Raman Spectroscopic Determination of Hydration Number of Methane Hydrates

Tsutomu Uchida, Takashi Hirano, Takao Ebinuma, Hideo Narita, Kazutoshi Gohara, Shinji Mae, and Ryo Matsumoto
Hokkaido National Industrial Research Institute, Sapporo-city, Hokkaido 062-8517, Japan

Hydration numbers of methane hydrates with various water/gas ratios of the sample were measured by Raman spectroscopy. Artificial methane hydrates were formed at temperatures ranging from 273.2 to 278.4 K, and pressures from 3.0 to 7.0 MPa, with a stirring rate of approximately 500 rpm. Under such nonequilibrium conditions, the obtained hydrate samples had a water/gas ratio ranging from 6.4 to 17.4, which was determined by mass measurements. The spectroscopic analysis revealed, however, that the crystallographic hydration number was almost constant at 6.2 ± 0.2, which corresponds to the hydration number estimated from the thermodynamic model. The same measurements were carried out on natural gas hydrate samples obtained from the deep-sea floor of Blake Ridge. The coincidence of the hydration numbers between natural and artificial samples indicated that the crystallographic hydration number is independent of the formation conditions and the large variation in the water/gas ratio of samples is described by the ratio between pure hydrate and free water.

Introduction

Methane hydrate ($CH_4 \cdot nH_2O$) is a crystalline molecular complex that includes a large quantity of methane molecules, and is stable at high pressures and low temperatures. The molar ratio of water reacted with a mole of methane molecule is n, which is called the hydration number. The structure of methane hydrate is a unit cell consisting of 46 water molecules that construct two small cages and six large ones. At most one methane molecule can occupy each cage, so less than eight methane molecules are expected to be included in one unit cell. If the hydrate is fully occupied by methane molecules, n becomes 5.75. However, the cage occupancy of small cages, θ_S, and that of large cages, θ_L, is usually smaller than unity, so n is determined by $23/(\theta_S + 3\theta_L)$.

Since gas hydrates can contain large amounts of gases such as natural gases, they are expected to have applications in gas storage and transportation material. To study the feasibility of industrial applications, it is necessary to control the amount of gas and to determine the water/gas ratio of the products. The physical properties of the mixture of hydrate and water are also required to study the feasibility of the transportation material.

The water/gas ratio, sometimes referred to as the ‘‘hydration number,’’ of artificial methane hydrates has been determined by various methods. Ripmeester and Ratcliffe (1988) summarized the earlier studies and found that variations on the measured hydration numbers ranged from 5.8 to 6.3. However, the determination methods included both macroscopic measurements and microscopic ones. It is not well known what affects the variation of the ‘‘hydration number.’’ Moreover, most of samples for determining the hydration number were prepared under equilibrium conditions. These conditions are not useful for industrial utilization due to the slow formation rate. Therefore, it is necessary to control the water/gas ratios of the samples that are formed under nonequilibrium conditions in order to determine the gas concentration in hydrate-including materials. The relation between the water/gas ratio of bulk samples and the crystallographic hydration number may be useful in estimating the amount of gas processing and to characterize the flow of the hydrate slurry.

Deposits of natural gas hydrates under seafloors and in permafrost areas are expected to serve as unconventional natural gas resources that have the advantages of high con-

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Correspondence concerning this article should be addressed to T. Uchida.
Present addresses for: T. Hirano, K. Gohara, and S. Mae, Faculty of Engineering, Hokkaido University: N13 W8, Kita-ku, Sapporo-city, Hokkaido 060-0813, Japan; R. Matsumoto, Faculty of Science, Tokyo University: 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.

centrations and potentially high amounts of gas. Therefore, the possibility of exploiting gas-hydrate deposits has been investigated recently. In order to estimate the quantity of natural gas resources related to hydrates, it is very important to investigate the variation of the molar ratio of water to gas molecules at various sites. This value is usually determined on a drilling boat by measuring the mass of sample, the amount of melt water, and the volume of gas. For example, the water/gas ratio in core samples obtained in the Blake Ridge in 1995 by the ODP Leg 164 expedition was reported to be more than 7.2 (Paull et al., 1996). The kind of measurement is easy and directly represents the apparent water/gas ratio of natural gas hydrates. However, it may include many errors caused by problems such as contamination by free water.

Handa (1988) precisely measured the water/gas ratio of the natural gas hydrate by using a differential scanning calorimeter. He reported that the molar ratio of water/gas in natural gas hydrates obtained by the Leg 84 expedition of the Deep Sea Drilling Project (off Guatemala) ranged from 5.91 to 6.00. Even by such precise measurements, these values were considered to include some extra water. It is therefore necessary to use various methods to estimate the precise value of the hydrate water/gas ratio, or to measure the crystallographic hydration number directly.

Moreover, it is expected that nondestructive measuring methods will establish accurate water/gas ratio measurements. This is because only a small number of natural samples are usually obtained by an expedition, and they are used for many kinds of geochemical and geophysical measurements other than the physical property of the hydrate itself. From a crystallographic point of view, it is advantageous to use Raman spectroscopic measurement for the nondestructive analysis of the determination of the hydration number. This nondestructive method may be useful as an industrial tool to examine the quality of the hydrate products.

Artificial methane hydrates were formed under various conditions to prepare samples with variations of the apparent water/gas ratio. Raman spectroscopic analysis was then carried out to determine the crystallographic hydration number of the hydrates included in the sample. In the present study, the relations between the apparent water/gas ratio and the crystallographic hydration number of hydrates were used to investigate the feasibility studies of the development of the engineering utilization of gas hydrates. Spectroscopic analysis determined that the hydration number of methane hydrates was constant ($n \fallingdotseq 6.2$), independent on the bulk water/gas ratio. The spectroscopic analysis on the natural gas hydrate retrieved from the deep-sea floor of Blake Ridge verified that the hydration number of hydrates is independent of the formation conditions.

Sample Preparations of Artificial Methane Hydrates

A system for forming artificial methane hydrates was previously demonstrated (Narita and Uchida, 1996). This experimental system consists of a reaction vessel with thermometers (type-T thermocouple), a gas inlet/outlet with pressure gage (Nagano Keiki Seisakusho, Ltd., type KH15), and a temperature-controlled bath with cold media. The volume of the reaction vessel is 232.2 ± 0.2 cm^3, including the dead space, and the contents can be agitated up to 1,000 rpm with a stirrer installed. The accuracy of temperature control is ± 0.1 K.

The formation conditions were measured at temperatures ranging from 273.2 K to 278.4 K, and at pressures ranging from 3.0 MPa to 8.1 MPa. Then the initial molar ratio $n_0 = N_w/N_g$ was varied from 2.5 to 11.4, where N_w and N_g are the molar concentrations of water and methane gas, respectively. The stirring condition in this study was fixed at approximately 500 rpm.

Deionized water (electrical conductivity of 5 mho or below) and pure methane gas (99.995 vol %) were used in the experiments. Air in the introduced water and dead space of the reaction vessel was purged twice with approximately 2 MPa of methane gas while being agitated at room temperature. The reaction vessel was then cooled to the experimental temperature and pressurized to the specific pressure by methane gas. After both the pressure and temperature conditions stabilized, the mixture was stirred. While the formation reaction proceeded, the pressure decreased over time. When the reaction finished, the temperature of the system was decreased to approximately 263 K before the depressurization process. It was necessary to cool the sample to prevent serious damage to the sample during the sample processing from the vessel for several minutes at atmospheric pressure. The samples obtained were stored in a freezer at a temperature of approximately 77 K.

The apparent water/gas ratio of the formed sample was determined by measuring the mass of the sample. Some pieces of the sample were inserted into a double-sealed tube to measure the mass of hydrate sample m_h with a precise microbalance. Several millimeters of samples were removed to prevent measurement error due to sample damage. The tube was designed to reduce errors caused by water condensation in the tube. The accuracy of the microbalance was ± 0.2 mg. After measuring m_h, the sample was completely dissociated at room temperature and degassed to measure the mass of water, m_w. We thereby used the following equation to obtain the bulk water/gas ratio of the sample, n_m:

$$n_m = m_w/(m_h - m_w) \cdot M_g/M_w, \qquad (2)$$

where M_g and M_w are the molar masses of methane and water. In the present study n_m varied between 6.4 and 17.4. The measurement error of n_m was estimated to be less than 12%. This result indicates that methane hydrate samples with various n_m can be prepared by changing the formation conditions. Therefore, the variation in the ‘‘hydration number’’ of artificial methane hydrates in the literature may have resulted from the difference between the samples themselves, even though they were formed under equilibrium conditions. Differences in the formation conditions at various sites in nature may also result in the variation of the bulk water/gas ratio of natural gas hydrates.

Natural Gas-Hydrate Samples Retrieved from Deep-Sea Floor of Blake Ridge

Natural gas-hydrate samples were recovered from the Blake Ridge sediment during leg 164 of the Ocean Drilling Program (ODP) at site 997 off South Carolina in the autumn of 1995. This site is located at the top of the ridge, where a strong bottom-simulating reflection (BSR) is observed. A large massive sample (core 42X) ws recovered from site 997, Hole 997A, at a depth of approximately 3,100 m below sea level (330 m below the seafloor). Some dispersed small hydrate samples were obtained at depths ranging from approximately 190 m to 460 m below the seafloor (Matsumoto et al., 1999).

The sample was stored in a high-pressure vessel just after core recovery. This vessel was pressurized by helium gas up to approximately 10 MPa. The sample vessel was kept in a freezer at a temperature of approximately 253 K to prevent the sample from decomposing. Under these pressure and temperature conditions, the massive sample was transported to Hokkaido National Industrial Research Institute nine months after recovery. The sample was removed from the vessel after arrival and stored in a cold chamber at 77 K.

Experimental Procedures for Raman Spectroscopic Analyses

A piece of solid specimen was chosen for this measurement and the surface of the specimen was flattened with the edge of a knife to reduce signal losses by light scattering due to surface roughness. This flattening process also had the advantage of removing the damaged sample-surface. The specimen was placed in a cryostat specially designed for microscopic Raman spectroscopy. The temperature of the specimen was kept below 230 K during measurement by controlling the sample-cell temperature with the flow speed of nitrogen gas. The magnification of the system was approximately 10^3 and a $20\times$-long working-distance objective lens was used. The diameter of the incident laser-beam focused on the specimen was approximately 8 μm.

The Raman spectrometer (SPEX RAMALOG-100) is a 1-m double-dispersed monochromator system. The spectra were recorded with a photomultiplier-tube detector system. The excitation source was an Ar-ion laser emitting a 514.5-nm beam, providing approximately 120 mW at the specimen. A computer system (SPEX DM1B) provided control and data acquisition for the spectrometer system. The scattered radiation was collected through a slit with 180 degree geometry at 300 μm. Spectra collected at a resolution of 5 cm^{-1} were obtained from a measuring range of 100 to 4,000 cm^{-1}. Using the sensitivity of the Raman scattering, this wide-range measurement provided a means for measuring the content of guest molecules. Narrow-range measurements were performed from 2,800 to 3,000 cm^{-1} to investigate precisely the methane-molecule vibrations in the hydrate. Spectra were collected with a 0.5-cm^{-1} scanning step and 5-s integration time/step. The Raman scattering line of a silicone plate, 520.0 cm^{-1}, was measured for the routine calibration of the monochromator.

Results and Discussion

Figure 1 shows typical Raman spectrum of methane hydrate (solid line) and ice (dashed line). Raman peaks of methane molecules in the hydrate were observed at approxi-

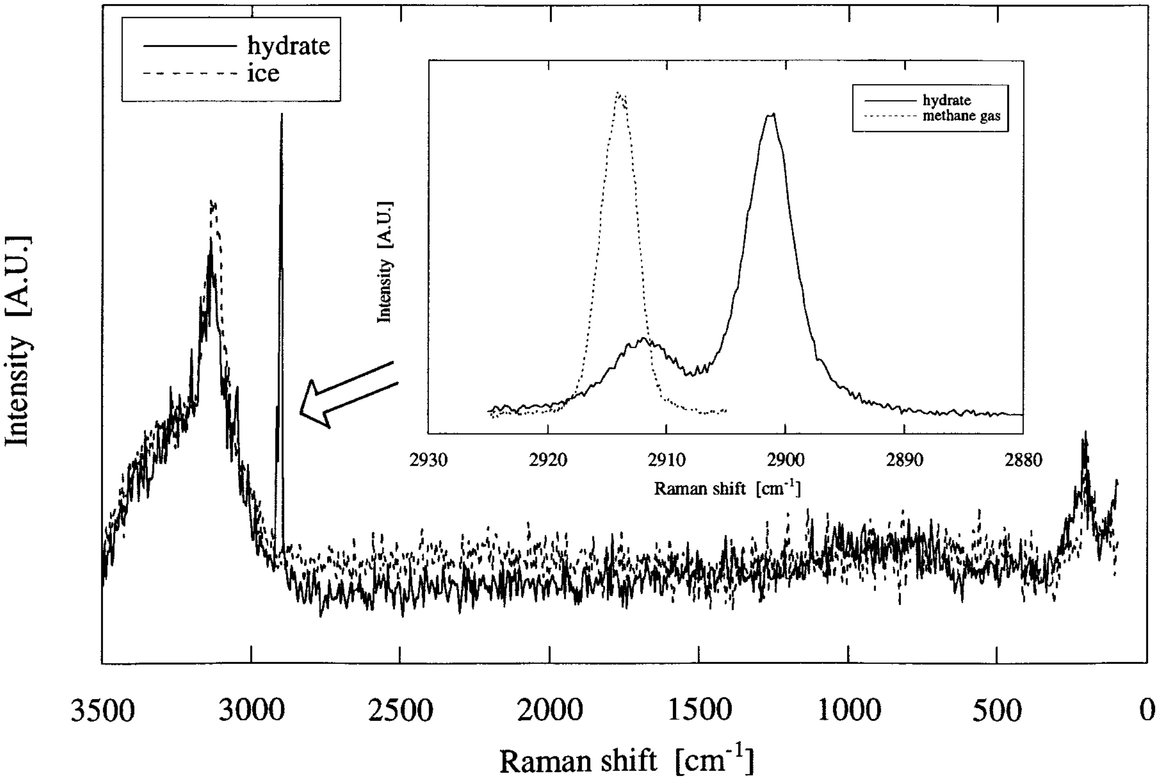

Figure 1. Typical Raman spectrum of methane hydrate (solid line) and ice (dashed line).

Raman peaks of the C-H stretching mode of methane molecules in the hydrate and gas phases are shown in the inset by the solid line and the dotted line, respectively.

mately 2,904 and 2,915 cm^{-1} (see the inset in Figure 1), while that in the gas phase was observed at 2,917 cm^{-1} (measured at room temperature and approximately 2 MPa), shown by the dotted line in the inset. The full widths of the half maximum of the twin peaks of the hydrates and the gas peak were 4.5 cm^{-1}, 6.3 cm^{-1}, and 3.5 cm^{-1}, respectively. The Raman peak in the gas phase correlated well with the C-H stretching mode of methane molecules ($\nu_1 = 2916.7$ cm^{-1}) (Schroetter and Kloeckner, 1979). The twin peaks in the hydrate phase were considered to be the C-H stretching mode (ν_1). However, they shifted lower than that in the gas phase and split into two peaks. These peaks resulted from the methane molecules included in different cages. Using these peak shifts and the peak existence, we can distinguish hydrate from free gas or ice in the specimen. These results were consistent with the experiments reported by Sum et al. (1997).

The Raman intensities of each hydrate peak were calculated using Lorentzian curve fitting on the intensity data, whereas those of the gas peak were fitted by the Gaussian curve. We obtained two Raman intensities from hydrates: I_L and I_S, where I_L is that of the larger peak (2,904 cm^{-1}) and I_S is that for the smaller one (2,915 cm^{-1}). The deconvolution of two mixed bands was accomplished by the curve-fitting routine in the commercial package Origin from Microcal Co.

In order to measure the crystallographic hydration number quantitatively, the intensity ratio I_L/I_S was investigated. Here we assumed that the cross section of methane molecules and their polarizabilities in both cages were almost the same. The intensity ratio can consider the Raman intensity quantitatively because several factors can be canceled. This results from the instrumental setup and from the sample condition. After allowing for the fact that there are three times as many large cages as small ones in type I hydrate, the cage occupancy ratio, θ_L/θ_S, is obtained by $I_L/3I_S$. The crystallographic hydration number is estimated from the data of θ_L/θ_S with the thermodynamic model for the hydrate (Ripmeester and Ratcliffe, 1988). In the absence of guest–guest interactions and host-lattice distortions, the chemical potential difference of the water molecules in the empty lattice of a structure I hydrate relative to ice, $\Delta\mu_w^0$, is given by

$$\Delta\mu_w^0 = -RT\left[3\ln(1-\theta_L) - \ln(1-\theta_S)\right]/23. \qquad (5)$$

The data of θ_L/θ_S, together with the value of $\Delta\mu_w^0$ which is 1297 $J \cdot mol^{-1}$ (Davidson et al., 1986), gives absolute occupancies θ_L and θ_S.

The measured crystallographic hydration number, n_c, can then be found from $n_c = 23/(3\theta_L + \theta_S)$. The calculated values of θ and n_c on various samples formed under various P, T conditions are listed in Table 1. Each value is the average of several measurements on the same sample. The variations of n_c among various n_m samples are shown in Figure 2. Table 1 and Figure 2 indicate that n_c is almost constant, $n_c = 6.2 \pm 0.2$, and independent on the formation conditions. This result indicates that the amount of gas in the hydrate is independent of the formation conditions, and that the large variation of n_m for the artificial methane hydrates mainly results from the variations in the hydrate/free-water ratio. Comparison between n_c and n_m represents the hydrate concentration in the sample. In the present study, the concentration of methane hydrate is estimated to be in the range from 0.36 to 0.98.

Table 1. Absolute Occupancies for Large and Small Cages and Crystallographic Hydration Number, Calculated from Raman Intensity Ratios Under Various P, T Conditions

Exp.		Absolute Occupancies		Crystallog. Hydration
T K	P MPa	θ_L	θ_S	No. n_c
273.6	2.99	0.980 ± 0.013	0.760 ± 0.010	6.22 ± 0.08
273.6	5.04	0.981 ± 0.013	0.722 ± 0.214	6.28 ± 0.29
273.6	6.37	0.980 ± 0.005	0.730 ± 0.149	6.27 ± 0.25
273.7	5.04	0.977 ± 0.017	0.823 ± 0.159	6.13 ± 0.24
273.8	5.00	0.976 ± 0.098	0.857 ± 0.156	6.08 ± 0.25
273.8	6.38	0.980 ± 0.004	0.747 ± 0.172	6.24 ± 0.29
273.8	6.89	0.978 ± 0.019	0.796 ± 0.176	6.17 ± 0.25
274.0	4.91	0.980 ± 0.014	0.756 ± 0.327	6.22 ± 0.24
274.2	5.92	0.978 ± 0.013	0.804 ± 0.146	6.15 ± 0.18
274.6	7.19	0.980 ± 0.006	0.723 ± 0.177	6.28 ± 0.30
275.3	6.13	0.978 ± 0.032	0.782 ± 0.203	6.19 ± 0.23
275.4	6.13	0.980 ± 0.006	0.715 ± 0.161	6.29 ± 0.22
275.6	6.04	0.979 ± 0.020	0.771 ± 0.198	6.20 ± 0.30
278.1	7.81	0.978 ± 0.133	0.787 ± 0.157	6.18 ± 0.19
278.3	8.08	0.979 ± 0.004	0.728 ± 0.150	6.28 ± 0.25
278.4	7.06	0.978 ± 0.010	0.760 ± 0.167	6.23 ± 0.23

We assumed that the gas–hydrate–water system was in equilibrium when the formation reaction finished, and that cage occupation was preserved during the sample storage and its measurement. Moreover, we should discuss the validity of the application of Eq. 5, because it is usually applicable to static conditions. The simulation of n by using Eq. 5 with various T and θ_L/θ_S conditions indicates that the variation of T within the range of the present study does not affect the variation of n. For example, if T varies from 273.2 K to 283.2 K, which includes the temperature range of our experiments, n ranges from 6.18 to 6.20. In the present study, however, such small variations were hidden within the experimental errors.

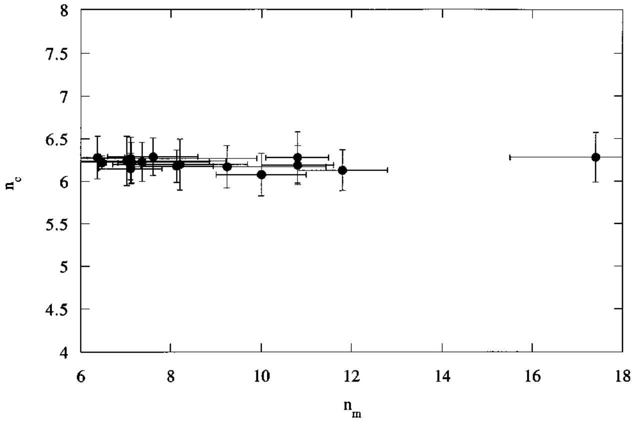

Figure 2. Relation between the crystallographic hydration member n_c and the water/gas ratio of bulk sample n_m.

Each error bar indicates the maximum scatter of the obtained data, as well as the maximum scattering of measured value.

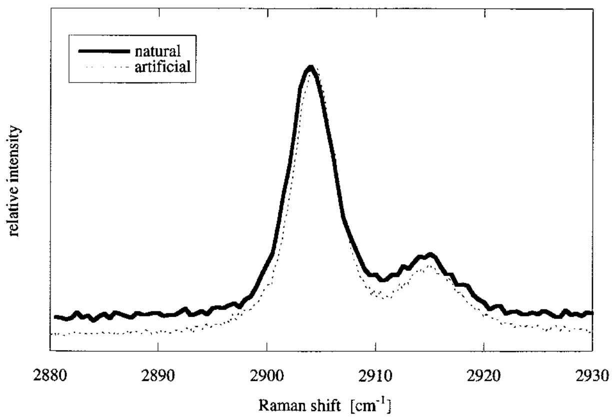

Figure 3. Raman spectra of the C-H stretching mode of methane molecules in the natural gas hydrate (solid line) and in the artificial methane hydrate (dotted line).

The relative intensities of both spectra were normalized by the maximum intensity near 2,905 cm^{-1}. (Modified from Matsumoto et al., 1999.)

The wide-range measurements of the Raman spectra for natural gas hydrate showed that spectra have several peaks that result from the vibration of H_2O molecules and the clearly resolved double peaks, which are the ν_1 symmetric band of methane. This result indicates that the specimen contains almost pure methane gas. The dissociated gas measurements of the natural gas hydrate by a gas chromatography showed that more than 99% of the content is methane. Figure 3 shows the mode of methane included in the natural hydrate sample (solid line; modified from Matsumoto et al., 1999). The same spectra of the artificial sample are also shown by the dotted line in this figure. The peak positions of the natural gas hydrate are 2,904.1 and 2,915.1 cm^{-1} for the larger peak and the smaller one, respectively. The full widths at half maximum of these peaks are approximately 4.4 cm^{-1} and 6.1 cm^{-1}, respectively. The values coincide well with those of artificial methane hydrates.

The intensity ratio I_L/I_S of the natural gas hydrate samples was 3.8 ± 1.2. Applying Eq. 5 to this result gives absolute cage occupancies $\theta_L = 0.97$ and $\theta_S = 0.78$. The crystallographic hydration number of the natural sample is then 6.2 ± 0.3. This value coincided well with those obtained in the artificial methane hydrates. Compared with the measurements of the water/gas ratio on the bulk sample (Paul et al., 1996), the concentration of gas hydrates in the sample is estimated to be at most 0.86 in pore space.

The coincidence of the crystallographic hydration numbers between artificial methane hydrates and natural gas hydrates gives us important information. At first, n_c of methane hydrates is not affected by n_m of the sample. The sample with small n_m contains almost pure methane hydrates, whereas the large n_m sample includes pure methane hydrates and a large amount of free water. Therefore the total amount of methane gas included in the sample is related to the concentration of hydration in the sample. Moreover, the formation conditions of the natural sample are completely different from those of artificial methane hydrate formed under stirring conditions. The formation rate of natural gas hydrates is thus assumed to be very slow compared with those of artificial samples, and to be almost under equilibrium conditions during formation. Therefore n_c of methane hydrates is also determined independently of the formation rate. It is then concluded that the crystallographic hydration number is almost constant and is independent of both the formation conditions and the amount of free water.

In conclusion, the methane hydrate is shown to be formed as a pure hydrate under various conditions, which provides the constant crystallographic hydration number, even if the product included a large amount of free water formed under nonequilibrium conditions. The variation in the water/gas ratio of the bulk sample thus results from the ratio between the amount of free water and pure hydrates included in the sample. It is important when estimating the total amount of natural gas resources to consider the change in hydrate concentration, not the change in the crystallographic hydration number. Because of the constant crystallographic hydration number, *in-situ* measurements of the gas/water ratio on the natural sample represent the hydrate concentration directly when the hydrate includes almost pure methane gas. Moreover, when we consider the engineering application of the methane hydrate, the product can be treated as the mixture of pure methane hydrate with water. At that moment, the total amount of processed gas can be estimated from the number of gas hydrates.

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Literature Cited

Davidson, D. W., Y. P. Handa, and J. A. Ripmeester, "Xenon-129 NMR and the Thermodynamic Parameters of Xenon Hydrate," *J. Phys. Chem.*, **90**, 6549 (1986).

Handa, Y. P., "A Calorimetric Study of Naturally Occurring Gas Hydrates," *Ind. Eng. Chem. Res.*, **27**, 872 (1988).

Matsumoto, R., T. Uchida, A. Waseda, T. Uchida, S. Takeya, T. Hirano, K. Yamada, Y. Maeda, and T. Okui, "Occurrence, Structure and Composition of Natural Gas Hydrates Recovered from the Blake Ridge, ODP Leg 164, Northwest Altantic," *Proc. ODP, Sci. Reps.*, College Station, TX (1999).

Narita, H., and T. Uchida, "Studies on Formation/Dissociation Rates of Methane Hydrates," *Proc. Int. Conf. on Natural Gas Hydrates*, Toulouse, France, p. 191 (1996).

Paull, C., R. Matsumoto, and P. Wallace, *Proc. ODP, Init. Reps. 164*, College Station, TX (1996).

Ripmeester, J. A., and C. I. Ratcliffe, "Low-Temperature Cross-Polarization/Magic Angle Spinning ^{13}C NMR of Solid Methane Hydrates: Structure, Cage Occupancy, and Hydration Number," *J. Phys. Chem.*, **92**, 337 (1988).

Schroetter, H. W., and H. W. Kloeckner, "Raman Scattering Cross Sections in Gases and Liquids," *Topics in Current Physics*, Vol. 11, *Raman Spectroscopy of Gases and Liquids*, A. Weber, ed., Springer-Verlag, Berlin, p. 123 (1979).

Sum, A. K., R. C. Burruss, and E. D. Sloan, Jr., "Measurement of Clathrate Hydrates via Raman Spectroscopy," *J. Phys. Chem.*, **101**, 7371 (1996).

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