Hydrate structural dependency of natural KHIs present in crudes compared to commercial KHI additives

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Kinetic Hydrate Inhibitors (KHIs) have been available on the market now for a number of decades. Although the exact mechanisms by which KHIs inhibit hydrates are not completely understood, modern CGI (crystal growth inhibition) test approaches have allowed the selection of additives that act to prevent or severely limit crystal growth: a property considered more robust than traditional nucleation inhibition (alone) for oil & gas field applications. The CGI procedure is based on evaluating KHIs in the presence of small quantities of hydrates (and/or hydrate 'history') in order to facilitate repeatability, and to test under 'worst case scenario' conditions. From a wide variety of studies using this method, it has been established that KHI failure appears most commonly linked to a sensitivity to structure-I hydrates in (nominally s-II forming) natural gas systems.

More recently, it has been established that some crude oils show clear KHI properties, in that they are able to delay and/or completely inhibit hydrate growth on practical timescales. Here, we report experimental results demonstrating this behaviour for a variety of different oils and laboratory test gases (CH4, 98% CH4 / 2% C2H6, 85% CH4 / 15% C3H8, and some multicomponent natural gases). Tests with some commercial KHI additives using the same gases with real condensate have also been performed for comparison.

Results show that when crudes display notable natural KHI properties, 'failure' / massive hydrate formation is seemingly governed by the most stable structure-I species present for the gas mix tested. In contrast, for crudes with little to no natural inhibition tendency, hydrate growth is in the form of the most stable structure-II species.

This behaviour is very similar to that seen for commercial additives, confirming that these natural crude oil KHIs are equivalent in action to synthetic KHI polymers. However, the identities of the crude compounds responsible are currently unknown.

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