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Interim Report

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Methane Hydrates in Russia and Europe

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Abstract

The oil and gas industry did thrive for more than a century on oil and gas resources present in a simple state, compressed gas for methane and a liquid for oil.

Actually gas and oil can appear in more complex form, in particular methane that can react with water and CO₂, producing stable solid compounds under certain conditions.

The stability is an asset from the point of view of holding methane in reserves that are not tight and do not require the complex geological conditions necessary for the formation of stable gas fields.

In fact, the reserves of solid methane appear to be immense and located in a great variety of geographical contexts. In the view of Thomas Gold's theory of the mineral origin of methane that is generated from a degassing of the earth mantle, this form of storage should be prevalent due to the looser conditions for holding methane in place.

In our study we limit the analysis to Eurasia where the methane in place appears to be present in extraordinary quantities. Efficient methods of extraction are, however, still to be developed.

About the Author

Cesare Marchetti started his career as a physicist, was then manager of research laboratories, and finally spent 30 years as a researcher in IIASA doing system analysis. He produced very simple predictive models, the physicist way, on the most variegated subjects, from the dynamics of energy markets to the evolution of transport systems. His papers are collected on his web site www.cesaremarchetti.org/.

Methane Hydrates in Russia and Europe

Cesare Marchetti

Executive Summary

Natural gas hydrates are known since Sir Humphrey David observed them experimentally in 1810. They got a bad press since the beginning of the oil industry as, in particular conditions, they tend to form into pipelines carrying natural gas (or oil) damaging the operation of the line with moving slurries or solid plugs (Table 1).

Natural gas hydrates form when water and gas are present, under certain conditions of pressure and temperature. Then highly charged dipole water molecules envelop (with a regular polyhedron) the electronically smooth and round methane molecule. This structure is thermodynamically fairly stable and can assemble into cubic crystals (water alone produces hexagonal crystals).

This "caging" is fairly efficient in terms of CH₄ retention and *one cubic meter of hydrate can contain up to 150 cubic meters of methane*. So much that there is talk of *transporting methane in this form instead of as LNG*, e.g., as a slurry suspended in crude oil cooled to -10°C or so.

Gas hydrates came to the limelight when, calculating the geological setting where they would be stable, especially on the continental shelves, scientists found really staggering, if potential, holding capacities.

Drilling here and there in an exploratory way showed that these hydrates really exist, filling the imagination of scientists and political economists with a possible, almost inexhaustible, source of methane (Figure 1). It must be clear that almost all is extrapolated from a few grams or tons of stuff recovered and mostly floats on scientific self-consistency and *very promising seismic soundings*.

The great advantage of hydrates is that they do not necessarily need a geological trap, with porosity and impervious cap, to contain gas, so accumulation can occur in the most varied geological settings, provided the relatively ample stability parameters for the hydrate formation are met. Furthermore, if a continuous plug of hydrate appears at a certain depth, the gas below is trapped as the plug blocks its ascent (Figure 2). In clays, where gas permeation is slow, the ascent, if not blocked, can be sleepy, and that may explain the large masses of gas even above the plug. Apart from diffusion speed there is also capillary action to keep the gas in place.

The amount of trapped gas has been calculated and the results from various authors are very different but they have in common immense quantities: 10¹⁵ - 10¹⁸ cubic meters. One fundamental question is where all that gas comes from.

The western dogma is that it comes from bacterial manipulation of organic ooze. Or from thermal decomposition of the same. In Eastern European countries, since Mendeleev, one had the suspicion, supported by many indicators, that some or most of the hydrocarbons are of inorganic, i.e., mineral origin, methane being primary and bacteria doing the rest. This thesis has been defended with great force and arguments by *Tommy Gold*, a planetary astrophysicist who applied his techniques to assess planet earth, whose last book "Deep Hot Biosphere" contains all the information and references about the theory.

In a nutshell, the earth has not been formed from a molten blob of sun, it would be helium and hydrogen, but from the concretion of meteorites, many of them being "chondrites" with fairly high carbon contents. Packed and heated in the earth mantle, this carbon slowly reacts with the oxygen and hydrogen in the rocks producing methane and carbon dioxide which are stable at the high temperatures and pressures that can be found in the mantle.

The methane (and some other light hydrocarbons which happen to be stable) *slowly moves up*, in rock "bubbles", being rock plastic at high pressure and temperature. Thus, in principle, methane simmers all over the place, although *the inhomogeneity of the earth crust can provide favorable channels for ascent*. Gold provides on this line a convincing interpretation of the extraordinary concentration of hydrocarbons in the Middle East, all ranged along the border of the Arabic plate, with no connection to the geological history of the various segments of land. He also points to the curious geographic coincidence of the petroleum, volcanoes and earthquake belt in southeast Asia (Figure 6).

Methane can also bubble up in solid granite cratons where certainly there are no botanic sediments, although bacterial life flourishes on the free energy carried up by the methane itself. The oxidizing power is taken from the rocks (typically by reducing iron and sulfur oxides). Microcrystals of ferrite of the kind produced by bacteria, has been found in the Silyan granites in Sweden, in deep perforations suggested by Gold, by the thousand of tons (estimated).

With the immense sedimental layers in the Caspian and in the Siberian area, and especially if the methane exhales from the mantle, the amount of methane fending its way up is immense. In the Caspian province one of the most typical manifestations are the mud volcanoes, where probably a mud diapir (a big blob of mud) arises in the sediments, supposedly due to its methane content, and at a certain point explodes as a volcano spitting in terms of days millions of tons of methane (that catches fire) and leaving behind a large cone of clay (Figure 3).

One could argue that with such an unlimited wealth under their feet the Russians would concentrate on geological mapping in terms of extensions and structures and also concentrate on the possible ways to bring this methane to the pipeline. The situation is certainly more torpid than the premises would suggest and in both directions the efforts appear limited and occasional. *One should not forget that Russia has the largest "conventional" gas fields in the world, if in faraway locations, and still struggles to bring this gas to the markets.*

Much of the gas hydrates seem to be in a more or less unstable situation, as changes in pressure and temperature can mobilize them. However, the decomposition of the hydrate is quite endothermic, and this puts a brake to the speed of decomposition.

Soil has negligible thermal conductivity. Actually a really explosive and macroscopic decomposition can occur only when a landslide on an ocean border brings down and *mixes with warm seawater* a large amount of hydrates. A megaphenomenon of this kind occurred, probably 7,000 years ago, when about 300 km of Norwegian shelf rolled down over the plains of the Atlantic bottom.

All this methane perched on unstable slopes and hidden by capillary retention in clays above, constitutes a source of preoccupation for ecologists and climatologists although really large and evident burps did not seem to have occurred in historical times. Climatic records in ice and rocks should tell it. A line still to explore is where the methane goes when continental plates slip under, as in western South America and also in Japan.

The old T. Gold formula is that the best way to protect the atmosphere from seeping (or exploding) CH₄ is to pierce the primary source, extract the methane and burn it (and dispose CO₂, I would add). If the seepages are moderate, usually a vigorous ecosystem establishes itself on these emissions and takes care of the disposal of CH₄ if not of the CO₂.

The North Sea and the Gulf of Mexico are spotted with bottom islands of flourishing ecosystems (Figure 4) where the food chain starts from seeping hydrocarbons and bacteria that metabolize them. Even worms living in methane chelates seem to have been discovered in the Gulf of Mexico. In front of Norway large mountains of coralline origin, but made by deepwater corals feeding on bacteria, are thought to have been located over large seeps much extended in time. The sheer mass of this emission excludes organic sediments and lends weight to Gold's hypothesis of earth mantle degassing, where "source" volumes are an order of magnitude larger.

According to Gold, also formation of peat from the slow growth of moss and aquatic plants in the northern regions of Europe is suspiciously linked to high levels of methane in the underground, and by the fact that peat is produced only in certain patches when the environment is substantially homogeneous. Actually, by digging *under* the peat bog and around, methane and more complex hydrocarbons are found, improbably coming from the decomposition of the organic material. Peat is also formed along faults in steep Swiss mountain sides (Gold).

This idea that the primary source of hydrocarbons is in the earth mantle revolutionizes the philosophy of hydrocarbon's search and wise oil companies should have separate prospecting teams competing, some based on the old dogma and some on the new. *Japan located on a piece of earth crust twisted and cracked by very active tectonics, might have privileged areas of methane upwellings* which does not form carbohydrate fields because of poor geologic traps, but *can be captured in their slow diffusion upward* (Figure 4).

Coming to brass tacks, the contribution of Russian scientists and engineers to the problem of harnessing gas hydrates appears very limited. This activity is mostly related to assessing, with computer models, the areas where gas hydrates should be present, and make some scattered checks. Even the much quoted Messoyakha gas field in the West Siberian Basin, where a sizable proportion of the output was attributed to decomposition of hydrates, is now under fine scrutiny. The free lunch was not there apparently. Even the presence of hydrates is questioned.

The Ukraine seems to be more active. She needs hydrocarbons and currently saps Russian gas pipelines going through her territory. According to a model produced by the Siberian Energy Institute in Irkutsk, large hydrate bodies could be present in the ooze facing Ukraine, in the Black Sea. Recent soundings seem to confirm the calculation of the model. The Ukraine certainly has the drive to look for and extract (Figure 6).

The final, and central, question is how to retrieve the methane. The most common proposal, even Russian, is to drill a well and leave it empty so to speak. Because the stability of the hydrate is linked to a certain level of pressure, it will decompose. As simple as that, but the decomposition is endothermic. The hydrate will cool down and decomposition stops. Because conductivity of rocks and soil is very low, it will take thousands of years for the appropriate amount of heat to flow in and reestablish the decomposition.

Russians have proposed "antifreezes" that lower the decomposition temperature, such as, e.g., methyl alcohol. In this case the heat for the decomposition comes from the cooling of the mass. Limited but interesting. The problem is the cost of the antifreeze. Natural gas is a very cheap product and one has to count the cents to be competitive.

The solution to the problem that for me takes the rank no. 1 comes from Japan. It proposes to mobilize the methane in the hydrate by substituting a methane molecule with a CO₂ molecule. The idea has been proposed and is being developed by Kazunari Ohgaki of the Department of Chemical Engineering at the University of Osaka.

Although the actual realization may require much skill in managing gases in and out of the fields without mixing them too much, the advantages of the system are:

- The problem of decomposition energy of the hydrate is neatly solved by the substitution.
- The problem of CO₂ disposal that looms high on the ecological policies can be neatly solved.

A plant reforms methane, more or less at the source, and sends CO₂ back to the fields and H₂ (as city gas, impure with CO and other things) to the final consumer.

Table 1. Gas hydrates as expensive nuisance

In 1984, Exxon insulated a North Sea pipeline to prevent hydrate flow stoppage; the incremental cost of that insulation was in the range $\$48\text{--}50 \times 10^6$. In another North Sea case, insulation costs were $\$6 \times 10^6$ for a 15 km subsea pipeline.

At one offshore field, one company reported hydrate inhibition through methanol injection at costs of $\$2.5 \times 10^6$ in 1990. Stange *et al.* reported that a typical rate of methanol injection was 51,000 lb_m/D for a 282 MM SCF/D production facility,⁷ amounting to a methanol operating cost of 1% of the revenue.

A typical offshore glycol inhibitor injection system, using a piggyback inhibitor supply line with onshore recovery, would cost $\$10 \times 10^6$ to inhibit a gas flow rate of 150 MM SCF/D.

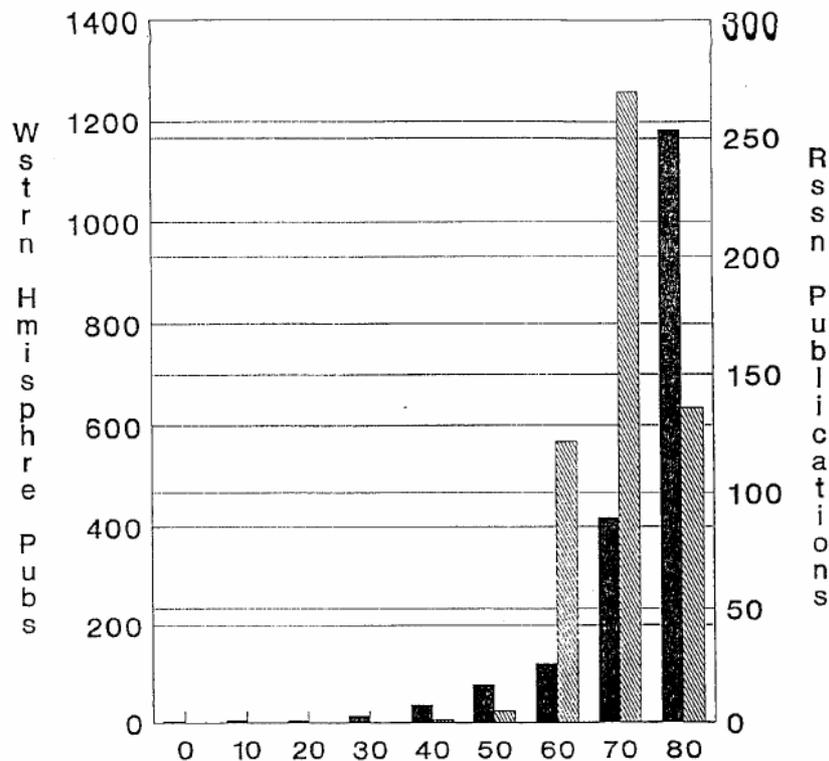


Figure 1.

Western (block and left scale) and Russian (stapled and right scale) publications, per decade, on gas hydrates. Western publications grow more or less exponentially, mirroring an increasing interest in the subject. Russian publications peaked in the seventies. Russians have no urgent interest in developing gas hydrates that, due to the particularly low surface temperature, may be stable also under land in Siberia. Actually, they have the largest world reserves of natural gas and their problem instead is to carry it to the markets. So their research is mainly stimulated by academic curiosity, although their recent agreements with Indian petroleum companies may leave the suspicion that they have some lines in terms of exploitation.

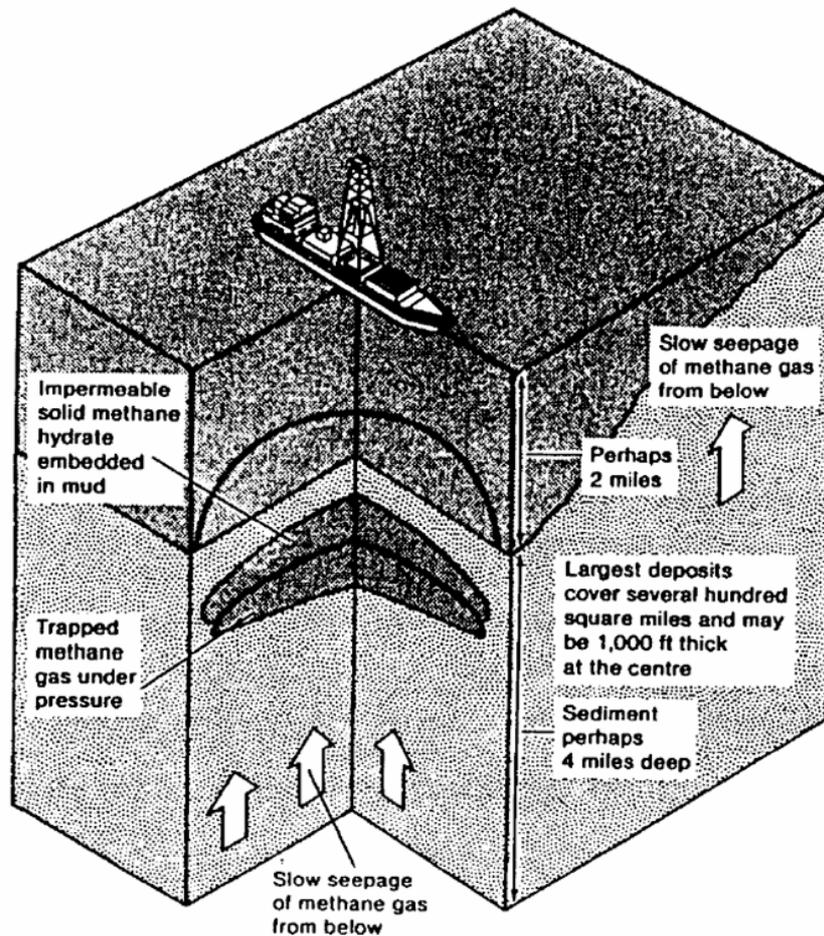


Figure 2.

The sketch gives an outline of the situation of methane hydrates in an idealized case and possible means to extract them. In the volume of hydrate stability a solid plug will form, impeding the movement of ascending gas and so creating a methane bubble underneath. This bubble of gaseous methane can be exploited by drilling through the plug. Some methane seeps out, refilling in time the bubble. And also some hydrate may decompose due to the change in pressure and provide some extra methane.

Hydrates are stabilized by their endothermicity when they decompose. If, e.g., a deposit of hydrate is drilled and the hole left at atmospheric pressure, the hydrate will start decomposing. However, due to the endothermicity of the process, it will cool and this will re-establish equilibrium at a lower pressure (1Atm) and lower temperature.

Because CO_2 can also form hydrates with somehow larger enthalpy than CH_4 , one can think of dislodging CH_4 from the hydrate by perfusing it with CO_2 . This is a Japanese proposal in that sense.



Black lines show geologically young (mesozoic and tertiary) faults and fold belts. The 13 most prominent mud volcano areas are marked, and they all fall on these belts.

Figure 3.

Mud volcanoes, spitting mud and methane by the million tons in a single burp, are located over very deep sediments that permit the formation of mud diapirs, balls of mud with kilometer dimensions, soaked with methane, slowly emerging probably helped by their load in gas, and finally discharging explosively. Now deep sediments exist in many places, but mud volcanoes are always located over geologically young faults and fold belts, giving much weight to Gold's theory that the methane ejected by the volcano comes from the earth mantle and not from the organic ooze which is present everywhere in the sediments.

Because Japan is traversed by one of these geological structures, as shown in the figure, one should expect methane emerging there and being trapped in clathrates or retained by capillary forces, as it does not have the deep sediments necessary for the formation of the diapir. Incidentally, Sakhalin, sitting on the same tectonic structure, has oil and gas.

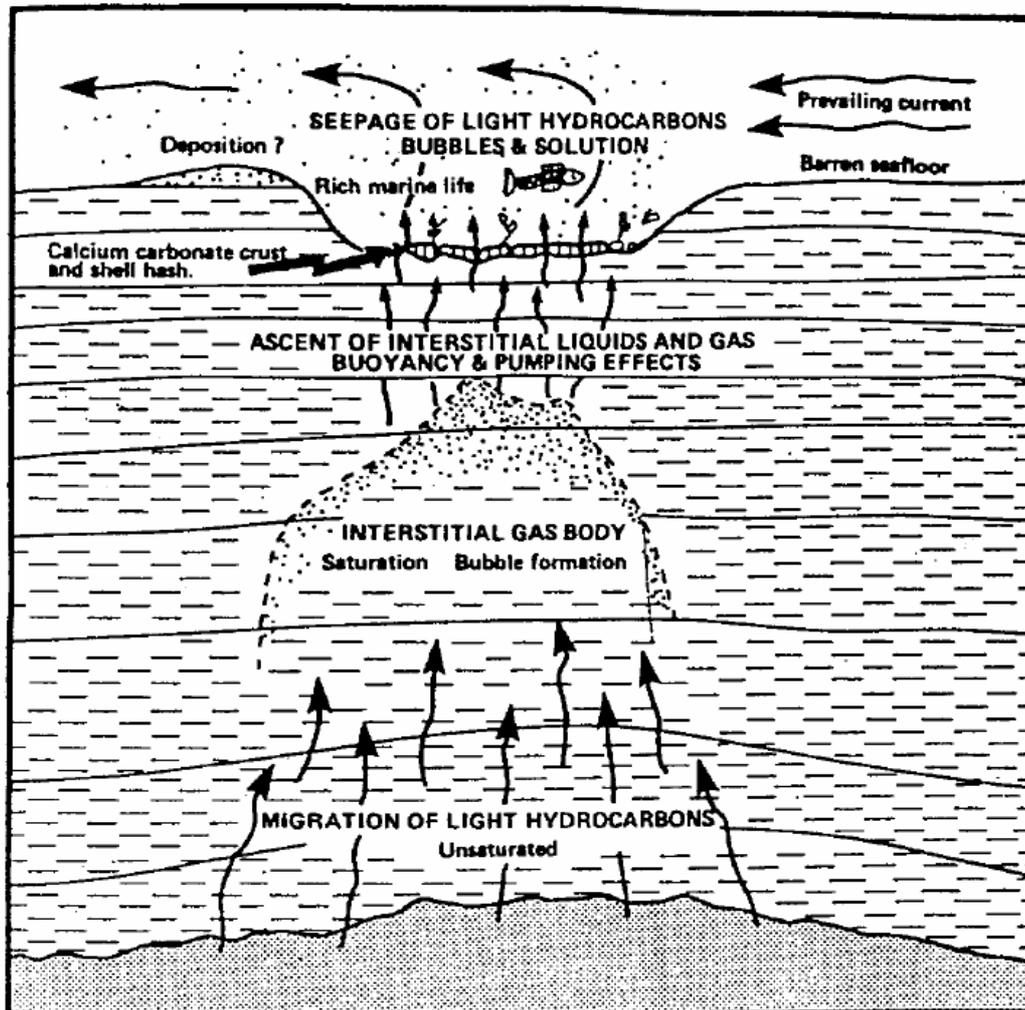


Figure 4.

Large amounts of methane percolate through the sea bottom and if the flow is not too turbulent, living colonies are established on this free energy source. The oxidant is oxygen dissolved in the water. The first clients are chemotropic bacteria, sitting at the base of a food chain that can reach fishes.

The residual clams and mineralization on the bottom are easily detectable with sonar and constitute a peculiar landscape at the bottom of the North Sea.

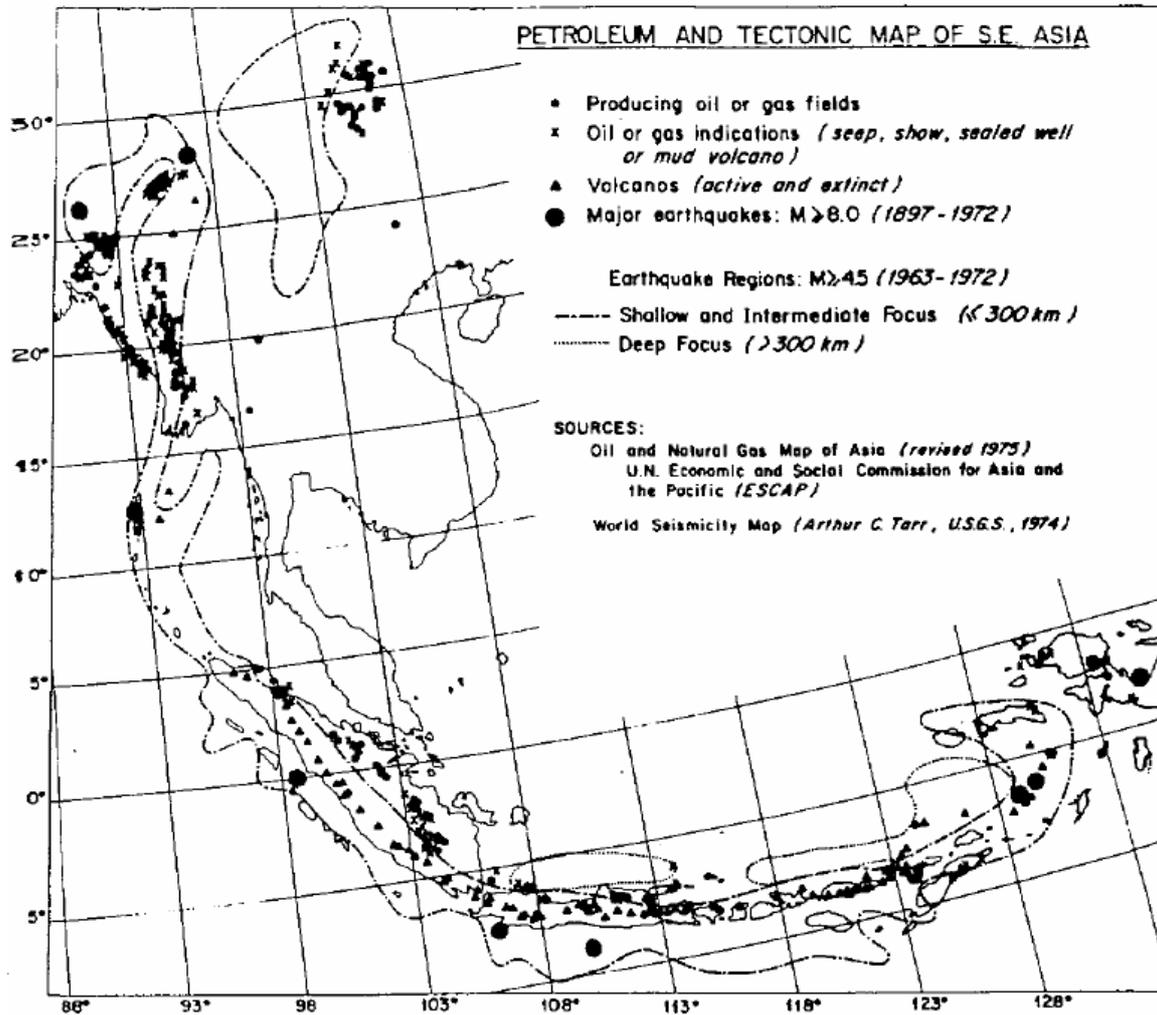
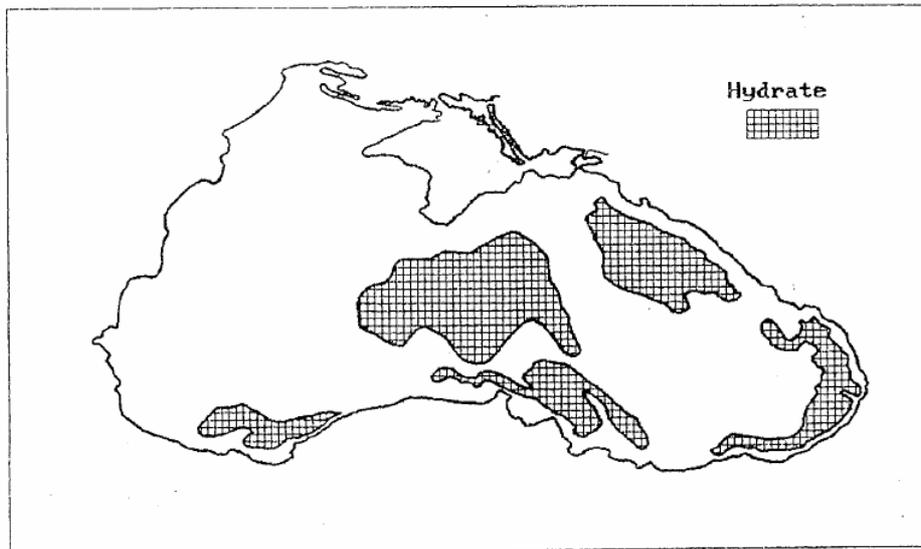


Figure 5.

A counterproof to the case of mud volcanoes is the parallelism, in southeast Asia, of the areas where oil and gas can be produced on one side and volcanoes and earthquakes are active on the other. The faults and twists of the ground generated by tectonic movements also constitute favored pathways for the eventual ascension of methane from the mantle. Where the conditions for stability apply, these areas should also be favored in terms of gas hydrate deposits.



Schematic map of Black Sea hydrate fields.

Figure 6.

This map is based on stability calculations for hydrates and some drilling in the Black Sea. Note the vast expanses of hydrate deposits in this closed sea.

Resumé

Ocean clathrates in just 20 years have gone from a scientific curiosity to an intensely searched subject. In the words of the optimists they promise an almost unlimited source of natural gas, spread more or less around the world, basically in the ocean boundaries. The estimates of methane contained range between 10^{15} and 10^{18} cubic meters.

Very little has been done on the technology of recovering them as a patent search has shown. Between various suggestions, the Japanese proposal to *undo natural gas clathrates by injecting CO₂* that forms itself clathrates in substitution appears the most valid, although the logistic of the two gases in and out is still to be architected.

The ideal machinery to exploit that in an ecological way would then be to reform CH₄ and send CO₂ underground again, with *city gas* produced in the reforming, piped to the final consumer. Transportation of hydrogen in pipelines has costs very near those for natural gas.

Research and experimentation have grown exponentially in the West (Figure 1). The *Russian situation* is simply described as of *mild interest* except for a few more or less academic initiatives. Their publications in fact peak in the seventies. Russia is probably endowed with very large gas clathrate deposits even underground, in Siberia, but also with enormous gas deposits and her real problem *now* is how to bring them to the markets in Europe and Asia.

It does not appear that the Russians have a particular experience in clathrate extraction, although their recent agreement with India may leave suspicions about that.

Even the case of the Messoyakha field, where part of the methane extracted was thought to come from clathrates is now put in doubt. Ukraine, however, has recently shown an interest, but presumably will wait for western initiatives to exploit her deposits in the Black Sea.

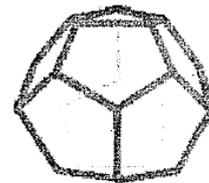
Natural Gas Hydrates and Their Properties

Methane hydrates are a type of "clathrate", which are compounds formed when molecules of one type form a lattice structure around a cavity and molecules of another type are included in the cavity.

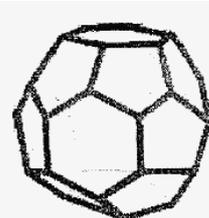
There are three structures of hydrates: I, II, and H. Each has different numbers of water and gas molecules. The ratio of water molecules is called the "hydrate number". The amount of gas actually contained in a hydrate is called the "degree of filling".

If completely filled:

- Structure I hydrates contain 46 water molecules per 8 gas molecules. The hydrate number is 5.75. The water molecules form two small dodecahedral voids and six large tetradecahedral voids. These voids can hold only small gas molecules (methane, ethane) with molecular diameters not exceeding 5.2 angstroms.
- Structure II hydrates contain 136 water molecules per 24 gas molecules. The hydrate number is 5.67. The water molecules form 16 small dodecahedral voids and 8 large hexakaidecahedral voids. They may contain gases with molecular dimensions from 5.9 to 6.8, such as propane, a three-carbon hydrocarbon, and isobutane. Structure II hydrate was first produced in laboratory experiments. It was first found in a natural environment in 1983 at a depth of 530 meters.



Structure I Hydrate
(Source: Sassen)



Structure II Hydrate
(Source: Sassen)

About 15% of the weight of gas hydrate is gas, and 85% is water. the density is about 950kg/cubic meter. These measurements vary with the gas composition and the pressure and temperature at the time the hydrate is formed.

Pressure and temperature must be above an equilibrium line for hydrates to form. In general, as pressure increase, so does the temperature at which hydrates can form. However, many factors may influence the temperature and pressure needed for formation, including the exact water and gas composition. Equilibrium curves for the hydrate structures are shown in Figure 7, and the property of methane hydrides and ice are reported in Table 2.

In some cases, inclusion can change the conditions under which hydrates can form. For instance, when propane and methane combine in one structure, hydrates can form over a broader range of temperature and pressure.

Why is it important to study methane hydrates? According to the U.S. Geological Survey's William Dillon,

- Hydrates have potential as a *future energy resource*.
- Hydrates may be a *source and also a sink for atmospheric methane*. Better understanding of these natural deposits may increase our understanding of climate change.
- Hydrates affect the *strength of the sediments* in which they are found. Areas with hydrates appear to be less stable than other areas of the seafloor. Consequently, it is important to assess their presence prior to the construction of underwater structures related to gas and oil exploration and production. Lack of stability might also be a factor in climate change.

Additional reasons include:

- Hydrates may be an *alternative to pipeline transmission* as a way to move natural gas from deep water to the terminals of existing offshore pipelines and also, on land, from production areas to consumption areas.
- Hydrates might be used as a *vehicular fuel*, especially for relatively large vehicles such as ships.

Where are hydrates located? Scientists are only just beginning to study of methane hydrate deposits. In the USA, deposits have been confirmed on all areas of the continental shelf and under Alaskan permafrost. Similar deposits have been confirmed in many locations throughout the world. But little is known about the actual size and location of even most hydrates that are presumed to exist.

Scientists are constantly making new discoveries about hydrate deposits that frequently challenge old assumptions. Only in the mid-1990s, for instance, were ice worms discovered living on hydrate outcroppings in the Gulf of Mexico. And new types of hydrate formations are being located. In 1995, for instance, scientists found an undersea volcano off the coast of Norway, approximately half a mile wide and under 4,000 feet of water. Further exploration in 1996 revealed that its slopes are covered with a layer of methane hydrate possibly spewed from the volcano. Future investigation is planned.

How much methane is found in the form of hydrates (Table 3). Estimates of the amount of gas sequestered in hydrates varies markedly. Today, most scientists estimate the low side as approximately 100,000 trillion cubic feet (TCF) to, on the high side, 270,000,000 TCF.

What are the expectations to recover gas from hydrates? It appears likely that some methods of extraction will be found. However, scientists urge caution until production feasibility is carefully assessed. Statements such as the following are common in research reports:

Recoverability of gas from these deep marine structures is very problematical at this stage. Important constraints such as permeability are

not usually taken into consideration, but new drilling technology, such as horizontal drilling through the reservoir to enlarge the drill hole face area, may compensate for the low permeabilities normally found in marine sediments. [Max and Lowrie, 1992]

It is possible that the volume of gas in the world's gas hydrate reservoirs exceeds the volume of known conventional gas reserves. However, the resource estimates include numerous assumptions that need careful testing, such as the concentration and extent to the hydrate accumulations. Moreover, little work has been performed on the production potential or the economic feasibility of gas hydrates. [Collett and Kuuskraa, 1998]

While the published estimates of methane hydrate abundance are enormous, it is likely that most of the hydrate occurs in low concentrations and has no commercial potential. [Johnson, 1998]

The Office of Fossil Energy of the US Department of Energy has recently tried to put somehow more indicative numbers on the US hydrate resources (Methane Hydrate Program, April 1998).

Region	Mean Estimate (TCF)	Percentage of Total U.S. Hydrate Resource
Atlantic Ocean	51,831	16.1
Gulf of Mexico	38,251	12.0
Pacific Ocean	61,071	19.1
Alaska Offshore	168,449	52.6
Alaska Onshore	590	0.2

Resource estimates are made by several methods that may be used in combination:

- The results of *seismic surveys*, which frequently indicate the presence of hydrate deposits that cap a deposit of free methane below. However, seismic analysis frequently does not give a good indication of hydrate deposits that do not cap free methane.
- *Core samples* taken either from oil and gas wells or from research sampling. Studies of geology, including knowledge both of the underground formations based on sampling/observation and of a region's geological history. Max and Lowrie's "*Natural Gas Hydrates: Arctic and Nordic Sea Potential*", for instance, is a good example of how an understanding of geology (including temperature changes throughout the millenia, the likelihood of organic deposits in regions no covered by water, etc.) can be used to develop hypotheses on areas likely to be rich in hydrates. And also the presence of weak or strongly deformed geologic structures that may facilitate the upwelling of mantle emissions. A rough map of the sites of interest is given in Figure 9.

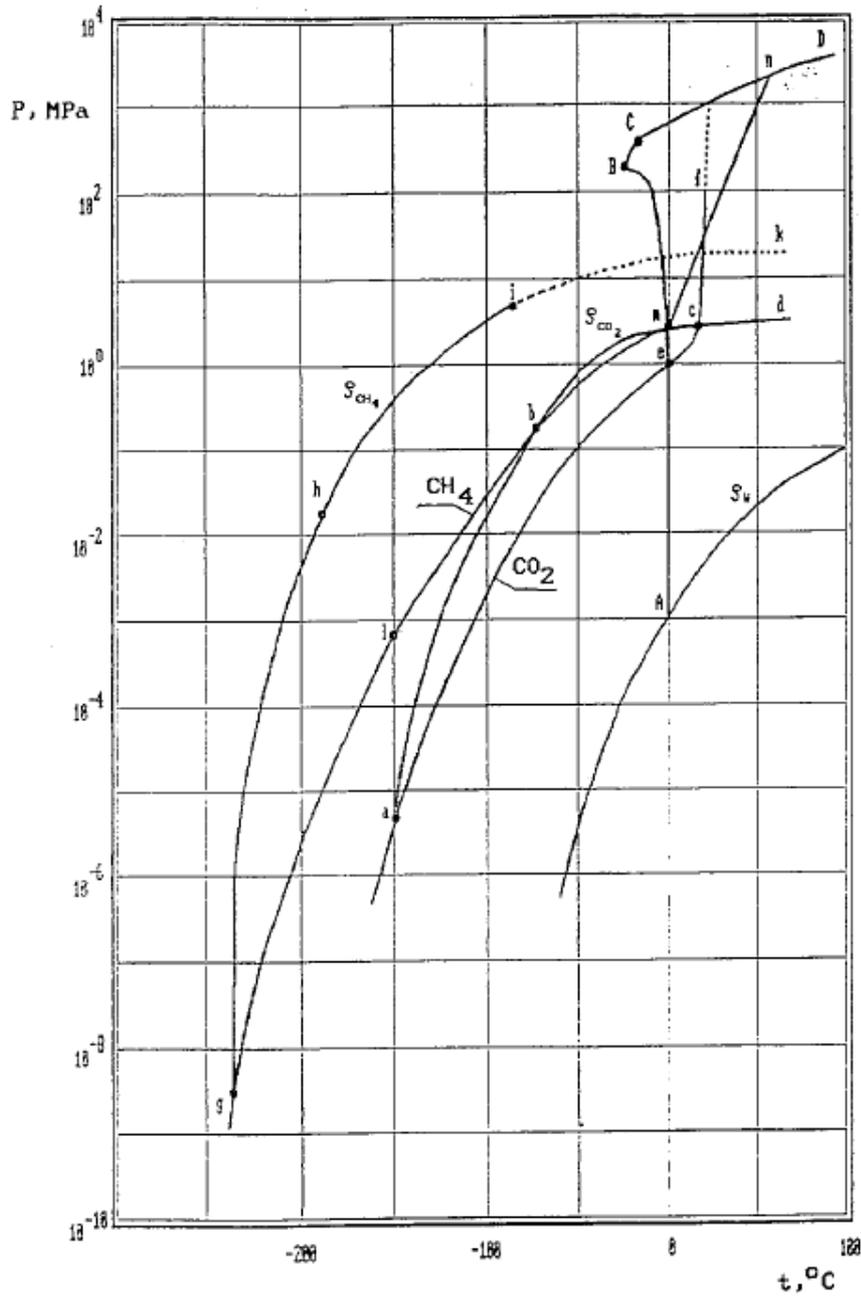
Table 2. Summary of published values for properties of ice and pure gas hydrates.

Property	Ice	Hydrate
Dielectric constant at 273 š	94	=58
NMR rigid lattice 2nd moment of H ₂ O protons (G ²)	32	33 ± 2
Water molecule reorientation time at 273 š (μ)	21	=10
Diffusional jump time of water molecules at 273 š (μ)	2.7	>200
Isothermal Young's modulus at 268 š (10 ⁹ Pa)	9.5	=8.4
Speed of longitudinal sound at 273 š	3.8	3.3
Velocity (km/sec)	80	92
transit time (μ/ft)		
Velocity ratio Vp/Vs at 272 š	1.88	1.95
Poisson's ratio	0.33	=0.33
Bulk modulus (272 š)	8.8	5.6
Shear modulus (272 š)	3.9	2.4
Bulk density (gm/cm ³)	0.916	0.912
Adiabatic bulk compressibility at 273 š 10 ⁻¹¹ Pa	12	=14
Thermal conductivity at 263 š (W/m-K)	2.23	0.49 ± 0.02

Ÿ '=' symbol of hydrate column of this table is wavy 'nearly equal' symbol in Prenskey (1995).

Table 3.

Year	Methane Volume (TCF x 10 ⁻¹⁵)		Reference
	Oceanic	Continental	
1997	1.8 - 8.8	0.02	Trofimuk, A.A., Cheraski, N.V., and Tsaryov, V.P., 1977, The role of continental glaciation and hydrate formation on petroleum occurrence, in Meyer, R.F., ed., The future supply of nature-made petroleum and gas: New York, Pergamon Press, p. 919-926.
1981	-	0.005	Meyer, R.F., 1981, Speculations on oil and gas resources in small fields and unconventional deposits, in Meyer, R.F., and Olson, J.C., eds., Long-term energy resources: Pitman, Boston, p. 49-72.
1981	1.1	0.011	Mclver, R.D., 1981, Gas hydrates, in Meyer, R.F., and Olson, J.C., eds., Long-term energy resources: Pitman, Boston p. 713-726.
1981	2700	12	Dobrynin, V.NIM., Korotajev, Y.P. and Plyushev, D.V., 1981, Gas Hydrates--a possible energy resource, in Meyer, R.F., and Olson, J.C., eds., Long-term energy resources: Pitman, Boston, p. 727-729.
1988	6.2	-	Kvenvolden, K.A., 1988, Methane Hydrate--a major source of carbon in the shallow geosphere?: Chemical Geology, v. 71, p. 51-51.
1990	6.9	-	MacDonald, G.J., 1990, The future of methane as an energy resource: Annual Review of Energy, v. 15, p. 53-58.
1994	9.3 - 49.1	-	GFornitz, V. and Fung, I., 1994, Potential distribution of methane hydrates in the world's oceans: Global Biogeochemical Cycles, v. 8, no. 3, p. 335-347.



P-T diagram of hydrate formation for CH₄ and CO₂.

Figure 7. Stability curves for hydrates of CH₄ and CO₂ are reported here.

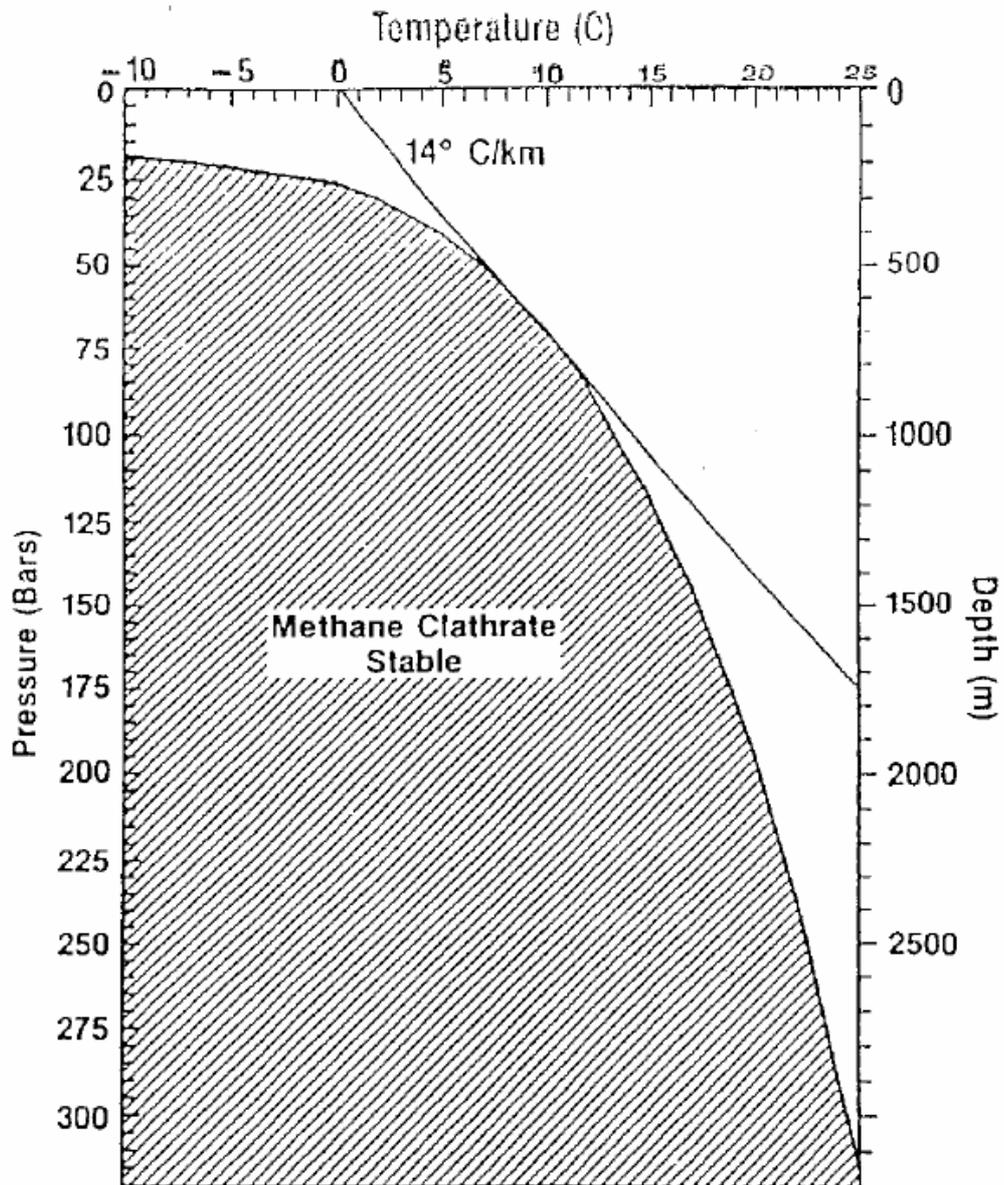
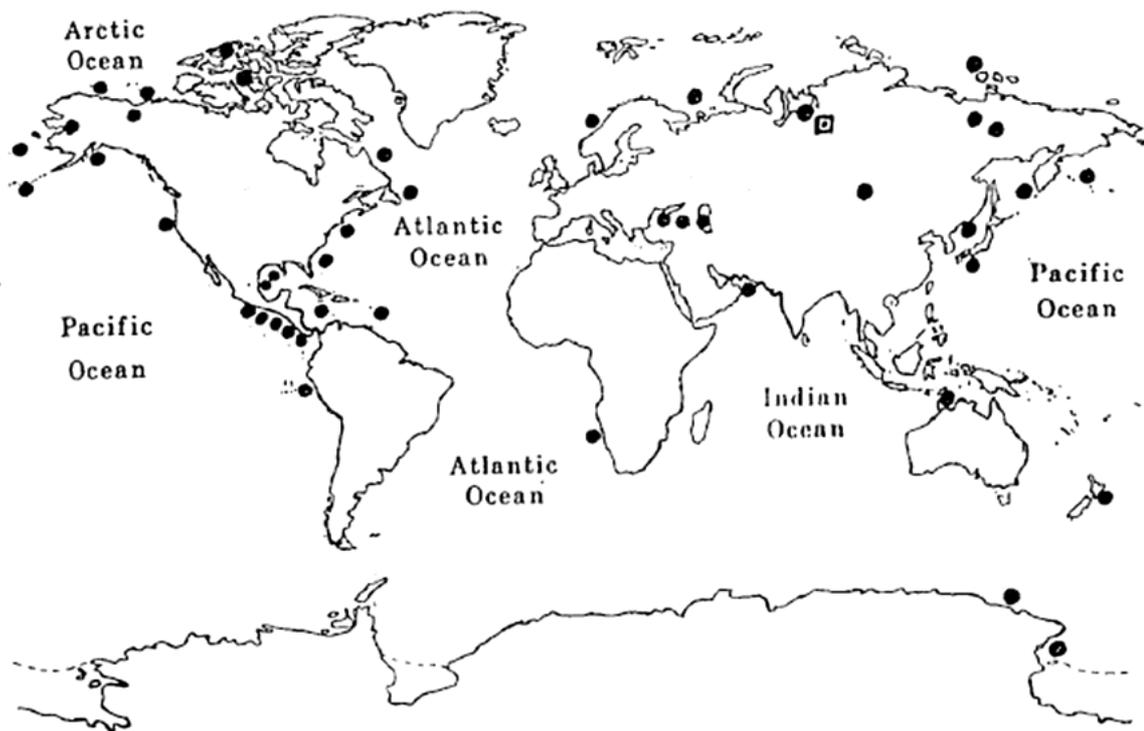


Figure 8.

Phase diagram showing the boundary between free methane gas and methane clathrate for the H₂O-CH₄ system. The ice-water phase boundary would be a vertical line through 0°C. The depth scale is drawn assuming hydrostatic equilibrium for pore water. The limiting geothermal gradient of 14°C km⁻¹ for the stability of methane clathrate outside permafrost regions is also indicated (from MacDonald, 1990).



Hydrate occurrences in the World (circles). Messoyakha field (square).

Figure 9.

Recovery of Gas Hydrates: Many Ideas, Any Solutions?

Gas hydrates have the basic problem that their endothermic decomposition requires heat that the poor conduction of rocks and soils cannot provide at the appropriate rate.

So the first idea is to try to bring heat from above. The imagination of the inventors produced some rudimentary paper proposals which we report as they may be the basis of more evolved ones.

As said before, in my opinion the best trick is to inject CO_2 in the hydrate layers, and use its heat of hydration to pull CH_4 out. This line is followed in Japan already.

The description of the various possibilities when injecting steam to heat the hydrates to decomposition are schematically given in Figs.7--14. To my knowledge there is no systematic experimentation yet on these methods although in many ways they resemble the ones used to extract thick oils.

A CO_2 injection system would work exactly with the same mechanism. However, fixation should be precise as CO_2 does not separate as easily as steam in case it is carried back by ascending methane.

In actual operation very little shows up. Filtering the outcome of a recent "Gas Hydrates" workshop at the University of Leeds (April 1998), one finds a sizable amount of explorations, even in out of hand oceanic places, but no actual extraction

experiments, except the ones *announced* by Japanese sources (Tokyo and Osaka Universities, JAPEx, and JNOC) for drilling in the Nankai trough.

Excellent papers on the physical chemistry of hydrates containing CH_4 , CO_2 , C_2H_6 and other components have recently been published by R.K. Bakker. These studies can be of fundamental importance in establishing the right strategy to extract CH_4 from hydrates.

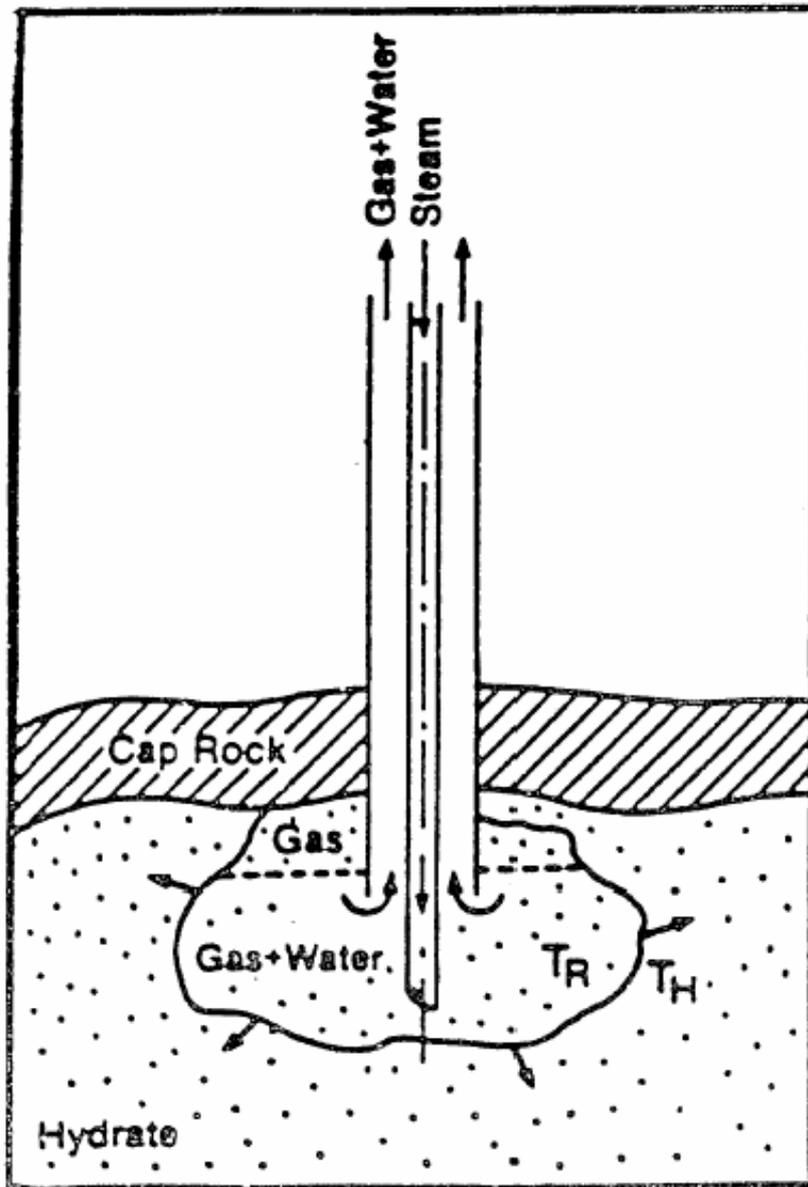


Figure 10. Schematic of steam injection into a hydrate reservoir.

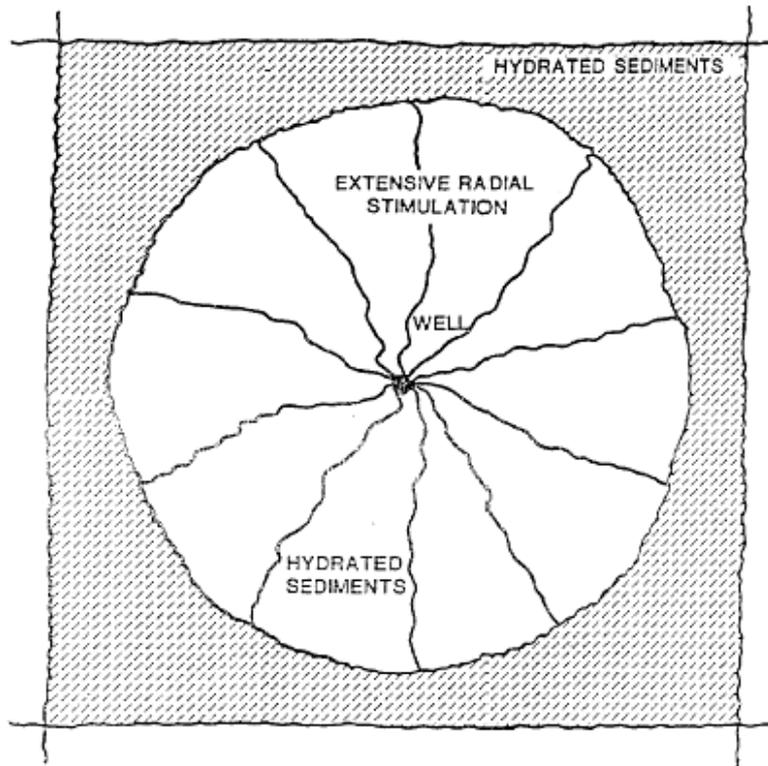


Figure 11. Illustration of radial stimulation (top view).

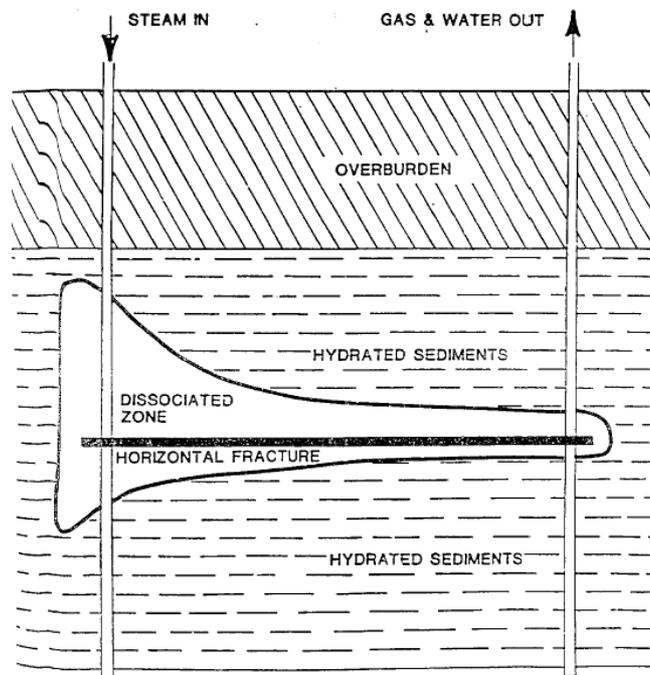


Figure 12. Continuous steam model with horizontal fracture (side view).

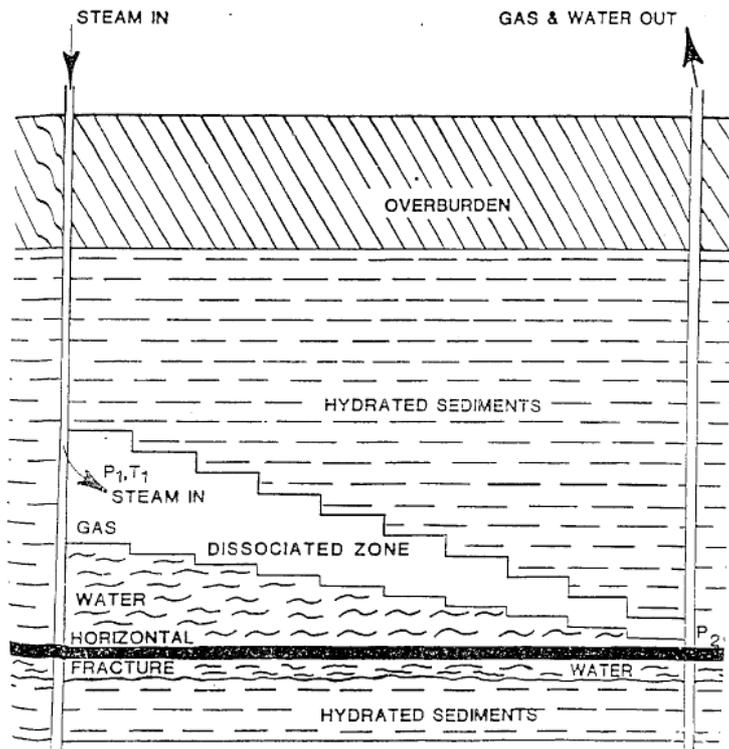


Figure 13. Detailed description of continuous injection model with horizontal fracture (side view).

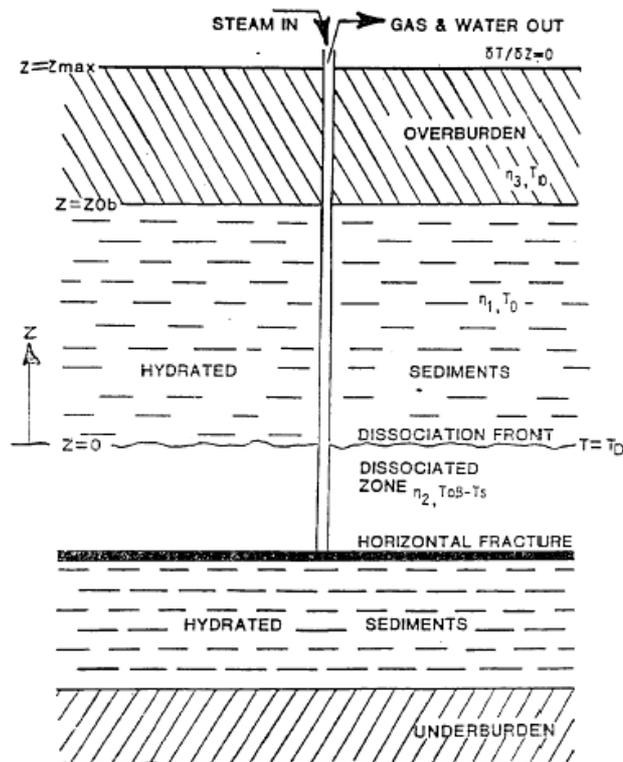


Figure 14. Heat conduction problem in vertical direction for horizontal fracture case - cyclic model (side view).

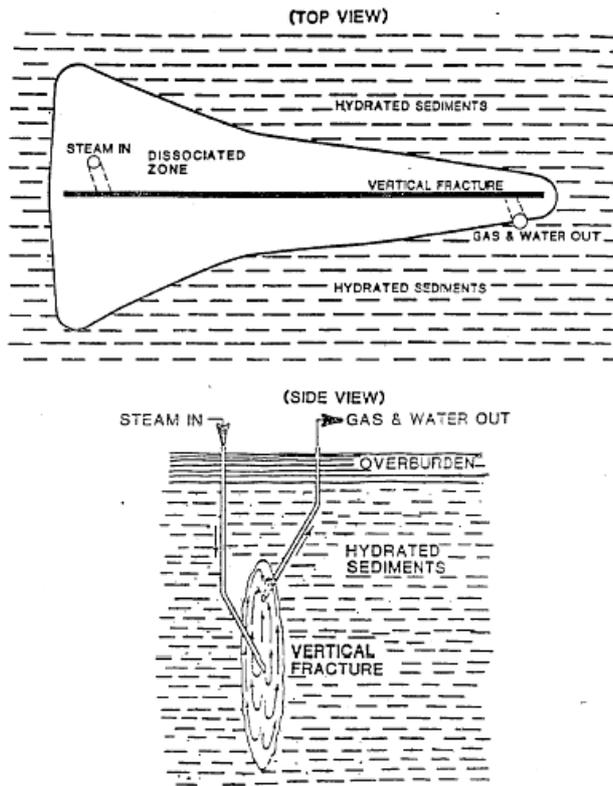


Figure 15. Continuous steam model with vertical fracture.

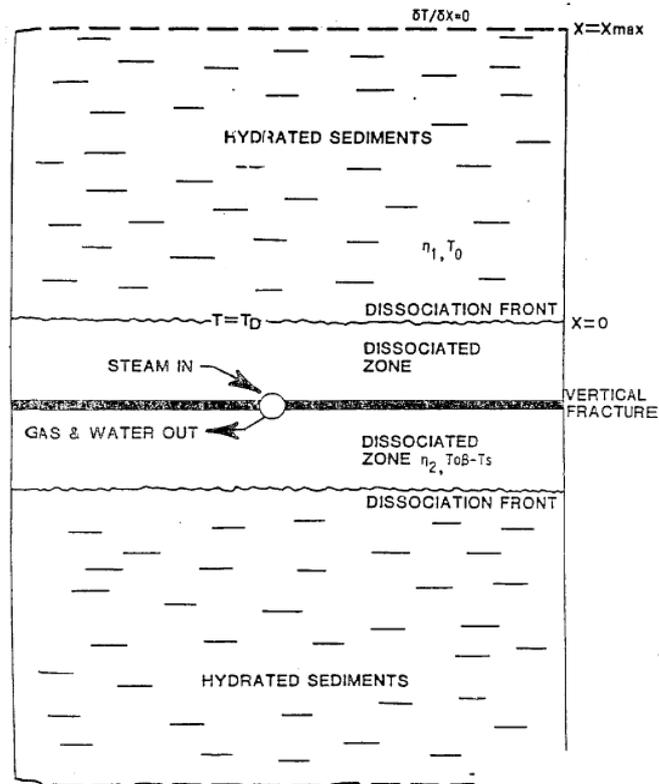


Figure 16. Heat conduction problem in horizontal direction for vertical fracture case - cyclic model (top view).

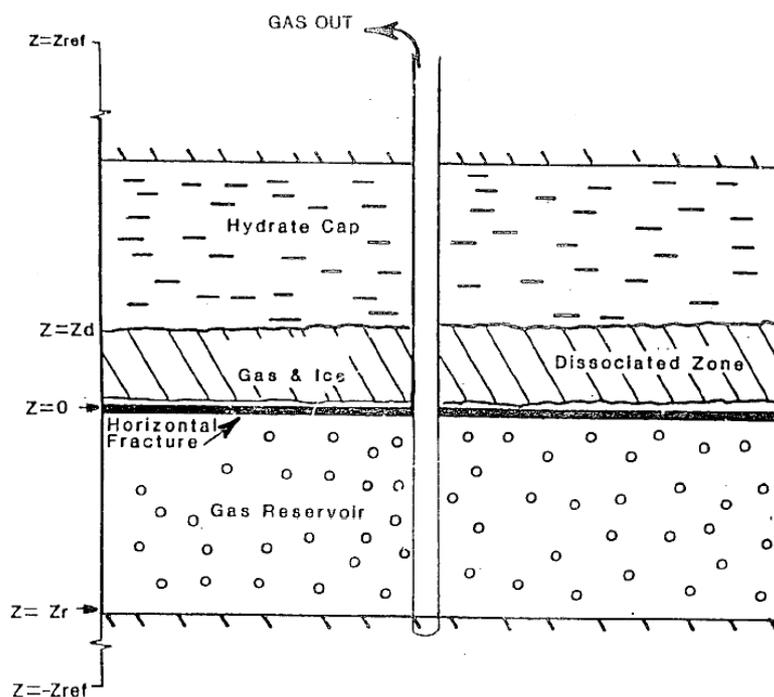


Figure 17. Decompression hydrate cap model with horizontal fracture (side view).

What about Hydrates Under Permafrost

Having a mean surface temperature around -10°C creates conditions for hydrate formation under the land. Normally, the geothermal gradient produces too high temperatures versus depth, i.e., pressure, to find zones of hydrate stability.

Because working on terra firma is much easier than working over the ocean, there is a special interest for detecting and hopefully exploiting gas hydrates under permafrost, i.e., geographically in boreal regions.

As Figure 18 shows, most permafrost land (and ocean) are located in Russia. The hydrate reserves could then be found at very convenient depths, between 300 and 1000 meters (Figure 19).

As said before, because these hydrate layers could accommodate CO_2 in place of CH_4 , it would be very ecological *if the Russians could reform their CH_4 to 4H_2 and CO_2 and pipe H_2 to the final consumers. It could be their best contribution to the Kyoto agreements.*

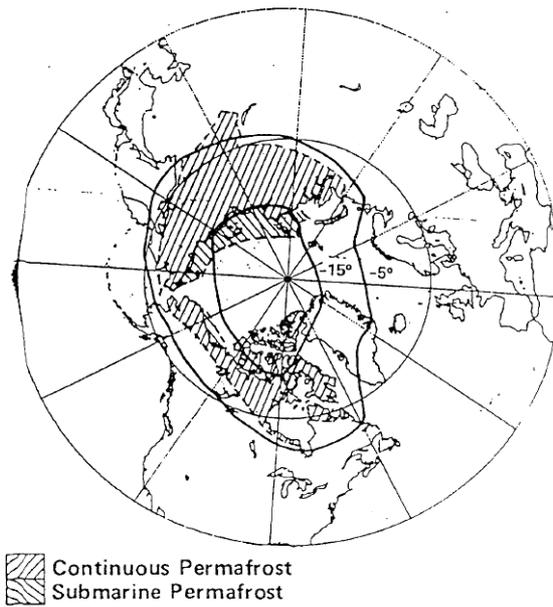


Figure 18.

The approximate location of the -5° and -15°C isotherms of annual mean surface air temperature and the areas of continuous Northern Hemisphere permafrost and identified subsea permafrost. (Permafrost data courtesy of Jerry Brown of the U.S. Army's Cold Regions Research and Engineering Laboratory.)

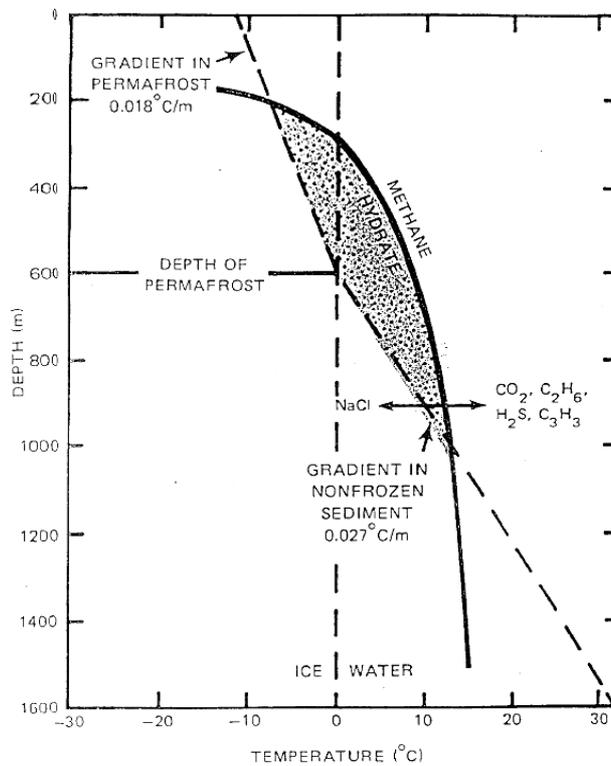


Figure 19.

Who Is Doing Research on Gas Hydrates

We scanned the listed literature, and some not listed, to try to find out whether there are centers of excellence, so to say, for research on hydrates.

We found really none. The papers come from disparate places, basically universities, showing that the driving force is just academic curiosity.

In the case of Russia, a number of papers come from Moscow inevitably, but also from Irkutsk (that has a computer model to establish where hydrates can be found) and Novosibirsk.

The coagulation points can be expected when real interest and proportionate money will start moving. The Russian--Indian deal may foster research in Russia. Gasprom is the richest company in Russia. And Japan is also condensing a line of action with various institutions collaborating.

Some driving forces in the study and practical handling of hydrate may come from the possibility, recently suggested, *to transport methane in form of hydrate*. A slurry of hydrate would be mixed with crude oils and shipped in current oil tankers, at atmospheric pressure. To ensure stability one should cool to -10°C or so, but decomposition of hydrate grains generate an ice skin on the grain and finally practice will suggest the best compromise. A certain decomposition level can be acceptable if the evolving gas can be used to propel the ship.

At present an amount of gas equivalent to the whole consumption in Europe is flared around the world because of the expense of transporting methane over long distances as LNG. A cheap way could mobilize important resources and incidentally *reduce CO_2 emissions in a very important measure* (equivalent to zeroing Europe's emissions, more or less). A fact which Kyoto legislators did not seem to have weighted sufficiently.

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Annex:

Japanese Papers on CO₂ and CH₄ Hydrates

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\$3.00 0.050 Hrs File5
\$5.80 4 Type(s) in Format 9
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\$0.15 TYMNET
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	4829	GASES
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03332260 JICST ACCESSION NUMBER: 96A0591411 FILE SEGMENT: JICST-E
Molecular Dynamics Simulation of Clathrate-Hydrate Formation.
HIRAI SHUICHIRO (1); OKAZAKI KEN (1); KURAOKA SHINSUKE (2); KAWAMURA
KATSUYUKI (3)
(1) Tokyo Inst. of Technol.; (2) Tokyo Inst. of Technology, Graduate School
; (3) Tokyo Inst. of Technol. Fac. of Sci.
Nippon Dennetsu Shinpojiumu Koen Ronbunshu, 1996, VOL.33rd,NO.Vol 1,
PAGE.339-340, FIG.3, REF.1
JOURNAL NUMBER: F0872CAE
UNIVERSAL DECIMAL CLASSIFICATION: 548.73:544.142.3/.4
LANGUAGE: Japanese COUNTRY OF PUBLICATION: Japan
DOCUMENT TYPE: Conference Proceeding
ARTICLE TYPE: Short Communication
MEDIA TYPE: Printed Publication
ABSTRACT: The phenomena of clathrate-hydrate formation has been conducted
by molecular dynamics simulation. Positions of Ar molecules(guest
molecules) were fixed and formation of cage structure by H2O molecules
around the Ar molecules were precisely simulated by the present
calculation. The interpretation of the formation mechanism was
discussed in detail. (author abst.)
DESCRIPTORS: clathrate compound; hydrate; water molecule; molecular
dynamics; argon; water; intermolecular interaction; hydrogen bond;
computer simulation; molecular orientation
BROADER DESCRIPTORS: molecular compound; addition compound;
compound(chemical); solvate; triatomic molecule; polyatomic molecule;
molecule; dynamics; rare gas; element; third row element; interaction;
binding and coupling; computer application; utilization; simulation;
orientation(direction)
CLASSIFICATION CODE(S): BK09050T

3/9/3

DIALOG(R)File 94:JICST-EPlus
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03166561 JICST ACCESSION NUMBER: 96A0155971 FILE SEGMENT: JICST-E
Formation and dissolution of CO2 clathrate hydrate under deep-ocean
disposal conditions.
WARZINSKI R P (1); CUGINI A V (1); HOLDER G D (2)
(1) Pittsburgh Energy Technol. Center, U.S. Dep., PA, USA; (2) Univ.
Pittsburgh, PA, USA
Ionics, 1995, VOL.21,NO.12 bessatsu, PAGE.5-7, REF.2
JOURNAL NUMBER: F0043BAT ISSN NO: 0388-659X
UNIVERSAL DECIMAL CLASSIFICATION: 628.511
LANGUAGE: English COUNTRY OF PUBLICATION: Japan
DOCUMENT TYPE: Journal
ARTICLE TYPE: Short Communication
MEDIA TYPE: Printed Publication
DESCRIPTORS: air pollution; global warming; carbon dioxide; exhaust gas
treatment; undersea storage; hydrate; clathrate compound; droplet;
covering; fixation; sea disposal
IDENTIFIERS: deep sea disposal
BROADER DESCRIPTORS: environmental pollution; pollution; warming(climatic);
climatic variation; fluctuation and variation; carbon oxide; oxide;
chalcogenide; oxygen group element compound; oxygen compound; carbon
compound; carbon group element compound; waste treatment; treatment;

storage; solvate; addition compound; compound(chemical); molecular compound; surface treatment; underwater disposal; waste disposal
CLASSIFICATION CODE(S): SC04020W

3/9/4

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02966629 JICST ACCESSION NUMBER: 95A0694225 FILE SEGMENT: JICST-E
High-pressure phase behavior of the mixed system including CO2 clathrate hydrate.

OGAKI KAZUNARI (1); HAMANAKA TAKAHIRO (1)
(1) Osaka Univ., Fac. of Eng. Sci.

Kagaku Kogaku, 1995, VOL.59,NO.8, PAGE.583-584, FIG.3, REF.3
JOURNAL NUMBER: F0099AAT ISSN NO: 0375-9253 CODEN: KKGKA
UNIVERSAL DECIMAL CLASSIFICATION: 66.021.4
LANGUAGE: Japanese COUNTRY OF PUBLICATION: Japan

DOCUMENT TYPE: Journal

ARTICLE TYPE: Short Communication

MEDIA TYPE: Printed Publication

ABSTRACT: A visible type high-pressure cell of 100MPa resistant provided with vibrational agitation was prepared. The coexistence relations of CO2 hydrate, liquid CO2 and H2O was measured up to a maximum pressure of 82MPa. With deep-sea bed storage of CO2 in mind, density reversion phenomena of CO2 hydrate, liquid CO2 and H2O phases depending on changes in temperature and pressure was observed. From these results, the possibility of a long-term stability storage of liquid CO2 in the Japan Deep was suggested.

DESCRIPTORS: carbon dioxide; clathrate compound; hydrate; high pressure; multiphase; phase diagram; mixture; water; liquefied gas; density; natural gas

BROADER DESCRIPTORS: carbon oxide; oxide; chalcogenide; oxygen group element compound; oxygen compound; carbon compound; carbon group element compound; molecular compound; addition compound; compound(chemical); solvate; pressure; phase(topology); diagram and table; object; liquid

CLASSIFICATION CODE(S): XD01030U

3/9/5

DIALOG(R)File 94:JICST-EPlus
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02955989 JICST ACCESSION NUMBER: 95A0744455 FILE SEGMENT: JICST-E
Molecular Thermo-fluid-dynamics. Investigation for the Stability of CO2 Clathrate-Hydrate Using Molecular Dynamics Simulation.

HIRAI S (1); OKAZAKI K (1); KURAKA S (1); KAWAMURA K (1)
(1) Tokyo Inst. Technol., Tokyo, JPN

Therm Sci Eng, 1995, VOL.3,NO.3, PAGE.69-74, FIG.7, TBL.1, REF.9
JOURNAL NUMBER: L1615AAS ISSN NO: 0918-9963
UNIVERSAL DECIMAL CLASSIFICATION: 544.142/.144

LANGUAGE: English COUNTRY OF PUBLICATION: Japan

DOCUMENT TYPE: Journal

ARTICLE TYPE: Original paper

MEDIA TYPE: Printed Publication

ABSTRACT: The stability of carbon dioxide clathrate hydrate which is the crystal solid in which the water molecule seems to be tied by the hydrogen combined by making cage grid structure filled up in the carbon dioxide molecule, is examined by the molecular dynamics simulation. Result shows that the clathrate hydrate of the carbon dioxide is more unstable than that of nitrogen and argon. This paper explains the reason for this instability on basis of the database which obtain from simulation.

DESCRIPTORS: hydrate; clathrate compound; carbon dioxide; argon; molecular dynamics; numerical calculation; stability analysis; interatomic potential

BROADER DESCRIPTORS: solvate; addition compound; compound(chemical); molecular compound; carbon oxide; oxide; chalcogenide; oxygen group element compound; oxygen compound; carbon compound; carbon group element compound; rare gas; element; third row element; dynamics; calculation; analysis; potential

CLASSIFICATION CODE(S): CE02000C

3/9/10

DIALOG(R)File 94:JICST-EPlus
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02261926 JICST ACCESSION NUMBER: 95A0139281 FILE SEGMENT: PreJICST-E
Diffusion of CO2 Gas and its Transformation to Clathrate Crystals in Polar Ice Sheets.

MAE SHINJI (1)

(1) Hokkaido Univ., Fac. of Eng.

Asahi Garasu Zaidan Josei Kenkyu Seika Hokoku(Reports of Researches Assisted by the Asahi Glass Foundation), 1994, VOL.1994, PAGE.583-590

JOURNAL NUMBER: G0061BAQ ISSN NO: 0919-9179 CODEN: AGSHE

LANGUAGE: Japanese COUNTRY OF PUBLICATION: Japan

DOCUMENT TYPE: Journal

MEDIA TYPE: Printed Publication

ABSTRACT: Microscopic observation of air-hydrate crystals were carried out with ice core samples retrieved at Vostok Station, Antarctica. It was found that the volume and number of air-hydrate varied with the climatic change. For example, the number concentration of air-hydrate crystals was about half in the interglacial ice compared with that in the glacial ice. The mean volume gradually increased as the depth increased and this means that the gas molecules can diffuse in the ice and their rearrangement takes place. Formation investigation of air-hydrate crystals shows that the nucleation of the crystals at the boundaries between ice and air is most predominant mechanism in the transformation process from air to air-hydrate crystals. (author abst.)

3/9/13

DIALOG(R)File 94:JICST-EPlus

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02142984 JICST ACCESSION NUMBER: 94A0130684 FILE SEGMENT: JICST-E

Research on the fixation technology of carbon dioxide by clathrate and hydrate.

SAJI AKIRA (1); NODA HIDETOMO (1); TANII TADAAKI (2); KAMATA TOSHIHIRO (3); KITAMURA HIKARU (3)

(1) Chubu Electric Power Co., Ltd.; (2) Mitsubishi Heavy Industries, Ltd., Takasago Technical Inst.; (3) Mitsubishi Heavy Industries, Ltd., Kobe Shipyard and Engine Works

Kagaku Kogaku Shinpojiumu Shirizu, 1993, VOL.38, PAGE.143-148, FIG.10, REF.19

JOURNAL NUMBER: F0807BAP

UNIVERSAL DECIMAL CLASSIFICATION: 628.52/.53 614.777:628.19:551.464

LANGUAGE: Japanese COUNTRY OF PUBLICATION: Japan

DOCUMENT TYPE: Conference Proceeding

ARTICLE TYPE: Original paper

MEDIA TYPE: Printed Publication

ABSTRACT: Generation principle supporting experiment, continuous generation experiment and sedimentation experiment of CO₂ clathrate (CC) were carried out in order to examine the system which stores large amount of CO₂ recovered from thermal power plants in deep-sea floor, and generation and sedimentation characteristics of CC which is reaction product between CO₂ and water were obtained. The generation speed of CC was in proportional to CO₂ - water interface, continuous generation and separation of 10-20mm size CC were possible, and it was proven that sedimentation velocity increased with the increase in particle size.

DESCRIPTORS: carbon dioxide; clathrate compound; hydrate; thermal power generation; power plant; gas recovery; undersea storage; system evaluation; reaction product; reaction rate; fugacity; particle size(diameter); settling tank; settling velocity

BROADER DESCRIPTORS: carbon oxide; oxide; chalcogenide; oxygen group element compound; oxygen compound; carbon compound; carbon group element compound; molecular compound; addition compound; compound(chemical); solvate; power generation; electric power energy operation; electric power facility; recovery; storage; evaluation; product material; velocity; activity(thermodynamics); thermodynamic property; diameter; length; geometric quantity; chemical equipment; equipment

CLASSIFICATION CODE(S): SC04040S; SB02040B

3/9/15

DIALOG(R)File 94:JICST-EPlus

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01833600 JICST ACCESSION NUMBER: 93A0429357 FILE SEGMENT: JICST-E

Recent heat pumps and applications. Technological trends in the development of electric and gas HPs. Ice-unused heat storage system. Clathrate heat-storage heat pump system.

SUZUKI MICHIIYA (1)

(1) Shimizu Construction Co., Ltd.

Shoenerugi(Energy Conservation), 1993, VOL.45,NO.4, PAGE.66-68, FIG.2, TBL.3

JOURNAL NUMBER: F0218ACY ISSN NO: 0387-1819

UNIVERSAL DECIMAL CLASSIFICATION: 621.577: 628.8+697.9 620.9.004.4

LANGUAGE: Japanese COUNTRY OF PUBLICATION: Japan

DOCUMENT TYPE: Journal

ARTICLE TYPE: Commentary

MEDIA TYPE: Printed Publication

ABSTRACT: This paper presents an introduction example of a heat-storage heat pump system using clathrate made up of CFC-11 and water as the cold heat storage material. Clathrate is formed at 8.5.DEG.C. and is a fluid. The heat-storage heat pump system was designed to be responsible for about 50% of a peak air-conditioning load for an office building with a total floor area of 8,480m². Operation performance for 102 days in the summer showed a midnight power utilization of 35%.

DESCRIPTORS: heat pump; heat storage; energy storage; clathrate compound; heat storage material; freon; thermal storage tank; heat exchanger; coefficient of performance; cold; air conditioning equipment

BROADER DESCRIPTORS: thermal operating device; storage and accumulation; storage; molecular compound; addition compound; compound(chemical); material; aliphatic chlorine compound; aliphatic halogen compound; organohalogene compound; organochlorine compound; aliphatic fluorine compound; organofluorine compound; storage tank; container; coefficient

; heat; equipment
CLASSIFICATION CODE(S): PC03020M; LC02000F

3/9/19

DIALOG(R)File 94:JICST-EPlus
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01411358 JICST ACCESSION NUMBER: 91A0560804 FILE SEGMENT: JICST-E
Study on Air Conditioning System Using the Clathrate Thermal Storage.
MIYAJI SHOZO (1); KOJIMA SHIN (2); KONDO FUMIO (2); YAMANAKA TOSHIHIKO (2);
ISAKA YASUO (2); MAKINO TAKASHI (2)

(1) Chubu Electric Power Co., Ltd.; (2) Mitsubishi Heavy Industries, Ltd.
Nippon Dennetsu Shinpoijumu Koen Ronbunshu, 1991, VOL.28th,NO.Pt 2,
PAGE.607-609, FIG.7, TBL.1, REF.2

JOURNAL NUMBER: F0872CAE
UNIVERSAL DECIMAL CLASSIFICATION: 628.81/.84:697.1/.7:697.9
LANGUAGE: Japanese COUNTRY OF PUBLICATION: Japan
DOCUMENT TYPE: Conference Proceeding
ARTICLE TYPE: Short Communication
MEDIA TYPE: Printed Publication

ABSTRACT: This paper discusses the high-performance thermal storage tank
for the air conditioning system using a gas hydrate, what is called a
"clathrate", which is formed from the mixtures of cooled water and
hydrating agent. In the thermal storage tank, the clathrate is formed,
stored and also dissolved. For making thermal storage tank more
efficient and smaller, we have analyzed the flow in the tank and found
the proper arrangement of heat exchangers and agitators. Based on the
results, an experimental unit with the high-performance thermal storage
tank has been manufactured and tested. The clathrate packing factor in
the tank has become greater than 40%. This proves that the "clathrate"
thermal storage system has the advantage of the conventional ice
thermal storage systems. (author abst.)

DESCRIPTORS: air conditioning equipment; energy system; thermal storage
tank; clathrate compound; agitated equipment; overall heat transfer
coefficient; accelerated test; heat transfer medium
BROADER DESCRIPTORS: equipment; system; storage tank; container; molecular
compound; addition compound; compound(chemical); machinery; mixing
equipment; heat transmission coefficient; coefficient; ratio; test
CLASSIFICATION CODE(S): PC02010U

3/9/23

DIALOG(R)File 94:JICST-EPlus
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00908782 JICST ACCESSION NUMBER: 89A0465919 FILE SEGMENT: JICST-E
Utilization of clathrate hydrates for strage of gas.
HONDO TAKEO (1); ANZAI HIDENORI (1); AZUMA NOBUHIKO (1); GOTO AKIRA (1);
MAE SHINJI (1)

(1) Hokkaido Univ., Faculty of Engineering
Kanchi Giijutsu Shinpoijumu Koen Ronbunshu, 1988, VOL.1988, PAGE.562-566,
FIG.3, TBL.3, REF.3

JOURNAL NUMBER: X0501AAF
UNIVERSAL DECIMAL CLASSIFICATION: 624.14+.139
LANGUAGE: Japanese COUNTRY OF PUBLICATION: Japan
DOCUMENT TYPE: Conference Proceeding
ARTICLE TYPE: Commentary

DESCRIPTORS: ice; clathrate compound; hydrate; hydrophobic; gas; safety;
crystal structure; property; utilization; CA storage
BROADER DESCRIPTORS: molecular compound; addition compound;
compound(chemical); solvate; structure; preservation(food); storage;
conservation

CLASSIFICATION CODE(S): RC03000S
?s forefront(f)methane(w)hydrate/ti
2370 FOREFRONT
1908 METHANE/TI
415 HYDRATE/TI
S4 13 FOREFRONT(F)METHANE(W)HYDRATE/TI
?t 4/9/2,3,4,8; t 4/9/4,6,7,10,11,13
5

4/9/2

DIALOG(R)File 94:JICST-EPlus
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.03553546 JICST ACCESSION NUMBER: 96A0894440 FILE SEGMENT: JICST-E
Forefront of the methane hydrate research. Promotion and interference of
the hydration of methane by additives.

OKUI TOSHIHARU (1); KAWASAKI TATSUJI (1); MAEDA YURIKO (1); KONDO TAKEHIKO
(1)

(1) Tokyogasu Furontiatekunorojiken
Gekkan Chikyu(Chikyu Monthly), 1996, VOL.18,NO.10, PAGE.690-694, FIG.3,
REF.23

JOURNAL NUMBER: L0342AAU ISSN NO: 0387-3498
UNIVERSAL DECIMAL CLASSIFICATION: 551.14:547
LANGUAGE: Japanese COUNTRY OF PUBLICATION: Japan
DOCUMENT TYPE: Journal
ARTICLE TYPE: Original paper
MEDIA TYPE: Printed Publication

DESCRIPTORS: methane gas; hydrate; additive; reaction rate;
pressurization(apply); chemical equilibrium; chemical synthesis;
natural gas
BROADER DESCRIPTORS: combustible gas; solvate; addition compound;
compound(chemical); admixture; material; velocity;
operation(processing); equilibrium; chemical reaction; synthesis
CLASSIFICATION CODE(S): DD01043K

4/9/3

DIALOG(R)File 94:JICST-EPlus
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03553545 JICST ACCESSION NUMBER: 96A0894439 FILE SEGMENT: JICST-E
Forefront of the methane hydrate research. Occurrence and resources of
methane hydrate distributed in Sea of Okhotsk. Review.

ODA HIROSHI (1)
(1) Univ. of Tokyo, Grad. Sch.
Gekkan Chikyu(Chikyu Monthly), 1996, VOL.18,NO.10, PAGE.675-679, FIG.2,
REF.8

JOURNAL NUMBER: L0342AAU ISSN NO: 0387-3498
UNIVERSAL DECIMAL CLASSIFICATION: 553.981/.982
LANGUAGE: Japanese COUNTRY OF PUBLICATION: Japan

DOCUMENT TYPE: Journal

ARTICLE TYPE: Review article

MEDIA TYPE: Printed Publication

DESCRIPTORS: submarine sediment; hydrate; methane gas; Sea of Okhotsk;
reserves of petroleum; natural gas

BROADER DESCRIPTORS: sediment; solvate; addition compound;
compound(chemical); combustible gas; Northwest Pacific Ocean; North
Pacific Ocean; Pacific Ocean; name of oceans

CLASSIFICATION CODE(S): DE09050D

4/9/4

DIALOG(R)File 94:JICST-EPlus
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03553544 JICST ACCESSION NUMBER: 96A0894438 FILE SEGMENT: JICST-E
Forefront of the methane hydrate research. Heat flow of the Kumano trough
gotten from gas-hydrate BSR.

AKAZAWA YASUHIKO (1); ASHI JUICHIRO (2); TOKUYAMA EIICHI (3)
(1) Shizuokakyoikuse; (2) Univ. of Tokyo, Grad. Sch.; (3) Ocean Res. Inst.,
Univ. of Tokyo
Gekkan Chikyu(Chikyu Monthly), 1996, VOL.18,NO.10, PAGE.660-666, FIG.5,
REF.19

JOURNAL NUMBER: L0342AAU ISSN NO: 0387-3498
UNIVERSAL DECIMAL CLASSIFICATION: 550.36+551.21 551.35
LANGUAGE: Japanese COUNTRY OF PUBLICATION: Japan

DOCUMENT TYPE: Journal

ARTICLE TYPE: Original paper

MEDIA TYPE: Printed Publication

DESCRIPTORS: hydrate; natural gas; ocean trough; submarine sediment;
terrestrial heat flow; reflection survey; reflection plane; Northwest
Pacific Ocean

BROADER DESCRIPTORS: solvate; addition compound; compound(chemical); ocean
basin(geomorphology); geomorphic element; sediment; flow rate;
seismic exploration; geophysical exploration; exploration;
investigation; face; North Pacific Ocean; Pacific Ocean; name of oceans

CLASSIFICATION CODE(S): DC03070D; DE06000F

4/9/8

DIALOG(R)File 94:JICST-EPlus
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03553305 JICST ACCESSION NUMBER: 96A0885124 FILE SEGMENT: JICST-E
Forefront of the methane hydrate research. Basic research of natural gas
production and the sea bottom isolation of carbon dioxide. Elucidation
of structure and physical property of the gas inclusion compound.

OGAKI KAZUNARI (1); MATSUBARA TAKUYA (1); NAKANO SHIN'YA (1)
(1) Osaka Univ., Fac. of Eng. Sci.
Gekkan Chikyu(Chikyu Monthly), 1996, VOL.18,NO.10, PAGE.685-689, FIG.6,
REF.7

JOURNAL NUMBER: L0342AAU ISSN NO: 0387-3498
UNIVERSAL DECIMAL CLASSIFICATION: 551.14 622.24.085.5
LANGUAGE: Japanese COUNTRY OF PUBLICATION: Japan

DOCUMENT TYPE: Journal

ARTICLE TYPE: Original paper

MEDIA TYPE: Printed Publication

DESCRIPTORS: clathrate compound; carbon dioxide; submarine sediment; mixed
gas; phase equilibrium; reaction rate; ocean floor resource; submarine
mining

BROADER DESCRIPTORS: molecular compound; addition compound;
compound(chemical); carbon oxide; oxide; chalcogenide; oxygen group
element compound; oxygen compound; carbon compound; carbon group
element compound; sediment; gas; mixture; object; equilibrium; velocity
; mineral resource; resource; underwater mining; mining operations

CLASSIFICATION CODE(S): DD01041C; UA09030M

4/9/5
DIALOG(R)File 94:JICST-EPlus
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03553543 JICST ACCESSION NUMBER: 96A0894437 FILE SEGMENT: JICST-E
Forefront of the methane hydrate research. On the characteristics of BSR
of Nankai Trough and the offing of Abashiri.
SAKAI AKIO (1)
(1) Jpn. Pet. Explor. Co., Ltd.
Gekkan Chikyu(Chikyu Monthly), 1996, VOL.18,NO.10, PAGE.652-659, FIG.6,
TBL.1, REF.14
JOURNAL NUMBER: L0342AAU ISSN NO: 0387-3498
UNIVERSAL DECIMAL CLASSIFICATION: 550.834
LANGUAGE: Japanese COUNTRY OF PUBLICATION: Japan
DOCUMENT TYPE: Journal
ARTICLE TYPE: Original paper
MEDIA TYPE: Printed Publication
DESCRIPTORS: ocean trough; Northwest Pacific Ocean; reflection plane;
reflection survey; well logging; geothermal gradient; submarine
sediment
IDENTIFIERS: Nankai Trough
BROADER DESCRIPTORS: ocean basin; basin(geomorphology); geomorphic element;
North Pacific Ocean; Pacific Ocean; name of oceans; face; seismic
exploration; geophysical exploration; exploration; investigation;
temperature gradient; gradient; sediment
CLASSIFICATION CODE(S): DE10030B

4/9/6
DIALOG(R)File 94:JICST-EPlus
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03553307 JICST ACCESSION NUMBER: 96A0885126 FILE SEGMENT: JICST-E
Forefront of the methane hydrate research. Analysis of the methane hydrate
natural sample using X-ray CT and NMR. Example of the natural sample
gotten from ODP Leg164.
UCHIDA TAKASHI (1); YAMAMOTO JUNJI (1); OKADA SHIN'ICHI (1); OKATSU KOMEI
(2)
(1) Jpn. Pet. Explor. Co., Ltd., JAPEX Res. Cent.; (2) Technol. Res. Center
Jpn. Natl. Oil Corp.
Gekkan Chikyu(Chikyu Monthly), 1996, VOL.18,NO.10, PAGE.704-709, FIG.5,
TBL.1, REF.4
JOURNAL NUMBER: L0342AAU ISSN NO: 0387-3498
UNIVERSAL DECIMAL CLASSIFICATION: 551.14:547
LANGUAGE: Japanese COUNTRY OF PUBLICATION: Japan
DOCUMENT TYPE: Journal
ARTICLE TYPE: Original paper
MEDIA TYPE: Printed Publication
DESCRIPTORS: hydrate; methane gas; submarine sediment; Northwest Atlantic
Ocean; boring core; excavation; X-ray computed tomography; 13C NMR;
natural gas
BROADER DESCRIPTORS: solvate; addition compound; compound(chemical);
combustible gas; sediment; North Atlantic Ocean; Atlantic Ocean; name
of oceans; geological sample; sample; X-ray inspection; radiographic
inspection; nondestructive inspection; inspection; computed tomography;
diagnostic imaging; diagnosis; tomography; image technology; technology
; radiography; NMR; magnetic resonance; resonance
CLASSIFICATION CODE(S): DD01043K

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DIALOG(R)File 94:JICST-EPlus
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03553306 JICST ACCESSION NUMBER: 96A0885125 FILE SEGMENT: JICST-E
Forefront of the methane hydrate research. Methane hydrate synthesis
experiment and examination of the stable condition.
MAEKAWA TATSUO (1); IMAI NOBORU (1)
(1) Geol. Surv. of Jpn., Agency of Ind. Sci. and Technol.
Gekkan Chikyu(Chikyu Monthly), 1996, VOL.18,NO.10, PAGE.695-699, FIG.2,
REF.11
JOURNAL NUMBER: L0342AAU ISSN NO: 0387-3498
UNIVERSAL DECIMAL CLASSIFICATION: 551.14
LANGUAGE: Japanese COUNTRY OF PUBLICATION: Japan
DOCUMENT TYPE: Journal
ARTICLE TYPE: Original paper
MEDIA TYPE: Printed Publication
DESCRIPTORS: methane gas; hydrate; natural gas; chemical synthesis; sodium
chloride; aqueous solution; stability constant
BROADER DESCRIPTORS: combustible gas; solvate; addition compound;
compound(chemical); chemical reaction; synthesis; alkali metal halide;
alkali metal compound; halide; halogen compound; chloride; chlorine
compound; sodium compound; solution(liquid); liquid; chemical
equilibrium; equilibrium
CLASSIFICATION CODE(S): DD01041C

4/9/10
DIALOG(R)File 94:JICST-EPlus
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03553303 JICST ACCESSION NUMBER: 96A0885122 FILE SEGMENT: JICST-E
Forefront of the methane hydrate research. Collapse sediment observed in
the Amazon submarine fan. Dissolution of gas-hydrate and slope
failure.
SO UON (1); SUZUKI KIYOFUMI (1); OKATSU KOMEI (2)
(1) Kyushu Univ., Faculty of Science; (2) Technol. Res. Center Jpn. Natl.
Oil Corp.
Gekkan Chikyu(Chikyu Monthly), 1996, VOL.18,NO.10, PAGE.667-674, FIG.5,
TBL.2
JOURNAL NUMBER: L0342AAU ISSN NO: 0387-3498
UNIVERSAL DECIMAL CLASSIFICATION: 551.35
LANGUAGE: Japanese COUNTRY OF PUBLICATION: Japan
DOCUMENT TYPE: Journal
ARTICLE TYPE: Original paper
MEDIA TYPE: Printed Publication
DESCRIPTORS: submarine fan; submarine sediment; slope failure; hydrate;
natural gas; dissolution; debris flow; South America; river
IDENTIFIERS: Amazon
BROADER DESCRIPTORS: alluvial fan; geomorphic element; sediment; decay;
solvate; addition compound; compound(chemical); Americas
CLASSIFICATION CODE(S): DE06000F

4/9/11
DIALOG(R)File 94:JICST-EPlus
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03553302 JICST ACCESSION NUMBER: 96A0885121 FILE SEGMENT: JICST-E
Forefront of the methane hydrate research. Physical property measurement,
well logging and BSR of the breaking ridge transect.
SATO MIKIO (1)
(1) Geol. Surv. of Jpn., Agency of Ind. Sci. and Technol.
Gekkan Chikyu(Chikyu Monthly), 1996, VOL.18,NO.10, PAGE.647-652, FIG.4,
REF.6
JOURNAL NUMBER: L0342AAU ISSN NO: 0387-3498
UNIVERSAL DECIMAL CLASSIFICATION: 550.834
LANGUAGE: Japanese COUNTRY OF PUBLICATION: Japan
DOCUMENT TYPE: Journal
ARTICLE TYPE: Original paper
MEDIA TYPE: Printed Publication
DESCRIPTORS: hydrate; natural gas; well logging; boring core; petrophysical
property; reflection plane; reflection survey; oceanic ridge; Northwest
Atlantic Ocean; submarine sediment
BROADER DESCRIPTORS: solvate; addition compound; compound(chemical);
exploration; investigation; geological sample; sample; lithologic
character; property; face; seismic exploration; geophysical exploration
; geomorphic element; North Atlantic Ocean; Atlantic Ocean; name of
oceans; sediment
CLASSIFICATION CODE(S): DE10030B

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DIALOG(R)File 94:JICST-EPlus
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03553300 JICST ACCESSION NUMBER: 96A0885119 FILE SEGMENT: JICST-E
Forefront of the methane hydrate research. Followings are investigated :
Solid methane and gas-hydrate under the sea bottom. Perspective on the
results of ODP Leg164 and the research about methane hydrate.
MATSUMOTO RYO (1)
(1) Univ. of Tokyo, Grad. Sch.
Gekkan Chikyu(Chikyu Monthly), 1996, VOL.18,NO.10, PAGE.633-639, FIG.6,
REF.5
JOURNAL NUMBER: L0342AAU ISSN NO: 0387-3498
UNIVERSAL DECIMAL CLASSIFICATION: 553.981/.982 551.14:547
LANGUAGE: Japanese COUNTRY OF PUBLICATION: Japan
DOCUMENT TYPE: Journal
ARTICLE TYPE: Review article
MEDIA TYPE: Printed Publication
DESCRIPTORS: methane gas; hydrate; submarine sediment; excavation; boring
core; Northwest Atlantic Ocean; international cooperation; natural gas
BROADER DESCRIPTORS: combustible gas; solvate; addition compound;
compound(chemical); sediment; geological sample; sample; North Atlantic
Ocean; Atlantic Ocean; name of oceans; cooperation(partnership)
CLASSIFICATION CODE(S): DE09050D; DD01043K
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\$0.25 TYMNET
\$23.94 Estimated cost this search
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