Quantification of Hydrate Formation Probability in Thermodynamically- and Kinetically-Inhibited Systems

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Gas hydrates are ice-like solids in which gas molecules are enclathrated within cages composed of hydrogen-bonded water molecules. Measuring gas hydrate formation in the presence of thermodynamic (THI, e.g. MEG) and kinetic hydrate inhibitors (KHI, e.g. PVP or PVCap) is not only of interest for probing the inhibition of multi-component nucleation processes but also has direct relevance to oil and gas production systems where such inhibitors are routinely used to avoid hydrate formation within subsea flowlines.

Since hydrate nucleation is stochastic, the quantification of performance for various inhibitors requires measurement of formation *probability* (e.g. as a function of subcooling and/or time). Here, high resolution curves describing gas hydrate formation probability were obtained with a second generation HPS-ALTA (high pressure stirred, automated lag time apparatus). This apparatus consists of steel pressure cells whose contents are magnetically stirred and whose temperatures are controlled by thermoelectric elements. The on-cell thermoelectric elements allow for rapid cooling and heating, enabling the collection of large numbers of hydrate formation events (up to around 20 per day per cell). In turn, this enables the generation of smooth formation probability curves within practical time frames.

Induction times for hydrate formation in water + gas systems were shown to be consistent with predictions from classical nucleation theory. The THI, MEG, was found to have no measurable effect on the form of the probability distributions, acting only to shift the boundary of the hydrate equilibrium region in *p*-*T* space. However, induction times obtained in the presence of a polymeric KHI (PVP:PVCap) were no longer exponentially distributed, instead being consistent with a Gamma distribution, suggestive of a multi-nuclei nucleation phenomena. The resultant distributions are also narrowed, a result which has ramifications for understanding risk in kinetically versus thermodynamically inhibited production systems.