7 through 12 (corresponding to the 100 mD medium in the 2.5" core). For reasons discussed in Section 3.2.1.2, we detect the same remarkable radial uniformity of pressure, the same rapid pressure decline with time, as well as the narrow depressurized region along the outer perimeter of the core. Similarly, the maximum pressure is observed at the bottom of the simulated half core, and confirms the general observation that better recovery may be achieved with longer cores. Note that the pressures observed in this larger-diameter core are higher than those in the 2.5" core despite the larger permeability (1000 mD vs. 100 mD). The reason for this behavior is lower initial temperature of the formation, which leads to slower dissociation and lower effective permeabilities over longer times because of a higher hydrate saturation.

3.2.2.2 Temperature distribution, 1000 mD case

Figures 28 through 33 show temperature distribution of the 1000-mD core corresponding to the pressure distribution discussed in Section 3.2.1. Temperature profiles observed here follow a pattern that is very similar of those in Figures 1 through 6 (corresponding to the 100 mD medium in the 2.5" core). The temperature distribution appears quite uniform in z at a given r, the radial distribution shows a strong gradient, and temperature of the hydrate-impregnated core continuously declines during the 30-min simulation period for the reasons discussed in Section 3.2.1.1. Temperatures are generally lower than those of Figures 1 through 6, consistent with the lower initial temperature.

3.2.2.3 Hydrate saturation distribution, 1000 mD case

Figures 34 through 38 show the hydrate saturation distribution of the 1000 mD core corresponding to the pressure and temperature distribution discussed in Section 3.2.1 and 3.2.2. Note that the first observation time is t = 10 min, as little apparent dissociation is observed at earlier times.

Figure 34 shows that at t = 10 min, dissociation is limited to a narrow band along the outer surface of the hydrate-impregnated core, while the inner portion of the core is at the initial formation hydrate saturation. As time advances, the dissociated region keeps expanding by moving inward radially, while the high-saturation region shrinks continuously. As expected, the

highest concentration of hydrates is encountered near the center of the core. Note the curvature of the saturation contours, caused by the effect of core boundaries and easier communication of the top of the core with its surroundings.

3.2.2.4 Hydrate saturation distribution, 100 mD case

Figures 39 through 43 show the hydrate saturation distribution when the medium permeability is 100 mD and all other conditions are the same as in the case discussed in Section 3.2.3. Comparison of Figures 39 through 43 to those in Section 3.2.3 shows that the two sets of graphs follow similar dissociation patterns, but the lower permeability leads to 1) slower advancement of the radial dissociation front, 2) a smaller dissociated zone, 3) a steeper radial saturation gradient, and 4) higher hydrate preservation.

3.2.2.5 Hydrate saturation distribution, 10 mD case

Figure 44 shows the hydrate saturation distribution when the medium permeability is 10 mD, $S_H = 85\%$, $T_m = 0^{\circ}C$ and $T = 9^{\circ}C$, and D = 2.5". Although the conditions here are markedly different from those discussed in Sections 3.2.3 and 3.2.4, the figure is included for reference.

A review of Figure 44 reveals that dissociation patterns discussed in Sections 3.2.3 and 3.2.4 persist here despite very significant differences in underlying conditions. This uniformity of saturation behavior reduces uncertainty and allows improved predictability of hydrate dissociation in cores.

3.2.2.6 Effects of T, S_H and D

Figure 45 shows hydrate preservation (as a fraction of the original hydrate mass or saturation) in the core when S_H varies from 50% to 85%, T varies from 4°C to 9°C and D varies from 2.5 in to 3.345 in.

3.3 Conclusions and Recommendations

Enhanced core preservation in recovered samples is promoted by

- 1. Low formation temperature
- 2. High hydrate saturation

For a given formation, hydrate preservation increases with

- 1. Increasing core diameter
- 2. Increasing core length
- 3. Decreasing mud temperature. Note that salts and alcohols must not be present in the mud because they act as hydration inhibitors and result in rapid hydrate dissociation.
4. Gas Production from Hydrate Accumulations

This component of the study addresses evaluation of the production potential of natural hydrate accumulations on Anadarko-owned properties in the North Slope. At the time of the study, information on geology and reservoir properties and conditions was incomplete. Consequently, the Anadarko-provided geologic/reservoir system description was based on reasonable assumptions based on data from adjacent properties. Additionally, there was no direct evidence of hydrate occurrence at the proposed site at the time of this study because of no prior drilling activity at the site. Thus, hydrate-related data provided by Anadarko were based on reasonable extrapolations from known permafrost hydrate accumulations in the North Slope of Alaska and in Northern Canada.

For the purposes of this study, two formations were considered: Ugnu and West Sak. Following the classification system of Moridis and Collett (2003), both hydrate-bearing formations were assumed to constitute Class 3 hydrate accumulations. In this class of hydrates there are no mobile fluid (gas or water) zones, and the formation coincides with the hydrate interval. When the hydrate saturation S_H is high, such accumulations are generally challenging to fluid flow because of low effective permeability conditions.

4.1 System Description

The gas hydrate was assumed to be pure methane hydrate. In both the Ugnu and West Sak cases, a single vertical well was considered. Production potential of the two formations was investigated by using 1) thermal stimulation and 2) depressurization as hydrate dissociation methods. Because the focus of this production study was identifying important processes and parameters for the design of a field test, the period covered by the simulation was very short (30 days), reflecting the limited operating window for such a test in the Arctic.

System properties and specifics of the simulations are listed in detail below:

4.1.1 Reservoir Properties

Thickness of the hydrate-bearing formation: H = 20 m (Ugnu and West Sak)

Porous medium permeability: k = 400 mD (Ugnu and West Sak)

Porosity $\phi = 0.30$ (Ugnu and West Sak)

Uniform and isotropic porous medium

4.1.2 Initial Conditions

Pressure P:	At Ugnu, P = 700 psig (4.93x10 ⁶ Pa)
	At West Sak, $P = 970 \text{ psig} (6.80 \times 10^6 \text{ Pa})$

Temperature T: At Ugnu, T = 36°F (2.25°C) At West Sak, T = 45°F (7.25°C)

Hydrate saturation: $S_{H} = 80\%$ and 50% (Ugnu and West Sak)

Irreducible water saturation: $S_{wr} = 15\%$ (Ugnu and West Sak)

Relative permeability and capillary pressure parameters: Consistent with a sand

4.1.3 Operational Parameters (Both Cases)

Water temperature at the well: $T_w = 50^{\circ}C$ and $80^{\circ}C$ (for thermal stimulation-induced production under constant well-T conditions)

Heat addition rate at the well: $Q_H = 6$ kW (for thermal stimulation-induced production for production under constant well heat addition conditions)

Pressure at the well: $P_w = 440$ psia (3.0x10⁶ Pa) for depressurization-induced production

Well completed in the entire formation

4.1.4 Grid of the Domain

Cylindrical system (r, z)

Discretization in r: non-uniform, with min $\Delta r = 0.05$ m and max $\Delta r = 0.25$ m

Discretization in z: non-uniform, with min Δz = 0.25 m and max Δz = 2 m

Total number of grid blocks: 32x32 = 1024 in (r, z)

4.2 Simulation Results in the Production Study

4.2.1 Ugnu Accumulation – Thermal Stimulation

4.2.1.1 Effect of initial formation temperature

Figure 46 shows the effect of initial formation temperature on cumulative gas methane production from the Ugnu hydrate accumulation. In the base (reference) case, $S_H = 80\%$, $T = 2.25^{\circ}C$ and thermal stimulation of the gas hydrate was caused by warm water circulating in the well at a constant temperature of $T_w = 50^{\circ}C$.

Results clearly demonstrate that initial formation temperature is among the most important factors affecting CH₄ production from hydrates, and confirms earlier observations (Moridis, 2004; Moridis et al., 2004). This is because a higher temperature indicates a higher energy state, requiring less heat for dissociation. An increase in initial temperature from 2.25°C to 6.75° C (i.e., the equilibrium dissociation temperature at the prevailing pressure) results in a five-fold increase in the production volume. For an increase in temperature to 6.25° C, production increases by a factor of about 2, while the effect of an initial temperature of 4.25 is on the order of about 20%. This indicates that proximity to the equilibrium temperature substantially increases production volume. The obvious implication is that accumulations with high initial temperatures are the most promising targets for hydrate exploitation.

4.2.1.2 Effect of T_w and Q_H

Increase in temperature T_w of the water in the circulating well from 50°C to 80°C results in an increase in produced volume by about 50%, and appears roughly proportional to the increase in the well water temperature (**Figure 47**). This conforms to expectations because the additional heat (provided through the higher T_w) leads to dissociation of larger amounts of gas hydrate. If instead of circulating water at the well, heat is added through well walls at a rate of 6 kW (roughly equal to the initial rate of heat addition when the circulating water temperature at the

well is 50°C), the increase in production is similar to that effected by raising T_w to 80°C. This result indicates that direct heat addition appears more effective than water circulation in thermal dissociation of hydrates.

4.2.1.3 Effect of S_H

Figure 48 shows the effect of hydrate saturation S_H on gas production. A reduction of S_H from 80% (in the base case) to 50% results in a reduction of the produced CH_4 volume. This reduction is observed for both $T_w = 50^{\circ}C$ and $T_w = 80^{\circ}C$, and is consistent with expectations. In a given volume, a lower S_H directs larger amounts of energy to increasing the temperature of the pore water, with correspondingly less heat available for dissociation of gas hydrate.

4.2.2 West Sak Accumulation – Thermal Stimulation

4.2.2.1 Effect of T, T_W and Q_H

Figure 49 shows the effect of initial formation temperature T on cumulative gas methane production from the West Sak gas hydrate accumulation. Additionally, it presents the effects of the well water temperature T_w and of the rate of heat addition Q_H . In the base (reference) case, $S_H = 80\%$, T = 7.25°C and thermal stimulation of the gas hydrate was caused by warm water circulating in the well at a constant temperature of $T_w = 50$ °C.

Results are entirely analogous to those for the case of the Ugnu accumulation. A higher initial formation temperature leads to larger CH_4 volume production because it requires less heat for dissociation. Note that the increase in produced volume when T = 8.25°C (equilibrium dissociation temperature at the West Sak pressure) is proportionally lower than that for the colder Ugnu formation. This is due to the proximity of the initial West Sak temperature to the dissociation temperature.

As in the case of Ugnu, an increase in T_w leads to a higher produced volume. Similarly, adding heat directly to the formation through the wellbore (e.g., by electrical heating) appears to be more effective in thermally dissociating the gas hydrate than circulating 50°C water in the well.

4.2.2.2 Effect of S_H

Figure 50 is consistent with the previously discussed Figure 49 that pertains to the Ugnu case. A reduction of S_H from 80% (in the base case) to 50% results in a reduction of the produced CH₄ volume. This reduction is observed for both $T_w = 50^{\circ}$ C and $T_w = 80^{\circ}$ C, as well as in the case of constant heat addition at a rate Q_H, and is consistent with expectations for the reasons discussed in Section 4.2.1.3.

4.2.3 Depressurization-Induced Production

In the simulation, depressurization was effected by imposing a boundary condition of constant pressure P_w at the well. This pressure was chosen to be slightly above that of the quadruple point of methane hydrate, thus ensuring that no ice be formed during production.

Figures 51 and 52 show cumulative gas and water production, respectively, from the Ugnu and West Sak fictitious hydrate accumulations with the initial hydrate saturation $S_H = 50\%$. The important conclusion that can be drawn from this figure is that depressurization appears to be far more effective than thermal dissociation (at least, within the limited 30-day period of the

planned production test). Gas evolves earlier, and the cumulative produced gas volume is orders of magnitude larger than that for thermal stimulation (Figures 48 and 50). Regarding relative performance of the Ugnu vs. the West Sak formations, the deeper and warmer West Sak is evidently a better target for production. This is attributed primarily to its higher temperature (leading to easier hydrate dissociation), as well as to its higher pressure (resulting in a larger depressurization-induced driving force for dissociation when produced at a constant well pressure. An additional observation is that the released water volumes are relatively large, and may pose a disposal problem. This is an inevitable issue in production from hydrate accumulations, given the stoichiometry of gas hydrates.

Figure 53 demonstrates the effect of initial gas hydrate saturation on depressurization-induced production. When hydrate saturation increases from 50% (in Figure 52) to 80%, cumulative gas production in both the Ugnu and West Sak fictitious cases is significantly reduced to levels similar to those from thermal dissociation. The reason for this behavior is the extremely low permeability of the formations at S_H = 80% (a persistent feature in Class 3 hydrates), which makes fluid flow extremely slow. Thus, depressurization is limited to a relatively narrow zone in the vicinity of the well, with a corresponding reduction in the released methane volume.

4.3 Conclusions and Recommendations

A West Sak-type gas hydrate accumulation would be a consistently better target for the planned test. Such a hydrate accumulation (if it indeed exists) yields larger production volumes from either depressurization- or thermally-induced dissociation. The major reason for the superiority of such a West Sak deposit is its higher temperature.

- 1. Gas production from either formation under any set of reasonable conditions is possible using either thermal stimulation or depressurization.
- Depressurization appears to be a significantly more effective method for gas production from gas hydrate deposits, leading to earlier gas emergence and significantly larger volumes. This is caused by the speed and effectiveness of the pressure wave in reaching large reservoir volumes.
- 3. Thermal stimulation appears to produce limited gas volumes. This is attributed to the slow rate of heat conduction (the only heat transport mechanism under the conditions of the thermal stimulation study) through the formation.
- 4. In thermal dissociation, production increases with an increasing initial reservoir temperature, an increasing hydrate saturation, and a higher well water temperature. Direct heat addition appears to be more effective than circulation of warm water in the well.
- 5. Under depressurization-induced dissociation, gas volumes produced at a constant well pressure increase with an increasing initial pressure and temperature. An increasing hydrate saturation may lead to severe reduction in the produced volumes because of the adverse permeability conditions that drastically reduce flow to the well.

5. Discussion of Results from Field Tests

The Maurer/Anadarko Hot Ice No. 1 field test was conducted in the winters of 2003 and 2004. During drilling, no hydrates were encountered within the expected hydrate stability zone that extends in the interval from the bottom of the permafrost to about a depth of 1150 m.

Reasons for the absence of hydrates are outside traditional realms of numerical simulation of subsurface processes, and can be best explained by an analysis of regional geology and reservoir conditions. In this section we provide a short discussion addressing some of the issues related to the discrepancy between expectations and field realities, and possible explanations for the observations.

It is not possible to conduct a numerical simulation to illuminate the subject of hydrate absence from the site. The main reason for this inability is lack of knowledge on the processes and sequence of events that lead to hydrate formation and dissociation in natural systems. Without solid evidence on the origin of the gas, changes of climate regimes in the area, changes in regional geothermal gradient, large-scale geological processes (such as zone subductions), it is not possible to reconstruct a credible scenario explaining the absence of hydrates.

A review of the temperature profile in the subsurface indicates that the geothermal gradient is somewhat steeper than generally expected. This leads to a reduction in the size of the gas hydrate stability zone, but the reduction is rather limited and affects the bottom part of the stability field (i.e., decreases the maximum depth where hydrates can occur). Thus, hydrates cannot occur at a depth of 1150 m at the site, but the bottom of the stability zone is rather certain to occur at a depth of 970 m or less. This provides a comfortably wide hydrate-stability zone, about 400 m in thickness.

A review of the texture of the subsurface sediments does not provide any indication of impedance to gas flow. There are several zones within the hydrate stability zone that have desirable reservoir properties, i.e., significant porosity and permeability. Thus, it is rather safe to exclude the possibility of a subsurface barrier to gas flow.

Consequently, the obvious focus of attention has to shift to the issue of resources. The presence of the hydrate stability zone that exists at the site is a necessary, but not a sufficient condition for hydrate occurrence. Therefore, absence of gas hydrates has to be tracked to one possible reason: lack of gas at the site.

An authoritative opinion on the subject can be rendered by reservoir geology specialists with access to detailed information on regional distribution of gas resources, hydrates, and reservoir zones. The presence of hydrates in the vicinity (relatively speaking) of the drilling site suggests that it possible for pre-existing hydrate deposits to have dissociated in response to warming climatic trends, and to have migrated toward the upper parts of the regional reservoir structure (outside the Anadarko property) toward neighboring sites with known hydrate accumulations. It is also possible that hydrate deposits were never present at the site because the available gas volume in the formations was limited, and migrated toward the upper part of the regional structure. In terms of numerical simulation, the multitude of possible hydrate formation scenarios and the non-uniqueness of possible dissociation scenarios at the regional scale do not permit an informed foray into the subject.

6. References

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Figure 1. Temperature distribution in core at t = 5 min (2.5" core)



Figure 2. Temperature distribution in core at t = 10 min (2.5" core)



Figure 3. Temperature distribution in core at t = 15 min (2.5" core)



Figure 4. Temperature distribution in core at t = 20 min (2.5" core)



Figure 5. Temperature distribution in core at t = 25 min (2.5" core)



Figure 6. Temperature distribution in core at t = 30 min(2.5" core)



Figure 7. Pressure distribution in core at t = 5 min, corresponding to temperature distribution of Figure 1 (2.5" core)



Figure 8. Pressure distribution (in Pa) in core at t = 10 min, corresponding to temperature distribution of Figure 2 (2.5" core)



Figure 9. Pressure distribution (in Pa) in core at t = 15 min, corresponding to temperature distribution of Figure 3 (2.5" core)



Figure 10. Pressure distribution (in Pa) in core at t = 20 min, corresponding to temperature distribution of Figure 4 (2.5" core)



Figure 11. Pressure distribution (in Pa) in core at t = 25 min, corresponding to temperature distribution of Figure 5 (2.5" core)



Figure 12. Pressure distribution (in Pa) in core at t = 30 min, corresponding to temperature distribution of Figure 6 (2.5" core)



Figure 13. Pressure distribution (in Pa) in core at t = 5 min when k = 10 mD (2.5" core)



Figure 14. Pressure distribution (in Pa) in core at t = 10 min when k = 10 mD (2.5" core)



Figure 15. Pressure distribution (in Pa) in core at t = 15 min when k = 10 mD (2.5" core)



Figure 16. Pressure distribution (in Pa) in core at t = 20 min when k = 10 mD (2.5" core)



Figure 17. Pressure distribution (in Pa) in core at t = 25 min when k = 10 mD (2.5" core)



Figure 18. Pressure distribution (in Pa) in core at t = 30 min when k = 10 mD (2.5" core)



Figure 19. Effect of medium permeability on hydrate recovery in core when T_m = 0°C (S_H = 85%, D = 2.5")



Figure 20. Combined effects of permeability and a colder mud temperature ($T_m = -5^{\circ}C$) on hydrate recovery ($S_H = 85\%$, D = 2.5"). Consistently higher recoveries are observed.



Figure 21. Combined effects of hydrate saturation on recovery in the 100 mD core. Recovery increases with hydrate saturation.



Figure 22. Pressure distribution in 1000-mD core at t = 5 min (D = 3.345", T = 4°C)



Figure 23. Pressure distribution in 1000-mD core at t = 10 min (D = 3.345° , T = 4° C)



Figure 24. Pressure distribution in 1000-mD core at t = 15 min (D = 3.345° , T = 4° C)



Figure 25. Pressure distribution in 1000-mD core at t = 20 min (D = 3.345° , T = 4° C)



Figure 26. Pressure distribution in 1000-mD core at t = 20 min (D = 3.345° , T = 4° C)



Figure 27. Pressure distribution in 1000-mD core at t = 30 min (D = 3.345° , T = 4° C)



Figure 28. Temperature distribution in core at t = 5 min, corresponding to pressure distribution of Figure 22



Figure 29. Temperature distribution in core at t = 10 min, corresponding to pressure distribution of Figure 23



Figure 30. Temperature distribution in core at t = 15 min, corresponding to pressure distribution of Figure 24


Figure 31. Temperature distribution in core at t = 20 min, corresponding to pressure distribution of Figure 25



Figure 32. Temperature distribution in core at t = 25 min, corresponding to pressure distribution of Figure 26



Figure 33. Temperature distribution in core at t = 30 min, corresponding to pressure distribution of Figure 27



Figure 34. Hydrate saturation distribution in core at t = 10 min, corresponding to pressure and temperature distributions of Figures 22 and 28, respectively



Figure 35. Hydrate saturation distribution in core at t = 15 min, corresponding to pressure and temperature distributions of Figures 23 and 29, respectively



Figure 36 Hydrate saturation distribution in core at t = 20 min, corresponding to pressure and temperature distributions of Figures 24 and 30, respectively



Figure 37. Hydrate saturation distribution in core at t = 25 min, corresponding to pressure and temperature distributions of Figures 25 and 31, respectively



Figure 38. Hydrate saturation distribution in core at t = 30 min, corresponding to pressure and temperature distributions of Figures 26 and 32, respectively



Figure 39. Hydrate saturation distribution in 100-mD core at t = 10 min (all other conditions as in Figure 33)



Figure 40. Hydrate saturation distribution in 100-mD core at t = 15 min (all other conditions as in Figure 34)



Figure 41. Hydrate saturation distribution in 100-mD core at t = 20 min (all other conditions as in Figure 35)



Figure 42. Hydrate saturation distribution in 100-mD core at t = 25 min (all other conditions as in Figure 36)



Figure 43. Hydrate saturation distribution in 100-mD core at t = 30 min (all other conditions as in Figure 37)



Figure 44. Hydrate saturation distribution in 10-mD core at t = 30 min (D = 2.5", T = 9°C)



Figure 45. Effect of initial formation temperature, core diameter and hydrate saturation on hydrate preservation in core



Figure 46. Effect of initial formation temperature on gas production from a hydrate deposit located in the Ugnu formation (thermally-induced dissociation of gas hydrates)



Figure 47. Effect of water well temperature and of method of heat addition on gas production from a hypothetical hydrate deposit located in the Ugnu formation (thermally-induced dissociation of gas hydrates)



Figure 48. Effect of hydrate saturation on gas production from a hypothetical hydrate deposit located in the Ugnu formation (thermally-induced dissociation of gas hydrates)



Figure 49. Effect of initial formation temperature, well water temperature, and method of heat addition on gas production from a hypothetical hydrate deposit located in the West Sak formation (thermally-induced dissociation of gas hydrates)



Figure 50. Effect of hydrate saturation on gas production from a hypothetical hydrate deposit located in the West Sak formation (thermally-induced dissociation of gas hydrates)



Figure 51. Gas production from hypothetical hydrate deposits in the Ugnu and West Sak formations (depressurization-induced dissociation of gas hydrates)



Figure 52. Water production from hypothetical hydrate deposits in the Ugnu and West Sak formations, corresponding to gas production in Figure 51 (depressurization-induced dissociation of gas hydrates)



Figure 53. Effect of hydrate saturation on gas production from hypothetical hydrate deposits in the Ugnu and West Sak formations (depressurization-induced dissociation of gas hydrates)

Appendix C: On-Site Geologic Core Analysis at Hot Ice No. 1 Using a Portable X-ray Computed Tomographic System

By: Barry M. Freifeld and Timothy J. Kneafsey Lawrence Berkeley National Laboratory, Berkeley, CA, USA

Abstract

Hot Ice No. 1 is a dedicated methane hydrate research borehole, located near the Kuparuk Field on the North Slope of Alaska. As part of the on-site core analysis program, a field portable x-ray computed tomography (CT) system was deployed for nondestructively characterizing recovered cores. CT provides information on sediment structure, diagenetic alteration, fractures, flow channels and barriers, porosity, and fluid-phase saturation. Images of Hot Ice No. 1 cores reveal the varied lithologies, which consist of thick sequences of sandstones, mudstones, and conglomerates. A methodology for determining hydrate saturation with high spatial resolution was developed and tested using synthetic hydrate samples. To demonstrate use of CT to quantitatively interpret hydrate kinetic processes, we calculated 95% confidence intervals for density changes occurring during laboratory methane hydrate dissociation experiments. The field deployment of a CT represents a paradigm shift in core characterization, opening up the possibility for rapid systematic characterization of three-dimensional structural features and leading to improved subsampling and core-processing procedures.

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Exhibit A. X-Ray CT Reconstructions Representing 1-mm Vertical Plane Through Lon Axis of Each Core2	g 1

Hot Ice No. 1

The Hot Ice No. 1 drill boring is located south of the Kuparuk River Field and approximately 100 km west of Deadhorse, Alaska. The Hot Ice No. 1 well was drilled as part of a two-year costshared partnership between the U.S. Department of Energy's Office of Fossil Energy, Anadarko Petroleum Corp., Maurer Technology Inc., and Noble Engineering and Development to explore hydrate occurrence on the Alaskan North Slope. The well was spud March 31, 2003, and drilled down to 1403 ft (428 m), when drilling was halted for the season on April 21, 2003. Drilling resumed on January 30, 2004 and the well was cored down to 2300 ft (701 m) on February 7, 2004. No hydrates were encountered during drilling, although a gas-bearing sand within the hydrate stability region (approximately 1510 ft to 1520 ft) could potentially be hydrate-bearing strata.

System Description

The portable x-ray CT was operated as part of a mobile laboratory to nondestructively image cores recovered during drilling operations. A schematic layout and photograph of the portable CT are shown in **Figure 1**. The photograph shown was taken when the CT was installed on the D/V *Joides Resolution,* not on the North Slope. The closet-sized room the CT was installed in at Hot Ice No. 1 had a footprint of 1.5 meters \times 2.3 meters. The room was situated between the core reception/sectioning area, and the main core laboratory. Because of the close proximity between the equipment operator and the x-ray CT, it was critical that the equipment meet the cabinet safe radiological requirements demanded by U.S. CFR 1020.40. The room in which the x-ray CT was operated was kept at temperatures between -10°C and -5°C, to prevent deterioration of the permafrost cores and to minimize dissociation of any recovered hydrates.

The core is installed vertically in the instrument and rotated around its vertical axis. A horizontal gantry holding the x-ray source and detector is raised and lowered by a belt-driven actuator to facilitate imaging selected regions of the core. The x-ray source has a tungsten target and a 250 μ m thick beryllium window, delivering up to 130 kV at 0.5 mA, with a variable focal spot size that increases from 5 microns at 4 watts to 100 microns at 65 watts. Computer control permits adjustment of both anode voltage and current. To be able to efficiently capture the cone-beam projection of the core, we used a dual-field 100 mm/150 mm cesium iodide image intensifier. The image intensifier exhibits some geometrical distortion (commonly referred to as pincushioning) and lacks the dynamic range of available solid-state x-ray detectors, but rapidly acquires images and has high sensitivity. Rapid imaging is important for imaging large numbers of cores and for performing transient studies.

Resolution of the CT system is dependent on numerous system parameters, including x-ray source focal spot size, image intensifier phosphor properties, location of the core between the x-ray source and the image intensifier, CCD camera resolution, and the image intensifier field of view. For the CT images shown in this paper, x-ray spot size varied from 60 to 100 μ m depending on power setting, the image intensifier input window was kept fixed at 150 mm in diameter, and the camera resolution was 768 × 494. With these settings, pixels on the acquired radiographs were approximately 200 μ m², resulting in reconstructed voxels (200 μ m on a side) that have a volume of 8 nanoliters.

To reduce noise and increase dynamic range of the system, great care was taken to optimize the x-ray beam path for core imaging. A beam collimator mounted on the x-ray source was used to minimize albedo, which degrades image quality. To reduce camera noise, multiple frames are acquired and averaged without moving the object, leading to a noise reduction proportional to the square root of the number of frames. Ten frames acquired over a 0.4second period was considered a reasonable trade-off between speed and image quality for the images acquired in this paper, although that number can be adjusted to match the requirements of a user's particular application.

As part of the beam collimator, a computer-controlled copper shutter mounted in front of the beryllium exit window can optionally be used to reduce the soft x-ray content of the beam. This is normally only performed at energies above 100 kV to reduce the influence that the effective atomic number has on x-ray attenuation, and lead to more precise density estimates. Below 100 kV, there is a significant component of photoelectric absorption, which is proportional to effective atomic number. Reducing the x-ray voltage (softer x-rays) results in increased photoelectric absorption and serves to highlight contrasting media and differences in fluid-phase saturation. This also leads to greater uncertainty in the density estimates because of increased beam-hardening effects (filtering of soft x-rays). A concise discussion of the effects of spectral energy, including implications for core analysis, is provided by Wellington and Vinegar [1987].

An aluminum compensator (**Figure 2**), installed between the sample and x-ray imager, reduces the dynamic range of the x-rays incident upon the image intensifier and increases sensitivity to attenuation variations within the sample. Because of the geometry of passing a cone-shaped beam through a cylindrical object, the x-rays passing beyond the outside edge of the core holder are not attenuated by the object; thus, the compensator is thickest in this region. By greatly attenuating the x-ray beyond the edge of the core holder, the aluminum compensator eliminates image blooming, an image defect that involves pixels on a CCD approaching their electron charge capacity and spilling over into nearby pixels, washing out the image. Where the core is thickest, in the center, the attenuator is thin, providing minimal additional attenuation of the x-rays. The result is an image of fairly uniform intensity striking the image intensifier. The aspherical compensator is designed using a fan-beam x-ray path simulation, assuming a core of uniform density. The slight variation in attenuation that occurs along the vertical axis of the core (as x-ray cone-beam angle increases) is ignored.

While the qualitative benefits of using the compensator have been mentioned above, **Figure 3** provides a quantitative example of how density resolution can be improved by using the compensator, without having to resort to cameras with increased dynamic range. For this discussion, it should be mentioned that every radiograph is composed of pixels with an intensity spanning a range that can be digitally represented, i.e., 10 or 12 bits. Similarly, a dynamic range, or bit depth, can be assigned for any region of interest. The dynamic range of a region of interest will be less than or equal to that of the whole image. As noted previously, without the compensator in place, a large variation in intensity occurs, from the outside of the core image to the inside. With the compensator in place, the dynamic range across the image is reduced, and greater contrast can be seen in any particular region of interest.

Figure 3 shows radiographic images of sandstone cores taken with the x-ray energy set below the threshold at which significant image blooming occurs, along with a histogram of pixel intensity for the region of interest enclosed in the white rectangles. The image taken without using the compensator was taken with the x-ray source set to 90 kV and 250 μ A, whereas the image with the compensator was taken at 110 kV and 300 μ A. For the region of interest without the compensator, the histogram reveals an image bit depth of 6 bits. The image with the compensator has a bit depth of 7.7 bits, representing a more than three-fold increase in the xray attenuation resolution. The increased performance provided by the compensator is significant. The aluminum compensator also contains milled flats that extend beyond the edges of the acylindrical region, used for correcting for fluctuations in x-ray tube intensity. By normalizing each image by the average image intensity in the reference region, one source of errors in density estimates is eliminated. This is particularly important for experiments that span long time periods, such as petroleum core floods, which can span several weeks duration. Note that large variations in x-ray current can be corrected for using this method, but because of photoelectric absorption, changes in x-ray voltage beyond small ripples produce nonlinear changes in the image intensity. Thus x-ray tube current can vary over a broad range and all of the images can be normalized to each other. Any change in the voltage setting, however, will require an independent system calibration for each selected voltage.

The image reconstruction software, Imgrec (developed at Lawrence Livermore National Laboratory), was employed to perform fan-beam convolution back projection (CBP) and Feldkamp reconstruction of the acquired cone-beam radiographs [Feldkamp et al., 1984]. The CBP algorithm is used for rapid reconstruction of acquired radiographs to verify correct parameter settings (only a few seconds are required to reconstruct a single horizontal slice), but does not account for the divergent cone-beam projection geometry. This limits CBP to the region near the radiograph's mid-plane. The Feldkamp algorithm corrects for the divergent cone beam geometry and can be used to accurately reconstruct images with x-ray projection angles up to 6 or 7°. However, beyond that point, the approximations that make the Feldkamp algorithm computationally tractable result in noticeable geometric distortions. The images shown here have used cone-beam angles from 6 to 10°. Reconstruction of 180 radiographs into a 10-cm three-dimension volume data set takes approximately 10 minutes on a 3-GHz PC. For either the CBP or the Feldkamp algorithm, it is important to acquire both a dark image from the camera (an image with the x-ray beam off) and a background image (where no object is in the beam path), which is subtracted from subsequent images of the object to account for x-ray intensity variations across the imaging plane.

Several innovations in the CT system make it both portable and radiologically safe for use in a core laboratory. The key to transportability is minimizing the volume enclosed within lead shielding. The usual shielding method for a fixed system, encapsulation of the entire unit or room within a lead enclosure, would have resulted in a unit of limited portability. We minimized the shielding required to enclose the x-ray path, by forming a cross that translates along the core axis (see Figure 1). One arm of the cross encompassed the main x-ray beam, and the other arm reduces radiation scattered along the core axis. To permit loading and unloading of the core, we split the vertical arm of the cross, allowing it to open and close by telescoping back over the horizontal arm. The entire system is designed to meet the United States radiological requirements for a cabinet safe system (U.S. Title 21 Code of Federal Regulations §1020.40). Redundant safety interlocks are located both on the access door and the shielding, to prevent energizing the x-ray unit while personnel are manipulating the core.

To convert x-ray attenuation to density, we scan the reference materials and perform a threedimensional CT reconstruction. A slice from a CT reconstruction of a calibration standard containing a variety of materials is shown in **Figure 4**. This standard consists of a 7.62 cm diameter PVC cylinder with a series of vertical holes, each of which contains a rod of different materials. For this standard, **Figure 5** shows density versus attenuation, along with regression analysis of the data. The data for PVC are not used for creating the calibration curve, because the high atomic number of chlorine contributes to a significant photoelectric absorption component in the x-ray attenuation, resulting in an overestimated density. The CT reconstructed image of the calibration cylinder displays artifacts and aberrations that are worth noting. Geometrically, because of image intensifier pin-cushioning, there is some visible elongation of the reference rods, which should appear circular. This aberration can be removed by remapping the pixels on each radiograph to eliminate the distortion prior to performing CT reconstruction. Quantitatively, there are negligible changes in the estimated material densities due to geometrical distortion. Beam-hardening, due to the polychromatic nature of the x-ray beam, is a reconstruction artifact responsible for the PVC cylinder appearing brighter in the center than at the edges. Unlike typical beam-hardening that make the outer edges of an object appear more dense (since it attenuates soft x-rays) and the center appear less dense (due to the interaction with harder x-rays), the aluminum compensator adds a counterintuitive beam-hardening aberration. This is because the background correction image used to normalize for intensity variation across the image intensifier suffers from beam-hardening effects, making the image appear disproportionately dark at the edges and bright at the center. The background corrected CT core images thus appear bright (less dense) at the edges, and dark (more dense) in the center.

There are several ways to eliminate or correct for beam-hardening effects when using the compensator. The simplest method is to perform a polynomial correction to the radiographs that removes the beam-hardening trend. This is the method that has been applied to the images in this paper. The second method, which will be carried out in the future, is to design the compensator using a polychromatic ray-path simulation.

Imaging Synthetic Hydrate

Prior to the initial mobilization to Hot Ice No. 1, hydrate dissociation studies were conducted using the x-ray CT scanner to spatially and temporally track the conversion of methane hydrate to methane and water ice. Synthetic methane hydrate samples were used. **Figure 6** shows a simplified schematic of the hydrate dissociation experiment. Synthetic hydrate was manufactured by the method detailed in Stern et al. [1996] and combined with water, ice and sand in a sealed pressure vessel. Hydrate dissociation, stimulated by allowing room air to warm the sample in the pressure vessel, was monitored by measuring temperature and pressure and periodically acquiring CT data [Freifeld and Kneafsey, 2003]. The goal was to determine how sensitive CT imaging is to spatial and temporal changes that occur during the hydrate dissociation process, so that these measurements can be applied to natural hydrate-bearing samples recovered during the Hot Ice No. 1 coring operation.

Figure 7 shows a sequence of reconstructed CT slices tracking the progression of dissociation of synthetic methane hydrate. Differential images, created by subtracting the baseline image from subsequent images, are used to highlight relatively subtle changes in density as dissociation progresses. The difference in the images taken prior to the start of the dissociation process, and after dissociation is complete (as verified by the pressure in the vessel), yields estimates of total hydrate saturation and spatial distribution. Quantifying hydrate dissociation changes in the CT data depends on accurate system calibration, and high resolution densiometry. Since any one voxel has considerable noise, confidence in density estimates can be increased by averaging multiple voxels, assuming that the region averaged over is homogeneous, and any variation in measured attenuation results from normally distributed noise. The 95% confidence interval for an estimate can be expressed as

$$\rho_{0.95}(x) = \rho(x) \pm t_{0.95,n} \frac{\sigma}{\sqrt{n}}$$

where n is the number of voxels, σ is the standard deviation of density estimates, and *t* is Student's *t* distribution. Water ice is used as a reference material because its density will remain constant throughout this experiment. The 95% confidence interval for estimating the density change for the water ice is shown in **Figure 8a** as a function of the length of a cubical region of interest. As the cubic region of interest is increased to a few millimeters in length, the uncertainty declines to ±0.01 g/cc.

Figure 8b shows the 95% confidence intervals for hydrate density changes during dissociation as a function of cubic region of interest, taken at three different times after the start of the experiment. As the hydrate dissociates and methane gas evolves, the density of the hydrate is seen to decrease. At the start of the experiment, the density of the methane gas encaged in the porous hydrate is calculated to be 0.084 g/cc, based on the stoichiometric ratio between water and methane. The density reduction as calculated from the x-ray images at 44 minutes, after dissociation concluded, is 0.088 g/cc. These density changes rely upon an initial baseline CT calibration curve, using regions of interest containing sand, hydrate and ice and their known densities. Figure 8b shows that even though x-ray CT system resolution may be 200 μ m, if the objective is to determine small changes in hydrate saturation, then the smallest region of interest that yields reasonable confidence has a minimum spatial dimension of approximately a 2.5 mm cube, or roughly 2,000 voxels.

Hot Ice No. 1 Core

The sedimentary structure at Hot Ice No. 1 contains thick sequences of conglomerates, sandstones, mudstones, and coals. Coring operations recovered no hydrates, which was corroborated by standard geophysical logs and the general absence of finding significant thick gas bearing formations. The core recovered from the gas bearing region between 1510 ft to 1520 ft did not exhibit any indication of containing hydrates, although it can not be conclusively ruled out that dispersed hydrates did not dissociate during core retrieval. X-ray CT images were acquired of 185 one-meter-long core tubes. The only operational problem to arise with the x-ray CT from work at the Arctic Platform Mobile Laboratory in a space maintained at -10°C to -5°C, was the failure of a coating on one of the objective lenses in the image intensifier during the 2003 drilling season. The coating appeared to delaminate, causing a distortion in one portion of the image. It is possible that this damage occurred during transport and set-up, when the imager was exposed for a limited duration of time to -40°C. This problem did not occur when the system was operated at the warmer, 2°C to 6°C temperatures within the Ocean Drilling Program's Gulf Coast Core Repository or reoccur during the 2004 drilling season. As a result of the failure of the coating of the lens, the images acquired from Hot Ice No. 1 during the first drilling season (down to 1403 ft MD) had a characteristic of being brighter near the center in an ellipsoidal region and darker at the edges.

Exhibit A (at end of this report) contains x-ray CT reconstructions that represent a 1-mm thick vertical plane running through the long axis of each core. These images are reduced in resolution from the available full size data sets that have been reconstructed from the x-ray attenuation images. Because the data sets are true three-dimensional estimates of density, image planes can be displayed in any orientation. Typically the images are either horizontal slices through the core as seen in Exhibit A, or vertical slices. As vertical slices, each CT reconstruction data set contains 400 200-µm thick planes. These images reveal the sequences of major lithologies: sandstones, mudstones, conglomerates and coals. For the images acquired between ground surface and 1400 ft MD, each subimage, denoted by horizontal lines, represents a section that is 9.5 cm long. For the images below 1400 ft MD, each subimage is 6 cm long. The subimages are stacked together to give the impression of a continuous core.

Reconstructed CT images reveal the textural features of the core. Figure 9 shows vertical and horizontal CT images taken of three different core samples collected during Hot Ice No. 1. Figure 9(a) shows vertical CT images of an unlithified sand with numerous mollusk-shell fragments. The dense (bright) region near the top of the core is an iron claystone concrete. Figure 9(b) shows horizontal CT images of a conglomerate cemented in a sand/ice matrix bearing numerous ice lenses. Individual gravel-sized fragments and small claystone clasts are visible. In Figure 9(c), horizontal CT images reveal the dense mussel fossils contrasting with the lower density fine sand matrix.

Images were reconstructed from a series of either 60 or 180 radiographs. The images reconstructed from 60 radiographs lack the higher resolution of the images reconstructed from 180 images, but still allow for assessment of density and show gross structural features. The CT reconstructions from 180 radiographs can resolve features as small as 200 µm. Calibrations during the first Hot Ice No. 1 drilling season were performed using a reference standard that consists of three different density materials: a 50% MeOH 50% H2O standard (density 0.937 g/cc), a 20/40 mesh sand saturated with MeOH (density 2.025 g/cc), and a dry 20/40 sand (density 1.75 g/cc). During the second drilling season at Hot Ice No. 1 a plastic calibration standard containing vertical cylinders of reference materials was used. Figure 4 shows an x-ray CT image of a horizontal slice through this reference standard. A graph of a calibration performed with this standard is shown in Figure 5.

Density Logs

To create a density log, reconstructed images were corrected for variations in apparent density due to x-ray artifacts. The most significant artifact is caused by the use of the compensator to normalize the beam across the imaging plane. Without the compensator, the beam would be overexposed at the edge and underexposed at the center and significant data would be lost. Most of the influence of the compensator is corrected for by performing a background correction. This is performed during the creation of attenuation radiographs (the natural log of the image radiograph) by subtracting off the log of the background image. The background image is the image acquired at the same x-ray beam potential with no core in the beam path. Since this image needs to be acquired without a core in place, the beam current is turned down considerably to prevent overexposure of the image intensifier. The background image subsequently needs to be multiplied by the ratio between beam currents used for acquiring the core images and the background image. Because of beam hardening and the use of the compensator, a background correction still leaves the center of the core apparently more dense then the edge. This effect is normalized by dividing the core image by a polynomial correction that accounts for the radial trend in apparent core density. The images shown in **Figures 10**, **11**, and **12** show density logs next to x-ray CT reconstructed images of the core.

Figure 10 reveals textural features in a mudstone core recovered from 137.5 to 139 ft MD. The bright streaks are mineral secondary precipitates that occur in subhorizontal and subvertical planes. The density log was created by plotting the density in a series of 1-mm³ voxels (each represents 125 averaged 200 µm³ voxels) taken near the midline of the cores vertical axis.

A CT image of permafrost sandstones in recovered at Hot Ice No. 1 (692 ft MD and 1298.9 ft MD) is shown in Figures 11 and 12. The figures show vertical planes through the core. Each image results from averaging five 200 µm thick vertical slices taken near the cores midline. The core in Figure 11 displays numerous interbedded laminae, ranging from wispy millimeter-sized fining layers, as displayed at 692.2 ft MD, to organic interbeds containing small claystone clasts as seen at 693.0 ft MD. The dark subhorizontal feature near the top of the core is an ice lens.

Ice lens were observed throughout the permafrost and were typically horizontally oriented. Changes in bedding strike and dip are clearly visible and can be used to define strike set thicknesses for various sedimentary layers. Sandstone recovered from near the base of the permafrost is shown in Figure 12. Only very subtle changes in density shown as slight contrasts in subhorizontal planes were noted, although there was significant fracturing that can be attributed to stress relief during core recovery and handling.

Conclusions

X-ray CT imaging of recovered core adds significantly to the amount of information that can be systematically obtained in the field. High-resolution images of whole core permit intelligent subsampling locations to be chosen so that they either intersect or avoid specific features. The portable system detailed here offers significant improvements in image quality over previous x-ray CT systems by incorporating specially designed collimators and filters to optimize the x-ray beam path.

By minimizing the sample volume enclosed by radiation shielding, carefully selecting ruggedized components, and by severely limiting infrastructure requirements, the x-ray CT we developed is able to be easily transported and operated. The vertical core orientation minimizes the footprint of the instrument, so that it can be easily incorporated into working lab space. Performing imaging at the drilling location ensures collection of the highest quality data, before transport and storage lead to core degradation.

The x-ray CT has been shown to be extremely sensitive to changes in density – on the order of ± 0.01 g/cc. For imaging hydrates, a time sequence of difference images has been used to track reductions in hydrate saturation with high spatial resolution in synthetic samples. This technique can be used to determine the distribution of hydrates in natural hydrate-bearing core. By carefully controlling pressures and temperatures during this process, an understanding of hydrate thermodynamics and dissociation kinetics in porous media can be gained.

While the portable CT system shown here represents a paradigm shift from previous systems, numerous areas are open for continued development. These areas include incorporation of dual-energy techniques for mineral identification and improved density estimation, data mining software for identifying particular features or structures, and integration of the CT system into multiproperty measurement systems. The interface for accessing the enormous volume of data acquired in high-resolution three-dimensional imaging needs improvement, requiring advances in data handling and interpretation software.

Acknowledgments

This work was supported by the Assistant Secretary of the Office of Fossil Energy, Office of Natural Gas and Petroleum Technology, U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The project was performed in collaboration with Anadarko Petroleum Corp., Maurer Technology Inc., and Noble Engineering and Development.

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Figures





Figure 1. (a) Schematic layout of portable x-ray CT system. (b) CT system installed in Bridge Deck *Joides Resolution* core laboratory for ODP Leg 210.

(b)



Figure 2. An aluminum acylindrical x-ray compensator used to increase sensitivity of the x-ray CT by reducing variation in intensity of the image striking the image intensifier. The flat regions at the edge of the compensator provide a reference area on each radiograph for normalizing for variations in x-ray intensity.



Figure 3. Radiographs taken with and without the aluminum x-ray compensator. Histograms for the mid-region of each image show how the compensator permits use of greater x-ray energy resulting in a broader distribution of pixel values. This translates into CT reconstructions with greater density resolution.



Figure 4. A single horizontal slice from a CT reconstruction of a cylindrical density reference standard.



Density Calibration

Figure 5. Linear regression of mean attenuation values obtained using a density reference standard containing an assortment of materials. The PVC data point is not used in the regression because the high effective atomic number of the chlorine atoms increases the attenuation.


Figure 6. A simplified schematic of a hydrate dissociation experiment.



Figure 7. X-ray CT images of a synthetic hydrate dissociation experiment. The baseline image shows the location of hydrate and water ice in a sand matrix. The difference images reveal the progression of dissociation within the hydrate nodules. The gray scale bar only applies to the difference images. Rectangular highlighted regions in the difference image, acquired at 61 minutes, were used to calculate changes in hydrate density.



Figure 8. (a) Estimated change in density for water ice used as a reference material in a hydrate dissociation experiment, showing the upper and lower 95% confidence intervals as a function of region of interest size. Density changes were calculated using the difference between the baseline CT data set and a data set acquired after 44 minutes. The expected change is 0.0 g/cc. (b) Time progression for changes in density of hydrate as dissociation progresses, expressed with upper and lower 95% confidence intervals as a function of region of interest size. The final data set, taken at 44 minutes, was acquired after dissociation was determined to be complete by independent pressure measurements.



Figure 9. X-ray CT images of core recovered at Hot Ice No. 1. (a) Vertical slices through an unlithified sand, with abundant fossil shells. The large bright region is a clay ironstone concrete. The rounded dense objects are quartz pebbles. (b) Horizontal images of a permafrost conglomerate cemented together by a sand/ice matrix. (c) A sandstone core with abundant mussel fossils.



Figure 10. Hot Ice No. 1 mudstone core (137.5 ft to 139 ft) showing the density profile averaged over 1-mm³ regions of interest. The profile reflects density along a vertically oriented line along the core's long axis. The vertical and horizontal virtual detail images reveal a filamentary network of secondary mineral precipitates.



Figure 11. A sandstone core from Hot Ice No. 1 showing the density profile for the core averaged over 1-mm³ regions of interest vertically oriented along the cores long axis. Reductions in density due to organic laminae (692.6 ft and 693.0 ft) and increases in density due to reduced porosity fine sand laminae (692.2 ft) are evident.



Figure 12. Sandstone core near the base of the permafrost showing the density profile averaged over 1-mm³ regions of interest, vertically oriented along the cores long axis. The upper detail reveals very subtle subhorizontal laminations. The lower detail shows a rounded gravel, approximately 3 cm in diameter, in the sandstone matrix.

Exhibit A. X-Ray CT Reconstructions Representing 1-mm Vertical Plane Through Long Axis of Each Core











































Hydrate Reservoir Characterization & Modeling 27 Appendix C









































Appendix D: Investigating Methane Hydrate in Sediments using X-Ray Computed Tomography

By: Barry M. Freifeld and Timothy J. Kneafsey Lawrence Berkeley National Laboratory, Berkeley, CA, USA

Keywords: gas hydrate, x-ray tomography, core imaging, hydrate kinetics

Abstract

A portable x-ray computed tomography (CT) system constructed for imaging core at drill sites was used to characterize methane hydrate within porous media. A series of experiments was performed using synthetic methane hydrate in a sand matrix, demonstrating the capabilities of x-ray CT imaging to spatially and temporally track hydrate dissociation. The method is demonstrated to be sufficiently sensitive to image and measures density changes in millimeter-sized nodules of hydrate in full-size (75 millimeter whole round) core. Portability of the imaging system is significant because it allows field deployment of the measurement system, thus avoiding the difficulties and uncertainties associated with preservation, storage, and transport of methane-hydrate-bearing samples. Determining the CT system's sensitivity to changes in hydrate saturation was a goal in conducting these experiments. Confidence intervals for estimating hydrate saturation changes have been established based on the volume of the region of interest. For a hydrate nodule as small as a few millimeters in diameter, dissociation of 10% of the contained methane can be discerned.

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Introduction

Thermal and kinetic properties of naturally-occurring hydrates are important to evaluate whether a hydrate deposit can be exploited as an economic resource [1]. Investigation of hydrate in sediment samples has been performed using visual and microscopic examination [2], x-ray diffraction [3], Raman spectroscopic methods [4], and x-ray computed tomography (CT) [5][6]. The most common experimental method employed to investigate hydrate kinetics consists of measuring gas production (or uptake) from a dissociating (forming) hydrate sample, while monitoring sample pressure and temperature [7][8][9]. By starting with hydrates of known grain size, researchers have developed kinetic models of hydrate dissociation based on assumptions of hydrate grain geometry. Unfortunately, batch experiments reveal little about processes as they occur within heterogeneous, natural samples. To understand the influence that the sediment matrix has on entrained hydrate, researchers require a nondestructive technique to visualize hydrate processes within the sample.

Using a medical x-ray CT scanner, Mikami et al. [5] showed dissociation occurring in an unlithified sand sample containing natural hydrate that was retrieved from the Mallik 2L-38 gas hydrate research well. This work was significant because it demonstrated the ability for x-ray CT to spatially and temporally track hydrate dissociation. Gas production was measured using a gas flow meter. Freifeld et al. [6] used a medical scanner to track an advancing dissociation front created by thermal stimulation of a synthetic hydrate/sand mixture. This work compared the amount of gas evolved with the observed spatial progression of the dissociation front through a cylindrical sample. Location of the hydrate dissociation front was compared to a simple moving boundary model that incorporated the latent heat of dissociation. The effective thermal conductivity of the hydrate/sediment mixture was estimated based on the velocity of the phase change boundary.

The purpose of this paper is to describe a series of experiments performed using a portable xray CT system to quantify the dissociation process in a synthetic methane hydrate-sand system. It differs significantly from previous work, demonstrating the use of the CT system to estimate the quantity of hydrate dissociated with high spatial resolution, independent of pressure or gas flow-rate measurements. Gas production is still used to quantify the total amount of hydrate contained within the sample, but this measurement is independent of the CT system's independent determination of the percentage of hydrate dissociated both spatially and temporally throughout the sample. Tracking dissociation with detailed spatial information is important for understanding (at a macroscopic level) the influence hydrate/sediment textural fabric has on the hydrate dissociation process. Such tracking can also answer important questions about whether dissociation is a kinetic or equilibrium process. Portability of the x-ray CT scanner is significant because it allows for hydrate dissociation experiments to be performed at the location of core recovery. This overcomes the difficulty of having to preserve the hydrates at high pressures and low temperatures for transportation to a remote laboratory.

X-ray Imaging System

Geometry and layout of the portable x-ray CT system are shown in **Figure 1** [10]. The most significant advantage of this system over the more commonly used medical style CT scanners, which typically scan 1 slice at a time, is that a 10 cm volume of core can be imaged simultaneously at high resolution. This is important for imaging transient processes, such as hydrate dissociation, since it allows rapid imaging of a large volume.

To obtain complete volumetric information, we perform a computer reconstruction on 180 radiographic images, acquired using a 2° rotation of the core between each image. The

resulting volumetric data set consists of an x-ray attenuation assigned to each 200 μ m voxel, or volume element. By calibrating to known standards, we can convert attenuation to density. To accurately discern small changes, we employ the technique of differential imaging, whereby all images acquired are subtracted from a baseline image set.



Figure 1. Schematic layout of the portable x-ray CT unit

For the experiments presented here, the beam energy was set at 130 kV and 200 μ A. Because the x-ray beam is polychromatic, it will undergo beam-hardening as it transverses the sample, and soft x-rays will be more attenuated, yielding a beam containing a steadily higher proportion of harder x-rays. Without being corrected, beam-hardening makes the center of the sample appear denser than the outer edges. To reduce beam-hardening aberrations, we placed a 1.6-mm thick copper between the x-ray beam and the sample being imaged. The reconstructed image is post-processed using a polynomial correction to remove beam-hardening artifacts that the copper filter does not eliminate.

Methane Hydrate Dissociation Experiments

Methane hydrate dissociation experiments were performed using cylindrical synthetic porous methane hydrate samples. For brevity, two of them will be shown here. The 28.6-mm diameter cylinder of synthetic, 30%-porosity hydrate was fabricated by the USGS in Menlo Park, California by the process detailed in Stern et al. [3]. To preserve the hydrate and prevent dissociation, the hydrate was initially stored in a refrigerator at -80°C and then transported in a liquid nitrogen (LN) dry shipping dewar to Berkeley Lab.

In each of the experiments, synthetic hydrate was added to a matrix of 12/20 mesh Ottawa sand. To prevent hydrate dissociation while preparing the sample at atmospheric pressure, we cooled the sand and hydrate using LN. Ice made from de-aired water and cooled with LN was

used as a reference material. Ice provides a stable reference material because of its low porosity, only influenced by thermal expansion as it warms. The unconsolidated sand is susceptible to thermal-mechanical effects and changes in the density of the gas in the pore space as the sample warms and hydrate dissociates. Early in the experiment, apparent density of the unconsolidated sand will be influenced by LN evaporation and the release of sorbed nitrogen.

The sand, hydrate, and ice samples were placed in a high-density polyethylene bottle (7.0 cm diameter × 12.7 cm high) and placed in an aluminum pressure vessel for imaging. Figure 2(a) shows an idealized schematic of the experimental set up, and Figure 2(b) shows a photograph of the pressure vessel used to hold the sample during x-ray CT scanning. Actual geometry of the hydrate and ice contained within the samples are shown in the reconstructed CT images.



Figure 2. (a) Schematic of hydrate experiment and (b) pressure vessel used to hold hydrate sample during CT scan. Note thermocouple wires and pressure gage on top end cap.

Pressure in the closed vessel was monitored using a pressure gage to track the amount of hydrate dissociated. A thermocouple installed near the center of the sand/hydrate mixture provided a local indication of sample temperature. The exact thermal profile within the pressure vessel was unknown. However, temperature as reported lagged average temperature of the sample, which lay close to the temperature indicated by the thermocouple, but somewhere between the indicated temperature and room temperature. This was clearly the case, because pressure in the vessel increased, indicating hydrate dissociation, prior to the indicated temperature rising above the hydrate stability temperature (-76°C at 0.1 MPa).

Dissociation was induced by allowing the sample to warm through the stability point using room heat. Temperature and pressure were recorded using a thermocouple with a digital readout and a borden tube pressure gage. Acquiring a set of 180 CT radiographs took 3 minutes, and was performed approximately every 10 minutes. (The experiment conditions are presented in **Table 1**.) The Feldkamp reconstruction algorithm was applied to the radiographic data to give volume density information. For each reconstructed data set, a file containing $430 \times 430 \times 400$ voxels was created, each element representing the density of a 200-µm cubical volume element.

First Experiment

The first dissociation experiment used a 32-mm long section of the 28.6-mm diameter porous hydrate sample. A cube of water ice made from de-aired water was used as a reference

material. **Figure 3** shows vertical and horizontal cross sections from reconstructed CT images, revealing the layout of the sample. The thermocouple junction is located at the tip of the temperature probe in the sand close to the water ice. Measured pressure and temperature are plotted in **Figure 4(a)**. The time indicated is referenced to the time the baseline set of CT images were acquired. The pressure rise that occurs prior to acquisition of the baseline image set is due to the boiling of residual LN in the sample. When pressure in the vessel stopped increasing (at about 40 minutes), dissociation was considered complete. **Figure 5** shows a horizontal slice taken through the hydrate cylinder in the sand matrix, along with difference images calculated by subtracting later images from the baseline image. The bright spot near the hydrate is caused by the stainless steel sheath around the thermocouple wires.



Figure 3. (a) Vertical and (b) horizontal cross-sections taken during Experiment 1 revealing hydrate and ice in a sand matrix

Second Experiment

The second dissociation experiment used a 19 mm long section of the 28.6 mm diameter hydrate. Prior to mixing with sand, the hydrate was broken into several pieces of assorted sizes. The smallest clearly discernable hydrate piece was approximately 2.4 mm \times 3.2 mm \times 4.8 mm, having a total volume of about 0.037 cm³. Similar to Experiment 1, a cube of ice was used as a reference standard. **Figure 4(b)** shows measured pressures and temperatures. **Figure 6** shows a horizontal slice taken through the sample, with the baseline image revealing various nodules of hydrate and the one large water ice piece. The difference images were calculated by subtracting subsequent images from the baseline image.



Figure 4. Pressure, temperature, and percent hydrate dissociated, as estimated from x-ray CT images, for (a) Experiment 1 and (b) Experiment 2

Discussion

Pressure and Temperature Data

Pressure and temperature data recorded for each experiment are presented in Figure 4. Table 1 shows the estimated moles of methane gas evolved calculated using the measured increase in gas pressure and the gas-filled volume of the pressure vessel. Both experiments show increases in pressure prior to when the temperature of the sample was above the dissociation temperature for the hydrate. This early rise is due to the nitrogen boiling off. The subsequent increases in pressure were due to hydrate dissociation. The evolved gas volume, estimated using the ideal gas law, roughly matches the known volume initially contained by hydrate for these two experiments.

Table 1. Experimental Conditions						
Experiment	Hydrate Geometry	Hydrate Volume (cm ³)	Moles Methane	Estimated Methane Evolved (moles)		
1	Cylindrical segment	20.4	0.12	0.13		
2	Nodules	12.2	0.074	0.053		

rimontal Conditions

CT Data

CT data were collected periodically during the dissociation experiments. **Figures 5** and **6** show a baseline image and difference images for Experiment 1 and Experiment 2, respectively. Significant reductions in hydrate density were observed during dissociation, whereas only minor changes in the density of ice and the bulk density of sand were observed. Percent hydrate dissociated for each experiment was estimated using measured attenuation data from a volume of interest in the interior of the hydrate and plotted along with temperature and pressure on **Figure 4**. These regions are highlighted on the last difference image shown for each experiment. The volume of interest for Experiment 1 was a central region of the cylindrical hydrate sample. For Experiment 2, which contained many small hydrate nodules, the percent dissociated was based on an average of three different interior volumes. To convert from x-ray attenuation to density, a calibration used the measured x-ray attenuation from the baseline image for the known materials: sand, hydrate and water ice.



Figure 5. Sequence of horizontal images from Experiment 1. Baseline image shows cylinder of hydrate surrounded by sand. Subsequent images are differences taken from the baseline image. Dissociation starts as a faint halo at edge of hydrate, steadily progressing throughout hydrate. The black circle indicates the region of interest used to calculate the change in hydrate density.

Difference images from Experiment 1 (**Figure 5**) show the dissociation of a single large cylinder of hydrate. A small halo at the edge of the cylinder first appears in the difference image acquired 15 minutes after baseline. Dissociation progresses inward. The image at 24 minutes

shows a continuous ring of dissociated hydrate at the edge of the cylinder with more pronounced dissociation at the warmest area, the edge closest to the pressure vessel wall. At 34 minutes, dissociation has occurred throughout the entire volume of the hydrate, with only a slight change noticeable at 43 minutes. The final image, at 61 minutes, reveals a drastic reduction in density at the edges of the hydrate cylinder and the estimated percent hydrate dissociated has jumped up to 130% of the theoretical value. This large reduction in density results from mechanical expansion of the sample. The bright ring around the final image shows the increase in volume of the original hydrate cylinder, now consisting of water ice.



Figure 6. Sequence of horizontal slices from Experiment 2, showing both methane hydrate and water ice in a sand matrix. All images after baseline have been differenced with baseline image. Rectangles in last image (61 min) show regions of interest used to calculate change in hydrate density.

Difference images from Experiment 2 (**Figure 6**) show changes similar to those from Experiment 1. Dissociation occurs in the hydrate nodules earliest near the walls of the pressure vessel and progress inward. The image acquired at 28 minutes shows that hydrate at the edge of the vessel has undergone significant reduction in density, whereas the interior hydrate nodules are unchanged. At 35 minutes, dissociation is visible throughout the hydrate, becoming more pronounced at 44 minutes. The image acquired at 61 minutes shows a large density reduction (130% of the expected value for hydrate dissociation), again accompanied with apparent displacement of sand and expansion of the hydrate sample.

Experimental Uncertainty

There are numerous sources of noise, error, and uncertainty in the estimation of density from xray CT images. Some of these errors are systematic and arise from the reconstruction process, since the Feldkamp Algorithm used for processing the data is an approximate method. These can be corrected during postprocessing. Beam hardening is one of the largest sources of error in making accurate density estimates. To eliminate beam hardening beyond what is removed by passing the x-ray beam through a copper filter, the reconstructed data set is normalized using a polynomial that is a function of the distance from the rotational axis of the core sample. To perform this correction, we normalize the reconstructed image set by the reciprocal of the beam-hardening trend, fitted by a second-order polynomial.

Other errors, such as camera noise, are Gaussian, and can be quantified using standard statistical analysis, so that confidence intervals can be determined for the density estimates. There is a significant amount of error in any one 200-µm cubical voxel. The 95% confidence interval for a density estimate can be expressed as:

$$\rho_{0.95}(x) = \rho(x) \pm t_{0.95,n} \frac{\sigma}{\sqrt{n}}$$

where n is the number of voxels, σ is the standard deviation of measured voxel densities, and t is Student's t distribution. The 95% confidence interval for estimating the density change for the water ice in Experiment 2 is shown in **Figure 7(a)** as a function of the length of a cubical region of interest. The density estimate as one approaches a region a few millimeters in length decreases to an uncertainty of approximately ±0.01 g/cc. For the ice shown, no change in density is expected. Similarly, confidence intervals for a region in the interior of a nodule of hydrate in Experiment 2 are shown in **Figure 7(b)** for each of the acquired image sets. Changes in hydrate saturation of 10% can easily be discerned for regions of hydrate greater than a few millimeters in diameter.

Conclusions

We have used x-ray computed tomography to determine spatial distribution of hydrates in whole-round cores with high resolution. By repeatedly imaging the same section of core as dissociation occurs, hydrate kinetics can be investigated. Because the location of the dissociation front represents a region of known thermodynamic conditions, locating and tracking movement of the front provides information on rates of energy flux and mass transport. Estimation of density confidence intervals indicates that even relatively modest reductions in hydrate saturation can be accurately determined. Future studies will use the x-ray CT to measure hydrate kinetic parameters and determine thermal parameters of hydrate sediment systems.



95% Confidence Interval

Figure 7. (a) Estimated change in density for water ice in Experiment 2 with upper/lower confidence intervals as function of region size. (b) Reduction in hydrate density during dissociation. Density changes were estimated using attenuation data contained within a cubical region of hydrate in Experiment 2.

Acknowledgments

This work was supported by the Assistant Secretary of the Office of Fossil Energy, Office of Natural Gas & Petroleum Technology, U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The authors are grateful to Laura Stern from the USGS for supplying the synthetic methane hydrate sample used in this paper. The authors would also like to thank Dan Schneberk for making the CT image-processing code, Imgrec, available to us and Jacob Pruess for assistance in data analysis. In addition, we would like to thank Liviu Tomutsa and an anonymous reviewer for providing careful reviews of this manuscript.

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