A SPECIAL CORE ANALYSIS APPROACH TO CREATE GAS HYDRATES IN SEDIMENT SAMPLES

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ABSTRACT

A method for experimentally forming hydrates in pore systems has been developed. Technology commonly used in special core analysis is applied to create controlled amounts of gas hydrates. By using this method on outcrop sand stone samples, gas hydrates occupying up to 45% of the pore volume were made.

A detailed description of the method, equipment, and experimental set up will be presented.

System pressure, differential pressure, temperature, resistivity, and flow rate of water and gas were measured, controlled, and monitored during all attempts of forming hydrates. Quantity and distribution of the hydrate, as well as the physical nature of it, and how it grows within the pore system are explained from interpretation of the experimental measurements when hydrates were successfully formed. Plots of pressure and resistivity versus time are presented.

The experimental procedure has been developed and tested with Bentheim sandstone samples as the porous medium, with brine and methane gas as hydrate forming agents. The experimental set up is designed as a recirculation unit, with the sample-part of the closed loop located in a cooling cabinet. To determine the quantity of formed hydrate, gas and water consumption were recorded using high precision pump, acoustic separator, and pressure and temperature sensors.

The proposed method forms realistic gas hydrates by simulating the same physical hydrate forming mechanism as in real reservoirs.

As reservoir hydrate samples are difficult and expensive to obtain, realistic synthetic hydrates should be a welcome contribution for understanding the formation of hydrates in porous medium and for tuning the interpretation tools of seismic data with regards to hydrate occurrence.

INTRODUCTION

Occurrence of natural hydrates in hydrocarbon reservoirs may represent an environmental risk factor. Global warming and the man-made warming of the seafloor by recovery related activities may cause dissociation of gas hydrates from marine sediments, and may therefore relate to the hazard of near shore submarine slides and consequent tsunami waves. It is also a potential energy reserve, as methane extracted from hydrate reservoirs is being considered among non-conventional hydrocarbon resources likely to be exploited in the future. Released gas can be used in recovery purposes as propellant gas, or as object of recovery itself. In any case, localising, and even quantifying, hydrate occurrence is important in reservoirs predisposed with pressure and temperature conditions within the gas hydrate stability zone.

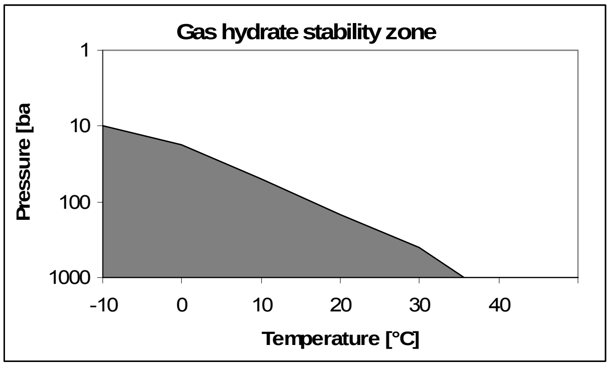

Figure 1: Free hand sketch of the gas hydrate stability zone (grey area).

The conventional way of localising hydrates below sea level is by combining pressure and temperature data with interpretation of seismic data. From the seismic data, a bottom-simulating reflector (BSR) at the base of the hydrate stability zone may indicate the presence of hydrates. However, detecting BSRs is not a reliable way to localise hydrate-bearing sediments. The BSR does not guarantee the presence of hydrates. And, vice versa, hydrates may occur even if no BSR is clearly pronounced on the seismic map [4, 5, 6, 7].

Also, by combining the Archie's [1] resistivity correlations determined in the core laboratory scale with down hole resistivity logs, valuable information about the localisation and quantity of natural hydrates will be acquired.

Clearly, in order to tune the hydrate detection technology, it is desirable to study seismic properties of hydrate-bearing sediment samples. But, due to the fact that keeping the sample at the proper temperature and pressure conditions is difficult, raw material available for such a study comes in short supply. The new method for experimentally forming hydrates in sediment samples may help eliminate this problem.

The new method not only provides gas hydrates in sediment samples, but also a known and desired quantity, with a known distribution.

GENERALLY ABOUT THE APPROACH

Hydrates In Bulk

The conventional way of quantifying hydrate growth in the laboratory is to measure the gas consumption during the process. The number of gas molecules needed to form a certain number of hydrate molecules is a known relation.

When creating hydrates in bulk (no porous media); known quantities of the basic forming agents (water, and refined gas or reservoir gas) and additives (e.g. reservoir condensate, inhibitors, anti-agglomerates etc.) are pressurized in a visual cell. The cell is equipped with a pressure gauge, and a stirring device to help initiating hydrate growth.

The closed cell is brought to hydrate creating conditions by cooling. The system pressure is monitored for the pressure decreases due to ordinary PVT relations, and for gas consumption required for hydrate formation.

The amount of hydrate formed is calculated from the gas consumption, which is estimated from the pressure decrease in the process [2].

All attempts and work of creating hydrates in sediment samples were based on this procedure for forming bulk hydrates.

Two-Phase Recirculation Rig

The experimental set-up was a standard recirculation flooding rig for two phases. Generally, the advantage of such set-up is that it works as a closed system. A minimum amount of test fluids are required, and the fluids are continuously kept in thermodynamic equilibrium. This is also a very flexible set-up, which allows various ways of attempting to form hydrates, such as gas or water injection, injection at constant rate, injection at constant pressure etc.

Resistivity Measurements

Monitoring resistivity across the sample is a useful way to obtain information about the situation inside the pores. In principal, the water phase is the only electrical conductive unit in the system. Hence, the resistivity is a measure of the water phase's ability to conduct electricity. It has shown to be very sensitive to water saturation, and is therefore an excellent tool for determining equilibrium in the pore system. Any change in water saturation or distribution, or anything else affecting the conductivity through the sample, will be detected. This is useful in all core analysis and petrophysical procedures involving measurements at equilibrium.

To aid the interpretation of electrical logs, formation factor (FF) and resistivity index (RI) measurements are made in the laboratory on rock samples taken from the formation of interest.

The formation factor of a plug sample can be estimated by the relation r_o/r_w, where r_o is the resistivity measured across a plug sample fully saturated with water of resistivity r_w. Hence, it quantifies the formation or matrix contribution to the measured resistivity.

METHODS

Three different methods were approached to create hydrates in porous media.

Static Tests

In some of the tests, a gas and water saturation was established prior to cooling down the system. This would be equivalent to the procedure for creating hydrates in bulk.

These tests were performed with various saturations, all resulting in only minor hydrate formation.

Calculations of saturations and gas consumption indicated that the hydrate creation stopped before either gas or water was fully consumed i.e. the pores contained free water; free gas and hydrates at the end of hydrate formation.

This indicates that hydrates form a grid or film separating the water phase and gas phase. When the interface between water and gas is totally covered, the hydrate formation stops. The hydrate film encapsulates the gas regime, and is therefore distributed by the gas phase, which initially is distributed by capillary forces.

Dynamic Tests

By starting gas injection into a fully water saturated pore system initially at favourable conditions for hydrate creation, it was anticipated that larger amounts of hydrates would be formed. This formation would be enhanced as the hydrate film creation and breaking cycle could repeat several times.

Measurements from these dynamic tests indicate that hydrate film was created and broken. However, no additional hydrates were formed after gas breakthrough. Not much water is displaced by gas injection before breakthrough, nor was much hydrate formed.

Porous Plate, Semi-dynamic Tests

Based on observations of the dynamic tests, it was assumed that larger amounts of hydrates would be created if gas could break towards the hydrate film with gradual increased gas pressure. Applying the porous plate method [3] by mounting a water-wet semi-permeable porous disc at the outlet of the plug sample, gas could be injected continuously at gradual increasing differential pressure over the gas/hydrate/water interfaces.

This resulted in a stepwise forming and collapse of hydrate films, with corresponding stepwise advancing gas regime. Each new hydrate film would amount more hydrates than the previous, and demand higher gas pressure to collapse. This semi-dynamic, stepwise behaviour was detected by the pressure and resistivity log.

As the semi-dynamic method with a porous plate was able to form significant amounts of hydrates, all further development work was based on this technique.

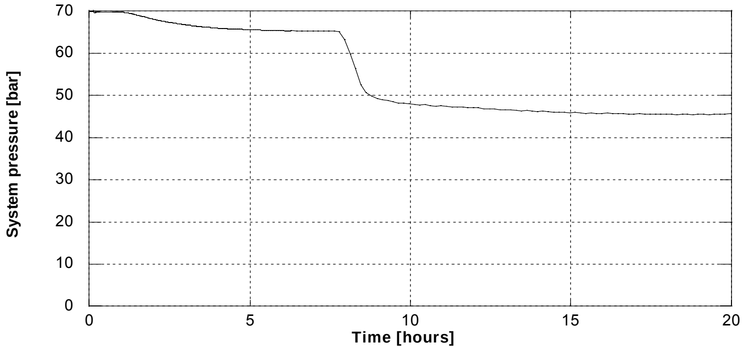

Figure 2: System pressure development with time.

Figure 2 shows the first successful hydrate creation during the development phase of the RF-method. It demonstrates how the pressure data can be used for quantifying hydrates in a closed system. A Bentheim sand stone plug saturated with saline water and methane gas initially at 70 bar and 17°C was brought to hydrate creating conditions (65 bar, 2°C) by cooling. The pressure decrease from 70 bar to 65 bar is caused by temperature fall in the closed system. After 7 hours the pressure suddenly falls as a result of gas consumption during hydrate formation.

RESULTS

The main result is the development of a new procedure where hydrates up to a saturation of 45% of the pore volume were created. The RF-method will be presented along with descriptions of how the calculations of hydrate amount were carried out.

Gas hydrates in real reservoirs are assumed to form as a result of gas migrating into pores saturated with connate water. With the right pressure- and temperature conditions, hydrates form on the interface between water and gas, where the forming agents coexist. This goes for both pore level and matrix level. The same forming mechanism is simulated in the proposed method.

Apparatus and Set-up

To ensure the fluids in the system are in thermodynamical equilibrium, the gas is circulated through the sample and/or the bypass and into the bottom of the separator and bubbled through the water zone. The pump will be filled with gas from top of the separator, and re-injects it into the plug. Similarly with water flooding; water from the sample enters the separator at top (gas zone), while the pump is filled with water from the bottom, and re-injects it into the core plug. This continues until equilibrium which is indicated by a constant system pressure and constant resistivity across the sample. This rig is designed to measure any volume and pressure in a closed, 2-phase system. It can quantify volumetric changes in a constant-pressure system, or pressure changes in a constant-volume system, with or without flooding. The rig can also measure electrical conductivity through the sediment sample (i.e. the water phase), and differential pressure across the sample of any flooding phase. A Hassler-type core holder is used. The rig is computer interfaced, and all measurements are logged throughout the test.

Specifics About The Final Experimental Set-up

In addition to a conventional recirculation flooding rig, this set-up contains a semi-permeable porous disc in capillary contact with the plug sample at the outlet end.

This set-up allows small, cylindrical, sediment samples (diameter 3.8 cm – i.e. standard 1.5 inches, and length up to 30 cm) to be flushed with various pore fluids under effective pressures of 60 – 70 bar and temperatures of 22 to -2°C.

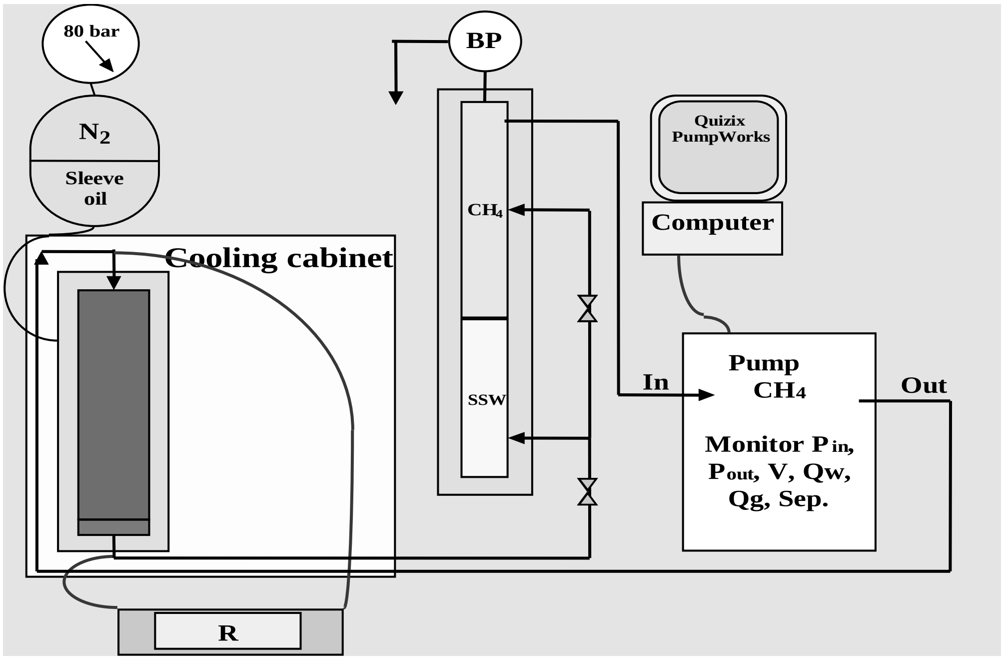

Figure 3: Schematic view of the RF-method Rig

A closed system is used, where CH4 is forced into, and through, the sediment sample towards the semi-permeable porous plate. At favourable pressures and temperatures, this system creates hydrate in the sediment's pores. Note that part of the system; the separator is outside the cooling cabinet, while the sediment sample is inside the cooling cabinet. This way hydrates can form on the water-gas interface in the pores, but not on the water-gas interface in the separator. To be able to accurately calculate the hydrate content, it is necessary to know the equilibrated system pressure with and without hydrates. This is done by recirculation through bypass tubing.

The Procedure

The final procedure for creating hydrates in sediment samples follows these steps:

a. A water (SSW) saturated sediment sample is mounted in a core holder along with a porous plate (water-wet semi permeable disc) at the outlet end

b. Initial conditions: Overburden pressure of 80 bar is applied to ensure any flooding through the sample. The system is pressurised (system pressure = 60-65 bar) and closed

c. Methane gas is circulated bypassing the sediment sample. System pressure, P_{1sys}, and temperatures, $T_{1outside}$ and $T_{1cabinet}$, at equilibrium before cooling are monitored. All water in the system is now located in the pores, and in the separator. Volumes of water and gas at equilibrium before cooling are monitored

d. System is brought to hydrate creation region by cooling. Temperature is set to 1-2°C (held constant during the rest of the test)

e. Start of test: Bypass is closed. Methane gas is injected into the sediment sample at a constant, low rate displacing water from the pore system through the porous plate

f. After an initiation time of 1-15 hours, hydrate starts to form, and covers the water-gas interface

g. With the flow path blocked by hydrates on the water-gas interface, the continuous injection of gas causes a differential pressure across the hydrate film, and eventually the hydrate film will break. Fresh water-gas interface is established, and the gas regime advances, letting additional hydrate to form and cover the interface

h. This hydrate forming process continues while:

1. Water saturation decreases due to displacement
2. System pressure decreases due to gas consumption in hydrate formation
3. Water salinity increases due to consumption of distilled water in hydrate formation (saline water is used to be able to measure electrical properties during the test)

i. As long as the supply of gas and water is sufficient, the hydrate formation continues until a combination of increased water salinity, and decreased system pressure is unfavourable for hydrate formation at the fixed temperature

j. When no more hydrate is formed, the bypass is opened to equilibrate the pressure. System pressure after test, P2sys and temperatures (T2cabinet and T2outside) are monitored at equilibrium. The volume of gas injected into the sediment, and volume of water displaced during the test is monitored.

Procedure Of Estimation Of Hydrate Content, And Water And Gas Saturation

Estimating the amount of hydrate is done using the calculation program by Sloan, E.D. [2]. In formation of a certain amount of gas hydrate, a certain amount of gas and water is consumed. In a closed, constant volume system, this consumption causes a pressure drop. The system is designed so that any pressure drop will be caused by either temperature decrease, or hydrate formation. Pressure drop caused by hydrate formation and pressure drop caused by temperature decrease are both known relations, and can be distinguished. Hence, by knowing the volumes (total, and of gas and water) of the closed system, and the changes of temperature (constant in these tests) and pressures in the system during the test, the amount of hydrate in the sediment sample can be estimated.

The separator and pump provide the volumes of gas injected and water displaced. From these data there are a number of relations which can be used to calculate water and gas (and hydrate) saturations in the pore system:

- Total pore volume ÷ volume of water consumed in hydrate formation ÷ volume of water displaced equals the volume of free water left in the pore system
- The rest is free gas: Total pore volume ÷ volume of hydrate ÷ volume of free water in the pore system equals the volume of free (unused) gas in the pore system
- Volume water displaced from the sediment sample equals the sum of hydrate volume and free gas volume inside the pore system

Principle Estimation Of Hydrate Content In The System

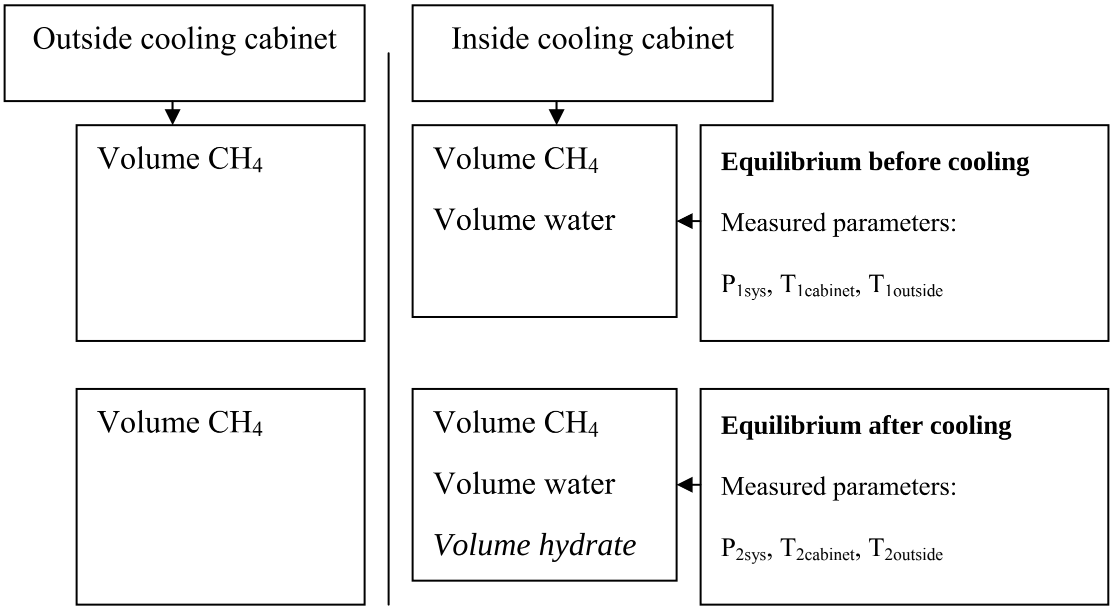

Figure 4: Schematic view of necessary measurements to calculate amount of created hydrates.

Procedure For Calculating Volume Of Created Hydrate:

1. Before cooling: Total amount of methane gas in the system is estimated by the ideal gas law (temperature inside and outside the cabinet may be slightly different even before cooling):

Inside the cooling cabinet: $$P_{1sys}V_{cabinet} = n_{1cabinet}RT_{1cabinet} \quad (1)$$

Outside the cooling cabinet: $$P_{1sys}V_{outside} = n_{1outside}RT_{1outside} \quad (2)$$

Total amount (# of moles) of methane gas in the closed system:

$$n = n_{1cabinet} + n_{1outside} \quad (3)$$

2. After cooling (and hydrate formation):

Inside the cooling cabinet: $$P_{2sys}V_{cabinet} = n_{2cabinet}\,RT_{2cabinet} \quad (4)$$

Outside the cooling cabinet: $$P_{2sys}V_{outside} = n_{2outside}\,RT_{2outside} \quad (5)$$

Total amount (# of moles) of free methane gas after hydrate formation:

$$n_2 = n_{2cabinet} + n_{2outside} \quad (6)$$

3. Amount of methane gas consumed in hydrate formation, $\Delta n_{methane}$, equals the difference between the amount of gas before and after hydrate formation:

$$\Delta n_{methane} = n - n_2 \quad (7)$$

4. The ideal structure of S_I –hydrate is $8CH_4 \cdot 46H_2O$ built with 2 small and 6 large cavities. The real (average) structure over average sized cavity is $7.68CH_4 \cdot 46H_2O$. Hence, the real amount of consumed water, Δn_{water}, in hydrate formation is provided by:

$$\Delta n_{water} = \Delta n_{methane} \frac{46}{7.68} \tag{8}$$

5. The mass of consumed methane gas and water in hydrate formation is given by the molar mass of CH_4 and H_2O:

$$m_{water} = \Delta n_{water} \cdot M_{H2O} \tag{9}$$

$$m_{methane} = \Delta n_{methane} \cdot M_{CH4} \tag{10}$$

6. Total mass of hydrate created is the sum of consumed water and methane:

$$m_{hydrate} = m_{water} + m_{methane} \tag{11}$$

7. S_I hydrate has density $\rho_{hydrate} = 0.914$ g/ml.
Volume of hydrates formed is given by: $V_{hydrate} = m_{hydrate} / \rho_{hydrate}$ (12)

DISCUSSION

Analysing the pressure plots is similar to the method we used to in our routine tests that created hydrates in bulk. Usually the set point for hydrate creation is clearly indicated by a sudden drop in system pressure. To estimate the final amount of hydrates created, the equilibrated system pressure before and after formation must be determined from the start and end of the plots.

The transient data of both pressure and resistivity give important information about the hydrate creation process. Repeating collapse and building of hydrate film is visualized by repeating drops and build-ups of the pressure and resistivity as seen in Figure 5. The initial pressure is 62 bar. During the hydrate formation, the system pressure decreases from 62 bar to 56 bar (first 50 hours). The peaks represent build-ups and drops in the injection pressure corresponding to hydrate film blocking the flood path, and hydrate film breaking due to high pressure difference. From 50 hours and onwards only smaller amounts of additional hydrate is formed, while the pressure build-up and drop is continuous. The system pressure (going from 62 bar to 56 bar) shows that most hydrate is formed in the first 75 hours.

Figure 5 also shows that injection pressure and resistivity have correlated behaviour to the process. Due to initially high water saturation, the resistivity increase has a slow start, but increases rapidly after 60 hours. This shows that the resistivity is, as expected, relatively insensitive to smaller hydrate saturations, i.e. high water saturations. After 75 hours only smaller amount of additional hydrate is formed, but the water displaced has an effect on the resistivity.

The "stable" portion of the resistivity plot alternating between 8,000 Ω to 15,000 Ω is very high, indicating a low water saturation. The peak at 25,000 Ω at the end is an indication of a nearly discontinuous water phase.

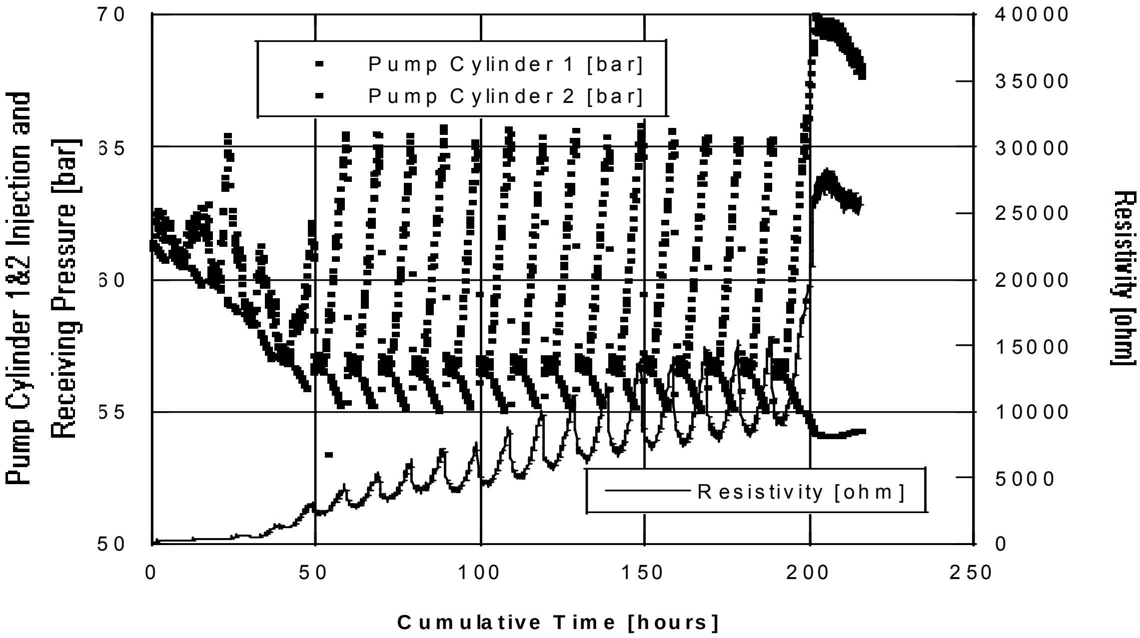

Figure 5: Pressure and resistivity as function of time during formation of hydrates. Resistivity data are indicated by the lower, continuous curve. Both pump cylinders took part in recirculation of the gas, by alternately delivering and receiving. Hence, to display injection pressure or system pressure, or both as in this case, during the process, data from both cylinders must be presented. Pressure data are indicated as points, with the lower part as the system pressure, and the higher, spiky part as the injection pressure.

The plot shows both pressure (spotted curve) and resistivity (continuous curve). The gas injection pressure is the higher part of the pressure data, and the system pressure is the lower part.

Observations from the tests strongly indicate that hydrate, gas and water are homogenously distributed through the sediment sample. This model is based on a homogenous pore system. All sediment samples in our tests were strongly water wet. In a two-phase water-gas system, the water phase will spread on the pore walls, and the gas phase will be located in the centre of the larger pores. Our tests indicate that the hydrate formed is located on the water-gas interface, and hence is distributed by the gas phase.

Initially, at low capillary pressure, hydrates form as a thin film constructing a grid through the pore system. This grid encapsulates the gas phase. No additional hydrate will be formed before new water-gas interface occurs. This requires the hydrate film to break, which will happen by applying sufficient capillary pressure by further gas injection.

Further Work

Natural continuance of this work would include in-situ visualization of a hydrate-bearing sediment sample, and preferably also of hydrate creation during the process.

Seismic studies of experimentally made hydrate-bearing sediment samples could also prove to be valuable, as the seismic properties as function of hydrate saturation and distribution will provide data for calibrating necessary prediction algorithms.

The mechanism of how the resistivity relates to hydrate saturation would be of interest. Combined with exact resistivity data, the Archie's saturation exponent n [1] could be determined. This could be used in evaluating hydrates-in-place from resistivity logs.

CONCLUSION

A method for creating gas hydrates in porous media has been developed.

The method uses conventional and easy accessible equipment, and is feasible in most core analysis laboratories.

The hydrates form at realistic conditions. The method works at initial pressure down to 60 bar, and hydrate creating temperature at 1˚C - 4˚C.

The method simulates a realistic hydrate formation. As assumed for real cases, gas advances into pores pre-saturated with water. At conditions within the hydrate creation region, a hydrate film forms on the interface between water and gas. The hydrate film increases throughout the pore system, dividing free gas from free water as the gas regime advances, which is caused by continuous gas injection into the pores.

The method is capable of creating significant hydrate quantities. Hydrate saturations up to 45% of the pore volume can be controlled and measured, and is adequate for most studies involving hydrates in porous media.

NOMENCLATURE

(In order of appearance)

RF	Rogalandforskning (Rogaland Research)
BSR	Bottom simulating reflector
PVT	Pressure Volume Temperature
FF	Formation factor
RI	Resistivity index
r_w	Resistivity of the water phase
r_o	Resistivity across a sediment sample fully saturated with water of resistivity r_w
SSW	Synthetic seawater
N_2	Nitrogen gas
CH_4	Methane gas
BP	Back pressure
R	Resistivity. Also Avogadro's number, the gas constant
P_{in}	System pressure. Pressure of the pump's receiving cylinder
P_{out}	Injection pressure. Pressure of the pump's delivering cylinder
Q_w	Injection rate of water
Q_g	Injection rate of gas

V	Accumulated volume injected from the pump
Sep.	Water-gas interface level in the separator
P_{1sys}	Initial system pressure (i.e. before cooling)
$T_{1outside}$	Initial temperature of the part of the system outside the cooling cabinet
$T_{1cabinet}$	Initial temperature of the part of the system inside the cooling cabinet
P_{2sys}	Equilibrated system pressure after hydrate creation
$T_{2outside}$	Temperature of the part of the system outside the cooling cabinet, after hydrate creation
$T_{2cabinet}$	Temperature of the part of the system inside the cooling cabinet, after hydrate creation
$V_{cabinet}$	Volume of methane gas in the part of the system inside the cooling cabinet
$n_{1cabinet}$	Initial number of moles of methane gas in part of the system inside the cooling cabinet
R	Gas constant, Avogadro's number, R=8.3145 J/mol K
$V_{outside}$	Volume of methane gas in the part of the system outside the cooling cabinet
$n_{1outside}$	Initial number of moles of methane gas in part of the system outside the cooling cabinet
n	Total number of moles of methane gas in the system, $n = n_{1cabinet} + n_{1outside}$. n is also denoted as the Archie's saturation exponent
$n_{2cabinet}$	Number of moles of free methane gas in part of the system inside the cooling cabinet, after hydrate creation
$n_{2outside}$	Number of moles of free methane gas in part of the system outside the cooling cabinet, after hydrate creation
n_2	Total number of moles of free methane gas in the system, after hydrate creation, $n_2 = n_{2cabinet} + n_{2outside}$
$\Delta n_{methane}$	Number of moles of methane gas consumed in hydrate formation, $\Delta n_{methane} = n - n_2$
Δn_{water}	Number of moles of water consumed in hydrate formation
m_{water}	Mass of water consumed in hydrate formation
M_{H2O}	Molar Mass of water
$m_{methane}$	Mass of methane gas consumed in hydrate formation
M_{CH4}	Molar Mass of methane
$m_{hydrate}$	Mass of hydrate created, $m_{hydrate} = m_{water} + m_{methane}$
$\rho_{hydrate}$	Density of S_1 type hydrate, $\rho_{hydrate} = 0.914$ g/ml
$V_{hydrate}$	Volume of created hydrate
Ω	Ohm, unity of resistance

REFERENCES

1. Archie,G.E., "The Electrical Resistivity Log as an Aid in determining Some Reservoir Characteristics", Trans. A. I. M. E. (1942), 146, 54

2. Sloan, E. D., ”The Colorado School of Mines Hydrate Prediction Program CSMHYD”, (Released August 5, 1996), Center Of Hydrate Research, Department of Chemical And Petroleum-Refining Engineering, Colorado School Of Mines, Golden, CO 80401

3. Welge, H.J. and W.A. Bruce, "The Restored State Method for Determination of Oil in Place and Connate Water", Drilling and Production Practices, American Petroleum Institute, 1947

4. Mienert, J., Bünz, S., Guidard, S., Vanneste, M., Berndt, C., 2005. ”Ocean bottom seismometer investigations in the Ormen Lange area offshore mid-Norway provide evidence for shallow gas layers in subsurface sediments”. Marine and Petroleum Geology, 22 (1-2), 287-297.

5. Holbrook, W.S., Hoskins, H., Wood, W.T., Stephen, R.A., Lizzaralde, D., 1996. “Methane hydrate and free gas on the Blake Ridge from vertical seismic profiling”. Science 273 (5283).

6. MacKay, M.E., Jarrard, R.D., Westbrook, G.K., Hyndman, R.D., 1994. ”Origin of bottom-simulating reflectors: Geophysical evidence from the Cascadia accretionary prism”. Geology 22

7. Berndt, C., Bünz, S., Clayton, T., Mienert, J., and Saunders, M., 2004. “Seismic character of bottom simulating reflectors: examples from the mid-Norwegian margin”. Marine and Petroleum Geology, vol. 21, issue 6.