**Some Fundamental Experiments on Apparent Dissolution Rate of Gas Phase
in the Groundwater Recovery Processes of the Geological Disposal System - 12146**

Taiki Yoshii, Yuichi Niibori, and Hitoshi Mimura
Dept. of Quantum Science & Energy Engineering, Graduate School of Engineering,
Tohoku University, 6-6-01-2, Aramaki, Aza-Aoba, Aoba-ku, Sendai 980-8579 JAPAN

ABSTRACT

The apparent dissolution rates of gas phase in the co-presence of solid phase were examined by in-room experiments in this study. The apparent dissolution rate of gas phase q (mol/m^3·s) was generally defined by $q = aK_L(\gamma P_g - c)$, where a (1/m) is specific surface area of the interface between gas and liquid phases, K_L (m/s) is overall mass transfer coefficient, γ (mol/(Pa·m^3)) is reciprocal number of Henry constant, P_g (Pa) is partial pressure of gas phase, and c (mol/m^3) is the concentration of gas component in liquid phase. As a model gas, CO_2 gas was used. For evaluating the values of K_L, this study monitored pH or the migration rate of the interface between water/gas phases, using some experiments such as the packed beds and the micro channel consisting of granite chip and rubber sheet including a slit. In the results, the values of K_L were distributed in the range from 5.0×10^{-6} m/s to 5.0×10^{-7} m/s. These values were small, in comparison with that (7.8×10^{-4} m/s) obtained from the bubbling test where gas phase was continually injected into deionized water without solid phase. This means that the solid phase limits the local mixing of water phase near gas-liquid interfaces.

INTRODUCTION

In a Japanese-conceptual design of the geological disposal system, the HLW and some TRU waste are disposed deeper than 300 m from the ground surface [1,2]. Such a depth level in Japan is generally under the water table. Therefore, the repository is predicted to be saturated with groundwater after the backfill. However, the ventilation process to the repository for a long term (at least 100 years including monitoring period) would form an unsaturated situation in the backfill and in its surrounding. Since an unsaturated zone plays a role in preventing an inflow of groundwater to beyond the backfill, the timing of groundwater recovery also affects the repository design, e.g., the intervals between waste packages, the permissible maximum temperature and so on [3].

So far, many studies have focused on the migration of radionuclides (RNs) through the unsaturated zone above unconfined aquifer such as Yucca mountain site [e.g., 4-7]. However, the recovery processes of the unsaturated zone temporarily formed in a confined aquifer have not been sufficiently discussed. Besides, supposing that the groundwater flow is relatively fast, the unsaturated zone would be replaced with groundwater in relatively short term. Such phenomena are similar to dynamic behaviors of fluids artificially produced from an oil or gas reservoir [8-11]. On the other hand, if the groundwater flow is sluggish under a natural condition, the dissolution of the gas phase to the liquid phase would become dominant in the recovery process of

groundwater. As a fundamental study, this study examined the apparent dissolution rate of the gas phase to deionized water in the co-presence of the solid phase, using various experimental set ups such as the column packed with silica sands or glass beads and the micro channel consisting of granite chip and rubber sheet including a slit.

EXPERIMENTAL

Column experiment with flow (Open system)

An ideal co-presence system of liquid, gas and solid phases, some kinds of vertical columns packed with silica sands or glass beads were prepared. The average particle diameters and the permeabilities are shown in Table I. The porosity was constant within the range of 0.38 to 0.40 in any column. The column was made of the plastic tube of 78 mm in height and 14 mm in inner diameter. The silicone rubber sheet serving as a cushion was put on the inside wall of the column in order to maintain a uniform porosity in the bed [12]. The edges of the column were shielded by a rubber stopper which has a flow path. Stainless net was put on the inside of the rubber stopper to avoid the outflow of solid particles from the column.

CO_2 gas was used as a gas phase. In the initial condition, the packed bed was saturated only with gas phase. Then, using the overflow to keep the hydraulic head (30 cm, 40 cm, or 50 cm), deionized water was continuously injected. The liquid phase and the gas phase flows out of the column were separated by a gas/liquid separation tube. The changes of permeability and pH were monitored during the experiments. Hereinafter, this experimental setup is referred to as "Column with flow (open system)".To calculate the permeability of the liquid-phase, Darcy's Law was used.

$$u = \frac{Q}{A} = -\frac{k}{\mu}\frac{\partial p}{\partial x}$$

(Eq.1)

where u is Darcy's fluid flow velocity (m/s), k is permeability (m^2), μ is viscosity of liquid phase (8.54×10^{-4} Pa·s), p is pressure (Pa), x is distance of flow path (m), Q is volume flow rate (m^3/s), and A is the cross section area of the column (m^2). The gradient of pressure $-\partial p/\partial x$ is approximated by $\Delta P/L$, where ΔP is the pressure difference between the overflow and the outlet of the column, and L is the length of column.

From the experimental results, this study tried the overall mass transfer coefficient between gas and liquid phases defined by

$$q = \frac{d[H_2CO_3]}{dt} = aK_L(\gamma P_g - [H_2CO_3])$$

(Eq.2)

where q is the apparent dissolution rate of gas phase to liquid phase (mol/(m^3·s)), a is apparent specific surface (interface) area between liquid phase and gas phase in column (m^2/m^3), P_g is partial pressure of gas phase (Pa), γ is conversion factor between pressure and concentration, it is inverse number of Henry' constant, and $[H_2CO_3]$ is the concentration of H_2CO_3 in liquid phase. Considering the successive reaction of carbonic acid, the charge balance is $[HCO_3^-] \approx [H^+]$ around neutral pH, then $[H_2CO_3]$ is described by $[H^+]^2/K_1$, where K_1 is the dissociation constant of

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

(Eq.3)

Besides, when at the initial condition $[H_2CO_3]$ is almost equal to 0, q can be described by $aK_L\gamma P_g$. Therefore, this study calculated the initial value of q from the initial change of pH, by using the relation of $[H_2CO_3]=[H^+]^2/K_1$ and evaluated aK_L. Furthermore, since it was observed from the outlet of the column that the area where fluid can flow was limited to the area saturated partially in column, this study approximately evaluated the value of a by using the diameter (d_{wet}) of the saturated area and the column length (L), i.e., $a= \pi d_{wet}L/V$, where V is the volume of column. However, this calculation method includes some uncertainties. Therefore, this study tried the other experimental methods, as mentioned next, in order to discuss the validity of K_L evaluated.

Column experiment with no flow (closed system)

Using the same columns mentioned above, the dissolution rates were examined under the condition in which fluid flow does not exist. That is, the outlet of the column was closed by the rubber stopper. The bottom end of the column was connected to the overflow (holding pressure constant) through the Tygon tube saturated with deionized water. Then, from the changes of the location of interface between gas phase and liquid phase with a given time-interval, the apparent dissolution rate of gas phase to liquid phase q was estimated. Hereinafter, this experiment is referred to as "Column with no flow (closed system)". The method to estimate the interface area is explained in the next section.

Micro channel experiment with no flow

Figure 1 shows the overview of micro channel. This setup consisted of granite chip [13] and rubber sheet including a slit whose size is described by the width w and the height b. The combination of w and b (w,b) was set to (3 mm, 3 mm), (2 mm, 2 mm) and (1 mm, 1 mm). Furthermore, the two types of granite-chips were prepared, i.e., one was the chip roughly ground with #2000 (grinding powder; ϕ7.9 μm SiC particles) (hereinafter referred to as "rough surface") and another was that polished up to mirror-like surface (referred to as "mirror-like surface"). In the experiment, the slit of the inlet (the left side illustrated in Figure.1) was connected to the overflow. Then, the apparent dissolution rate q was estimated by directly monitoring the location of interface between gas phase and liquid phase with a given time intervals. Here, the interface area was approximated by wb.
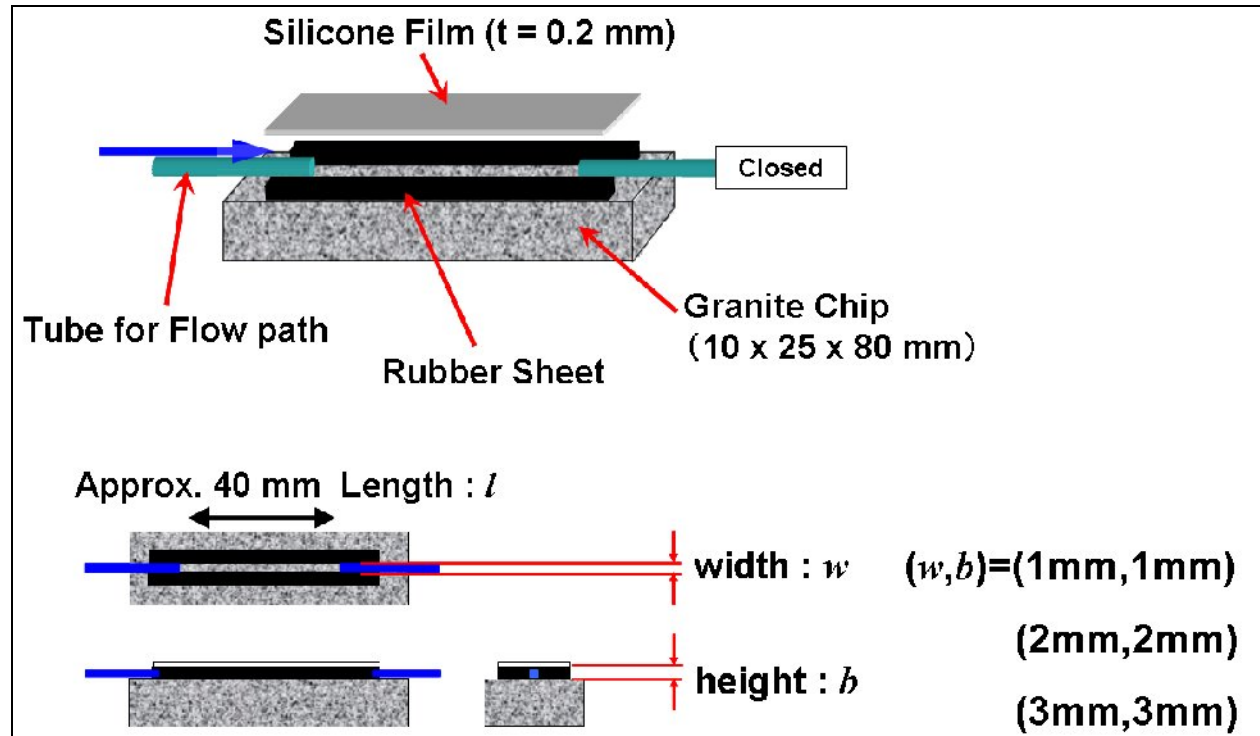
Fig. 1. Overview of Micro channel experiment.

RESULT AND DISCUSSION

Result of column experiment (open system)

Figure 2 shows the examples of permeability and pH measured in the column experiments with flow (open system, ϕ0.5 silica sands). As shown in Figure 2 (a), the recovery of pH was slower than that of the permeability. Since the mean residence time was approximately 30 seconds in these experiments, the delay of pH recovery means that the gas phase continued dissolving to liquid phase also after the breakthrough of the fluid through the column. Besides, the hydraulic head set in the range from 30 cm to 50 cm did not affect the experimental results.

In this study, the overall mass transfer coefficients K_L were calculated from the initial changing of pH as shown in Figure 2(a). Figure 2(b) shows the results of K_L in the column experiment with flow (open system). These values were remarkably small, in comparison with that (7.8×10^{-4} m/s) obtained from the "Bubbling test" where gas phase was continually injected into deionized water without solid phase. This means that the solid phase limits the local mixing of water phase near gas-liquid interface.

Furthermore, the overall mass transfer coefficient did not strongly depend on the particles size and its distribution. (The standard deviation of particle diameter of silica sands is larger than that of glass beads.) This suggests that the mass transfer was controlled by relatively macro gas-liquid interface formed in the column with flow.
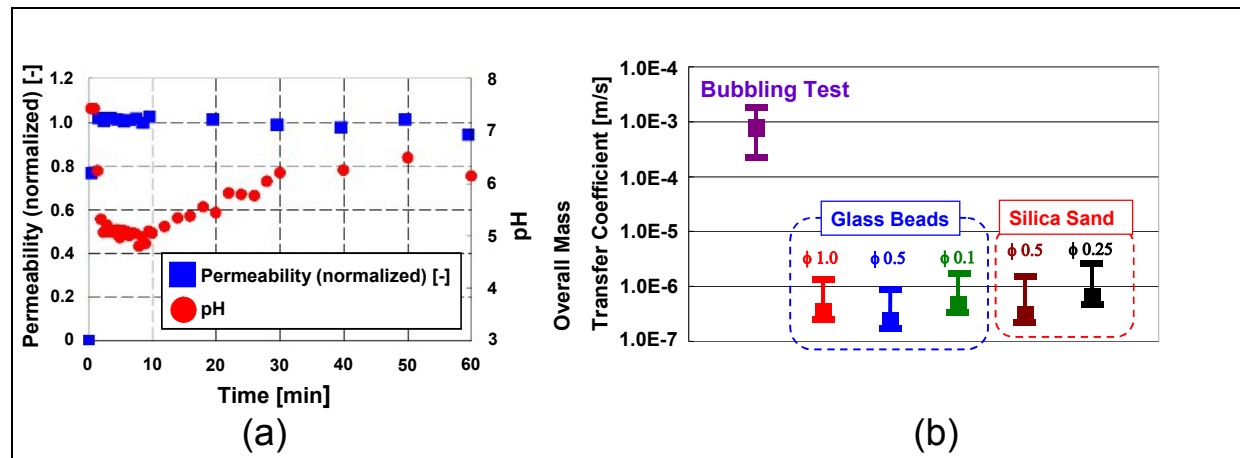
Fig. 2. Experimental results of column experiment with flow (open system) (a) An example of normalized permeability and pH (ϕ0.5 silica sands, the hydraulic head = 30 cm, and (b) Overall mass transfer coefficient K_L.

Result of column experiment (closed system)

Figure 3 shows the interface locations in the column experiment (with no flow), where the location of interface was monitored as the top height H_L. There was no large difference between silica sands of ϕ 0.5 and ϕ 0.25. These interfaces reached to the top end of column at 4 hours. On the other hand, in the cases of glass beads, the interfaces of gas-liquid water phases were not able to reach to the 50% of column height in the experiment time up to 10 hours. These results suggest that the apparent dissolution rate depends not on the average size of solid particles but on the size-distribution. Since the silica sands compared to the glass beads have a wider range in the diameter of particles, the capillary force strongly affects the shape of the interface formed in column. This study roughly estimated the area of the interface by using the top height H_L of the interface and the column diameter d. That is, the surface area of the interface was approximated by $d^2\pi/4$ in the glass beads column, and $d^2\pi/4+dH_L$ in the silica sands column. In the results, the area of interface of silica sands was 5.5 times larger than that of glass beads. The difference remarkably influences the apparent dissolution rate of gas phase to liquid phase.

Table I summarizes the overall mass transfer coefficients K_L obtained from the column experiments of the open system and the closed system. The K_L-values of the closed system were calculated by using the interface location and the surface area mentioned above. While in the cases of the closed system the value of K_L depends slightly on the particle size, the values of K_L were similar within the range from 5.0×10^{-6} m/s to 5.0×10^{-7} m/s. Although the apparent dissolution rates in the column of silica sands remarkably exceeded those of glass beads as shown in Figure 3(a), the surface area of the interface estimated in the column of silica sands was several times large compared to that of glass beads. Therefore, the value of K_L itself was similar to each other in this study.
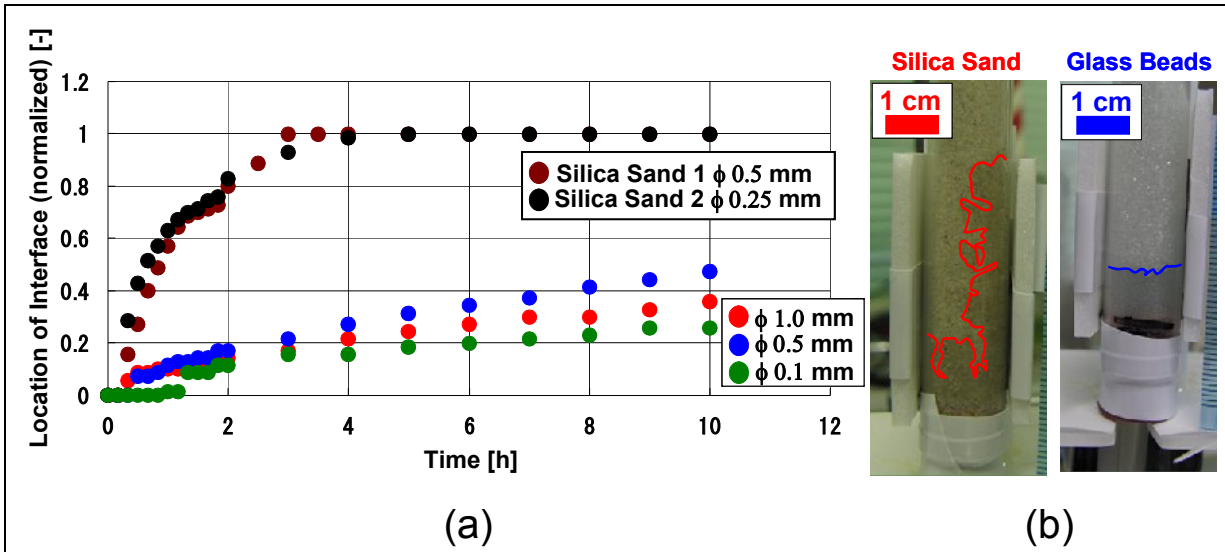
Fig. 3. Result of column experiments with no flow (closed system) (a) The locations of interface and (b) The examples of interface formed in the column (closed system) where the average diameters of silica sands and glass beads are ϕ 0.5 mm, and the hydraulic head was 30 cm.

Table I. Result of overall mass transfer coefficients at column flow/dissolution experiments (k = permeability (m^2) defined by Eq. 1 under the condition saturated with deionized water)

	Glass beads			Silica Sand	
	$\phi 1.0$ (k=2.0×10^{-11} m^2)	$\phi 0.5$ (k=1.6×10^{-11} m^2)	$\phi 0.1$ (k=0.7×10^{-11} m^2)	$\phi 0.5$ (k=2.1×10^{-11} m^2)	$\phi 0.25$ (k=2.3×10^{-11} m^2)
Column with flow (open system)	3.57×10^{-7}	2.46×10^{-7}	4.73×10^{-7}	3.05×10^{-7}	6.48×10^{-7}
Column with no flow (closed system)	4.99×10^{-7}	6.56×10^{-7}	7.87×10^{-7}	3.41×10^{-6}	2.71×10^{-6}

Result of micro channel experiment with no flow

Figure 4 (a) and (b) show the interface locations and the K_L-values given from the micro channel experiment with no flow. The hydraulic head was fixed at 30 cm through the overflow. In the experiments, this study focused on a relation of the overall mass transfer coefficient to the surface roughness of the granite-chip. As shown in Figure 4(c), the chip samples of "rough surface" and "mirror-like surface" are apparently different in the irregularity of surface shape. In other words, the net wetting surface area of the rough surface exceeds that of mirror-like surface. This tendency might locally deform the shape of the gas/liquid water interface. Such a

deformation of the gas/liquid interface increases the net exchange surface area between gas phase and liquid water phase. In fact, as shown in Figure 4(a), the migration of the interface location in "rough surface" chip always exceeds that in mirror-like surface. Besides, when the combination of (w,b) was (1 mm, 1 mm), its apparent dissolution rate exceeded the other combination such as (2 mm, 2 mm) and (3 mm, 3 mm). If the wetted surface area per unit volume of liquid-phase can be described by $1/b$, the combination of (1 mm, 1mm) has the largest $1/b$ in the three cases. That is, its largest $1/b$ may lead relatively large deformation of the interface of gas/liquid phases compared to the other combinations.
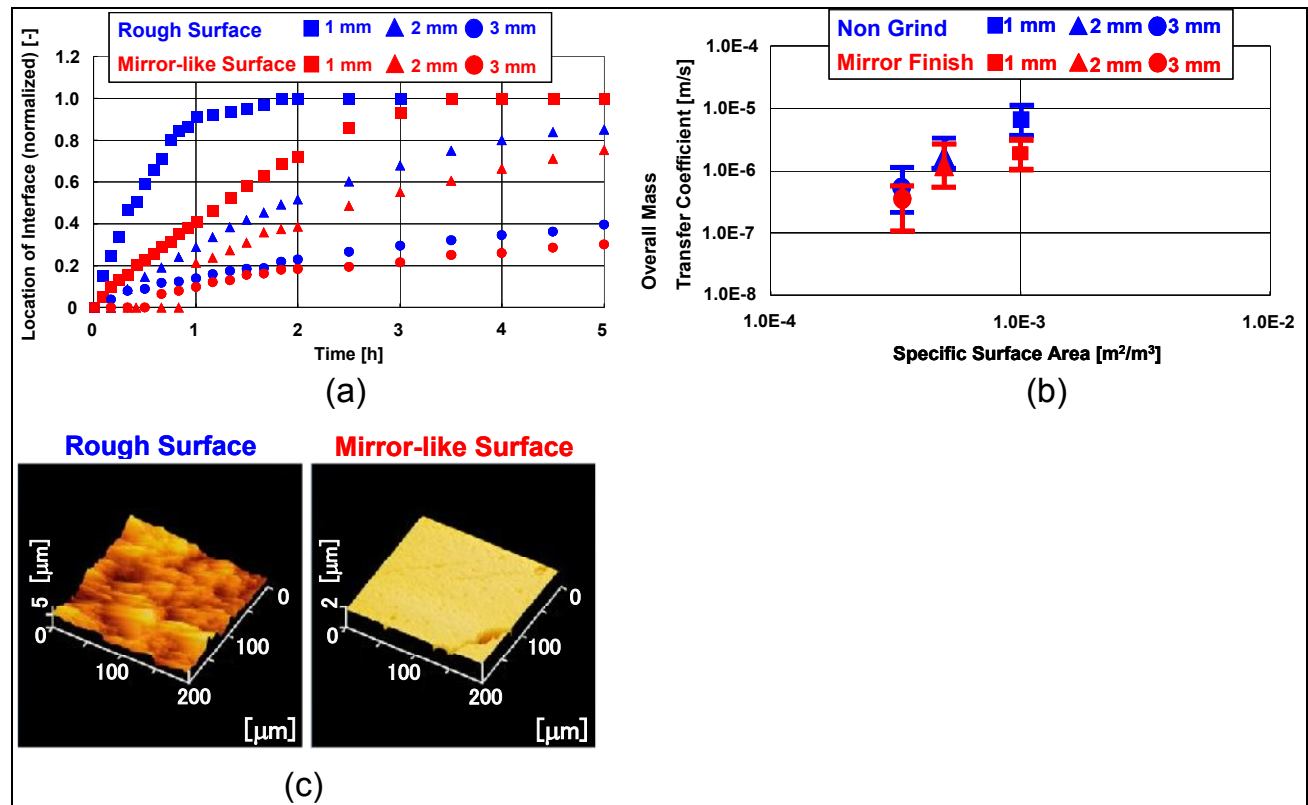

Fig.4.   The experimental results of micro channel experiment with no flow. ((a) the location of the interface of gas/liquid water phase, (b) the overall mass transfer coefficients, (c) the surface roughness observed by atomic force microscope (AFM).)

CONCLUSIONS

In a Japanese conceptual design of the geological disposal system the repository is constructed under the water table. Such a repository will be saturated with groundwater after the emplacement of the backfill. However, the ventilation process (at least 100 years including operating and monitoring periods) would form an unsaturated situation in the backfill and its surroundings. Therefore, in order to predict the timing of groundwater recovery, we need also the dissolution rate of gas phase to liquid-water phase in the co-presence of solid phase.

Through the various experimental setups, the overall mass transfer coefficients were in the range

from 5.0×10^{-6} m/s to 5.0×10^{-7} m/s. This value was remarkably small, compared to that obtained from the bubbling test with no solid phase (7.8×10^{-4} m/s). This means that the solid phase limits the local mixing of water phase near gas-liquid interfaces. Furthermore, the capillary force and the net wetted surface area deformed the shape of the interface formed in column or in channels, increasing the interface surface area of gas/liquid water phase. These results suggest that a more reliable model for estimating the detail of groundwater recovery around the repository should consider both the overall mass transfer coefficient in the co-presence of solid phase and the deformation of the interface between gas and liquid-water phases.

REFERENCES

1. JNC (Japan Nuclear Cycle development institute). (2000). H12: Project to Establish the Scientific and Technical Basis for HLW Disposal in Japan, Project Overview Report. JNC TN1410 2000-001.

2. FEPC (Federation of Electric Power Companies of Japan) and JNC. (2005). Second TRU progress report. JNC TY1400 2005-013, FEPC TRU-TR2-2005-02.

3. Niibori, Y., Joonhong, A., and Mimura, H. (2011). Uncertainty of Relative-permeability to Describe Two-phase Flow in Geological Disposal System. *NUCLEAR TECHNOLOGY*, 175.

4. DOE (U.S. Department of Energy). (1998). Viability Assessment of a Repository at Yucca Mountain. DOE/RW-0508.

5. Pruess, K. (1998). Two-Phase Unsaturated Flow at Yucca Mountain, Nevada, A Report on Current Understanding. LBNL-42075 Earth Sciences Division, Lawrence Berkeley National Laboratory.

6. Wu, Y., Haukwa, C., and Bodvarsson, G.S. (1999). A site-scale model for fluid and heat flow in the unsaturated zone of Yucca Mountain, Nevada. *Journal of Contaminant Hydrology, 38*, 185.

7. DOE. (2001). Yucca Mountain Preliminary Site Suitability Evaluation. DOE/RW-0540.

8. Aziz, K., and Settari, A. (1979). Petroleum Reservoir Simulation. Applied Science Publishers Ltd. London.

9. Huyakorn, P.S., and Pinder, G.F. (1983). Computational method in subsurface flow. Academic Press, New York, 186-187.

10. Seol, Y., Kneafsey, T.J., Tomutsa, L., and Moridis, G.J. (2006). Preliminary Relative Permeability Estimates of Methane Hydrate-Bearing Sand. Proc. TOUGH Symp., Berkeley, California, May 15-17, 2006, Lawrence Berkeley National Laboratory.

11. Haga, D., Niibori, Y., and Chida, T. (1999). Hydrodynamic Dispersion and Mass Transfer in Unsaturated Flow. *Water Resourc. Res., 35*, 1065.

12. Yang, Y.G., Niibori, Y., Inoue, C., and Chida, T. (2005). A Fundamental Study of Microbial Attachment and Transport in Porous Media for the Design of MEOR. *JOURNAL OF THE JAPANESE ASSOCIATION FOR PETROLEUM TECHNOLOGY VOL.70,* 459-468.

13. Niibori, Y., Nakata, R., Tochiyama, O., and Mimura, H. (2009). Evaluation of Solute Transport through a Fracture by Considering the Spatial Distributions of Retardation Effect in Grain Scale. *Journal of Hydrologic Engineering, ASCE (American Society of Civil Engineers), 14,* 1214-1220.

ACKNOWLEDGMENTS