Formation Efficiency of CO₂ Hydrate under Low Temperature and Low Pressure by Ultrasonic Mist

Shinichiro Hirabayashi¹, Motoki Takeuchi², Atsushi Murata², Yoshitaka Yamamoto¹, Taro Kawamura¹, Yuichi Tsukada¹, and Tomoya Tsuji²

¹Methane Hydrate Research Center, National Institute of Advanced Industrial Science and Technology
Tsukuba, Japan
²College of Industrial Technology, Nihon University
Narashino, Chiba, Japan

ABSTRACT

Formation efficiency of CO₂ hydrate from submicron ice was investigated by laboratory experiments and numerical models. Since formation rate of hydrate changes as the surface area of reaction interface decreases, temporal variation of formation rate was taken into account in this study. In the experiment, fine ice particles, the diameter of which was about 0.5 μm, generated by an ultrasonic mist generator, was confined in a reaction cell with pure CO₂ gas under the condition of 0.7 MPa and 253 K to form CO₂ hydrate. The conversion rate of ice to hydrate was obtained as a time history by measuring its weight at different reaction period. In the numerical part, a fugacity-driven formation model incorporated with a shrinking-core model of a single ice particle was applied to a spherical ice particle. Unknown parameters such as formation rate constant and coefficient of diffusion of CO₂ in hydrate film were determined by fitting the model to the experimental results. It was found that the most of the formation phenomena was diffusion-limited process and the estimated diffusion coefficient almost agreed with that proposed in the literature for relatively larger ice particles with diameter of about 100 μm.

KEY WORDS: CO₂ hydrate formation, submicron ice, ultrasonic mist, formation rate constant, diffusion coefficient, shrinking-core model

INTRODUCTION

Clathrate hydrates are crystalline water-based solids in which small molecules are trapped inside cages of hydrogen bonded water molecules. Recently large amount of natural gases such as methane have been found to exist in sand sediments under the seabed and exploitation of those gases as alternative energy sources is expected. The distinctive difficulty of their recovery compared with the conventional oil and natural gases is attributed to the physical characteristics of hydrate which is normally stable at low temperature and high pressure. Therefore, understanding of dissociation characteristics of hydrate is important for the purpose of efficient gas production. In addition, it has been proposed that injection of carbon dioxide (CO₂) in the neighboring sediment layer enhances the dissociation of methane hydrate by the formation heat of CO₂ hydrate (Ohgaki et al., 1996). Komai et al. (1999) paid attention to the generation of CO₂ hydrate at higher temperature and a lower pressure than those for methane hydrate, and suggested the production of methane by replacement of CO₂ hydrate. In these technologies, it is also important to comprehend the formation mechanism of CO₂ hydrate and to increase its formation rate.

Aside from the exploitation of fossil fuels, utilization of hydrate is getting more and more attention in many engineering technologies. For example, separation of CO₂ from mixed gas in a form of gas hydrate is expected to be an alternative method for capturing carbon at the extensive emission sites such as power plants and cement production factories. One of the most cost-consuming factors in forming CO₂ hydrate is to keep its pressure high, e.g. 1.3 MPa at 273.1 K (Sloan, 1998), in a pressure-resistant tank. Instead, when CO₂ hydrate is formed at lower temperature, for example 253 K, the required pressure for stable condition is reduced as low as about 0.4 MPa. If we make use of the cold energy which is usually abundant in gas companies for liquefied natural gas storage, the cost associated with this method may become competitive with those of other conventional capturing methods such as chemical absorption by amine solution or physical absorption by porous media.

The efficiency of hydrate formation is also important in reducing the processing cost. It is easily expected that increase of the interface area at which hydrate formation occurs directly lead to increase of the speed of hydrate formation. It is also expected that the smaller the volume of each water mass becomes, the more easily all the water is made into hydrate because of the rapid supply of CO₂ to the reaction interface. From these expectations, fine ice particles have often used for increasing the efficiency of CO₂ hydrate formation. Takeya et al. (2000) measured growth rates of CO₂ hydrate from small ice particles with average diameter of about 150 μm by X-ray diffraction experiments. They applied two-stage model to interpret the formation mechanism and estimated the initial reaction rate and diffusion coefficient of CO₂ through hydrate layer under various temperature conditions. Staykova et al. (2003) observed the formation process of CO₂ hydrate from ice grains with a typical diameter of 40 – 80 μm by neutron diffraction experiments and proposed a multi-staged model for hydrate growth. They obtained the same order of diffusion coefficient