Effect of Gas Composition on Hydrate Growth Rate and Agglomeration Tendency

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While the past decade has seen significant advances in kinetic hydrate inhibitor (KHI) evaluation, gas hydrate AA (anti-agglomeration/agglomerant) / natural transportability testing remains notably disparate by comparison, suffering from a lack of standardisation and persistent gaps in knowledge regarding the generic fundamentals of hydrate plugging. This problem is in a significant part responsible for the more limited use of AA based approaches as a hydrate mitigation strategy – be that by chemical treatment or utilising natural transportability properties – when compared to complete hydrate inhibition by KHI / THI (thermodynamic inhibitor) injection.

Historically, AA studies have primarily focused on the liquid hydrocarbon and aqueous phases, with oil composition (notably the presence of natural surfactants), water cut and salinity seen as the main controlling factors. In contrast, much less attention has been paid to the gas and hydrate phases, particularly the compositions of these.

Following delineation of the hydrate phase boundary, either by measurement or prediction, the gas is generally only considered in terms of total moles consumed for the purposes of calculating the fraction of solid hydrate formed. The hydrate phase is treated in a similar manner, being assumed as a single structure of largely fixed composition ('s-II natural gas hydrates'…'s-I methane hydrates'), with the fraction present viewed as the dominant controlling factor in plugging.

However, recent work in an ongoing industry funded JIP (joint industry project) demonstrates that both gas and hydrate composition play a major role in slurry transportability, controlling the rate of hydrate growth, plugging tendency, and LDHI performance (both AAs and KHIs).

As described in a companion article, in both single (e.g. methane) and multi-component gas systems, rather than just one hydrate phase forming, a number of hydrates of differing composition/structure nucleate and grow at variable (by up to one order of magnitude) rates as subcooling is increased, including a largely unknown low pressure s-II methane hydrate. The relatively rapid growth rates of some phases means that hydrates formed initially may not be the most thermodynamically stable, making subsequent solid-solid and/or complete dissociation-reformation transitions a common feature. Crucially, different gases show variable plugging tendencies as a function of subcooling for identical test conditions, and it is proposed that this is structural and/or structure change related, e.g. through melting/regrowth cementation mechanisms. These structure related plugging processes also give rise to novel 'un-agglomeration' behaviour, where 'plugs' disintegrate to flowing slurries at fixed PT, sometimes well inside the hydrate region, for both gas-water and gas-liquid hydrocarbon-water systems.