



Continuous Complex Conductivity Measurements During Methane Hydrate Formation and Dissociation in Sandstone

Mathias Pohl^a, Cesar Mapeli^a, Manika Prasad^a

Colorado School of Mines, Center for Rock Abuse

Contact email: mpohl@mines.edu

Introduction

Natural gas hydrates are crystalline structures consisting of water molecules that encage guest molecules with small molecular diameters, most commonly methane and occasionally larger molecules such as ethane, propane, and carbon dioxide (Sloan & Koh, 2007). Low temperatures, elevated pressures, adequate amounts of free water as well as gas, either in free- or in dissolved-phase, are required for hydrates to occur in nature. These conditions exist in marine environments, along continental slopes, or in permafrost regions (Kvenvolden & Lorenson, 2001).

Mapping gas hydrate occurrences in nature is fairly well established, estimating gas hydrate saturation is less so. Since pure methane hydrates are insulators (Edwards, 1997, Du Frane et al, 2011 & 2015), their presence in sediments can influence electrical properties. The formation of gas hydrates replaces the conductive brine, thereby reducing water saturation and restricting the flow of electric current leading to an increase in bulk resistivity of the sediment (Yuan & Edwards, 2000). The formation of hydrate withdraws fresh water from the formation and excludes ions. Thus, hydrate formation causes a competing effect between decrease in water saturation and increase in salinity. Additionally, hydrate formation causes a drop in permeability which reduces potential conductivity paths. Kerkar et al. (2014) found that methane gas dissolved in water forms gas hydrates within the pore-space. Using electrical measurements, we detect the combined effects of free water surrounding hydrate grains as well as unreacted water within the hydrate structure in hydrate-bearing systems.

Methodology

We performed conductivity measurements at the low-frequency range (1.5 Hz to 12 kHz), variously known as the Induced Polarization (IP) method, the Complex Resistivity (CR) method, or the Complex Conductivity (CC) method, using four electrodes. IP is sensitive to the ability of the porous material to store electrical charges as well as conduct electrical charge.

The measured in-phase or real conductivity is the combined effect from the electrical current influenced by pore bulk water conductivity and surface conductivity (Revil et al., 2013a, Revil et al., 2013b). The out-of-phase or quadrature conductivity is exclusively affected by surface polarization and can therefore provide information relating to pore structure. Our continuously recorded conductivities (in-phase and quadrature) during various stages of hydrate formation and dissociation help us to better understand and characterize hydrate – sediment systems.

Results

Figure 1 shows real (top panel) and quadrature (lower panel) conductivity changes during the experiment. The Cooling Stage (Arrow I) marks onset of hydrate formation with an exponential drop in conductivity. The Freezing Stage (Arrow II) marks onset of ice formation accompanied by a sharp drop

in conductivity. As ice is thawed (Thawing Stage: Arrow III), conductivity increases back to Cooling stage levels for sediment plus hydrate. And finally during hydrate dissociation (Warming Stage: Arrow 4), the part of conductivity reaches initial values. Although the real and the imaginary parts of the conductivity track each other, they differ during hydrate dissociation (Warming Stage: Arrow 4). The real conductivity shows an increase whereas onset of hydrate dissociation leads to a prominent peak that drops back to initial values before start of the cycle. Once conductivity values remained constant for at least 5 hours at each stage, the reaction was considered as completed.

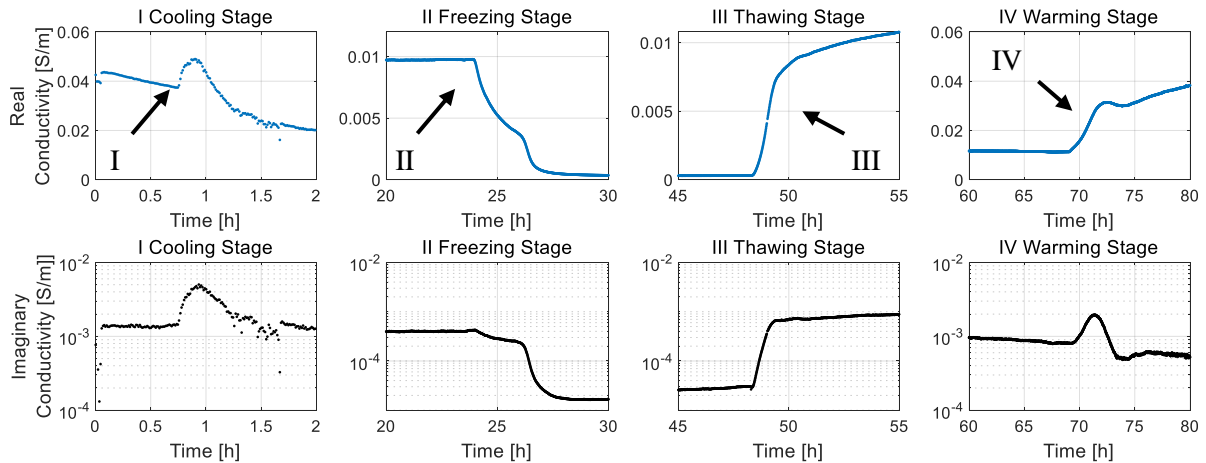


Figure 1: Real (blue) and Imaginary (black) part of the conductivity displayed for a single frequency (94 Hz). The arrows mark distinct stages: Arrow I – Cooling Stage with onset of hydrate formation, Arrow II – Freezing Stage with ice formation, Arrow III – Thawing Stage, Arrow IV – Warming Stage with onset of hydrate dissociation.

Discussion

The beginning of hydrate formation is marked by an increase in conductivity. This increase is the result of a combination of factors such as increase salinity, decrease water saturation, diffusion of ions, and the exothermic reaction of hydrate formation where the latter is the most dominant effect. This increase in conductivity is observed over all frequencies, though the amplitude is greater at higher frequencies, and can be used in the field to monitor the hydrate formation front during CO₂ sequestration. As the hydrate dissociation is the reverse effect and is as detectable, this method can also be used to determine hydrate dissociation front in field data during gas production out of hydrate deposits.

Temperature reduction to below the freezing point of water results in a sudden drop in conductivity values. This indicates that layers of water between the hydrates and sediment grains were still present in the sample. The presence of free water pockets between the hydrate crystals can explain the increase in acoustic wave attenuation properties of hydrate-bearing sediments (Pohl et al., 2017).

Conclusions

We present electrical conductivity measurements to help detect hydrate formation and dissociation fronts. Overall, the hydrate-forming process is more complex than previously thought and can be challenging to detect in the field when not considering short-term effects of hydrate formation or dissociation.

Acknowledgements

This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Fossil Energy, under Award Number DE-FE 0009963.

References

Du Frane, W. L., Stern, L. A., Weitemeyer, K. A., Constable, S., Pinkston, J., Roberts, J. J., (2011), *Electrical properties of polycrystalline methane hydrate*. *Geophys. Res. Lett.*, 38, L09313,

- Du Frane, W. L., Stern, L. A., Constable, S., Weitemeyer, K. A., Smith, M. M., & Roberts, J. J. (2015), *Electrical properties of methane hydrate + sediment mixtures*. *J. Geophys. Res. Solid Earth*, 120, 4773–4783, doi:10.1002/2015JB011940.
- Edwards, R. N., (1997), *On the resource evaluation of marine gas hydrate deposits using seafloor transient electric dipole-dipole methods*. *Geophysics*, 62, 63–74.
- Kerkar, P. B., Horvat, K., Jones, K. W., & Mahajan, D. (2014), *Imaging methane hydrates growth dynamics in porous media using synchrotron X-ray computed microtomography*, *Geochem. Geophys. Geosyst.*, 15, 4759–4768, doi: 10.1002/2014GC005373.
- Kvenvolden, K., & Lorenson, T. (2001), *The global occurrence of natural gas hydrate*, in *Natural Gas Hydrates: Occurrence, Distribution, and Detection*. *Geophys. Monogr. Ser.*, vol. 124, edited by C. Paull and W. Dillon, pp. 87–98.
- Pohl, M., Prasad, M. & Batzle, M. L. (2017), *Ultrasonic attenuation of pure THF hydrates*. *Geophysical Prospecting*, doi: 10.1111/1365-2478.12534
- Revil, A., Woodruff, W. F., Torres-Verdín, C. et al. (2013a). *Complex conductivity tensor of anisotropic hydrocarbon-bearing shales and mudrocks*. *Geophysics* 78 (6): D403-D418. <https://doi.org/10.1190/geo2013-0100.1>.
- Revil, A., Eppehimer, J. D., Skold, M. et al. (2013b). *Low-frequency complex conductivity of sandy and clayey materials*. *Journal of Colloid and Interface Science* 398: 193-209. <https://doi.org/10.1016/j.jcis.2013.01.015>.
- Sloan, E., & Koh, C. (2007), *Clathrate Hydrates of Natural Gases*. Boca Raton, FL: CRC Press
- Yuan, J., & Edwards, R. N. (2000), *The assessment of marine gas hydrates through electrical remote sounding: Hydrate without a BSR?* *Geophys. Res. Lett.*, 27, 2397–2400, doi:10.1029/2000GL011585.