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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; Østergaard 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; ¬Østergaard 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)

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