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Modelling hydrate formation in porous media: Capillary inhibition effects

Monday, 31 May 2021 16:25 (15 minutes)

Marine sediments hosting methane hydrates (MH) cover pore sizes ranging from coarse-grained sands to fine-grained silts and clays. Coarse-grained sediments favour methane gas and methane saturated water flow and hence the formation of large concentrations of MH in pores (~60-90%) (e.g., Weinberger and Brown, 2006). However, most of the world's MH inventory exists disseminated within fine-grained sediments in very low saturations (below 10%) (e.g., Max et al., 2016). Experimental tests (e.g., Anderson et al., 2009; Chuvilin et al., 2005; Handa and Stupin, 1992; ∅stergaard et al., 2002; Uchida et al., 1999, 2004) and theoretical models (e.g., Clennell et al., 1999; Henry et al., 1999; Sun and Duan, 2007) have evidenced that MH confined in narrow pores (<100 nm) are subjected to capillary effects that disturb their thermodynamic stability. These studies show that capillary pressure hinders MH stability by decreasing the pore water activity and increasing aqueous methane solubility. Then, as pore size decreases, capillarity effects shift the MH equilibrium phase boundary towards higher pressures and/or lower temperatures than those predicted from bulk conditions (no sediment); similar and in addition to the shift generated by chemical inhibitors like salt. Understanding the stability conditions of natural MH is critical for a reliable prediction of the methane budget stored in hydrate systems as well as to assess the feasibility of its extraction for energy purposes (Ruppel and Waite 2020). Here, we first propose an equilibrium model to simulate MH formation conditions accounting for capillary effects. Analogously to water freezing behaviour in pores (e.g., Nishimura et al., 2009), our model assumes MH formation to be controlled by the sediment pore-size distribution and the balance of the capillary forces developed at the liquid-hydrate interface. Our model uses the Clausius-Clapeyron relation for the thermodynamic equilibrium of methane and water chemical potentials in hydrate systems. It defines the thermodynamic equilibrium conditions that need to be satisfied by the liquid and MH phase pressures and the system temperature in a single pore size. Our model captures the depression of the MH equilibrium temperature observed experimentally during hydrate formation/dissociation tests performed in narrow pores (≤30.6 nm) (e.g., Deaton and Frost, 1946; Jhaveri and Robinson, 1965; McLeod and Campbell, 1961; ¬∅stergaard et al., 2002; Anderson et al. 2003, Anderson et al. 2009). Then, the model is combined with van Genuchten's capillary pressure (van Genuchten, 1980) to relate the thermodynamic properties of the hydrate system to the host sediment pore-size distribution. The model is finally applied to simulate and quantify MH formation in sand, silt and clays with different content of fine-particles, under equilibrium conditions and without mass transfer limitations. The simulations evidence that capillary effects are negligible in sand and almost negligible in silty sediments but exert a key control in MH stability and saturation within clayey sediments. In particular, the results show that at thermodynamic conditions typically found in the seabed, capillary effects may reduce the maximum hydrate saturation expected in sediments with a high content of fines up to 50%.

Time Block Preference

Time Block B (14:00-17:00 CET)

References

Anderson, R., Llamedo, M., Tohidi, B., and Burgass, R. W. (2003). Experimental measurement of methane and carbon dioxide clathrate hydrate equilibria in mesoporous silica. J. Phys. Chem, B(107):3507-3514

Anderson, R., Tohidi, B., and Webber, J. B. W. (2009). Gas hydrate growth and dissociation in narrow pore networks: Capillary inhibition and hysteresis phenomena. Geol. Soc. Spec. Publ., 319:145-159.

Chuvilin, E., Kozlova, E., Makhonina, N., and Yakushev, V. (2005). Experimental investigation of gas hydrate and ice formation in methane-saturated sediments. In Proceedings of the 5th International Conference on Gas Hydrate, Thermodynamic Aspects, Trondheim, Norway, 2005 13-16 June, 1562-1567.

Clennell, M. B., Hovland, M., Booth, J. S., Henry, P., and Winters, W. J. (1999). Formation of natural gas hydrates in marine sediments: 1. conceptual model of gas hydrate growth conditioned by host sediment properties. Journal of Geophysical Research, 104 (B10):22985-23003.

Deaton, W. M. and Frost, E. M. J. (1946). Clathrate hydrates and their relation to the operation of natural gas pipe lines. U.S. Bureau Mines Monograph 8.
Handa, Y. P. and Stupin, D. (1992). Thermodynamic properties and dissociation characteristics of methane and propane hydrates in 70 a˚ radius silica gel pores. J. Phys. Chem, 96 (21):8599-8603.

Henry, P., Thomas, M., and Clennell, M. (1999). Formation of natural gas hydrates in marine sediments: Thermodynamic calculations of stability conditions in porous sediments. J. Geophys Res. B (104), pages 23005-23022.

Jhaveri, J. and Robinson, D. B. (1965). Hydrates in the methane-nitrogen system. The Canadian Journal of Chemical Engineering, 43(2):75-78.
Max, D., Michael, H., and Arthur, H. J. (2016). Exploration and Production of Oceanic Natural Gas Hydrate.

McLeod, H. and Campbell, J. (1961). Natural gas hydrates at pressures to 10,000 psia. J. Petroleum Technol., (222):590-594.

Nishimura, S., Gens, A., Jardine, R. J., and Olivella, S. (2009). THM-coupled finite element analysis of frozen soil: formulation and application. Geotechnique, 59(3):159-171.

∅stergaard, K., Anderson, R., Llamedo, M., and Tohidi, B. (2002). Hydrate phase equilibria in porous media: Effect of pore size and salinity. Terra Nova, 14:307 - 312.

Ruppel, C. D., & Waite, W. F. (2020). Grand challenge: Timescales and processes of methane hydrate formation and breakdown, with application to geologic systems. Journal of Geophysical Research: Solid Earth, 125, e2018JB016459
Sun, R. and Duan, Z. (2007). An accurate model to predict the thermodynamic stability of methane hydrate and methane solubility in marine environments. Chemical Geology, 244(1):248-262.

Uchida, T., Ebinuma, T., and Ishizaki, T. (1999). Dissociation condition measurements of methane hydrate in confined small pores of porous glass. J. Phys. Chem. B, 103 (18), pages 3659-3662.

Uchida, T., Takeya, S., Chuvilin, E., Ohmura, R., Nagao, J., Yakushev, V. S., Istomin, V. A., Minagawa, H., Ebinuma, T., and Narita, H. (2004). Decomposition of methane hydrates in sand, sandstone, clays, and glass beads. J. Geophys. Res., 109(B05206).

Weinberger, J. L. and Brown, K. M. (2006). Fracture networks and hydrate distribution at hydrate ridge, Oregon. Earth Planet. Sci. Lett., 245:123-136.

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