

Estimation of Surface Area of Methane Hydrate in Sediments

Takafumi Nakayama⁽¹⁾, Keiichi Ogasawara⁽²⁾, Fumio Kiyono⁽²⁾, Akihiro Yamasaki⁽²⁾, Toru Sato⁽¹⁾

⁽¹⁾ Department of Environment Systems, University of Tokyo, Kashiwa, Japan

⁽²⁾ Environmental Fluid Engineering Group, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan

ABSTRACT

Surface area of methane hydrate in sediments is necessary to predict the amount of dissociated methane gas. It depends on the morphology how methane hydrate exists in sediments under the ground. The purpose of this study is to obtain a model equation for the surface area of methane hydrate in sediments as a function of porosity, hydrate saturation, and size of sediment particles. We conducted hydrate dissociation experiment in a pressure cell filled by glass beads. It is expected that the temperature in the cell first goes down to the equilibrium point due to hydrate dissociation, and that the dissociation ceases until heat is transferred from the surrounding cell walls. We simulated this process by using a numerical model with tentative surface areas. The surface area is, then, estimated by comparing the amounts of dissociated gas in the experiments and in the numerical simulations.

KEY WORDS: Methane hydrate; surface area; morphology; sediment.

INTRODUCTION

The surface area of the methane hydrate existing in sediments is necessary to estimate the dissociation rate, together with the dissociation speed of methane hydrate. The latter was given in a function of molecular fraction of methane, temperature and pressure by part of the authors. The surface area depends on the morphology how methane hydrate exists in sediments under the ground. In this study, it is assumed that the area is a function of the size of sediment particles, porosity, and hydrate saturation. We first conducted hydrate dissociation experiment by using a pressure cell filled by glass beads. To control the porosity, we mixed the beads with a couple of diameters. Water was filled in the cell and hydrate was generated. The amount of the water determines the hydrate saturation. The time change of methane gas dissociated from the hydrate was measured under the conditions of various porosity, hydrate saturation, temperature, and pressure of the experiment system. It is expected that the temperature in the experimental cell first goes down to the equilibrium point due to the hydrate dissociation. Then, the dissociation ceases until heat is transferred from the surrounding cell walls. Therefore, it is hard to know the hydrate surface area only by the dissociation experiments,

because we do not know the exact value of the transient temperatures at arbitrary points in the cell. In this study, we conducted the numerical case studies to simulate heat transfer and phase change taken place in the experiment cell by changing a coefficient of the hydrate surface area. When the calculated amount of the dissociation gas matches that of the experiment, we can obtain the coefficient. The systematic work of this process gave a form of the area coefficient as a function of bead size, porosity, and hydrate saturation, without knowing the existence morphology of methane hydrate.

MODELLING

Dissociation Model

Kim et al. (1987) proposed a rate equation (Kim-Bishnoi model) for the intrinsic dissociation rates based on the fugacity difference between the point at which dissociation takes place and the equilibrium condition, and the rate constants have been determined. More accurate measurements were performed by Clarke and Bishnoi (2001) with a particle-size analyzer. The Kim-Bishnoi equation has been used for a variety of dissociation process including a simulation of methane production from marine hydrate sediment. However, elimination of the heat transfer and mass transfer resistances was carried out simply by increasing the stirring rate in batch-type reactors in their treatments. This should be confirmed to prove the existence of rate constant.

Recently, Sean et al. (2007) suggested a new dissociation model (hereafter, SSAK model), the rate constant of which is based on the Gibbs free energy difference between the hydrate phase and the ambient aqueous phase, by a combination of experimental observations and numerical simulations with a computational fluid dynamics (CFD) method. The advantage of the SSAK model is that the intrinsic dissociation rate can be evaluated separately from the mass transfer rate, which enables us to investigate the dissociation processes at a wider range of water flow rates. In this study, the SSAK model is used for the estimation of amount of dissociated methane gas per unit surface area.

$$F = Ak_{bl}RT \ln \frac{x_H}{x_G} \quad (1)$$