

Simulation of Methane Hydrate Formation Employing a Model That Relates the Stochastic Nature of Crystallization and the Phase Equilibria.

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The aim of this work is the modeling of the thermal evolution inside a hydrate forming system which is submitted to an imposed steady cooling. Two study systems are considered, the first one is a w/o emulsion where the formulation considers the CCl_3F as the hydrate forming molecule dissolved in the oil phase. The second study system is an aqueous solution containing dissolved methane. The hydrate formation within the w/o emulsion submitted to steady cooling occurs in the aqueous phase of the emulsion, i.e. in the dispersed phase. The model equation is based on the resolution of the continuity equation in terms of a heat balance for the dispersed phase. The crystallization of the CCl_3F hydrate occurs at supercooling conditions ($T_c < T_F$), besides, the heat released during crystallization interferes with the imposed condition of steady decrease of temperature around the system. Thus, the inclusion of the heat source term has to be considered in order to take into account the influence of crystallization. The rate of heat released during the crystallization is governed by the probability of nucleation $J(T)$. Previous experimental measurements allowed to derive the corresponding function $J(T)$ of the w/o emulsion. The results provided by the model equation subjected to boundary conditions describe the evolution of temperature in the dispersed phase. The most singular point in the temperature–time curve is the onset time of hydrate crystallization. Three time intervals characterize the evolution of temperature during the steady cooling of the w/o emulsion: (1) steady cooling, (2) hydrate formation with a release of heat, (3) a last interval of steady cooling. Regarding the second study case, the probability of nucleation function $J(T)$ is elaborated employing the van der Waals and Platteeuw model with an activation energy of the Arrhenius type. In this manner the Gibbs free energy of nucleation may be linked to the equilibrium parameters of the methane hydrate formation. It is worth to highlight that the probability of nucleation $J(T)$ can be determined experimentally by differential scanning calorimetry, nevertheless, in the particular case of methane hydrates there has not been crystallization thermograms reported in the literature. Formation of methane hydrate during heating are reported in several work of Dalmazzone C. et al [1].

- [1] Dalmazzone C., D. Dalmazzone. *Differential scanning calorimetry: a new technique to characterize hydrate formation in drilling muds*. SPE 62962.
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- [3] O. Ye. Zatssepina, Buffett B. A. Nucleation of CO_2 - hydrate in a porous medium. *Fluid Phase Equilibria*, **200**, 263-275 (2002).