CRYSTAL GROWTH OF CLATHRATE HYDRATE AT THE INTERFACE BETWEEN SEAWATER AND HYDROPHOBIC-GUEST LIQUID: EFFECT OF ELEVATED SALT CONCENTRATION

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ABSTRACT
This paper reports the visual observations of the clathrate hydrate crystal growth at the interface of the seawater and a guest substance. Recently, Sakemoto et al. (Crystal Growth & Design 2010, 10, 1296-1300) reported the visual observations on the cyclopentane hydrate crystal growth in the seawater system. They concluded that the morphology of the hydrate crystals in water and seawater are generally similar at a given subcooling, $\Delta T_{\text{sub}}$. However, they performed the experiments exclusively with the seawater of the ordinary concentration, i.e., ~0.035 mass fraction of the salts and hence the effect of elevated salt concentration is not known. In this study, we performed the experiments with the mass fraction of NaCl in the aqueous solution from 0.035 to 0.3 to clarify the effect of elevated salt concentration on the crystal growth. Cyclopentane was used as the guest substance. Hydrate crystals grew along the interface of cyclopentane and the NaCl solution covering the interface. We visually analyzed the individual hydrate crystals and classified the morphology of the crystals according to $\Delta T_{\text{sub}}$ at atmospheric pressure. It was found that the size of the individual cyclopentane hydrate crystals decreased with increasing $\Delta T_{\text{sub}}$. The results showed that the morphology of the individual cyclopentane hydrate crystals in any seawater is qualitatively similar at a given $\Delta T_{\text{sub}}$. We also measured the lateral growth rates of the hydrate-film propagation.

Keywords: clathrate hydrates, crystal growth, seawater, desalination

NOMENCLATURE
$\Delta T_{\text{sub}}$: subcooling [K]
$T_{\text{eq}}$: equilibrium temperature [K]
$T_{\text{ex}}$: system temperature [K]
$X$: lateral growth rate of hydrate [mm/min]
x: length of the lateral growth of a crystal [mm]
$\Delta t$: time required for crystal growth [min]

INTRODUCTION
Clathrate hydrates are crystalline solid compounds consisting of hydrogen-bond water molecules forming cages that enclose other small molecules. Water molecules are called “host molecules”, while the encaged molecules are the “guest molecules”. Depending on the size and shape of the guest substances, water molecules form several different cage structures that interconnect to yield hydrates of different crystallographic structures, such as structure I, II, and H. Hydrocarbons and noble gases are the typical guest substances that form clathrate hydrates. Hydrates are typically stable at low-temperature and high-pressure conditions. Clathrate hydrates have several unique properties, such as a large heat of formation/decomposition, guest-substance selectivity, and a high gas storage capacity. Recently, research and development of novel energy and environmentally related technologies, exploiting these properties and characteristics of hydrates are being performed. Some of these novel technologies are transportation and storage of natural gases and hydrogen, ground/ocean sequestration of carbon dioxide, development of heat pump/refrigeration systems, removal of hydrogen sulfide from

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