

Formation of gas hydrates in a permeable medium*

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Abstract

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Gas migrating upwards in deep sea sediments can form a thin zone of solid gas hydrates, which can act as a seal below which free gas is trapped. The acoustical contrast between the water-bearing sediments above this seal and the gas-containing sediments below it could cause seismic reflectors with a negative polarity running subparallel to the sea floor. The gas hydrate seal itself would be too thin to be resolved by seismic methods.

To clarify whether gas hydrates could form such thin seals that are still effective, the formation of gas hydrates in a sediment has been simulated in laboratory experiments. An effective seal was formed from propane and water within 15 minutes in a coarse sand pack. This seal when 5 cm thick, could withstand a pressure difference of 2.4 bar. This finding supports the above model.

Introduction

Although the stability of hydrates of natural gas in deep water is well known, the form in which these frozen hydrates and associated gas exist is open to speculation. The presence of hydrates beneath the sea bed can be detected as a seismic reflector, which is more or less parallel to the sea floor (bottom simulating reflector or 'BSR', Stoll et al. 1971). The pressure and temperature conditions prevailing at the BSR match those of the stability boundary of pure methane hydrate. Since some hydrate layers have been drilled (Sheridan &

Gradstein 1981), there is no doubt that the BSRs occur at the lower boundary of a fully or partially hydrated sediment. In the early seventies, it was suggested at our laboratories that free gas could be trapped below a seal formed by gas hydrates in otherwise permeable sediments of the continental margin, more or less like the Messoyakha field in eastern Siberia which is described by Sapir et al. (1973A and B) as an active gas seep which is self-sealed at shallow depth by the formation of gas hydrates.

This model arose from the observation that on all the seismic sections over the continental margin that were available at that time at Shell Internationale Petroleum Maatschappij, the sound velocities in the interval between the sea floor and the BSR

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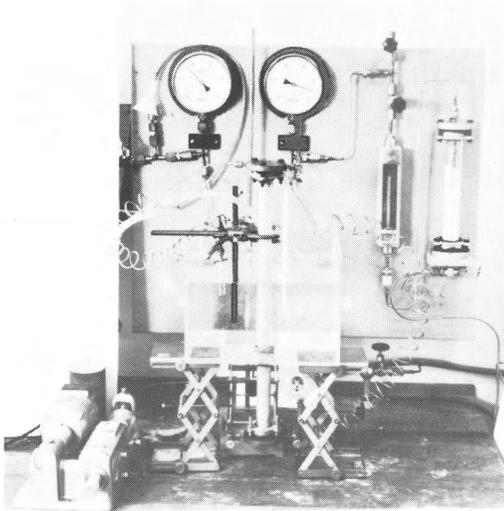


Fig. 1. Laboratory set-up for hydrate formation in sand packs.

were found to be normal. Abnormally high sound velocities above the BSRs, as reported from the Blake Bahama Outer Ridge, Tucholke et al. (1977) were not observed on these sections.

Moreover, in those cases where the BSR was strong enough to make polarity analyses, a negative polarity was found. Such 'bright spots' indicate lower sound velocities below the BSR than above it.

It was suggested that the BSRs observed were caused by the acoustical contrast between normal velocities from the water-bearing interval above the BSR and low velocities in a free-gas-bearing zone below the BSR. The seal below which the free gas was trapped then should be formed by a gas-hydrate-bearing zone which would be too thin (< 40 m) to be resolved by the seismic systems used, which were set for penetration rather than resolution.

The model obtained some additional support when, in a few very exceptional cases, a seismic expression of the gas/water contact ('flat spot') was found below a bottom-simulating bright spot.

The experiments described in this paper were set up firstly to learn something about the formation of hydrates in a permeable bed, and secondly to find out if a relatively thin (< 40 m) hydrate seal could be that tight and strong enough to trap gas columns sufficiently thick to cause a bright spot.

Experimental

The experimental set-up is shown in Figs. 1 and 2. The main unit consists of a vertical cylindrical glass

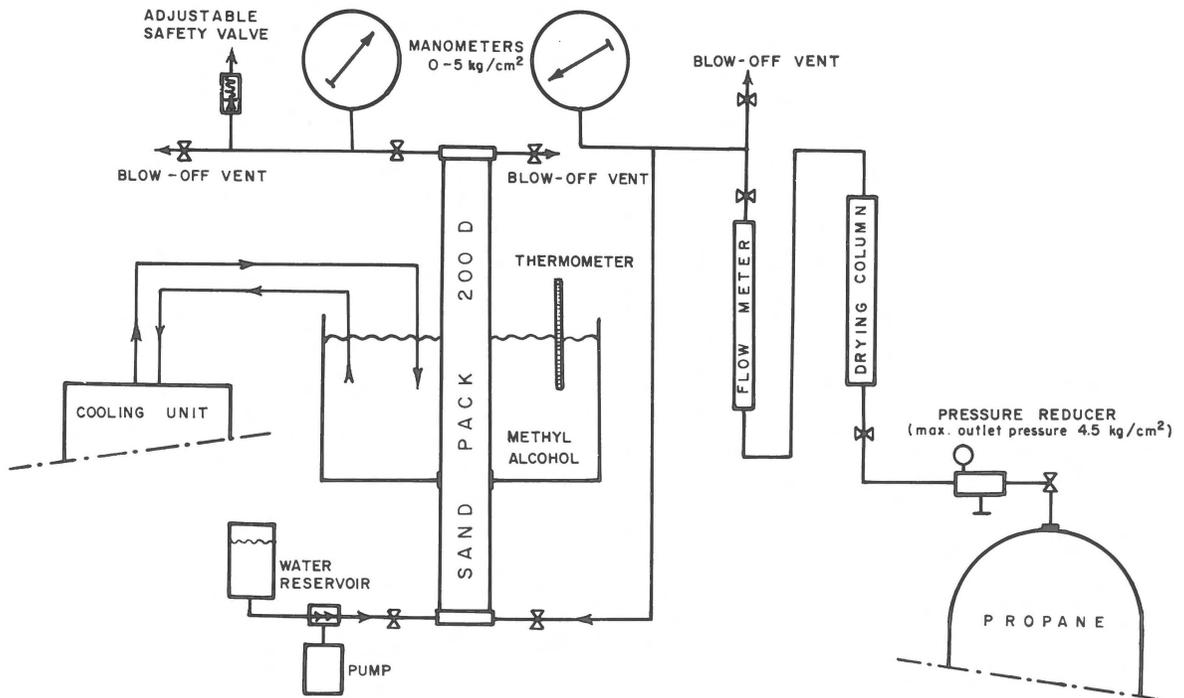


Fig. 2. Flow scheme for laboratory apparatus.

tube (internal diameter 2.5 cm, length 70 cm). The middle part with a height of approx. 15 cm can be cooled to bring the gas-plus-water mixture into the hydrate stability regime. The tube is filled with a coarse, very well sorted natural sand with an average grain size of 0.75 mm and a permeability of 200 D. The maximum allowed pressures for the apparatus meant that propane had to be used as a hydrating agent, instead of methane. A propane gas flow of 0.5 normal L/h (volume normalised to 1 atmosphere and room temperature) was established through the initially water-saturated sand pack at room temperature. The dry gas was first passed through a rotameter and then through a water-filled sand pack in the tube. Subsequently, it flowed through a back-pressure regulator and a wet-gas meter. The pressure difference across the sand pack at an average pressure of 4 bar abs. was only 0.01 bar. Cooling of the middle section of the

tube brought the pressure and temperature conditions into the stability regime of propane hydrate. When the first icelike crystals were observed at a temperature just below 0°C, the temperature was raised to 1.6°C to remove all ice. At this higher temperature, the crystals continued to grow, which indicates that they were not ice but hydrates. The continuing flow of gas through the preferentially gas-filled channels prevented the channels from being blocked by the gas hydrates because the water needed for their formation was absent in these channels and a more or less constant state could be maintained for many days. Apparently, the initially dry gas could not contact enough water in the lower part of the tube to keep the hydration reaction going.

However, the injection of only a few cubic centimetres of water resulted in a perfect hydrate seal within 15 minutes. During the one-week

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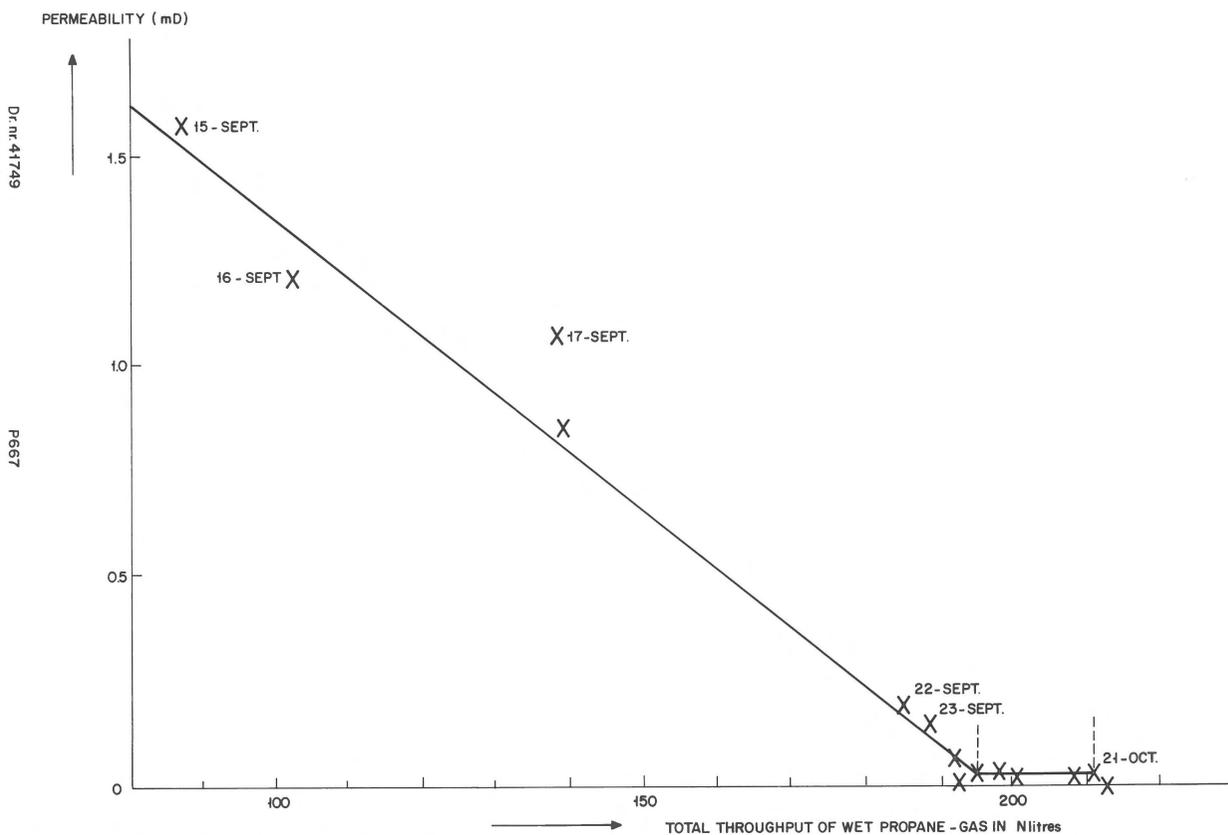


Fig. 3. Permeability of the sand pack for propane under influence of the growing hydrate layer.

observation period, no leakage of gas was detected. Instead, the seal seemed to grow at the inlet side of the tube. When the outlet pressure was reduced below 2.8 bar abs., the hydrates at the top of the cooled zone began decomposing until the seal was destroyed and the outlet pressure increased again. New seals could only be formed with either wetted gas or an admixture of water to the dry gas.

The sealing experiment was repeated with propane gas that was saturated with water, without an extra input of liquid water (see Fig. 3). Now the permeability of the sandpack decreased almost linearly with the total amount of propane passed through until the permeability reached a value of $\sim 3 \mu\text{D}$. After reaching this value the permeability remained constant for a week. It was assumed that the gas flow through the very narrow openings had become too fast to let the seal grow further. By decreasing the pressure difference over the seal from 1.8 to 1.5 bar the gas flow was slowed down slightly. Immediately, the permeability decreased further until it reached immeasurably small values. At the end of this experiment the flow through the hydrate seal was much smaller than accidental leaks from the apparatus itself, which was demonstrated by a significant difference between the inflow and the outflow rate of the gas.

The seal could withstand a pressure difference of 2.7 bar, the maximum possible in the given set-up (maximum inlet pressure 5.5 – condensation point of propane, minimum outlet pressure 2.8 bar abs. – decomposition point of propane hydrate).

By lowering the level of the cooling fluid, we could establish that the minimum thickness of the layer that could withstand a pressure difference of 2.4 bar was equal to 5 cm. This sealing capacity of about 0.5 bar per cm thickness would mean that a 10 metre thick hydrate seal can hold a free gas column of 500 metres or more, depending on the gas saturation and pressure. Hence, the results of this experiment support the model of free gas being trapped below a hydrate seal that is too thin to be resolved by seismic methods.

Figures 4 and 5 show the cooled zone of the sandpack. Only a part of the pore space is filled with gas hydrates. From the amount of gas pro-

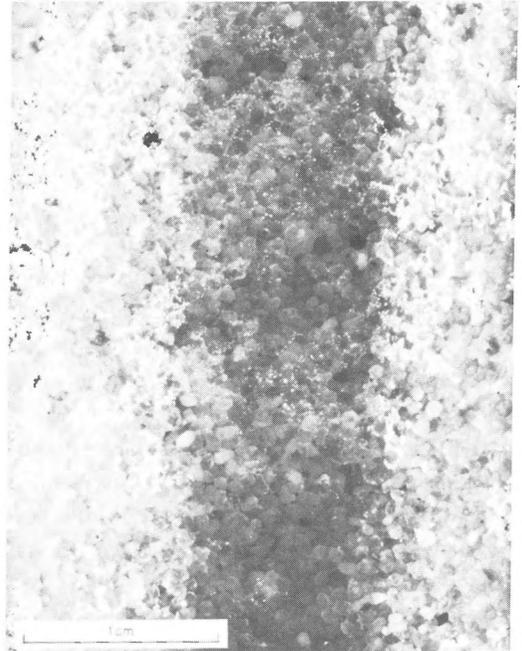


Fig. 4. Propane hydrates (shiny spots) in 200 D sand pack. (The black band in the middle is due to optical distortion of the cylindrical pipe).

duced by decomposition of the seal, it was estimated that approximately 50% of the pore space in the seal was filled with hydrates. Apparently the narrow passages were plugged before all the pore space could be filled with hydrate.

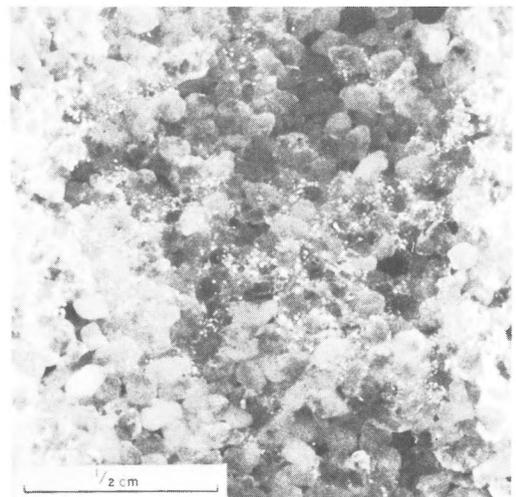


Fig. 5. Detail of figure 4.

Conclusions

The results of these experiments suggest that, given the proper conditions of pressure and temperature, upward flow of gas will readily lead to the formation of gas hydrates in deep-sea sediments. A hydrate seal that can easily withstand the maximum possible pressure (lithostatic pressure) will probably be formed near the bottom of the hydrate-stability zone, while the position of the top of this zone will be governed by the (extremely slow) diffusion of the dissolved gas to the sea-bottom.

A hydrate layer strong enough to trap a gas column of 1000 metres can nevertheless be too thin to be resolved by seismic methods.

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References

- Sapir, M.Kh., Ye.N. Khamenskov, I.D. Yefremov, G.D. Ginsburg, A.E. Benyaminovich, S.M. Lenka & V.I. Kislova 1973A. Geology and Geophysical logging of the gas hydrate pool of the Messoyakh gas field (Translated from: *Geologiya Nefti i Gaza*). *Petroleum Geology* 11: 243-249
- Sapir, M.Kh., G.D. Ginsburg, V.I. Kislova & R.S. Bogatyrenko 1973B. Effect of low formation temperatures on the hydrocarbon composition of natural gases and conditions of preservations of their pools (Translated from: *Geologiya Nefti i Gaza*). *Petroleum Geology* 11: 319-321.
- Sheridan, R.E. & F.M. Gradstein 1981 Early history of the Atlantic Ocean and gas hydrates in the Blake Outer Ridge: Results of the Deep Sea Drilling Project. *Episodes* 2: 16-22
- Stoll, R.D., J. Ewing & G.M. Bryan 1971 Anomalous wave velocities in sediments containing gas hydrates. *Journ. Geophys. Res.* 76 (8): 2090-2094
- Tucholke, B.E., G.M. Bryan & J.E. Ewing 1977 Gas hydrate horizons detected in seismic-profiler data from the Western north Atlantic. *Bull. Amer. Ass. Petr. Geol.* 61: 698-707