Subcooling and Induction Time Measurements to Quantify Hydrate Nucleation Probability

Vincent Lim, Peter Metaxas, Paul Stanwix, Zachary Aman, Michael Johns and Eric May^{C, S} Fluid Science & Resources Division, The University of Western Australia, Perth, WA, Australia eric.may@uwa.edu.au

The formation of gas hydrates in bulk water and at interfacial boundaries is a stochastic process. As such, large numbers of measurements of hydrate formation events are required to accurately determine formation probability as a function of subcooling or the time spent within the hydrate equilibrium region. However, traditional experimental techniques for quantifying hydrate formation (e.g. rocking cells and autoclaves) are typically not compatible with high throughput data collection. In an effort to accurately quantify hydrate formation probability and thus enable rigorous comparison with theories for hydrate formation, we have developed a High Pressure Stirred Automated Lag Time Apparatus (HPS-ALTA) for measurements of hydrate formation. The system enables the identification of hydrate formation and the measurement of hydrate growth rates under shear via a pressure-based detection technique. Each high-pressure cell (operating up to 20 MPa) within the multi-cell system is equipped with six Peltier elements, which, when combined with each cell's low thermal mass, enable cycling of the system's temperature at rates up to 5 K·min⁻¹. This enables the measurement of 100 or more hydrate formation-dissociation events in a matter of days. The HPS-ALTA array was used to investigate hydrate formation probability distributions as a function of both subcooling (in scanned temperature experiments) and induction time (at constant subcooling). The former type of measurement introduces experimental artefacts associated with the cooling rate; however, these can be overcome with appropriate corrections. Several different high-pressure systems including methane + water, a natural gas mixture + water, and a gas + water-in-oil emulsion were investigated with varying concentrations of kinetic hydrate inhibitor compounds. The observed distributions are gualitatively consistent with nucleation theory predictions: they are exponential in form, are representative of a mononuclear nucleation mechanism, and allow characteristic nucleation rates to be extracted that are consistent with other reported observations but with smaller uncertainties. Quantitative consistency with the predictions of nucleation theory is more challenging, although a method of how it might be achieved is proposed.