

# RECOVERY RATE OF CH<sub>4</sub> FROM CH<sub>4</sub>-HYDRATE IMMERSED IN CO<sub>2</sub>-CH<sub>4</sub> MIXTURES

S.Hirohama, Y.Shimoyama, A.Wakabayashi,  
Chiyoda Corp., Yokohama 221 Japan,  
S.Tatuda, I.Norikyo, Hokuriku Electric Power Co., Toyama 930, Japan,  
N.Nishida, Sugino Machine Ltd. Uozu 937, Japan.

## INTRODUCTION

Occurrence of subterranean CH<sub>4</sub>-hydrate layers is known and inferred in all over the world. A vast quantity of CH<sub>4</sub> contained in the hydrate layers can be one of the main energy sources in the next century (Holder et al.1984, Kvenvolden,1994). Injection of liquid CO<sub>2</sub> into the hydrate layers might be a promising technique to recover CH<sub>4</sub> simultaneously segregating CO<sub>2</sub> from the biosphere as CO<sub>2</sub>-hydrate, because some portion of CH<sub>4</sub>-hydrate is converted to CO<sub>2</sub>-hydrate by simply immersing it in liquid phase containing CO<sub>2</sub>(Hirohama et al. 1996). Mass-transfer in hydrate solid is presumed to determine the rate because CH<sub>4</sub>-hydrate at the interface with the liquid phase is initially converted to CO<sub>2</sub>-hydrate which can inhibit further conversion.

As CH<sub>4</sub> content in the liquid phase increases, the recovery rate can decrease because of decrease in the driving force. So that evaluation of this technique requires that the effect of the composition on the rate of the conversion is known in a wide composition range. However there has been no datum on the effect of the liquid composition. Although Hirohama et al. (1996) proposed a diffusion model to describe the mass-transfer in hydrate solid, its accuracy was not tested at altered compositions of the liquid phase.

This article proposes data on the conversion rate under varied compositions of the liquid phase. The accuracy of the model is discussed by comparing the data with the prediction.

## EXPERIMENTAL

The experimental setup is the same as that used by Hirohama et al.(1996). The apparatus consists of a reactor, a feeding system for each component, a temperature controlled water bath and a back pressure regulator. The experiments were conducted by the following procedure:

Formation of CH<sub>4</sub>-hydrate: Water and CH<sub>4</sub> were charged in the reactor. Quantity of consumed CH<sub>4</sub> was determined from the temperature, the pressure and the volume of the gas phase before and after the formation of CH<sub>4</sub>-hydrate.

Purging CH<sub>4</sub> in gas phase by gaseous CO<sub>2</sub>: Gaseous CO<sub>2</sub> was fed to the reactor to purge the CH<sub>4</sub> in the gas phase keeping the total pressure of the reactor above the dissociation pressure of CH<sub>4</sub>-hydrate at the temperature.

Injection of CH<sub>4</sub> and CO<sub>2</sub>: Liquid CO<sub>2</sub> and CH<sub>4</sub> were fed to the reactor. The change of the total pressure was monitored for about 600-1100 hours while the temperature was kept constant.

Discharge from the reactor: The total pressure of the reactor was reduced to the atmospheric pressure to vaporize all of the liquid and dissociate all the hydrate. The volume and the composition of the outlet gas were measured to determine the quantities of CH<sub>4</sub> and CO<sub>2</sub> existed in the reactor.

The experimental conditions and the results are listed in Table 1. The material balance of CH<sub>4</sub> and CO<sub>2</sub> through the procedures are between 90% and 105%. The change of the total pressure of the reactor is shown in Fig.1.

## CONVERSION RATE

Quantity of recovered CH<sub>4</sub> can be determined from the total pressure and the temperature by solving the following material balance and volume balance simultaneously.

$$n_{CO_2,i} - n_{CO_2,hy} = G(1 - y_{CH_4}) + L(1 - y_{CH_4}) \quad (1)$$

$$n_{CH_4,i} - n_{CH_4,hy} = Gy_{CH_4} + Ly_{CH_4} \quad (2)$$

$$V_i - V_{hy} = G / \rho_G + L / \rho_L \quad (3)$$

Eliminating  $G$  and  $L$  from the equations above gives:

$$n_{CH_4,i} - n_{CH_4,hy} = \frac{(n_{CO_2,i} - n_{CO_2,hy}) / \rho_L + (x_{CH_4} - 1)(V_i - V_{hy})}{(1 - y_{CH_4}) / \rho_L - (1 - x_{CH_4}) / \rho_G} y_{CH_4} + \frac{-(n_{CO_2,i} - n_{CO_2,hy}) / \rho_G + (1 - y_{CH_4})(V_i - V_{hy})}{(1 - y_{CH_4}) / \rho_L - (1 - x_{CH_4}) / \rho_G} x_{CH_4} \quad (4)$$

In Eq.(4),  $x_{CH_4}$ ,  $y_{CH_4}$ ,  $\rho_L$  and  $\rho_G$  were calculated by the Patel-Teja equation of state (Patel and Teja, 1982) from the temperature and the pressure. The effects of  $H_2O$  on the vapor-liquid equilibria and the material balance were neglected because the solubility of  $H_2O$  in liquid  $CO_2$  is less than 0.5 mol% (Wiebe and Gaddy, 1941). The value of  $n_{CO_2,hy}$  was estimated assuming that all the free  $H_2O$  was consumed to form  $CO_2$ -hydrate shortly after the injection of  $CO_2$ .  $V_{hy}$  was estimated from the superficial density of the hydrate solid measured by Hirohama et al (1996).

Figure 2 shows the quantity of  $CH_4$  recovered from the hydrate phase. As the initial mole fraction of  $CH_4$  in the liquid phase increased, the rate of the conversion decreased. A rapid increase in the pressure in the first 10 hours was not taken in account, because the homogenization of the gas and the liquid in the reactor takes about 10 hours. Figure 3 shows the effect of the liquid composition on the amount of methane recovered in 600h. As the  $CH_4$  content increased, the rate of the conversion decreased dramatically.

## DISCUSSION

$CH_4$ -hydrate at the interface with the liquid phase can be initially converted to the hydrate of  $CO_2$ - $CH_4$  mixture through which  $CO_2$ ,  $CH_4$  and/or  $H_2O$  permeate to continue the conversion. The following diffusion-like equation proposed by Hirohama et al.(1996) was applied to calculate the flux ( $N_i$ ) of  $CO_2$  and  $CH_4$  in hydrate solid.

$$N_i = -\rho_{hydrate} \theta_i^* \omega \left( \frac{\partial \mu_i}{\partial z} \right)_i \quad (5)$$

$$\text{where } \theta_i^* = (\theta_{i,1} v_1 + \theta_{i,2} v_2) / (v_1 + v_2) \quad (6)$$

Chemical potential ( $\mu_i$ ) was calculated by the following empirical equation of which parameter values were determined by fitting to the rigorous solution of the solid solution theory (Waals et al., 1959, Saito et al., 1964) which gave good prediction for the initial hydrate forming pressures of  $CH_4$ - $CO_2$  mixtures.

$$f_i = \frac{1}{K_i^*} \times \frac{\theta_i^*}{1 - \sum_k \theta_k^*} \quad (7)$$

In Eq.(7),  $K^{*CO_2}$  and  $K^{*CH_4}$  were 21.5  $MPa^{-1}$  and 9.98  $MPa^{-1}$  respectively at 274K. Quantity of  $CH_4$  recovered from the hydrate phase was calculated by solving Eqs.(4)-(7) simultaneously under the same boundary conditions as those used by Hirohama et al.(1996).

No single value of solute mobility was able to describe the effect of the  $CH_4$  content on the decrease in the conversion rate. So that the cause of the effect of the liquid composition can not be attributed only to the decrease in the driving force if the equilibrium model is applicable at the conditions. The fact implies that the composition of the liquid phase might influence the solute mobility in the layer of initially converted hydrate at the surface of the hydrate solid.

This work tempted to correlate the solute mobility as a function of the fraction of vacant cage as follows:

$$\ln(RT\omega) = A\theta_i^* + B \quad (8)$$

$$\text{where } \theta_v = 1 - \sum \theta_i \quad (9)$$

*A* and *B* are empirical parameters of which values were determined so as to describe the data of all runs. The values of *A* and *B* were 610 and 10.1 respectively. Simulation was carried out by solving Eqs.(4)-(9) simultaneously. The model was capable of describing well the tendency of the experimental results as shown in Figs.2 and 3.

## CONCLUSIONS

Conversion rate of CH<sub>4</sub>-hydrate to CO<sub>2</sub>-hydrate immersed in the liquid phase of varied compositions was determined. As the CH<sub>4</sub> content increased, the conversion rate decreased more rapidly than predicted from the decrease in the driving force calculated by the solid solution theory. An empirical equation was proposed to correlate the solute mobility as a function of the fraction of vacant cage.

## NOMENCLATURE

<i>A</i> :	empirical parameter in Eq.(8)	[-]
<i>B</i> :	empirical parameter in Eq.(8)	[-]
<i>G</i> :	quantity of gas phase	[mol]
<i>f</i> :	fugacity	[MPa]
<i>K</i> <sup>*</sup> :	Langmuir constant for simplified model	[1/MPa]
<i>L</i> :	quantity of liquid phase	[mol]
<i>n</i> <sub><i>i</i></sub> :	quantity of component <i>i</i>	[mol]
<i>P</i> :	pressure	[MPa]
<i>R</i> :	gas constant	[J/(mol·K)]
<i>T</i> :	temperature	[K]
<i>t</i> :	time	[s]
<i>V</i> :	volume	[m <sup>3</sup> ]
<i>x</i> :	mole fraction in liquid	[-]
<i>y</i> :	mole fraction in gas	[-]
<i>Z</i> :	depth	[m]
<i>μ</i> :	chemical potential	[J/mol]
<i>v</i> :	fraction of water of cage type <i>j</i>	[-]
<i>θ</i> <sub><i>i,j</i></sub> :	occupancy of component <i>i</i> in cage type <i>j</i>	[-]
<i>θ</i> <sub><i>i</i></sub> :	average occupancy of component <i>i</i>	[-]
<i>ρ</i> :	density	[mol/m <sup>3</sup> ]
<i>ρ</i> <sub>cage</sub> :	cage number in a unit volume of hydrate	[mol/m <sup>3</sup> ]
<i>α</i> :	effective mobility of solute	[m <sup>2</sup> /(s·J)]
<Subscript>		
<i>G</i>	gas phase	
<i>hy</i> :	hydrate solid	
<i>i, k</i> :	component identification number	
<i>j</i> :	cage type	
<i>L</i> :	liquid phase	
<i>t</i> :	total	
<i>v</i> :	vacant	

## LITERATURE CITED

- Adisasmito, S., R. J. Frank, III, and E. D. Sloan, Jr.; *J. Chem. Eng. Data*, 36, p68 (1991)
- Hirohama, S., Y. Shimoyama, A. Wakabayashi, S. Tatuda and N. Nishida; *J. Chem. Eng. Japan*, 29, p1014 (1996)
- Holder, G. D., V. A. Kamath and S. P. Godbole; *Ann. Rev. Energy*, 9, p427 (1984)
- Kvenvolden K.A.: "International Conference on Natural Gas Hydrate", *Annals of the New York Acad. of Sciences*, vol 715, The New York Acad. of Sciences, New York, U.S.A., p 232 (1994)
- Patel, N. C. and A. S. Teja; *Chem. Eng. Sci.*, 37, 3, p463 (1982)
- Saito, S., D. R. Marshall and R. Kobayashi; *A.I.Ch.E. Journal*, Sep., p734 (1964)
- Waals, J. H. van der, and J. C. Platteeuw; *Advances in Chemical Physics*, vol.2, 1st

ed., Interscience, New York, U.S.A. p1 (1959)  
 Wiebe, R and V.L.Gaddy, "Vapor Phase Composition of Carbon Dioxide-Water  
 Mixtures at Various Temperatures at Pressures to 700 Atmospheres,"  
 J. Am. Chem. Soc., 63, 475-477 (1941)

Table 1. Experimental conditions and results

items	unit	Hirohama et al. (1996)		This work	
Formation of CH <sub>4</sub> -hydrate					
H <sub>2</sub> O charged	[mol]	31.29	31.71	31.10	31.97
CH <sub>4</sub> trapped in hydrate	[mol]	4.23	3.74	4.16	4.52
H <sub>2</sub> O remained free	[mol]	6.95	10.23	7.18	5.98
Purging CH <sub>4</sub> in gas phase by CO <sub>2</sub>					
CH <sub>4</sub> remained in gas phase	[mol]	0.52	0.35	0.38	0.52
CO <sub>2</sub> existed in gas phase	[mol]	5.12	5.35	5.34	5.25
Soaking CH <sub>4</sub> -hydrate in CO <sub>2</sub> -CH <sub>4</sub> mixture					
liquid CO <sub>2</sub> charged	[mol]	10.3	10.3	10.94	10.16
CH <sub>4</sub> charged	[mol]	0	0	2.48	5.23
temperature	[K]	274	276	274	274
Material balance	CH <sub>4</sub>	[%]	96	91	103
	CO <sub>2</sub>	[%]	96	96	94
Reaction time	[h]	800	800	600	1100
CH <sub>4</sub> recovery	[%]	13	16	8	2

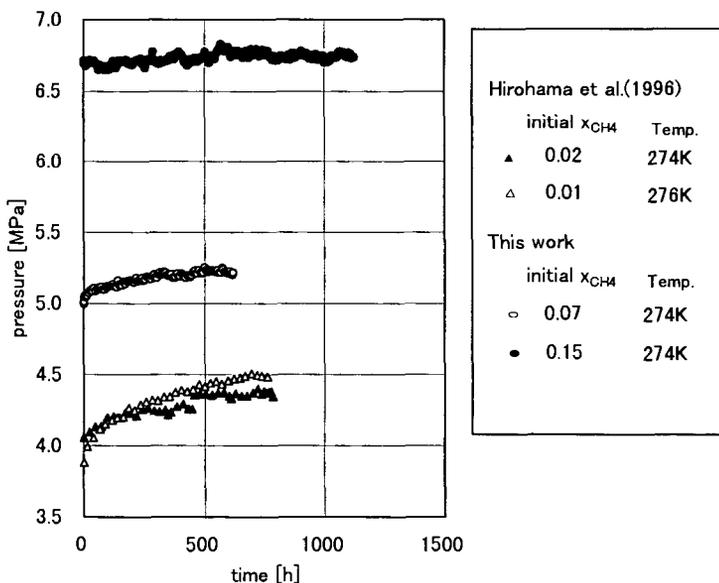


Fig. 1 Change of total pressure

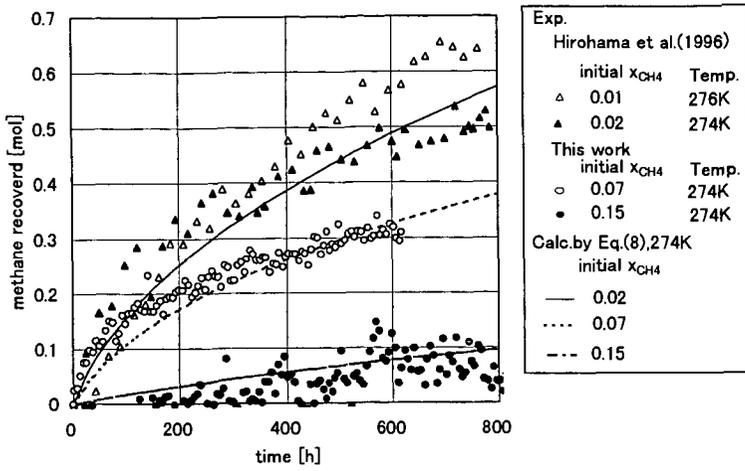


Fig.2 CH<sub>4</sub> recovered from the hydrate phase

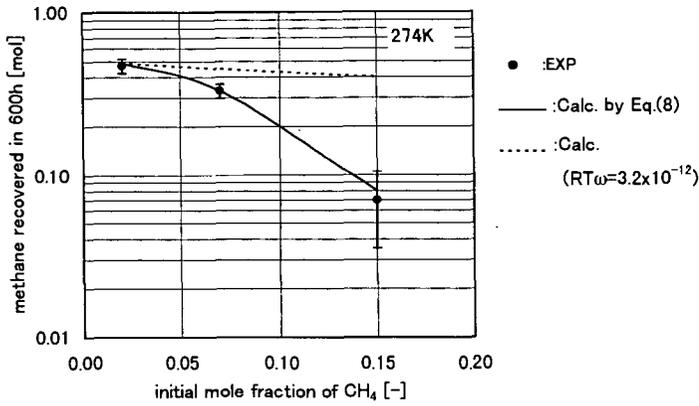


Fig.3 Effect of CH<sub>4</sub> content on methane recovery