



Laboratory formation of non-cementing hydrate using excess water and temperature cycling, supported by rock physics modelling.

S. K. Sahoo^{a,b}, H. Marín-Moreno^a, L. J. North^a, T. A. Minshull^b and A. I. Best^a

^aNational Oceanography Centre, University of Southampton Waterfront Campus, UK; ^bNational Oceanography Centre, University of Southampton, UK.

Contact email: sourav.sahoo@soton.ac.uk

Introduction

Seafloor methane gas hydrates occur naturally on continental margins around the world, and are considered as a significant alternative energy resource (Riedel et al, 2010). Accurate quantification of gas hydrates beneath the seafloor using geophysical remote sensing is hampered by uncertainties associated with the effect of hydrate content (saturation of pore space) and its distribution on measurable geophysical properties of hydrate-bearing sediments, such as seismic velocity and electrical resistivity.

Depending on hydrate content and the way hydrate forms within the mineral grain framework of the host sediment (e.g. sand), hydrate can be either cementing or non-cementing, i.e. either hydrate acts to bond sand grains and increases the stiffness of a sand pack, or it does not affect the sand pack stiffness because the hydrate floats in the pore space, suspended within the pore water; however, non-cementing hydrate is thought to be the dominant morphology in marine sediments. We conducted laboratory experiments to grow non-cementing methane gas hydrates in natural Berea sandstone (a convenient host porous medium). The challenge was to form a homogeneous distribution of non-cementing hydrate in the rock sample, suitable for ultrasonic-pulse echo measurements of P- and S-wave velocity and attenuation, and electrical resistivity. Non-cementing hydrate forms when hydrate nucleates away from grain contacts, which can be achieved in principle using methane super-saturated pore water instead of gaseous methane (Waite and Spangenberg, 2013). The solubility of methane in water is very low which makes hydrate formation from methane super-saturated water an expensive and slow process with the additional problem of clogging due to hydrate formation in inlet and outlet pipes (Waite and Spangenberg, 2013). This method can also result in a heterogeneous distribution of hydrates. Here, we present a faster method to obtain a more homogenous distribution of non-cementing hydrate without using methane super-saturated water. The results are interpreted with the aid of a novel rock physics model of velocity (and attenuation).

Methods

We used a standard stainless steel, high pressure cell, instrumented to monitor electrical resistivity, ultrasonic P- and S-wave velocity and attenuation (e.g. Best et al, 2007), pore fluid pressure, and temperature (both sample and ambient). We modified the existing excess gas method (Choi et al., 2014; Waite et al., 2004) by using an initial pore brine saturation of 80%, which created an excess water condition in the pore space. Methane gas was then injected to a pore fluid pressure of 11.8 MPa with a constant effective pressure of 10 MPa. The pore fluid system was sealed and then the temperature was reduced to within the hydrate stability field. There was a finite length of pipe containing methane gas which was allowed to enter the sample during hydrate formation in response to reductions in pore

pressure. Repeated cycles of hydrate formation and dissociation were carried out by controlling the temperature.

Results

In the first cycle, the increase in P-wave velocity due to hydrate formation is larger than in the second cycle even though the hydrate saturation is almost same (Figure 1). Using a novel rock physics model (Marín-Moreno et al, 2017), we deduce that the decrease in velocity is likely due to the formation of non-cementing hydrate in the second cycle. Similar changes were also observed in S-wave velocity, P- and S-wave attenuation and electrical resistivity (not shown here).

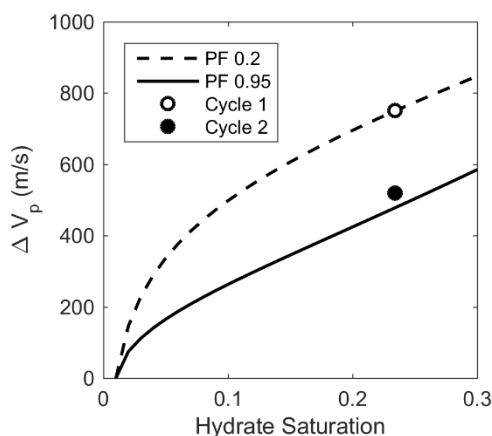


Figure 1: Comparison of measured (circles) and modelled (lines) P wave velocity for the first and second cycles of hydrate formation for a hydrate saturation of 22%. The modelled velocities were obtained using the rock physics model of Marín-Moreno et al. (2017). For simplification, cementing hydrate was considered to be in equal proportions of both grain contact and grain coating cement. Dotted lines represent 20% of the hydrate as pore filling (PF; a type of non-cementing hydrate) while solid lines represent 0.95 pore filling hydrate. The uncertainty in the saturation estimate is less than 0.25%.

Conclusions

The repeated cycling of hydrate formation and dissociation in the presence of excess water in the pore space results in conversion of initially formed cementing hydrate into non-cementing hydrate, as deduced from rock physics modelling of elastic wave velocity.

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References

- Best, A. I., J. Sothcott, and C. McCann (2007) A laboratory study of seismic velocity and attenuation anisotropy in near surface sedimentary rocks, *Geophysical Prospecting*, 55(5), 609-625.
- Choi, J.H., Dai, S., Cha, J.H., Seol, Y (2014) Laboratory formation of noncementing hydrates in sandy sediments. *Geochemistry, Geophys. Geosystems* 15, 1648–1656. doi:10.1002/2014GC005287
- Marín-Moreno, H., Sahoo S. K. and Best A. I. (2017) Theoretical modelling insights into elastic wave attenuation mechanisms in marine sediments with pore-filling methane hydrate, submitted to *Journal of Geophysical Research*.
- Riedel, M., E. C. Willoughby, and S. Chopra (2010) Gas hydrates - geophysical exploration techniques and methods, in *Geophysical characterization of gas hydrates*, edited by M. Riedel, E. C. Willoughby and S. Chopra, pp. 1-22, Society of Exploration Geophysicists, Tulsa, Oklahoma.
- Waite, W.F., Spangenberg, E. (2013) Gas hydrate formation rates from dissolved-phase methane in porous laboratory specimens. *Geophys. Res. Lett.* 40, 4310–4315. doi:10.1002/grl.50809
- Waite, W.F., Winters, W.J., Mason, D.H., (2004) Methane hydrate formation in partially water-saturated Ottawa sand. *Am. Mineral.* 89, 1202–1207.