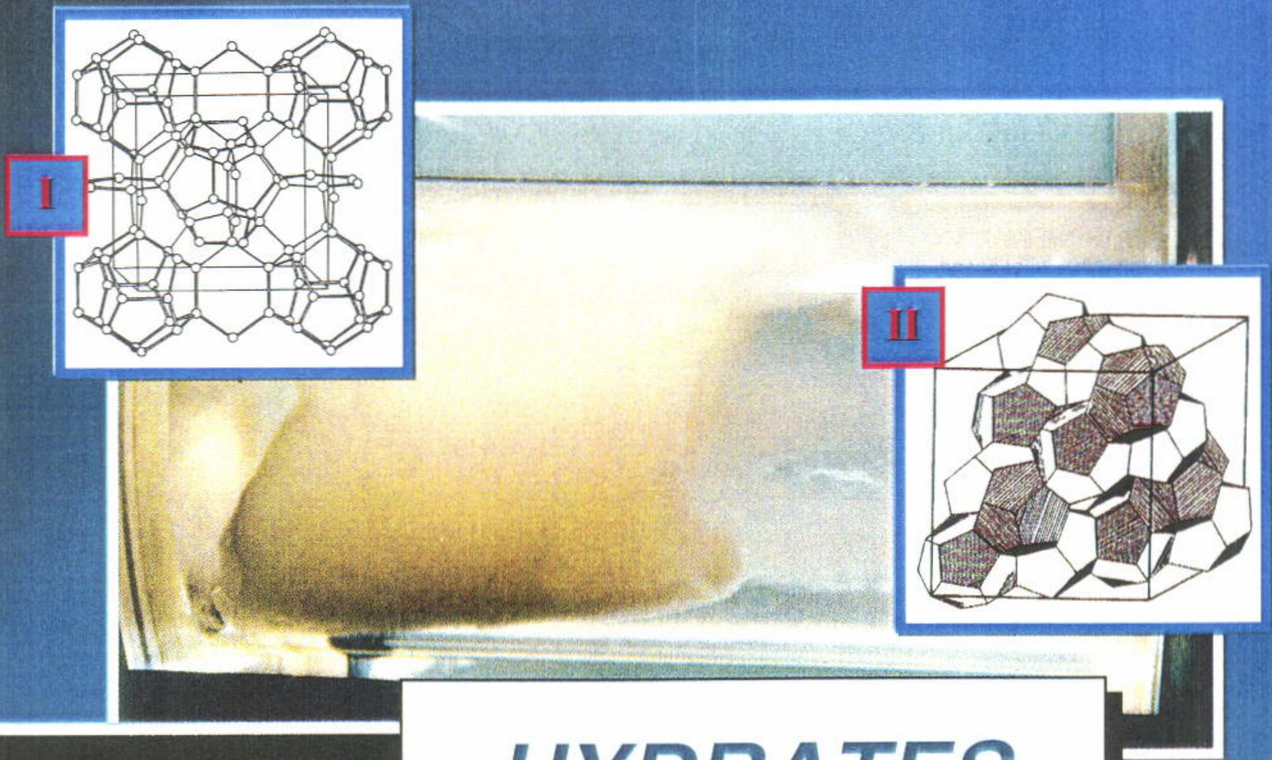
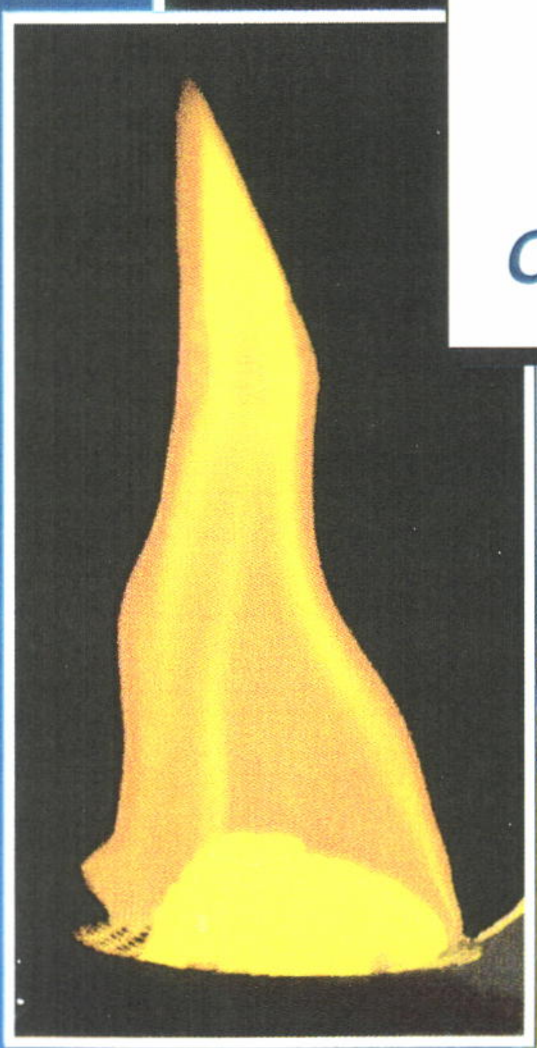
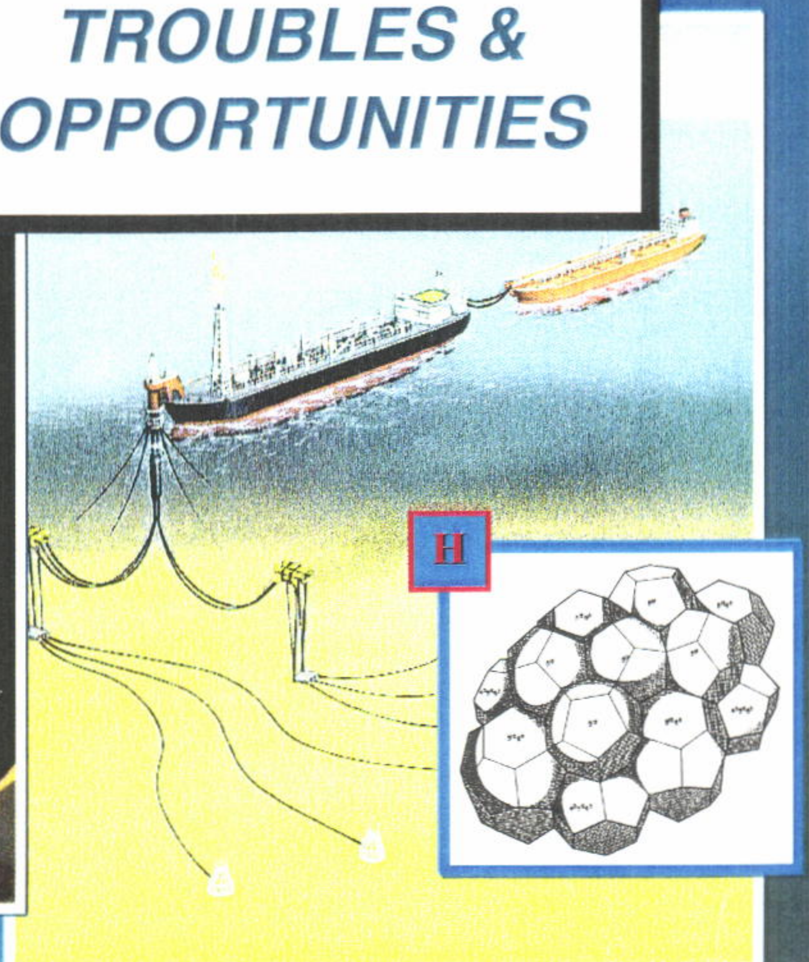
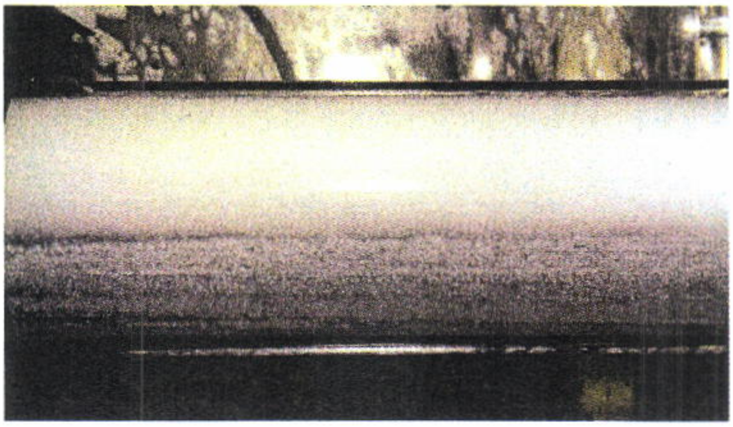


HYDRATES
TROUBLES & OPPORTUNITIES





The gas hydrates are deposits similar to ice. They occur when hydrocarbons come into contact with water at specific T and P. Gas, condensates and oil can produce hydrates in cold habitats (ex. deep waters, seabed conditions T=3÷4°C; sealine working pressure 70÷80 bar).



HYDRATE DEPOSITION ON PIPE WALL
(SINTEF-Annual report 1992
Hydrate formation and behaviour in flowing fluids)

1 - HYDRATES

Gas hydrates are crystalline solids similar to ice, consisting of water (about 85% of the total) and gas (e.g. methane, nitrogen, helium Fig. 1)[1-10]. These compounds are stable at high pressures and low temperatures.
The above conditions may occur in different points of the oil production system: pipelines, production facilities.
They may occur in subsea lines (e.g. North Sea, Gulf of Mexico) when oil and/or unstabilised wet gas are transported together (multiphase). In fact, the pressure in these pipelines is usually high and the temperatures low - being close to the seabed temperature.

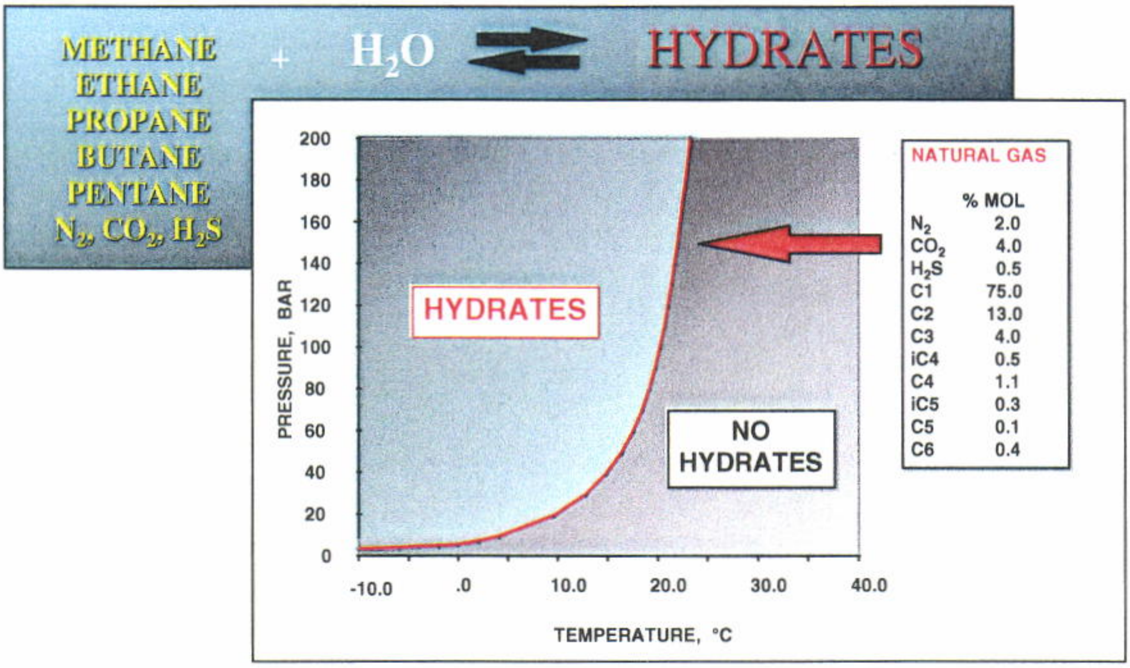


FIG.1 - STABILITY PREDICTION OF HYDRATES IN A GAS PIPELINE

Another example of hydrate occurrence is during the storage of gas in underground caves (Nixdorf and Oellrich 1996)[11]. Usually the temperature inside these caves is too high to enable the formation of hydrates, however the dry gas which is injected may become saturated with water. As the wet gas is collected during winter, temperatures close to the surface may be low enough to promote the formation of hydrates. The first reported case of hydrates forming outside the lab dates back to 1934 (Hammerschmidt)[12] and involved the attempt to distribute gas saturated with water during winter.

Gas hydrates are also present in the natural environment, below ocean beds and in the permafrost.

The structure of hydrates, their chemical - physical characteristics and thermo-dynamic behaviour have already been widely studied. However, as concerns the formation of these compounds, a great deal still has to be discovered about the kinetic aspects which govern the reaction and control the rate of formation.

The technologies related to hydrates have mainly been developed as a result of knowledge on the thermodynamics of these compounds. Thermodynamics make it possible to identify the stability conditions of hydrates in various compositional states (description of phase equilibria with various types of hydrocarbon mixtures) and to plan chemical treatments for inhibiting these products (calculation of the required amounts of methanol and glycol for inhibiting the hydrate formation, description of the phase equilibria in the presence of inhibitors).

To sum up this brief look at the main characteristics of hydrates, we shall mention a particular aspect of these compounds: an ice-cube is stable for a fairly long time - several hours - at ambient pressure and at temperatures below 0°C.

In fact the decomposition process of hydrates is slow. The most interesting aspect of these compounds is when the hydrocarbon gases, which are released through decomposition, are burnt. It is as if an ice-cube, which the gas hydrates resemble, were to burn (Fig.2).

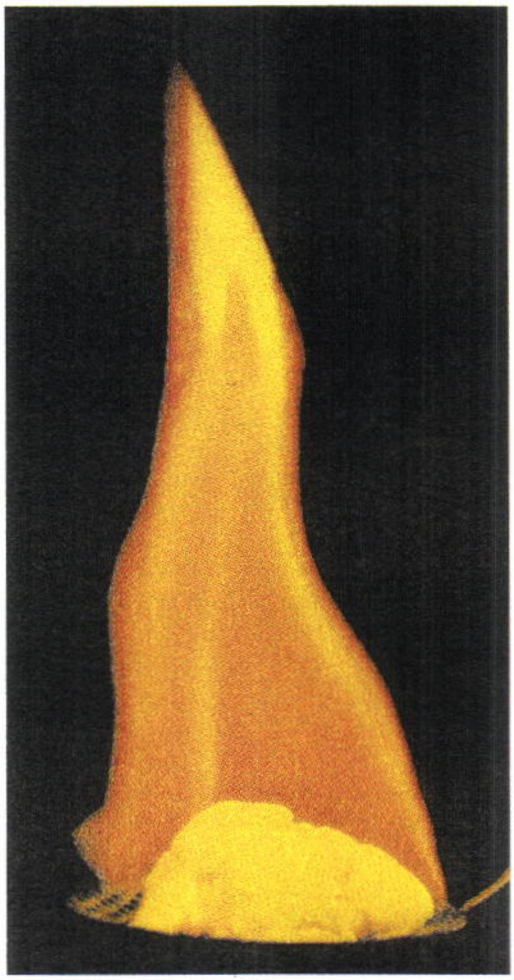


FIG. 2 - METHANE HYDRATE COMBUSTION
(M.BYLOV - Ph.D. Thesis - 1997
Institut for Kemiteknik-Danmarks Tekniske Universitet)

2 - WHY THE OIL AND NATURAL GAS INDUSTRIES DEAL WITH GAS HYDRATES

The oil industry deals with gas hydrates in terms of both problems and opportunities. Hydrates are a problem as they can form in many different situations at each level of the hydrocarbon (oil and gas) production cycle: drilling, production, processing[13-21].

Yet these compounds also represent an opportunity and a challenge to the present-day frontiers of hydrocarbon production, as through control of hydrates is essential in developing new areas such as: marginal reservoirs (the North Sea, the Gulf of Mexico) and gas hydrate reservoirs (Alaska section of the Kuparuk River; the Siberia-Messoyakha Field).

EXAMPLES OF HYDRATE OCCURRENCES IN PETROLEUM INDUSTRY

- *Hydrates and multiphase production (oil + gas+water) (Ref.19,20)*
- *Hydrate formation/inhibition during deepwater subsea completion operations (Ref. 21) and production (Ref. 22, 23)*
- *Gas hydrates formation and deposition in gas or gas condensate streams (Ref. 17, 39)*
- *Plugging problems in undersea natural gas pipelines under shutdown conditions (Ref. 14)*
- *Formation and control in long distance submarine pipelines (Ref. 15)*

3 - HYDRATES - THE PROBLEMS

Hydrates are solids, which increase and cake so quickly when they crystallise, that they obstruct the facilities: which may be anything from a pipeline to a well completion. For this reason the effects of their presence may be extremely serious for carrying out normal production operations.
The *formation of hydrates during drilling operations* is usually due to concomitant causes, such as low temperatures-high pressures-drilling mud make up-hydrocarbon composition water production. Two cases have been widely reported: the first concerns the drilling of a well offshore the western coast of the United States (depth 350m, mud-line temperature 7°C); the second, the drilling of a well in the Gulf of Mexico (depth 945 m, mud-line temperature 4°C)[22]. In both circumstances, the hydrates obstructed the choke and kill lines during gas kick control operations.

The *formation of hydrates during production* is mainly linked to operations performed in cold habitats (for example deep waters)[23-24] which cause major pressure increases. It has been demonstrated that these conditions usually occur during production start-up or during prolonged shut down of a well which has previously been in production.
The hydrates may also form while the well is in production. The figure 3 shows a deep water scenario, water may be present in the flow lines and T/P conditions (4-7°C;50-100 bar) can promote the hydrate deposition.

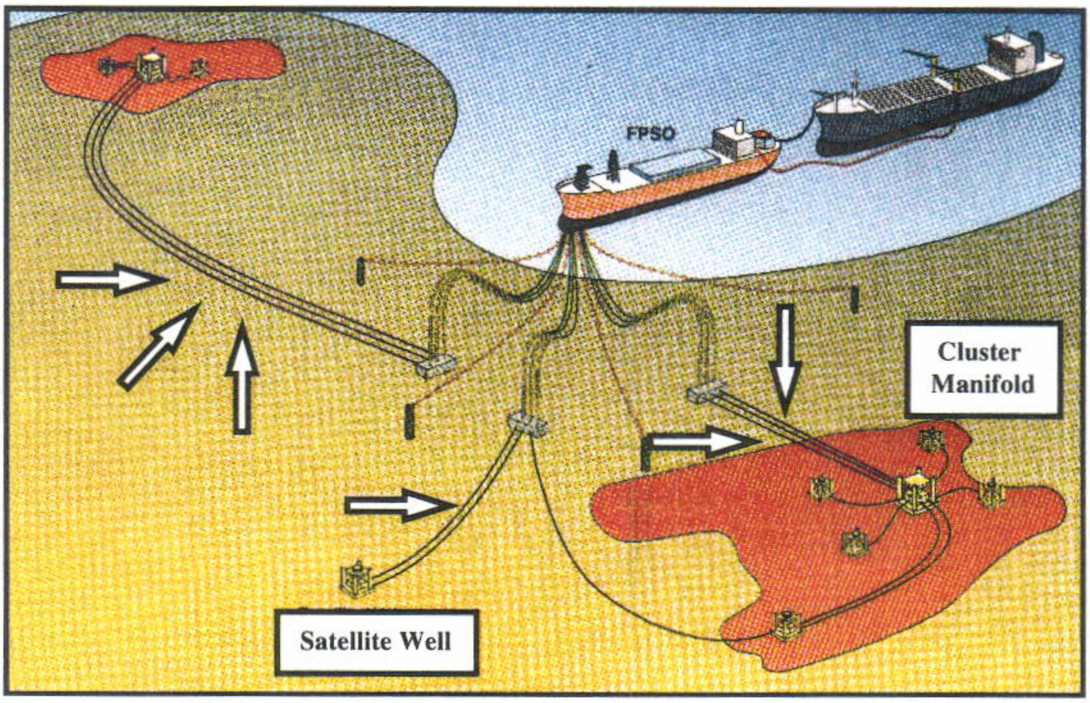


FIG. 3 - HYDRATE LOCATION (WHITE ARROWS)
IN DEEP WATER SCENARIO : TOTAL SUBSEA PRODUCTION
(AGIP-RIIN Dept.)

The formation of hydrate plugs can lead to various consequences: hydrocarbon production may drop significantly until it stops, obstructions can make it hard to control wireline tools in the tubings, the hydrate plugs may negatively affect the opening and closing of the downhole valves which control the flow of fluids produced in the tubing and the annulus.
The hydrate deposition experimented in a laboratory loop using different flow conditions showed that various types of hydrate can be produced: slurry-like or ball-like or wall adhesive thin layered . In the figure 4 are represented three different cases. The hydrate obstruction of the line is observed only in B and C.

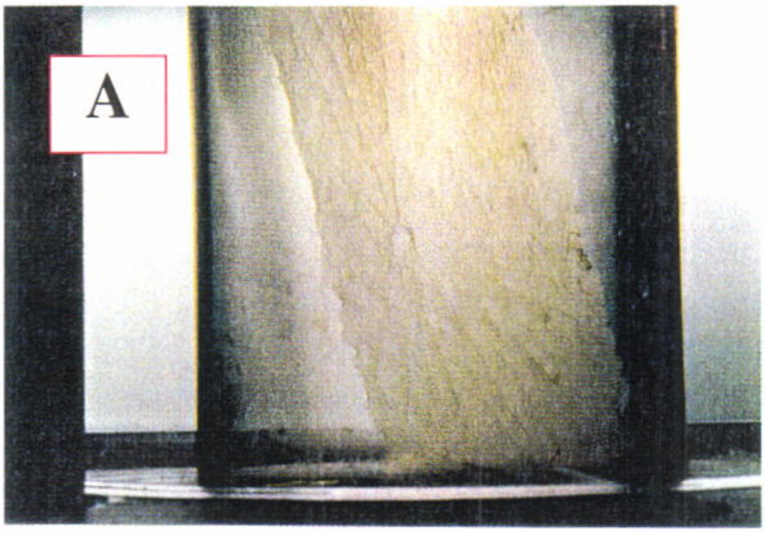
Formation of hydrates during transport

The presence of hydrates in the production cycle has even been identified during the pipeline transport of fluids and in this case too, the problem of hydrates affects both gas and liquid hydrocarbon transport. An oil, which consists mainly of heavier hydrocarbon components, also contains the lighter hydrocarbons which generate hydrates. Line obstructions due to the formation of hydrates have mostly occurred in the subsea transport of gas and condensate, as operative conditions are usually harsher in these cases (high pressures, low temperatures). The accumulation of these crystalline solids may also occur in horizontal sections, in particular locations (depressions and narrowings).
The entity of this problem may vary and depends on many factors: the length of the lines, the amounts of water transported, the operative conditions.

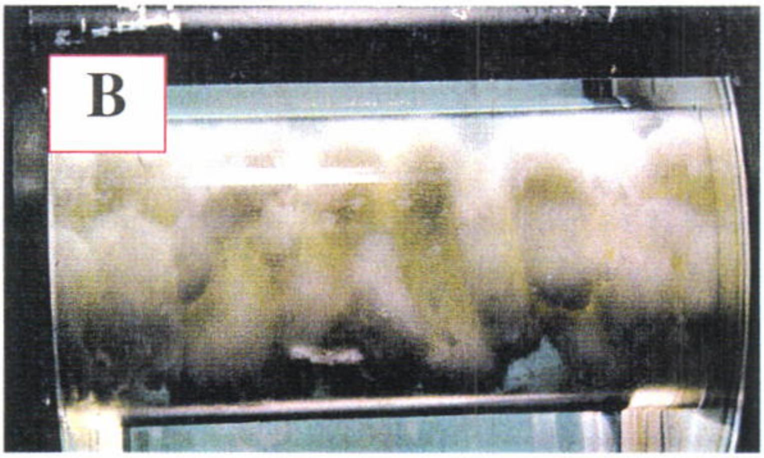
From 1990 to 1993 the Norwegian Petroleum Directorate (NPD), in association with SINTEF, performed two studies to define the type and entity of hydrate-based problems related to drilling activities on the Norwegian continental shelf.[25] A detailed questionnaire about hydrate formation events in sealines was handed out to 15 companies operating in the North Sea. The reported cases of hydrate formation concerned:

- a 12 km long, 9" oil/gas sealine, where a faulty valve led to an anomalous inlet of water, which in turn triggered on the formation of hydrates;
- a 12 km long, 6" oil/gas sealine, where hydrates formed during production start up. Suitable inhibition procedures had not been adopted;
- a 7 km long, 5" oil/gas sealine, where total obstruction occurred because of the hydrates. In this case the critical factor was identified as the sudden drop in temperature due to an unscheduled shut down operation.

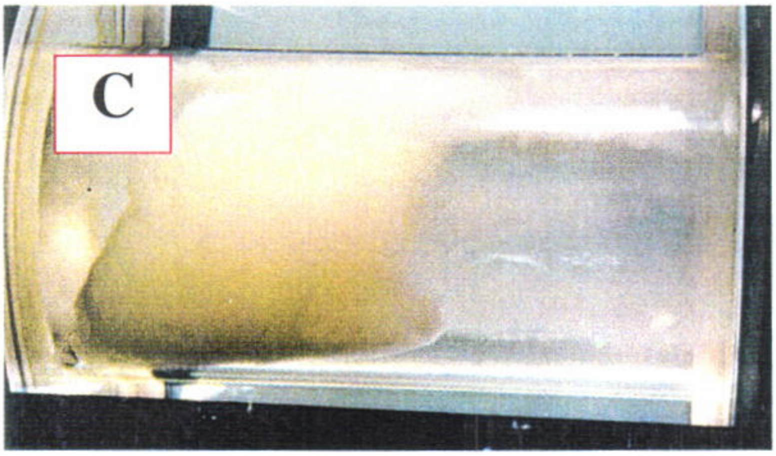
Another aspect of the problems related to hydrates is the potential safety risk during operations to eliminate these substances. One of the most common methods for eliminating hydrates is to melt them by depressurization. (Fig.7). It can be hard to control this operation, because of the characteristics of the solids which form. These solids are not usually homogeneous and may incorporate foreign bodies (sand, shale). Accidents related to damage to control structures and equipments have occurred during these operations, due to the uncontrolled movement of plugs along the line.



HARD HYDRATE DEPOSIT ON THE WALL



HYDRATE BALLS



SOFT HYDRATE PLUG AND ADHESIVE HYDRATE

FIG. 4 - HYDRATE MACROSCOPIC STRUCTURES IN AN EXPERIMENTAL FLOW LOOP.
(SINTEF-Annual report 1992
Hydrate formation and behaviour in flowing fluids)

4 - STATE OF THE ART OF CURRENT TECHNOLOGIES FOR CONTROLLING HYDRATES

Know-how on thermodynamic behaviour is now consolidated, and a great deal of work has been done on modelling the thermodynamic behaviour of hydrates. A variety of simulation programmes currently exist on the market and these can be used to successfully evaluate the T, P conditions for the formation of hydrates, describe the chemical-physical properties of the hydrates and calculate the effects of some inhibitors on the stability of these compounds. Agip uses the HYDSIM programme by CALSEP A/S.

Current strategies for controlling these compounds are based mainly on the knowledge of thermodynamics.[39-40] In fact the most common means for preventing the formation of hydrates are:

- *eliminating the water phase from the relevant system;*
- *increasing the system's temperature to values above the range where hydrates are stable at a given pressure;*
- *decreasing pressure to values below the range where hydrates are stable at a given temperature;*
- *injecting inhibitors, such as methanol, to move the thermodynamic stability curve of the hydrates so that the compounds do not form in the system's current temperature and pressure conditions (Fig.5).*

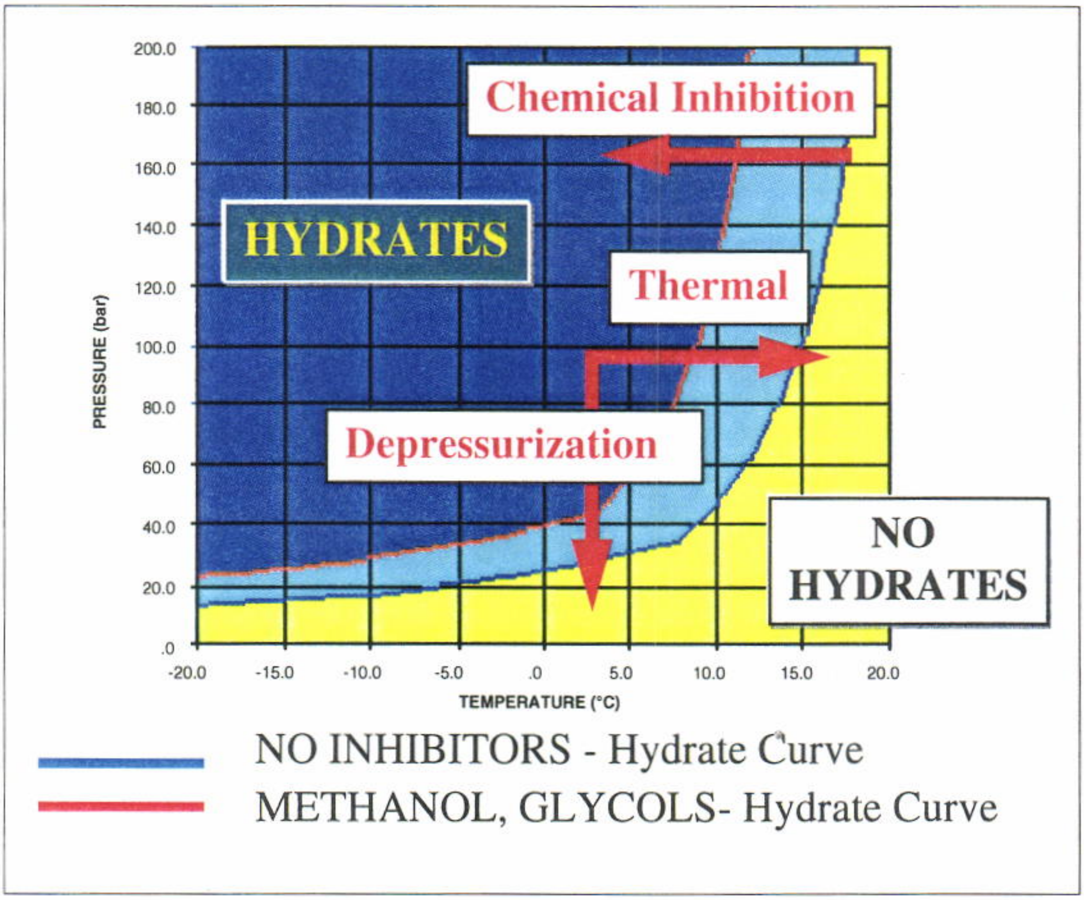


FIG. 5 - DEPRESSURIZATION, THERMAL AND CHEMICAL INHIBITION EFFECTS ON HYDRATE STABILITY.
(Modified from M.H.Yousif et al. ,SPE 30641, 1995)

4.1 - Treating hydrates with chemical products[40-43]

The conventional method for preventing the formation of hydrates, after optimising the T and P conditions, is to inject chemical products. The oil industry, including AGIP, mainly uses methanol and glycols (diethylene glycol and triethylene glycol). These inhibitors act on the thermodynamics of the system, by lowering the temperature and increasing the threshold pressure of the hydrates. In operative terms, these inhibitors are chosen on the basis of the efficiency-cost ratio of the products used. The figure 6 shows the main parameters selected for comparing methanol, monoethylene glycol, diethylene glycol and triethylene glycol: the quantities needed to obtain the same degree of inhibition, cost, irreversible losses of the chemical, possibilities of recycling the product, problems in using it.

Methanol is the most widely used of these products,because of its cost and efficiency. It reacts with the solid surface of the hydrate more quickly than the other products, however it is the hardest to recover. It is normally used as a disposable product, while glycols are recycled and put back into the system. Because of its high vapour pressure, irreversible losses of methanol are more likely. The product must also be handled with care, as it is inflammable and highly toxic upon direct contact.

Regardless of the choice of chemical, treatments with these products are no longer effective when the water cuts are high (30-60%). In these cases, such big amounts of product may be required that there are no longer any advantages in producing the hydrocarbons.

	METHANOL	MONO-ETHYLENE GLYCOL	DI-ETHYLENE GLYCOL	TRI-ETHYLENE GLYCOL
INHIBITOR AMOUNT ($Kg_{inhibitor}/Kg_{produced\ H2O}$)	0.15	0.29	0.43	0.51
COST (Lit/Kg)	1000	1200	1100	1350
INHIBITOR LOSS DURING THE TREATMENT	HIGH	LOW	LOW	LOW
CHEMICAL RETRIEVE	NO	YES	YES	YES
HAZARD	flammable toxic	non-flammable low toxicity	non-flammable low toxicity	non-flammable low toxicity

FIG. 6 - CHARACTERISTICS OF CLASSIC INHIBITORS

4.2 -Treating hydrates with thermal methods[44]

Hydrates can be eliminated by using external energy sources to increase the system's temperature and cause the decomposition of the hydrates. Hot water or steam re-circulation systems exist, as well as the use of thermal tracers and electromagnetic energy. However these systems alone are hardly ever efficient and are normally combined with depressurization and chemical inhibitor treatments.

Thermal insulation can be used to prevent the formation of hydrates. Insulation, with varying costs, may be applied for both hydrocarbon pipelines and for wells (tubing insulation). One of the most efficient insulation methods consists of a double walled line, with a vacuumed or gas-filled annulus to further reduce heat dispersion.

4.3 - Treating hydrates with depressurization[45]

Depressurization is practically the only way to eliminate hydrate plugs from gas and/or condensate gas subsea pipelines. This method is normally applied with a fairly limited knowledge of the location of the obstructions and their entity. During depressurization, the pipeline pressure is decreased to a value below the hydrate equilibrium pressure referred to the seabed temperature.

As a result, the solid hydrate begins to dissociate and produces heat which is absorbed by the surrounding environment. The generated heat expands towards the obstruction, further increasing dissociation which stops when a new thermodynamic equilibrium has been reached. The decomposition process of the hydrates is related to the line temperature and extent of the pressure variation applied (Fig.7). Eliminating hydrates by depressurization is usually a slow process (at times, it may take days), if applied at a low temperature and with slight drops in pressure.

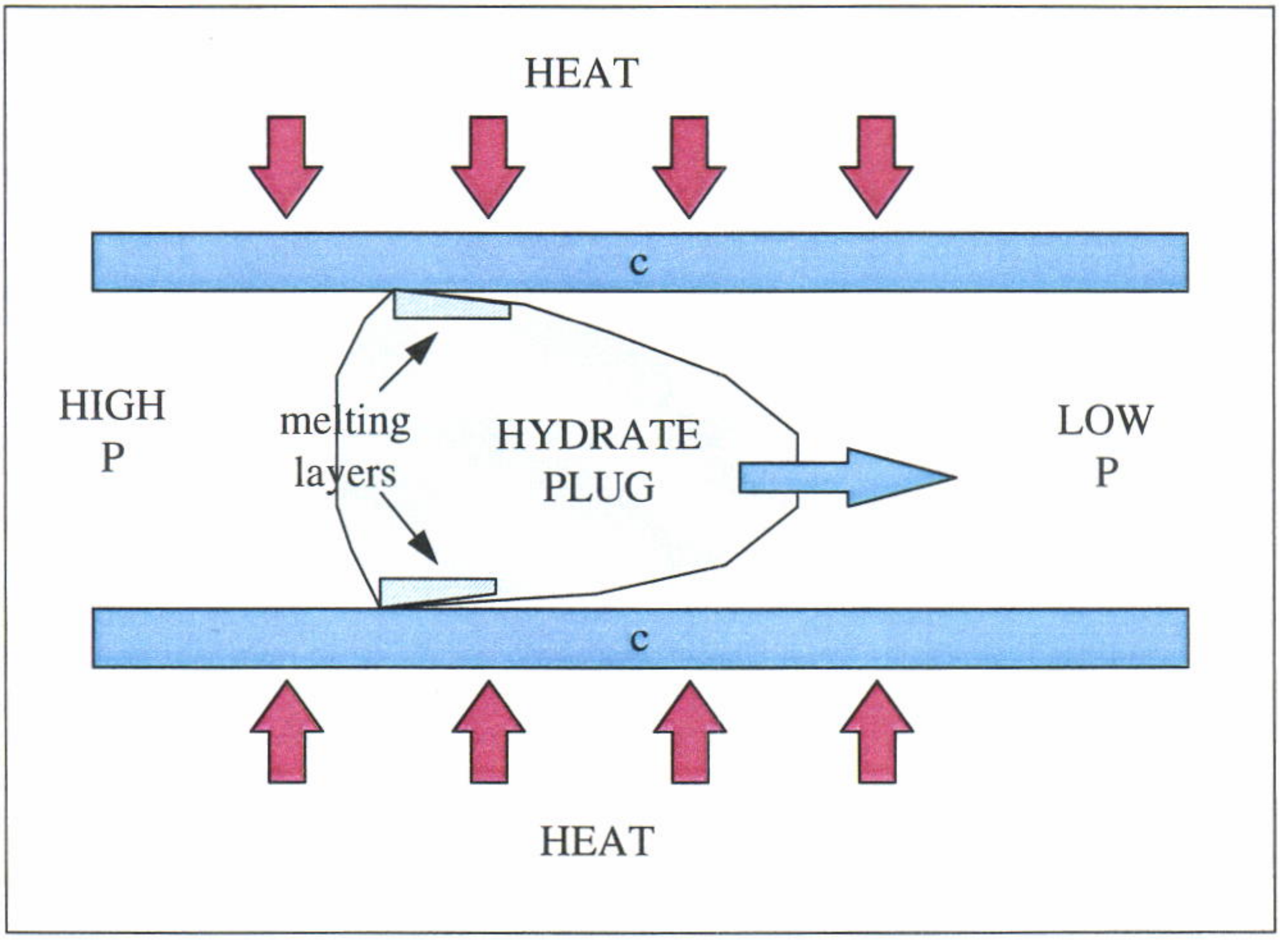


FIG. 7- SCHEMATIC OF MELTING PIPELINE HYDRATE DUE TO PRESSURE REDUCTION ON ONE SIDE ONLY. (R.LARSEN,T.Y.MAKOGON,C.A.KNIGHT,E.D.SLOAN JR., 1997, Preprint)

5- NEW DEVELOPMENTS IN HYDRATE TECHNOLOGY

New developments in hydrate technology have focused on three main aspects:

- *identifying new chemical inhibitors which will radically change the current approach to using chemical treatments;*
- *perfecting a new technology for transporting natural gas as gas hydrate;*
- *applying innovative technologies for putting hydrate fields into production.*

5.1 - Kinetic inhibitors, a new approach to treating hydrates[46-52]

At present, chemical treatments for hydrates are focusing on alternatives to thermodynamic inhibitors (methanol and glycol) (Fig. 8).

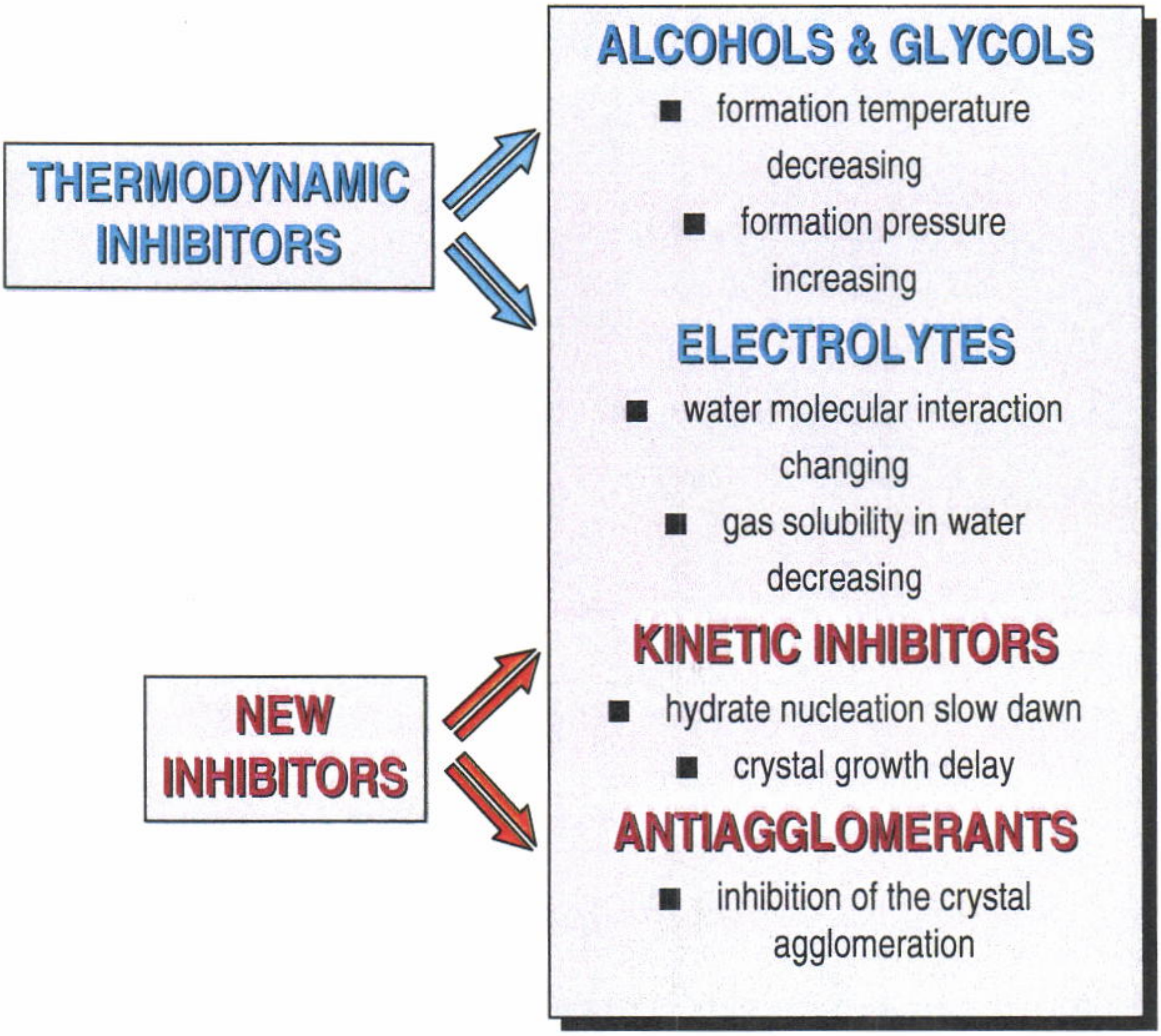
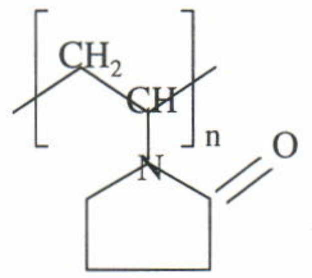


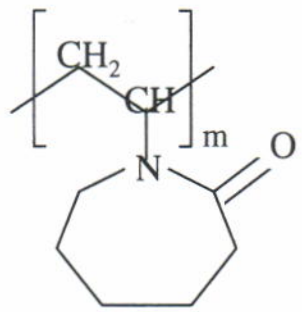
FIG. 8 - CHEMICAL TREATMENTS FOR HYDRATES

Suggestions have been made for a low dosage chemical treatment system, where the chemical is disposed of, so its environmental impact is reduced. The significantly lower dosage levels mean that costs for purchasing, treating and recovering the product are also reduced.
Agip, like many other oil companies (Conoco, Shell, Elf), is sponsoring research on the identification and selection of a new class of products: kinetic inhibitors.
Lab tests have already identified some new chemical products (e.g. polyamide polymers such as PVP, PVCap, VC-713, VP:VCap , Fig.9), however information on these products' efficiency in the field is still incomplete.

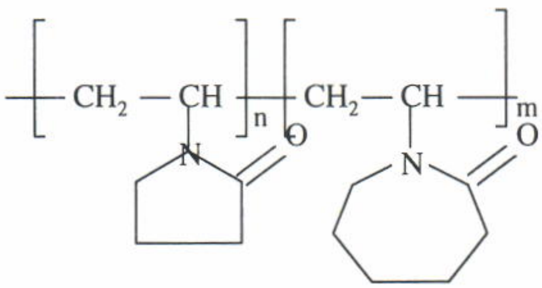
BP has tried out kinetic inhibitors (Corrigan 1995)[53] in the North Sea, on a pipeline which transports wet gas from the Ravenspurn field to the Cleeton field. The line is 13 miles long, with a temperature (8-9 °C) and pressure (75 bar) that are suitable for the formation of hydrates. During the test, methanol - which is normally used as the inhibitor - was successfully replaced for seventeen days with a kinetic inhibitor that was not specifically defined. The authors state that these inhibitors enabled efficient control of shut down and re-start operations, which are generally the most critical for hydrates.
The basic idea behind the use of kinetic inhibitors is to control hydrates, by controlling the kinetic processes of their formation and therefore their formation times (Fig.10). The fact that this new class of products acts on the kinetics of reactions has radically changed the concept of this treatment. The reason for this is that the kinetic inhibitors affect the mechanisms which the first stages of hydrate formation depend on: the formation of the first crystalline nuclei (nucleation) and the rate at which they grow. As far as we know, the kinetic inhibitors should act with water and gas on a molecular level as if they were catalysts, yet they should hinder, rather than favour, the onset of the reaction of hydrate formation.



PVP = POLYVINYLPYRROLIDONE



PVCap = POLYVINYLCAPROLACTAM



VP:VCap copolymers

FIG. 9 - CHEMICAL STRUCTURE OF SOME POLYMERIC KINETIC INHIBITORS

Like catalysts, these compounds should be active in very low concentrations and this is the very reason why these products have an innovative potential: the fact that very low amounts (<1% in weight, while methanol is normally used in concentrations ranging from 10 to 60 % in weight) of inhibitor can guarantee efficient inhibition.

Today's challenge is to identify chemical products which not only have the requirements described, but also offer a high level of compatibility with other chemicals, (e.g.: anti-corrosion products), minimum environmental impact and low production costs.

The experimented kinetic inhibitors may affect the phenomena of hydrate formation and hydrate growth. In the figure 10 are drawn the hydrate formation curves in three different cases:

1. ***absence of inhibitor***
2. ***kinetic inhibitors affecting induction time (necessary to form the first crystal of hydrate)***
3. ***kinetic inhibitors affecting the growth of hydrate.***

In the first case the hydrate formation is almost instantaneous.
In the second one the induction time is increased (the hydrate formation is slowed down), then the growth is very quick.
In the third case the growth of the crystals is controlled, so the precipitation process is globally slowed down.

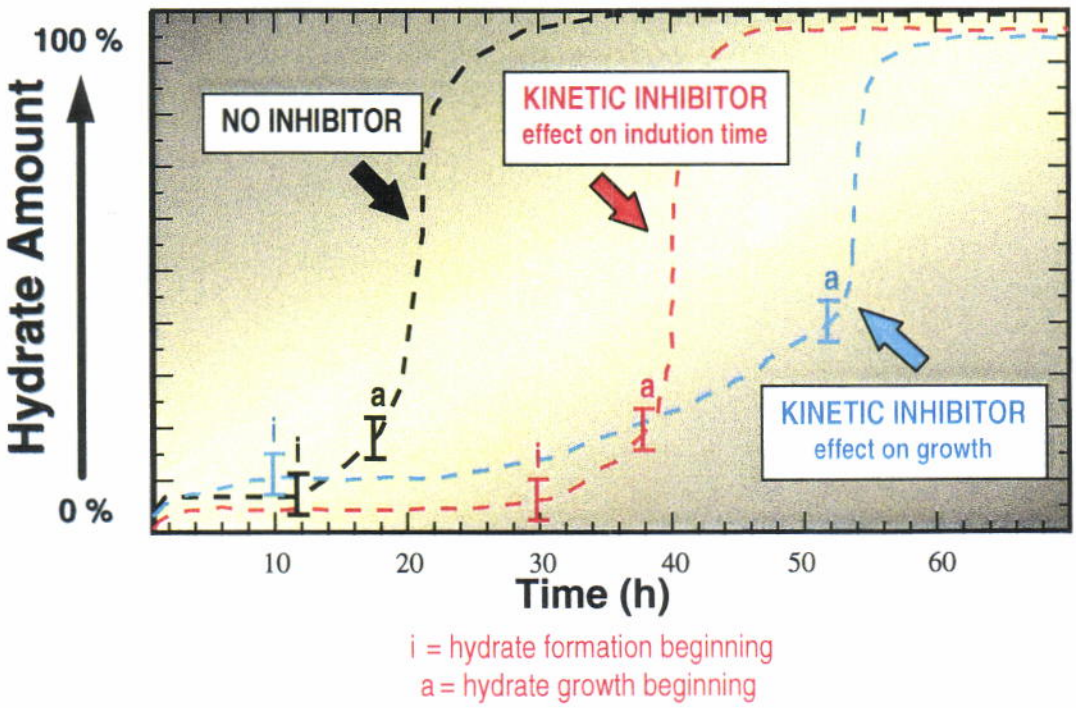


FIG. 10 - INFLUENCE OF KINETIC INHIBITORS ON HYDRATE GROWING CURVES

6-HYDRATES:THE OPPORTUNITIES

The opportunities provided by hydrates are linked to the search for new energy sources. The oil industry is advancing along two fronts, in this search: technological innovation to enable the commercial development of marginal reservoirs and identification of alternative hydrocarbon reserves.

As far as the identification of **alternative hydrocarbon reserves** is concerned, there is a great deal of evidence that major reserves of hydrocarbons in the form of gas hydrates exist in the subsurface (Fig.12)[26-34]

There are two factors which lend interest to gas hydrates as a potential energy source: the vast amount of natural gas apparently incorporated in the crystalline lattice of these compounds (1 cm^3 of methane hydrate produces up to 150 cm^3 of natural gas) and the extensive distribution of natural gas hydrates world-wide. Credible sources (Kvenvolden, 1993)[35] estimate world (natural hydrate gas reserves in the range of 1.4×10^{13} to 3.4×10^{16} m^3 for the permafrost and 3.1×10^{15} to 7.6×10^{18} m^3 of gas for oceanic sediments .

These are speculative figures, with a wide margin of uncertainty, however the leading experts in the sector agree on an overall estimated energy potential from natural hydrate reserves in the range of 2×10^{16} m^3 of natural gas. This figure represents an equivalent amount of carbon which is approximately twice the amount evaluated on the basis of known fossil hydrocarbon accumulations (Fig.11). At present, only Japan is developing new technologies for the production of natural gas from natural hydrate reservoirs. A five-year exploration plan (1995-99) for offshore hydrate drilling in the Nankai Trough area has been financed by the Ministry for Trade and International Industry (MITI) (Dagam-1995, Okuda-1996).[37-38]

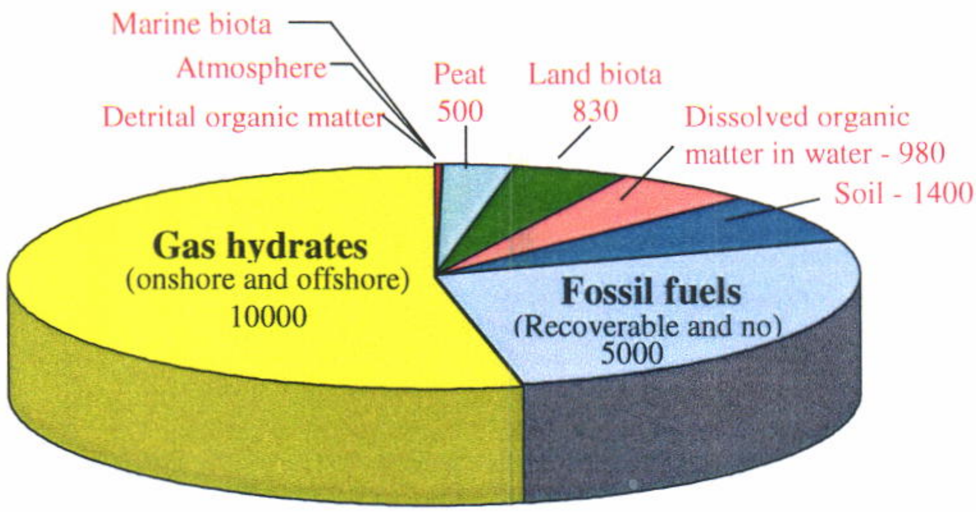


FIG. 11 - DISTRIBUTION OF ORGANIC CARBON IN THE EARTH. NUMBERS ARE IN UNITS OF 10^{15} G OF CARBON. (KVENVOLDEN, 1993)[35]

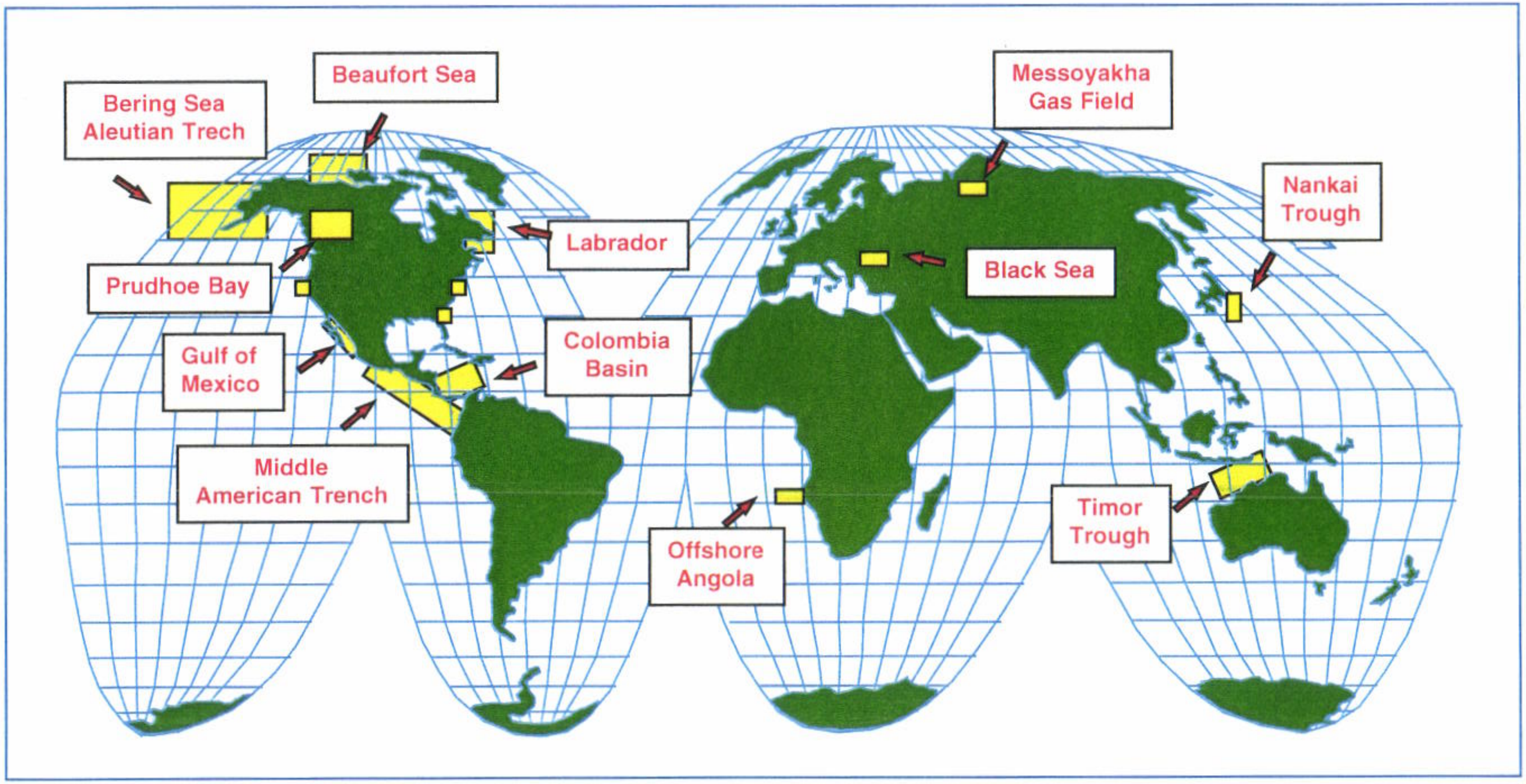


Fig. 12 - Global location where heavy occurrences of hydrates were studied J.Krason , OFFSHORE, August 1994[36]

6.1 - Transport and storage of gas as a hydrate[54-57]

The idea is to develop a technology for a new gas transport chain, where natural gas is stored as a hydrate, the solid hydrate is transported and the methane is finally released through decomposition of the hydrate.
This chain is called NGH (natural gas hydrate Fig.13) and has been suggested as an alternative to the natural gas liquefaction chain (LNG -liquefied natural gas).

Norway at the Norwegian University of Science and Technology (NTHU).
In 1990 Professor Gudmundsson patented a method for generating and preserving hydrates in conditions which were practically adiabatic. Gudmundsson experimentally demonstrated that at atmospheric pressure and at temperatures ranging from -5°C to -15°C, the decomposition process of hydrates is basically negligible.
A feasibility study for transporting large volumes of gas as a hydrate pointed to the possibility of major savings in operative

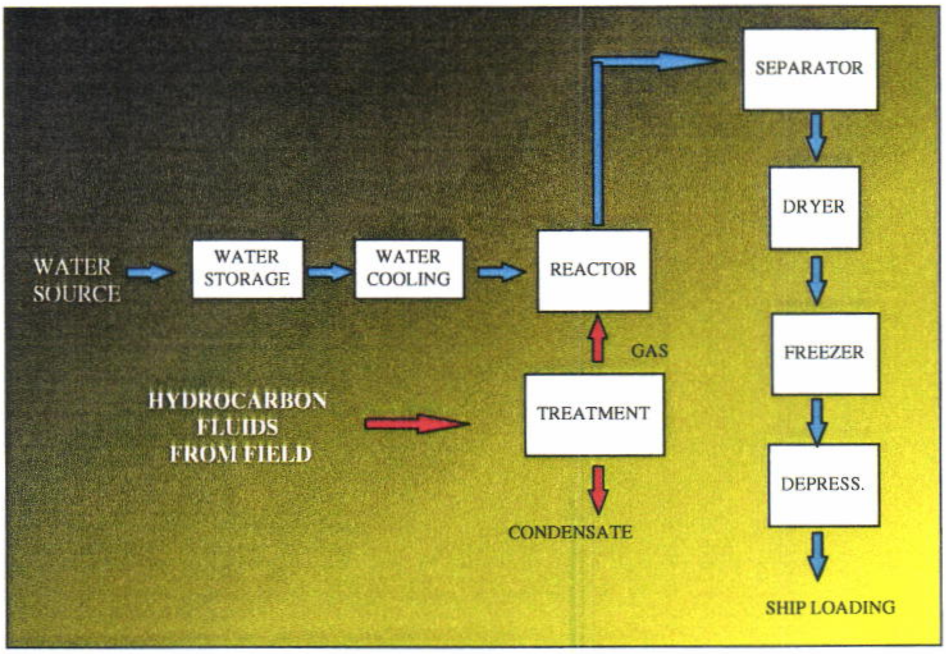


FIG. 13 - SCHEMATIC OVERVIEW OF THE NGH PRODUCTION PROCESS (J.GUDMUNDSSON, 1996)[56]

Significant amounts of hydrocarbons do exist in hydrates, in conditions which are not too harsh (atmospheric pressure, temperatures ranging from -10°C to -20°C), with figures standing at about 150 Sm^3 of gas per m^3 of hydrate.The idea of storing and transporting gas as a hydrate, at atmospheric pressure, was developed in

costs (about 24%) compared to the LNG technology (liquefaction-transport-regasification). Many people are confident that the NGH chain will be able to compete on the LNG market, in the future, at least for certain applications.

6.2 - Natural gas production from gas hydrate reservoirs[58-60]

A vast amount of natural gas is trapped as hydrate in the earth's crust and in oceanic sediments (2×10^{16} m^3 of gas). This resource cannot be developed, though, with current technologies as we are still not able to predict the effects in terms of material stability (subsidence), hydrogeological balance (besides gas, the decomposition of gas hydrate produces 85% water) and economics.

So far, a series of models for recovering the gas from gas hydrates (Fig.14) has been studied. The different techniques proposed are based on the common principle of decomposing the hydrate in order to produce the hydrocarbons it contains. The main solutions to achieve this are:

[1] reducing reservoir pressure to below hydrate equilibrium pressure (depressurization);

[2] heating the reservoir, to increase the temperature above the hydrate dissociation temperature (thermal stimulation by steam, hot water, hot brine injection, in-situ gas combustion, micro-wave stimulation, electromagnetic heating);

[3] injecting chemical products (chemical stimulation with methanol or glycols).

All these methods have advantages and disadvantages. The most commonly held opinion is that a synergetic approach to using these methods is the most effective solution, theoretically speaking.

In the West, (US, Europe) the study of these models is a long way off from actual operability and today, only Japan seems to be making rapid progress towards putting a development plan for hydrate fields into operation.

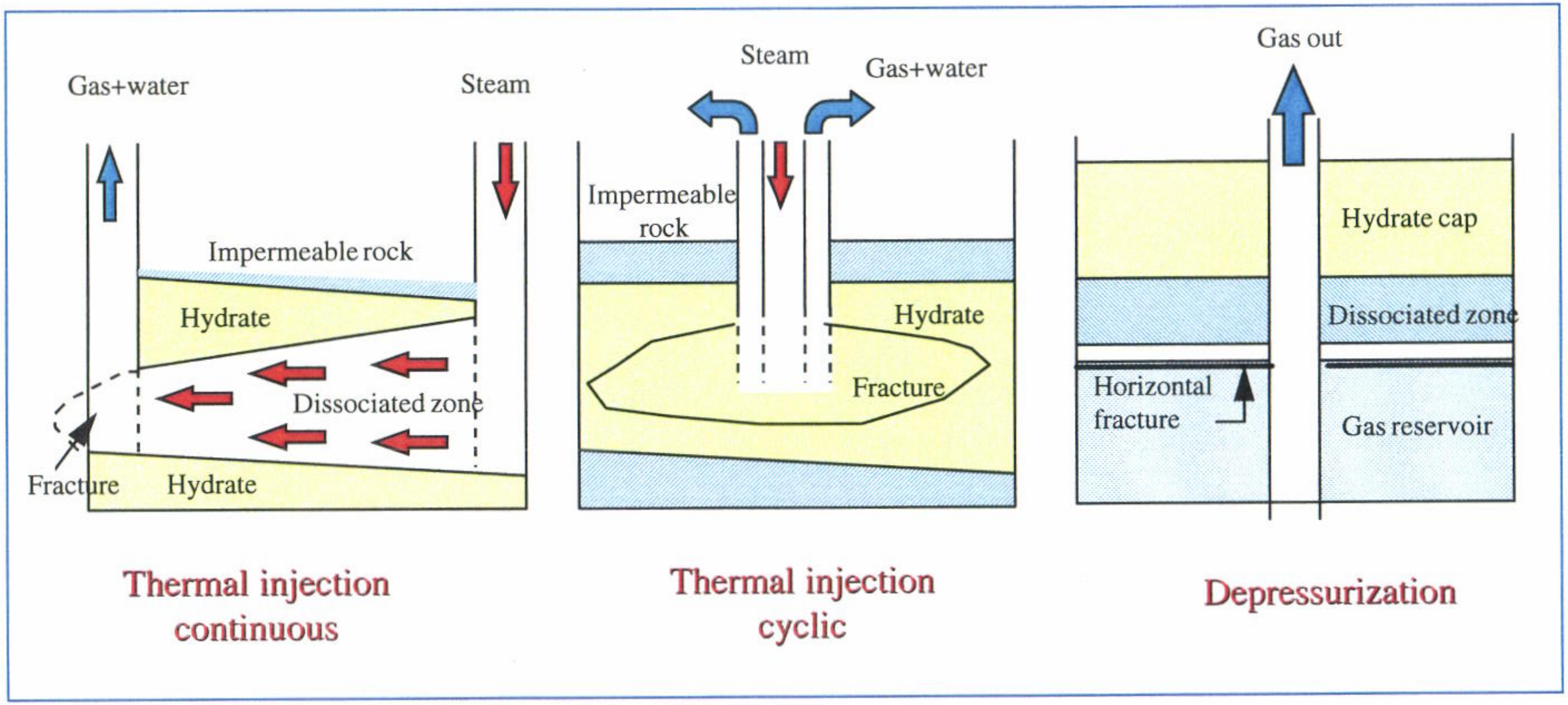


Fig. 14 - Proposed natural gas hydrate production techniques (U.S. Department of Energy, 1986)

7 - WHAT WE ARE CURRENTLY DOING ON THE SUBJECT OF GAS HYDRATES

Gas hydrates are studied by Agip especially in relation to the problems connected to natural gas and gas-condensate production. According to ENI's strategy to promote the exploitation of natural gas and gas-condensate so that oil production will be exceeded in the next two-three years, great improvements are expected in the optimisation of chemical treatments of gas. Most of these treatments regards the hydrate inhibitors for gas production at high pressure (Libya, Nigeria) and low temperature (Kazakhstan). Hydrate inhibitors as alternatives to methanol and glycols are being considered to decrease costs , to minimise the effects on environment, to improve the efficiency of the chemical treatments.
A project (*'New Hydrate Inhibitors'*-DSP 255) has been sponsored since 1995 with the aim of identifying new low dosage hydrate inhibitors (kinetic type). Agip's efforts are currently focused on the application of these chemicals in the field. Case screening where hydrate treatments are critical (high costs due to chemicals or to unscheduled stop of production by hydrates) is in progress.
Agip is advancing toward the commercial development of reservoirs in deep waters: Lower Adriatic Sea (Aquila Field), Nigeria (Abo Field), Congo, Gulf of Mexico (East Breaks). The development of deep water offshore fields is strictly connected to the more efficient solution of hydrate problems because the costs of present-day solutions (standard inhibitors such as methanol and glycol, insulation of the lines) are very high.
Last but not least, the technical involvement of Agip in hydrate inhibition during multiphase production and transport of crude oils and natural gases is to be considered. One of the challenges of the oil industry is to commercially develop the marginal reservoirs (areas characterised by fairly small hydrocarbon reserves, 2-3 x 10^6 m^3, located far from existing facilities). The fundamental idea is to transport in multiphase conditions (oil+gas+water) production fluids, directly onshore or to a centralised treatment facility. To realise this project innovative technologies are in development in various sectors (new pumping systems, new flow rate measurement systems, hydrate controls) in order to reduce cost and treatment facilities. In this context a very important role is played by the control of hydrate formation using new type of chemicals.

Agip's activities summary

Optimisation of chemical treatments in natural gas and gas condensate production at high pressure (Libya, Nigeria) and low temperature (Kazakhstan).

Problem prevention. Hydrate problems must be considered in the exploitation of hydrocarbons reserves in deep/cold seawaters (e.g. Lower Adriatic Sea, North Sea, Nigeria, Congo, Gulf of Mexico) .

Research and development is aimed at :

- *Decreasing costs, minimising the effects on environment, and improving the efficiency of chemical treatments.* Since 1995 we are sponsoring the project *New Hydrate Inhibitors* with Amoco, Conoco, Mobil, Elf, Norsk Hydro, Hoechst, Tros for the identification of new low dosage kinetic hydrate inhibitors. The screening of cases where the new hydrate treatments can be tested is in progress. Possible field test sites could be Cortemaggiore and Fornovo (operated by SPI).
- *Detecting the presence of natural hydrates in Mediterranean Sea.* A dedicated research project (*Ricerca di idrati di metano con metodi geofisici* DES 162) was launched in 1997 and results are expected in 1999. The seismic data already available are analysed to infer the occurrence of natural hydrates near the seabottom.

8 - BIBLIOGRAPHY

1. D.W. DAVIDSON *'GAS HYDRATES'* in Water:a Comprehensive Treatis; Frank F., Ed.;Plenum Press New York, **1973**; Vol 2,Cap.3, 115-234
2. Y.F.MAKOGON *'HYDRATES OF NATURAL GAS'* Penn Well Publishing:Tulsa, OK, **1981**
3. *' INTERDISCIPLINARY GAS HYDRATE LITERATURE BIBLIOGRAPHY* 'United States Department of Energy, Office of Fossil Energy, Morgantown Energy Technology Center Sept **1983**.
4. E.BERCZ,M.BALLA-ACHS *'GAS HYDRATES'* Elsevier Ed. **(1983)**.
5. G.D.HOLDER, S.P.ZETTS, N. PRADHAM *'PHASE BEHAVIOR IN SYSTEMS CONTAINING CLATHRATE HYDRATES'* Rev.Chem.Eng. 5(1), 1-69 **1988.**
6. E.D.SLOAN Jr *' CLATHRATE HYDRATES OF NATURAL GASES* ' Marcel Dekker Ed. **(1990)**.
7. E.D.SLOAN *'NATURAL GAS PHASE EQUILIBRIA AND KINETICS: UNDERSTANG THE STATE-OF-THE-ART'* Rev.Inst.Fr.Pet 45, 245-266 **1990.**
8. P.ENGLEZOS *' CLATHRATE HYDRATES* ' Ind.Eng.Chem.Res. 32, pp 1251-1274 **(1993)**.
9. PROCEEDING *' 1st INTERNATIONAL CONFERENCE ON NATURAL GAS HYDRATES'* ANN.N.Y.ACAD.SCI. VOL 715 **(1994)**
10. PROCEEDING **' 2nd** ***INTERNATIONAL CONFERENCE ON NATURAL GAS HYDRATES'*** Jun 2-6, Toulose (France) **(1996)**
11. J.NIXDORF, L.R. OELLERICK *' EXAMINATION OF NATURAL GAS HYDRATES FORMATION AND ITS PREVENTION UNDER GAS STORAGE CONDITIONS'* , Proc. 2nd Int.Conf. Natural gas Hydrates, June 2-6,**1996**, Toulouse, France, p.17.
12. E.G.HAMMERSCHMIDT *'FORMATION OF GAS HYDRATES IN NATURAL GAS TRANSMISSION LINES'* Ind.Eng.Chem. **1934**, 26 (8), 851-855.
13. C.J.KALLI, D.COWIE *' HYDRATES: TOWARDS THE COMPLETE SOLUTION* ' EUROPEC 90, The Hague 22-24 Oct. **1990.**
14. JAMALUDDIN, N. KALOGERAKIS, P.R. BISHNOI *' HYDRATE PLUGGING PROBLEMS IN UNDERSEA NATURAL GAS PIPELINES UNDER SHUTDOWN CONDITIONS* ' J.Petroleum Science and Engineering, 5, pp 323-335 **(1991)**.
15. LINGELEM,A.I.MAJEED *'HYDRATE FORMATION AND CONTROL IN LONG DISTANCE SUBMARINE PIPELINES'*, Trans IChemE, Vol 70, Part A, pp 38-42 Jan **1992**.
16. D.HERICKSON AND T.BROWN *'HYDRATE OCCURENCE IN MULTIPHASE FLOWLINES'* International Conference on Natural Gas Hydrates, pp 40-58 ANN.N.Y.ACAD.SCI. VOL 715 **(1994)**.
17. P.D.DHOLABHAI,N.KALOGERAKIS,P.R.BISHNOI *'EVALUATION OF GAS HYDRATE FORMATION AND DEPOSITION IN CONDENSATE PIPELINES: PILOT PLANT STUDIES'* SPE Production & Facilities, pp. 185-190 Aug **1993.**
18. E.BEHAR,A.DELION,A.SUGIER,M.THOMAS *' PLUGGING CONTROL OF PRODUCTION FACILITIES BY HYDRATES* ' International Conference on Natural Gas Hydrates, pp 94-105 ANN.N.Y.ACAD.SCI. VOL 715 **(1994)** .
19. E.BEHAR, A.S.DELION,J.M.HERRI, A.SUGIER, M.THOMAS *'HYDRATES PROBLEM WITHIN THE FRAMEWORK OF MULTIPHASE PRODUCTION AND TRANSPORT OF CRUDE OILS AND NATURAL GASES PART 1 - PHYSICAL-CHEMISTRY OF HYDRATES FORMATION AND DISSOCIATION* ' Rev.Inst.Fran.Petr. 49,3,265-280 **(1994)**
20. E.BEHAR, A.S.DELION,J.M.HERRI, A.SUGIER, M.*THOMAS 'HYDRATES PROBLEM WITHIN THE FRAMEWORK OF MULTIPHASE PRODUCTION AND TRANSPORT OF CRUDE OILS AND NATURAL GASES PART 2 - POSSIBLE SOLUTIONS TO EXPLOITATION DIFFICULTIES GENERATED BY HYDRATES* ' Rev.Inst.Fran.Petr. 50,4,627-640 **(1995)**
21. M.A.PEAVY,J.L.CAYIAS *'BRIEF: HAYDRATE FORMATION/INHIBITION DURING DEEPWATER SUBSES COMPLETION OPERATIONS'* JPT,pp 330-331, Apr. **1995**.
22. J.DAVALATH, J.W. BARKER *' HYDRATE INHIBITION DESIGN FOR DEEP WATER COMPLETIONS* ' 68th SPE Annual Technical Conference Houston , 3-6 pp 265-279 Oct. **1993**.
23. R.L.MCKEE, H.NESHAN *"PREDICTING AND MITIGATING HYDRATES IN DEEPWATER PRODUCTION'* International Conference on Natural Gas Hydrates, pp 59-72 ANN.N.Y.ACAD.SCI. VOL 715 **(1994)** .
24. PEAVY, J.L. CAYIAS *'HYDRATE FORMATION/INHIBITION DURING DEEPWATER SUBSEA COMPLETION OPERATIONS* ' 69th SPE Annual Technical Conference ,New Orleans, 25-28 pp 143-156 Sept. **1994**.

25. D.LYSNE,R.LARSEN,A.K.THOMSEN,A.LUND *'HYDRATE PROBLEMS IN PIPELINES: A STUDY FROM NORWEGIAN CONTINENTAL WATERS* ' Proc. 5th Int.Offshore and Polar Eng.Conf. pp. 257-262, June 11-16 **1995**.
26. B.L.BARRACLOUGH, P.L.MCGUIRE,S.P.KOCZAN *'METHANE HYDRATE RESOUCE ASSESSMENT PROGRAM JUL-SEP 1980* ' Los Alamos National Lab., NM (USA) Sep. 1981.
27. S.P.GODBOLE *'NATURAL GAS HYDRATES IN ALASKA: QUANTIFICATION AND ECONOMIC EVALUATION'* SPE13543 California Regional Meeting 27-29 Mar **1985**
28. T.S.COLLETT ' *POTENTIAL OF GAS HYDRATES OUTLINED* ' Oil & Gas Journal, pp 84-87 , Jun. **1992.**
29. T.S.COLLETT, K.J.BIRD, R.C.BURRUSS, M.W.LEE *'GAS HYDRATE RESERVOIR CHARACTERISTICS AND ECONOMICS* ' US DOE NATUR. GAS RES. & DEVELOP. CONTRACT.REV.MTG. (Morgantown, WV, 5/5-6/92) PAP.US DOE REP. NO. DOE/MC/20422-92/C0027 (DE92014351) **(1992)**.
30. T.S.COLLETT ' *NATURAL GAS HYDRATES OF THE PRUDHOE BAY AND KUPARUK RIVER AREA, NORTH SLOPE, ALASKA* ' American Association of Petroleum Geologists Bulletin, 77, pp. 793-812 **(1993)**.
31. K.A.KVENVOLDEN, G.D.GINSBURG, V.A. SOLOVIEV *'WORLDWIDE DISTRIBUTION OF SUBAQUATIC GAS HYDRATES'* Geo-Marine Letters 13,32-40 **(1993)**
32. R.L.FONTANA,A.MUSSUMECI ' *HYDRATES OFFSHORE BRAZIL* ' International Conference on Natural Gas Hydrates, pp 106-113 ANN.N.Y.ACAD.SCI. VOL 715 **(1994)**.
33. K.A.KVENVOLDEN ' *NATURAL GAS HYDRATE OCCURRENCE AND ISSUES* ' International Conference on Natural Gas Hydrates, pp 232-246 ANN.N.Y.ACAD.SCI. VOL 715 **(1994)**.
34. T.S.COLLETT ' *PERMAFROST-ASSOCIATED GAS HYDRATE ACCUMULATIONS* ' International Conference on Natural Gas Hydrates, pp 247-269 ANN.N.Y.ACAD.SCI. VOL 715 **(1994)**.
35. K.A.KVENVOLDEN (US Geological Survey). USGS Prof.pap. no.1570 *'GAS HYDRATES AS A POTENTIASL ENERGY RESOURCE - A REVIEW OF THEIR METHANE CONTENT* ' , pp.555-561 **(1993)**.
36. KRASON ' *STUDY OF 21 MARINE BASINS INDICATES WIDE PREVALENCE OF HYDRATES* ' Offshore , pp.34-35 **(1994)**.
37. DAGAM R. ' *GAS HYDRATES EYED AS A FUTURE ENERGY RESOURCE'* Chem. and. Eng. News, 6 March, **(1996).**
38. OKUDA J., ' *RESEARCH ON GAS HYDRATE FOR RESOURCE ASSESSMENT IN RELATION TO NATIONAL DRILLING PROGRAM IN JAPAN'* , Proc. 2nd Intl. Conference on Natural Gas Hydrates, Tolouse, France, 2-6 june **(1996).**
39. D.B.ROBINSON, H.J. NG *'HYDRATE FORMATION AND INHIBITION IN GAS OR GAS CONDENSATE STREAMS'* Jour. Can.Pet.Tech., pp. 26-30, Jul-Aug **1986.**
40. R.A.HUBBARD,J.M.CAMPBELL *'RECENT DEVELOPMENTS IN GAS DEHYDRATION AND HYDRATE INHIBITION'* SPE Gas Technology Symposium, Houstonpp 263-276, Jan 23-25 **1991.**
41. E.BEHAR, L.CREAGH *'HYDRATES INHIBITION BY PHYSICAL SOLVENTS IN THE TREATMENT OF NATURAL GAS FROM OFFSHORE RESERVOIRS'* 67th Annual Techincal Conference and Exhibition of SPE Washington, Oct. 4-7, SPE 24830 pp.661-673 **1992**.
42. SLOAN ET AL. ' *PREDICTION AND INHIBITION OF HYDRATE AND WAX FORMATION* ' GRI-92/0303, Aug. **1992.**
43. O.URDAHL,A.LUND, P.MØRK,T.L. *NILSEN 'INHIBITION OF GAS HYDRATE FORMATION BY MEANS OF CHEMICAL ADDITIVES* ' Chem.Eng.Sci 50, pp 863 (1995).
44. A.GILLESPIE ' *CONTRACTOR LAYS INSULATED LINE TO COMBAT HYDRATE FORMATION* ' Offshore pp 102-105 , Aug. **1994**.
45. M.H.YOUSIF, V.A.DUNAYEVSKY *'HYDRATE PLUG DECOMPOSITION: MEASUREMENTS AND MODELING'* SPE 30641 Ann. Tech.Conf. Dallas(USA) 22-25 Oct **1995**
46. M.A. KELLAND, T.M.SVATAAS,L.A. DYBVIK *'CONTROL OF HYDRATE FORMATION BY SURFACTANTS AND POLIMERS* ' SPE 69th Ann.Tech.Conf. and Exhib. New Orleans pp. 431-438 **(1994)**.
47. P.ENGLEZOS *'KINETICS OF GAS HYDRATE FORMATION AND KINETIC INHIBITION IN OFFSHORE OIL AND GAS OPERATION* ' Fifth Int.Offshore and Polar Engineering Conf., The Hague,The Netherlands pp.289-295 **(1995)**.
48. M.H.YOUSIF ' *THE KINETICS OF HYDRATE FORMATION* ' SPE 69th Annual Technical Conference and Exhibition , New Orleans, 25-28 Sept. **1994**.

49. G.D.HOLDER, R.M. ENICK *'SOLIDS DEPOSITION IN HYDROCARBON SYSTEMS - KINETICS OF HYDRATES AND DIAMONDOIDS IN NATURAL GAS SYSTEMS'* GRI-93/0285 **(1994)**.
50. P.SKOVBORG,P.RASMUSSEN *'A MASS TRANSPORT LIMITED MODEL FOR THE GROWTH OF METHANE AND ETHANE GAS HYDRATES'* Chem.Eng.Sci , 49 pp. 1131-1143 **(1994)** .
51. J.LONG *'GAS HYDRATE FORMATION MECHANISM AND KINETIC INHIBITION'* Colorado School of Mine Ph.D Thesis **1994.**
52. D.LIPPMANN, D.KESSEL,I. RAHIMIAN *'GAS HYDRATE NUCLEATION AND GROWTH KINETICS IN MULTIPHASE TRANSPORTATION SYSTEMS'* Fifth Int.Offshore and Polar Engineering Conf., The Hague,The Netherlands pp.250-256 **(1995)**.
53. A.CORRIGAN,S.N.DUNCUM,A.R.EDWARDS, C.G.OSBORNE *'TRIALS OF THRESHOLD HYDRATE INHIBITORS IN THE RAVESPURN TO CLEETON LINE'* SPE 30696, Ann. Tech.Conf. 22-25 Oct **1995**, Dallas,Texas.
54. A. BORREHAUG, J. GUDMUNDSSON, *'GAS TRANSPORTATION IN HYDRATE FORM'* EUROGAS 96, 3-5 June 1996, Trondheim, Norway.
55. J. GUDMUNDSSON *'METHOD FOR PRODUCTION OF GAS HYDRATES FOR TRANSPORTATION AND STORAGE'* International Pubblication Number WO 93/01153, 21 January 1993.
56. J. GUDMUNDSSON, A. BORREHAUG *' FROZEN HYDRATE FOR TRANSPORT OF NATURAL GAS'* Proceeding of 2nd Int. Conf on Natural Gas Hydrates, June 2-6 (1996), Toulouse, France p. 415.
57. J. GUDMUNDSSON, M. PARLAKTUNA, A.A. KHOKHAR, *' STORING NATURAL GAS AS FROZEN HYDRATE '* SPE Production and Facilities, **(1994)**, 69-73.
58. P.L. Mc.GUIRE *'METHANE GAS PRODUCTION BY THERMAL STIMULATION'* 4th Canedian Permafrost Conf.,Calgary, Alta **(1981)**
59. V.A. KAMATH, S.P. GODBOLE *' EVALUATION OF HOT BRINE STIMULATION TECHNIQUE FRO GAS PRODUCTION FROM NATURAL GAS HYDRATES '* J.Pet. Technol., 38(11), 1379-1388 **(1987).**
60. M.R.ISLAM *' A NEW RECOVERY TECHNIQUE FOR GAS PRODUCTION FROM ALASKAN GAS HYDRATES '* J.Petr.Sci.Eng. 11, pp. 267-281 **(1994)**.