Dependence of Hydrate Formation Kinetics on System-Size and Shear

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Gas hydrates (ice-like clathrate compounds) can pose a significant plugging risk to subsea hydrocarbon production. Unfortunately, quantifying this risk is challenging. This is partly because gas hydrate nucleation, the precursor to plug formation, is highly stochastic. Due to this stochasticity, large numbers of hydrate formation measurements are required to generate a robust quantification of hydrate formation probability.

Unlike many conventional apparatus, the low-thermal-mass HPS-ALTA cells (high pressure, stirred automated lag time apparatus) use thermoelectric (Peltier) elements to allow fast temperature ramping. This enables system conditions to be rapidly brought into and out of the hydrate stability region, subsequently enabling time efficient generation of high-resolution probability maps for gas hydrate formation. The probability curves can be fit with models from classical nucleation theory, enabling extraction of parameters that describe the kinetic and thermodynamic aspects of nucleation. However, it is critical to understand how to correctly interpret such results since formation probability is both system-size- and shear-dependent. Such knowledge is also important for informing the use of probability data in predictive industrial models.

In this presentation, we will detail the results of experiments aimed at understanding the role that shear and system size play in determining observable hydrate formation kinetics. Via measurements in multiple generations of HPS-ALTA, we extract rates of hydrate nucleation and growth across system volumes ranging from (1 to 54) mL under varying levels of shear and subcooling. Combining this data with results obtained in µL-scale, levitated water droplets reveals clear system-size dependencies which initially point towards the water-gas interface being the critical dimension that determines nucleation rate. Growth rates are also extracted and supported by top-down visual observations. These reveal that the growth rate and mode (including ring and slurry formation) depend strongly on the level of shear and gas-water interface perturbation.