Modelling of Hydrate Composition during Formation of Clathrate Hydrates from Gas Mixtures

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Since the 1930's it has been known that gas hydrates form plugs that block pipelines. Laboratory studies have investigated methods of preventing plug formation as well as methods to remove hydrate plugs. In the course of studying the relative dissociation times of structure I (sI) and structure II (sII) gas hydrates prepared from methane + ethane mixtures, X-ray diffraction analysis indicated the simultaneous presence of both hydrate structures at conditions where only one hydrate structure should form. The aim of this work was to develop a model describing the formation of gas hydrates from mixtures of methane + ethane in a closed system as the gas forms the hydrate and to validate the model by experiment. Two methods of laboratory hydrate preparation from ice particles were studied: (1) A closed system pressure-drop formation, and (2) A closed system constant pressure formation. Models were developed for both methods (1) and (2) and method (2) was also investigated by experiment. Experimentally a mixture of mole fraction 89.7 % methane + 10.3 % ethane was used in the hydrate plug formation. Mole fractions of each gas were monitored periodically during the hydrate formation by gas chromatography (GC). The water-free hydrate phase mole fraction of methane and ethane were also measured by GC at the completion of hydrate formation. During the hydrate formation the mole fraction of methane in the gas phase increased. The model showed the same trend, however there was a discrepancy between the model and experiment. The discrepancy is most likely due to the assumption in the model that there is equilibrium between the various phases. This work was performed at the University of Canterbury.