CRYSTAL GROWTH OF CLATHRATE HYDRATE IN LIQUID WATER SATURATED WITH A GUEST SUBSTANCE: OBSERVATIONS IN A HYDROCARBON-GAS MIXTURE + WATER SYSTEM

Sho Watanabe, Kota Saito and Ryo Ohmura
Department of Mechanical Engineering
Keio University
3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522
Japan

ABSTRACT
This paper reports the visual observations of the formation and growth of clathrate hydrate crystals in liquid water presaturated with methane + ethane + propane gas mixtures. The compositions of the methane + ethane + propane gas mixtures are (i) 90: 7: 3, (ii) 94.1: 5.8: 0.1 (iii) 99.47: 0.51: 0.02 in molar ratio. A hydrate film first formed to interven between mixed gas and liquid water, and then hydrate crystals grew in liquid water phase. The morphology of hydrate crystals grown in liquid water distinctly varied depending on the system subcooling \( T_{\text{sub}} \). When \( T_{\text{sub}} \) is smaller than \(-7\) K, hydrate crystal growth in liquid water was not observed. When \(-7\) K < \( T_{\text{sub}} \) < \(-12\) K, hydrate crystals with polygonal morphology were observed. At \( T_{\text{sub}} \) > \(-12\) K, polygonal crystals were replaced by dendritic crystals. These morphology changes were observed with all three gas mixtures. It was found that the morphology in the system with mixed gas of the molar ratio 99.47: 0.51: 0.02 was different from those of the other two systems. We also observed the hydrate crystals floating to the hydrate film from liquid water phase. Floating crystals formed in the bulk of the liquid water and attached the hydrate film then continued to grow in liquid water. The morphology of floating crystals varied with \( T_{\text{sub}} \) and the gas compositions.

Keywords: gas hydrate, crystal morphology, natural gas, energy storage

NOMENCLATURE
\( T_{\text{ex}} \) Experimental Temperature [K]
\( T_{\text{eq}} \) Equilibrium temperature [K]
\( \Delta T_{\text{sub}} \) System subcooling [K]
\( P \) Experimental pressure [MPa]
\( t \) time [min]

INTRODUCTION
Clathrate hydrates are crystalline solid compounds consisting of hydrogen-bonded water molecules called “host” to form cages and other different molecules called “guest” enclosed in the cage. Hydrates are known to form various crystal structures. The most common hydrate crystal structures are structure I, structure II and structure H. Recently, novel hydrate-related technologies attract attention in the energy and environmental fields. Some of these technologies are the transportation and storage of natural gas\(^1\) and hydrogen,\(^2\) cool-energy storage for air-conditioning,\(^3\) highly-efficient heat pump/refrigeration systems,\(^4\)\(^5\) etc. Various hydrates are studied for the development of these hydrate-based technologies. Natural gas hydrate is one of the most important hydrates because it is relevant to the natural gas transportation/storage and the plugging of the flow of oil or gas pipeline.\(^6\) Furthermore, natural gas hydrate naturally occurring in the seafloor is expected as the energy resource in the future.\(^7\) This study focuses on the formation and characteristic of the natural gas hydrate. Knowledge of the morphology of the hydrate crystals is necessary for the development of above-mentioned technologies utilizing hydrate since the morphology provide fundamental information on the mechanistic nature of hydrates. “Crystal