



## Mass transfer of trichloroethylene through the palladized iron coated reactive geomembrane

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### ARTICLE INFO

#### Article history:

Received 28 April 2011

Received in revised form 28 October 2011

Accepted 28 October 2011

Available online 9 November 2011

#### Keywords:

Reactive geomembrane (RGM)

Palladized iron (Pd/Fe)

Mass transfer

Trichloroethylene (TCE)

### ABSTRACT

Palladized iron coated reactive geomembrane (Pd/Fe RGM) was developed to mitigate the mass transfer of chlorinated volatile organic compounds through HDPE geomembrane. It had good performance in mitigating the mass transfer of TCE at the preliminary study. This study focused on the effects of Pd/Fe coating on the mass transfer parameters and the reaction rate constant of RGM. Also, the effects of sulfide and aging on the RGM were evaluated. It was proved that the effect of Pd/Fe coating on partition and diffusion coefficients of toluene was not significant by batch immersion test results with student's *t*-test. The reactivity of Pd/Fe RGM had a linear correlation with an increase in the Pd/Fe loading rate on RGM. However, it was lower than the reactivity of the Pd/Fe powder by a factor of one hundred because the effective surface area of Pd/Fe was blocked partially by the geomembrane and the opportunity to contact Pd/Fe and TCE was reduced. The reactivity of Pd/Fe RGM decreased severely at 10 mM sulfide concentration and with long-term aging of RGM in the atmosphere for three years. However, the reactivity of aged RGM was recovered slightly by acid treatment, but not completely.

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### 1. Introduction

Chlorinated volatile organic compounds (CVOCs) have been found in municipal and hazardous waste landfill sites and contaminated groundwater. Especially, trichloroethylene (TCE), known as a degreaser or solvent, is frequently detected in landfill leachate or groundwater [1,2]. The International Agency for Research on Cancer distributed TCE to “group 2A”, which meant that TCE was suspected to be carcinogenic for humans [3]. TCE also may have an adverse effect on kidneys, vessels, and the liver and so on if a human is exposed to TCE [4]. Since the density of TCE is greater than that of water, TCE seeps down below the water table and causes widespread contamination of soils and underground aquifers [5]. High-density polyethylene (HDPE) geomembrane is widely used as a landfill liner or vertical wall for the purpose of containment of hazardous waste and contaminated groundwater. HDPE geomembrane mitigates the mass transfer of aqueous and inorganic contaminants effectively. However, volatile organic compounds such as CVOCs (e.g., TCE) can readily permeate through HDPE geomembrane by the partition–diffusion process [6–9].

Several researches have been conducted to mitigate the mass transfer of CVOCs through geomembrane. The research of Sangam and Rowe demonstrated that surface fluorination of HDPE geomembrane reduced permeation coefficients 1.5–4.5 times less than those of non-treated geomembrane [10]. However, a guideline concerning the thickness required to prevent the mass transfer of certain CVOC was not provided. Shimotori et al. proposed the reactive geomembrane containing zero-valent iron (ZVI) and glycerol which supported ZVI in geomembrane to dechlorinate CVOCs [11]. Glycerol in the geomembrane, however, may weaken the physical properties of the geomembrane. Surdo et al. developed the sandwich-type composite membrane in which an aqueous clay suspension layer containing a sorptive and reactive scavenger such as powdered activated carbon or Fe<sup>0</sup> in a polytetrafluoroethylene spacer was inserted between two sheets of HDPE [12]. In the field application, however, consolidation of the reactive layer had the potential to squeeze water, which may result in separating clay and water layers, and finally affect the permeability and shear strength of the composite liner.

Seo proposed the reactive geomembrane (RGM) coated with reactive material such as grind precipitates dust (GP dust) on the surface of the geomembrane [13]. Although GP dust-coated RGM did not mitigate the problem because of the low reactivity of GP dust, this type of RGM has some practical advantages whereby the

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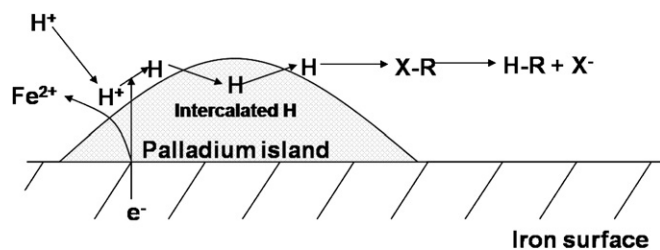


Fig. 1. Schematic diagram of dechlorination mechanism of Pd/Fe. (modified from Zhang et al. [18]).

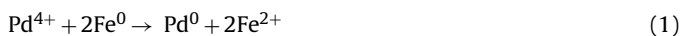
amount of coating reactive material can be controlled and the physical properties of the geomembrane as a hydraulic barrier did not change due to the coating. Shin et al. used palladized iron (Pd/Fe) of which the reactivity was higher than ZVI and GP dust as coating material of RGM [14,15]. The Pd/Fe coated reactive geomembrane (Pd/Fe RGM) showed good performance in mitigating the mass transfer of TCE because it was rapidly dechlorinated by Pd/Fe on the surface of geomembrane [14,15].

To have a better understanding of the mass transfer of Pd/Fe RGM, the effect of Pd/Fe coating on mass transfer parameters such as partition and diffusion coefficients was verified and the reaction rate constants of Pd/Fe RGM at various Pd/Fe types or different loading amounts on the unit area of RGM were evaluated in this present paper. Also, the effect of sulfide ion existing in the sulfate-rich subsurface environment and long-term aging of Pd/Fe RGM during storage or shipping was also verified to obtain some basic engineering parameters for field application.

## 2. Materials and methods

### 2.1. Pd/Fe reactive geomembrane (Pd/Fe RGM)

Pd/Fe was synthesized by mixing potassium hexachloropalladate (99.9 wt.%, Aldrich) solution with iron powder (100 mesh, Fisher Scientific Inc.) until the color of the solution was changed from purple to pale yellow (or transparent). Palladium particles were deposited on the surface of the iron electrochemically as follows:



The dechlorination of the Pd/Fe can be attributed to the following sequence of reactions: (a) evolution of hydrogen gas by the reduction of water molecules by elemental Fe (i.e., the “corrosion” of Fe in water), (b) the adsorption of the evolved hydrogen gas by Pd, and the formation of the powerful reducing species “Pd-H<sub>2</sub>” (i.e., hydrogen gas intercalated into the elemental Pd lattice), and (c) the reduction of the TCE that is adsorbed on the Pd/Fe surface (Fig. 1) [15–18].

Synthesized Pd/Fe was washed with deionized water for three times and dried completely. Scanning electron microscope (SEM) analysis of Pd/Fe was conducted to verify palladium particles on the surface of the iron (Fig. 2). In this study, Pd/Fe samples were classified according to the Pd content on the iron surface and drying methods. Two types of Pd/Fe sample were prepared that Pd content of Pd/Fe was 0.8% and 0.05%, respectively (by wt.). Also, drying methods included drying in an oven at 105 °C overnight (about 12 h) and drying in a anaerobic chamber with silica gel at 20 °C for one day to minimize oxidation of iron.

Pd/Fe RGM was manufactured by coating dried Pd/Fe powder on the surface of the HDPE geomembrane during the casting and pressing procedures (Fig. 3). Normal geomembrane (NGM) as control was manufactured by same ways of Pd/Fe RGM except Pd/Fe coating. The thickness of geomembranes used in this study was

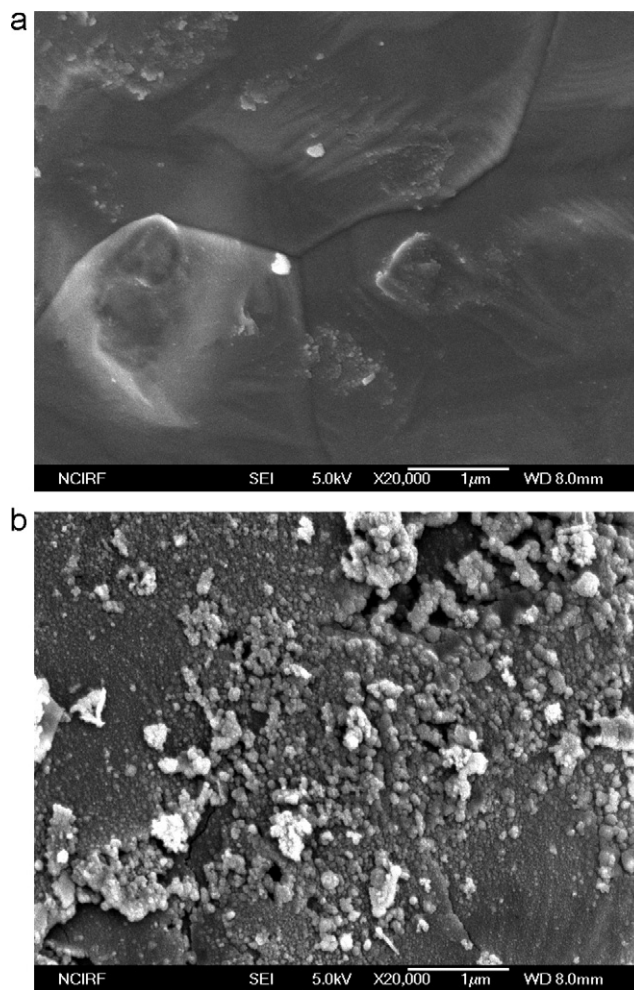


Fig. 2. SEM analysis of (a) surface of iron particle and (b) surface of palladized iron particles.



Fig. 3. Pd/Fe RGM manufactured.

**Table 1**  
Nomenclature of Pd/Fe and Pd/Fe RGM specimens.

Types	Pd content of Pd/Fe (% by wt.)	Drying condition	Pd/Fe loading amount per unit area of geomembrane <sup>a</sup> (mg/cm <sup>2</sup> )
Pd/Fe powder			
Pd/Fe-0.8A	0.8	105 °C oven in air (A)	–
Pd/Fe-0.8N	0.8	Anaerobic chamber (N)	–
Pd/Fe-0.05N	0.05	Anaerobic chamber (N)	–
Pd/Fe RGM			
Pd/Fe-0.8A-UK	0.8	105 °C oven in air (A)	Unknown <sup>b</sup>
Pd/Fe-0.05N-1.842	0.05	Anaerobic chamber (N)	1.842
Pd/Fe-0.05N-17.67	0.05	Anaerobic chamber (N)	17.67

<sup>a</sup> Total Pd/Fe amount used for RGM manufacture (mg)/total RGM area manufactured (cm<sup>2</sup>).

<sup>b</sup> In case of Pd/Fe-0.8A-UK, Pd/Fe amount used and RGM area manufactured were not recorded. However, loading rate may be maximum because Pd/Fe-0.8A was coated on RGM as much as possible.

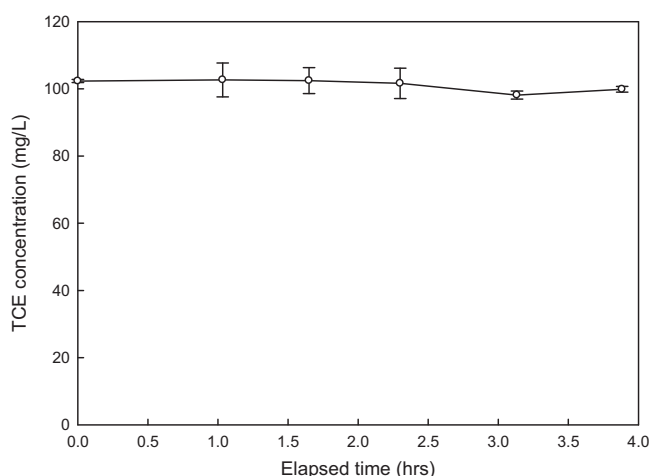
2 mm. Pd/Fe RGMs were classified according to the Pd/Fe loading rate per the unit area of geomembrane. The nomenclature of Pd/Fe and Pd/Fe RGM was listed in Table 1.

### 2.2. Batch test for TCE dechlorination by Pd/Fe

A 40 mL vial with a Mininert™ valve was prepared for the batch test. 1 g of Pd/Fe powder was added to a 40 mL vial containing 100 mg/L TCE (99.99%, Aldrich) solution without headspace. This vial was continuously tumbled by a rotary shaker. 0.4 mL of aqueous solution was withdrawn by a gas-tight syringe and the TCE in the sample was extracted by an n-hexane (GC Grade, MERCK). The extracted sample was analyzed by gas chromatography (Younglin M600D, Younglin Co. Ltd.). Sodium sulfide hydrate (60–62 wt.%, Scales, JANSSEN) was used after it was dried in an oven at 105 °C for 7 min to prepare the sulfide solution. The blank test was conducted to determine whether the loss of TCE may occur due to volatilization during the experiment. As shown by Fig. 4, the observed concentration change of TCE in the blank test was ±1–3%, which was negligible because the variation was within the measuring error which was 3%. All of the measured data were adjusted using the internal standard method.

### 2.3. Chemical composition analysis on the surface of Pd/Fe

The chemical composition analysis on the surface of Pd/Fe was analyzed by X-ray photoelectron spectroscopy (XPS) analysis (SIGMA PROBE, ThermoVG). The X-ray source was monochromatic Al K $\alpha$  (15 kV, 100 W, and 400  $\mu$ m).



**Fig. 4.** Blank test for TCE dechlorination batch test.

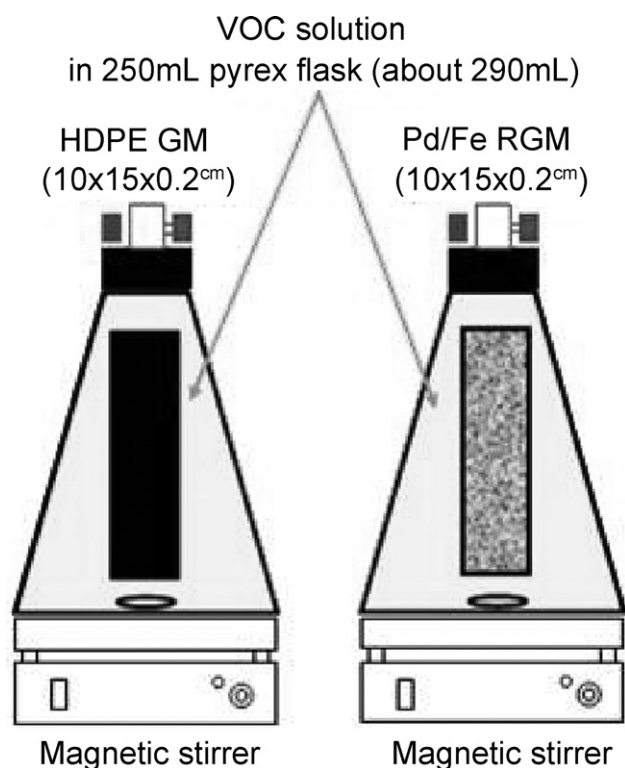
### 2.4. Batch immersion test for mass transfer of toluene through geomembrane instead of TCE

Pd/Fe RGM and NGM specimens were placed in 250 mL Pyrex flasks (total volume: 290 mL), which were filled completely with toluene solution as shown in Fig. 5. Each test was in triplicate and the headspace in the flask was minimized to prevent the loss by volatilization. As the mass transfer was steady-state, the partition coefficient was determined using Eq. (2):

$$K_{\text{HDPE-W}} = \frac{(C_{w,i} - C_{w,eq}) \cdot V_w}{M_{\text{HDPE}} \cdot C_{w,eq}} \times \rho_{\text{HDPE}} \quad (2)$$

where  $K_{\text{HDPE-W}}$  is the HDPE–water partition coefficient of an organic compound [dimensionless],  $C_{w,i}$  is the initial concentration of the organic compound in water [M/L<sup>3</sup>],  $C_{w,eq}$  is the equilibrium concentration of the organic compound in water [M/L<sup>3</sup>],  $M_{\text{HDPE}}$  is the mass of a HDPE geomembrane [M],  $V_w$  is the volume of the water [L<sup>3</sup>], and  $\rho_{\text{HDPE}}$  is the density of the HDPE geomembrane [M/L<sup>3</sup>].

The mathematical model of diffusion in a plane sheet in contact with a stirred solution of limited volume has been well defined. If



**Fig. 5.** Schematic diagram of batch immersion test.

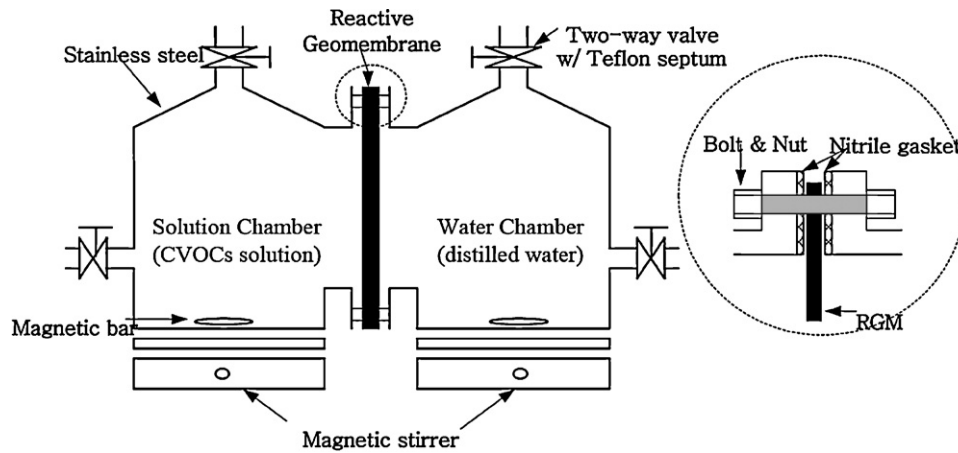


Fig. 6. Schematic diagram of confined double compartment apparatus (CDCA) test.

$M_t$  denotes the total amount of diffusing substance that has entered the sheet at time  $t$ , and  $M_\infty$  denotes the corresponding quantity after infinite time, the solution is as follows [19]:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2q_n^2} \exp\left(\frac{-Dq_n^2t}{l_{\text{half}}^2}\right) \quad (3)$$

where  $q_n$  is the non-zero positive roots of  $\tan(q_n) = -\alpha(q_n)$  and  $\alpha = V_c/K \cdot V_{\text{HDPE}}$ ,  $V_c$  is volume of solution [ $L^3$ ],  $K$  is partition coefficient of a plane sheet (HDPE geomembrane) [dimensionless],  $V_{\text{HDPE}}$  is volume of HDPE geomembrane specimen [ $L^3$ ],  $l_{\text{half}}$  is half the thickness of a HDPE geomembrane specimen [ $L$ ], and  $D$  is the diffusion coefficient [ $L^2/T$ ].

The diffusion coefficient of toluene through the geomembrane was determined by curve fitting using Eq. (3) as a function of  $D \cdot t$  to a series of data points of toluene concentration in solution.

### 2.5. Confined double compartment apparatus (CDCA) test for mass transfer of TCE through geomembrane

A confined double compartment apparatus (CDCA) test was conducted to monitor the mass transfer of TCE through RGM and to verify that RGM was an effective barrier to mitigate the mass transfer. RGM was installed between compartments to set the Pd/Fe side of RGM to the solution chamber and compartments were jointed with a nitrile butadiene rubber gasket by bolts and nuts to minimize absorption to gasket and TCE loss through joint part as shown in Fig. 6. A 100 mg/L TCE solution was prepared in the solution chamber (SC) and deionized water was prepared in the water chamber (WC) without headspace. Each compartment was fully stirred by a magnetic bar. The partition coefficient, diffusion coefficient, and reaction rate constant of Pd/Fe, which determined the mass transfer of TCE through RGM, were obtained by curve fitting to a series of observed concentration data points in both chambers using mathematical model as shown below. The mathematical model developed by Shin et al. was used [14]. The governing equation, initial condition and boundary conditions were as follows.

Governing equation:

$$\frac{\delta C(x, t)}{\delta t} = D \cdot \frac{\delta^2 C(x, t)}{\delta x^2} \quad (4)$$

Initial condition:

$$C(x, t) = 0, \quad 0 < x < l, \quad t = 0 \quad (5)$$

Boundary conditions:

$$C_{0,t} = K_0 C_{v,o}, \quad x = 0, \quad t > 0 \quad (6)$$

$$C_{v,t} = C_{v,o} - \frac{A_m}{V^d} \int_{x=0}^{x=l} C(x) dx - \frac{V^d}{V^v} C_{d,t} - K_{\text{obs}} \int_{t=0}^t C_{v,t} dt \quad (7)$$

$$C_{l,t} = K_l C_{d,t}, \quad x = l, \quad t > 0 \quad (8)$$

$$C_{d,t} = C_{d,o} + \frac{A_m D}{V^d} \int_{t=0}^t \left[ \frac{\delta C}{\delta x} \right]_{x=l} dt \quad (9)$$

where  $K$  is the partition coefficient [dimensionless],  $D$  is the diffusion coefficient [ $L^2/T$ ],  $K_{\text{obs}}$  is the observed first-order reaction rate constant [ $T^{-1}$ ],  $l$  is the thickness of the HDPE [ $L$ ],  $t$  is elapsed time [ $T$ ],  $V$  is the volume of the compartment [ $L^3$ ], and  $A_m$  is the area of specimen in direct contact with the aqueous solution [ $L^2$ ]. Superscripts  $v$  and  $d$  refer to the solution chamber (SC) and water chamber (WC), respectively.

## 3. Results and discussion

### 3.1. Effect of Pd/Fe coating on partition and diffusion coefficients

The coating of Pd/Fe powder may extend the molecular pore of HDPE, and can increase the diffusivity of TCE through the geomembrane. Moreover, it may decrease the hydrophobicity of the HDPE surface because Pd/Fe is hydrophilic. Therefore, it is necessary to prove whether the Pd/Fe coating changes the values of the partition and diffusion coefficients of organic compounds. Batch immersion tests of Pd/Fe RGM and NGM in triplicate were conducted with toluene instead of TCE (Fig. 5) in order to determine the effect of Pd/Fe coating on the partition and diffusion coefficients indirectly because TCE was rapidly degraded by Pd/Fe, so it could barely be determined whether the decrease of TCE concentration in solution was occurred by dechlorination or by mass transfer through the geomembrane, while toluene was not degraded by Pd/Fe at ambient temperature. Partition and diffusion coefficients were evaluated from the result of batch immersion tests using Eqs. (2) and (3) and the sorption curves were illustrated in Fig. 7. As a result of the student's  $t$ -test, the hypothesis that the partition and diffusion coefficients of toluene through RGM were identical to those through NGM was not rejected in both 90% and 95% confidence levels (Table 2). That is, partition and diffusion coefficients through RGM did significantly not differ from those through NGM. Therefore, it is available that partition and diffusion coefficients evaluated from NGM are applied to mathematical model instead of the partition and diffusion coefficients evaluated from RGM as mass transfer parameters of CVOCs through Pd/Fe RGM. In case of CDCA test, partition and diffusion coefficients of TCE evaluated from NGM were 211.07 (dimensionless) and  $1.69 \times 10^{-9} \text{ cm}^2/\text{s}$

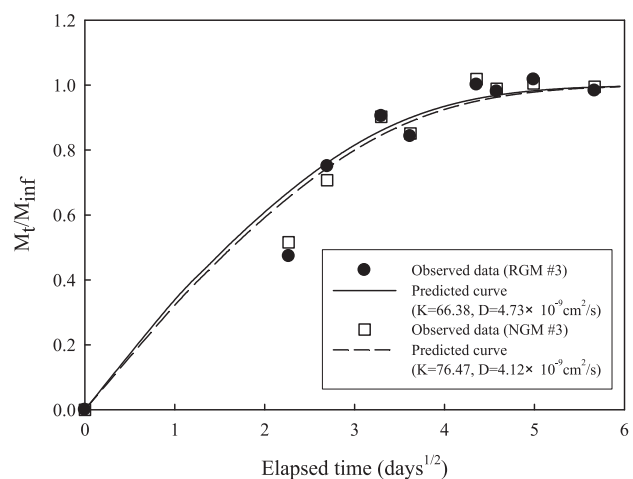
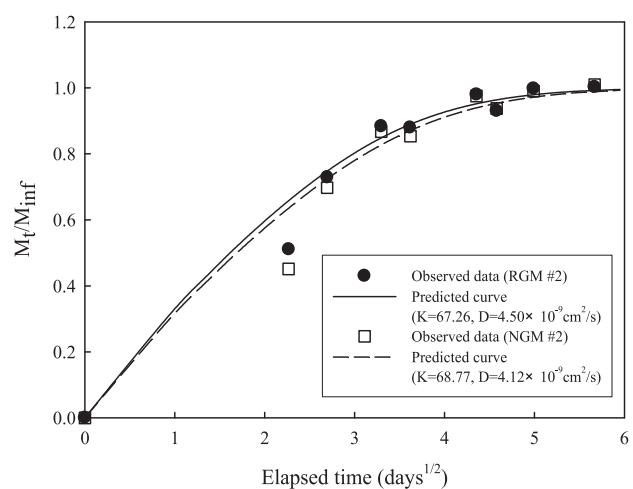
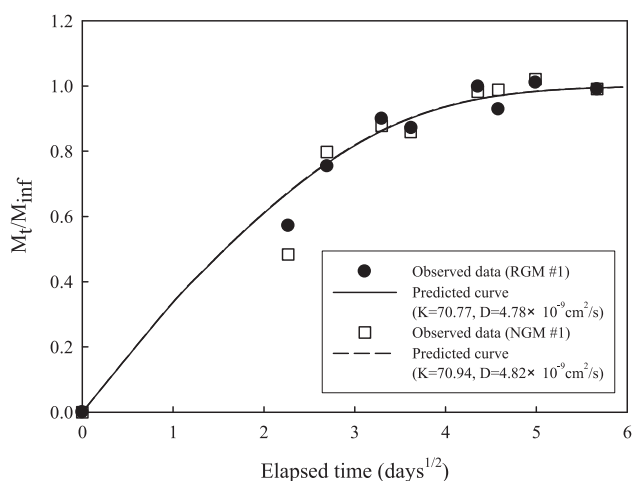


Fig. 7. Sorption curves of toluene on RGM and NGM in batch immersion test.

(the graph was not included), and its standard deviations were 14.17 and  $0.06 \times 10^{-9} \text{ cm}^2/\text{s}$ , respectively. These values were used as mass transfer parameters of Pd/Fe RGM.

### 3.2. Reactivity of Pd/Fe on surface of geomembrane

#### 3.2.1. Reaction rate constants of Pd/Fe powder at different conditions

The Pd/Fe-0.8A powder completely dechlorinated 40 mL of the 100 mg/L TCE solution in the batch test within 4 h and the reaction

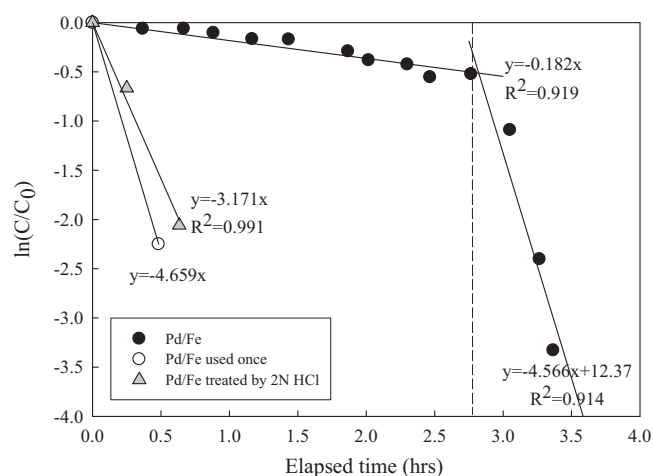


Fig. 8. TCE dechlorination by Pd/Fe-0.8A at different conditions.

of the Pd/Fe-0.8A powder seemed to be divided into two phases (Fig. 8). At the first phase, the observed reaction rate constant was  $0.182 \text{ h}^{-1}$ , and was higher than the  $0.0038 \text{ h}^{-1}$  reaction rate constant of zero-valent iron that was under the same conditions (i.e., ratio of Pd/Fe to solution, initial concentration, temperature, etc.) in the previous study [15]. The second phase began after about 2.8 h had elapsed from the start of the experiment and the reactivity of Pd/Fe suddenly increased. The observed reaction rate constant at the second phase was  $4.566 \text{ h}^{-1}$ , which was 25 times higher than that at the first phase. There was a significant difference in the reaction of Pd/Fe between this study and previous studies, which proposed that the reaction of Pd/Fe took place at constant rate over the whole time range [20,21].

It appears that the change of Pd/Fe reactivity may occur due to hydrogen accumulation in the solution or to surface transformation during reaction. As a result of a batch test with Pd/Fe-0.8A powder used once to determine the reason for the two phase-reaction, 40 mL of 100 mg/L TCE solution was dechlorinated rapidly within 30 min and the reaction rate constant of Pd/Fe-0.8A was  $4.659 \text{ h}^{-1}$ , which was similar to that in the second phase of the Pd/Fe-0.8A powder (Fig. 8). This meant that the change of Pd/Fe reactivity did not occur due to any changes in the solution such as hydrogen accumulation, but by transformation of the Pd/Fe surface such as removing the oxide film on the surface. In order to support this hypothesis, a batch test with Pd/Fe-0.8A powder treated by a 2 N HCl solution for 5 s was conducted under an identical condition. The observed rate constant of acid-treated Pd/Fe-0.8A powder was  $3.171 \text{ h}^{-1}$ , which was nearly similar to that of the second phase, though somewhat less, because some extent of Pd/Fe may be lost during acid treatment. In contrast to Pd/Fe-0.8A, the reaction of Pd/Fe-0.8N powder showed one-phase, with an observed reaction rate constant of  $4.566 \text{ h}^{-1}$ , which was similar to that of the Pd/Fe-0.8A powder at the second phase,  $4.564 \text{ h}^{-1}$  (Fig. 9). This result also supported the hypothesis that oxide film on the surface decreased the reactivity at the first phase.

To summarize, it seemed that the reactivity of Pd/Fe dried in air was less than that of Pd/Fe dried in nitrogen because the oxide film on the surface of Pd/Fe formed during the drying process. However, oxidation during drying in an oven overnight (about 12 h) did not decrease the reactivity of Pd/Fe permanently and this was recovered before long in a batch test. It was assumed that the surface of the Pd/Fe-0.8A powder was transformed because the oxide film was pelted off due to the collision of each particle of Pd/Fe during the batch test or unexpected chemical reaction. Further studies are needed to determine this. In order to evaluate the effect of the Pd content on Pd/Fe reactivity, two types of Pd/Fe powder (i.e., Pd

**Table 2**  
Batch immersion test results of Pd/Fe RGM and NGM and student's *t*-test.

	Partition coefficient (dimensionless)		Diffusion coefficient ( $10^{-9}$ cm <sup>2</sup> /s)	
	Pd/Fe reactive geomembrane (Pd/Fe RGM)	Normal geomembrane (NGM)	Pd/Fe reactive geomembrane (Pd/Fe RGM)	Normal geomembrane (NGM)
No. of sample	3	3	3	3
Average	68.14	72.15	4.67	4.47
Standard deviation	2.32	4.12	0.15	0.35
$T_{\text{calculated}}$		1.469		0.910
$T_{\text{table}}$ (confidence level)	2.776 (95%)	2.132 (90%)	2.776 (95%)	2.132 (90%)
Decision	Do not reject $H^0$	Do not reject $H^0$	Do not reject $H^0$	Do not reject $H^0$

$H^0$ : partition coefficient or diffusion coefficients of RGM are equal to those of NGM, respectively.

content is 0.8 and 0.05% (by wt.)) were manufactured. The batch tests were conducted to compare the reactivity of each type (Fig. 9). The observed reaction rate constant of Pd/Fe powder had a positive correlation with the Pd content. However, the observed reaction rate constant of Pd/Fe powder did not proportionally increase in accordance with an increment of the Pd content. Even though the Pd content of the Pd/Fe powder increased by a factor of 16, the observed reaction rate constant increased only by a factor of two.

### 3.2.2. Correlation between Pd/Fe loading rate and observed reaction rate constant of Pd/Fe RGM

Two Pd/Fe RGM specimens were prepared to determine the correlation between the Pd/Fe loading rate on the surface of RGM and the observed reaction rate constant of Pd/Fe RGM; the specimens contained approximately 1.842 and 17.67 mg/cm<sup>2</sup> of Pd/Fe-0.05N powder on the HDPE geomembrane, respectively. The observed reaction rate constant of the two Pd/Fe RGMs (Pd/Fe RGM-0.05N-1.842 and Pd/Fe-0.05N-17.67), were evaluated using the result of the CDCA test and the mathematical model and their reaction rate constants were  $1.0 \times 10^{-4}$  h<sup>-1</sup> and  $1.0 \times 10^{-3}$  h<sup>-1</sup>, respectively (Fig. 10). Therefore, the reactivity of RGM increased proportionally to the Pd/Fe loading rate on RGM, but not to the Pd content of Pd/Fe in the range.

### 3.2.3. Comparison between Pd/Fe coated on RGM and Pd/Fe powder

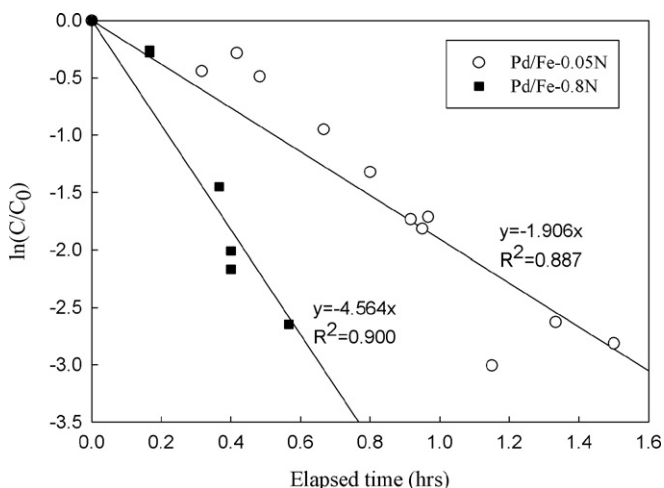
Dechlorination of TCE by Pd/Fe is known to be the pseudo first-order reaction [20]. Dechlorination of Pd/Fe appears to be surface-mediated reaction and first-order with respect to the amount of metal available to serve as reductant [22]. Therefore, the observed

reaction rate constant of Pd/Fe,  $k_{\text{obs}}$  [1/T] could be expanded as Eq. (10):

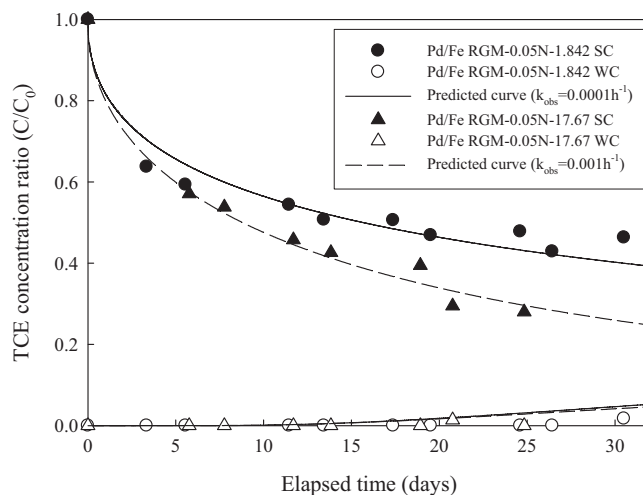
$$k_{\text{obs}} = k_{\text{SA}} a_s \rho_m \quad (10)$$

where  $k_{\text{SA}}$  = specific reaction rate constant [ $\text{L}^3/\text{L}^2/\text{T}$ ];  $a_s$  = specific surface area of Pd/Fe [ $\text{L}^2/\text{M}$ ]; and  $\rho_m$  = mass concentration of Pd/Fe [ $\text{M}/\text{L}^3$  of the solution].

It was expected that the reactivity of the Pd/Fe coated on the surface of the geomembrane was smaller than that of the Pd/Fe powder because the effective surface of the Pd/Fe powder coated on the geomembrane which was able to dechlorinate TCE was blocked partially, while the Pd/Fe powder was suspended in the TCE solution and the vial used in the batch test was tumbled completely to contact the Pd/Fe powder and TCE effectively. As shown in Table 3, the reactivity of the Pd/Fe-0.05N powder and Pd/Fe RGM-0.05N were compared. In the case of Pd/Fe RGM-0.05N-1.842 and Pd/Fe RGM-0.05N-17.67, the values of  $k_{\text{SA}} \times a_s$  were  $7.7 \times 10^{-4}$  Lg<sup>-1</sup> h<sup>-1</sup> and  $8.0 \times 10^{-4}$  Lg<sup>-1</sup> h<sup>-1</sup>, respectively. The two values were similar. On the other hand,  $k_{\text{SA}} \times a_s$  of the Pd/Fe-0.05N powder was  $7.8 \times 10^{-2}$  Lg<sup>-1</sup> h<sup>-1</sup> on average, and it was 100 times higher than Pd/Fe RGM-0.05N. This meant that the effective surface area of Pd/Fe-0.05N was larger than that of Pd/Fe RGM-0.05N because  $k_{\text{SA}}$  was the indigenous value of the material, so, the  $k_{\text{SA}}$  of Pd/Fe-0.05N and Pd/Fe RGM-0.05N were identical. Therefore, the amount of Pd/Fe required may be 100 times more than that expected through the batch test when Pd/Fe RGM was designed for field application.



**Fig. 9.** TCE dechlorination by Pd/Fe powders with different Pd content.



**Fig. 10.** Comparison of mass transfer of TCE through Pd/Fe RGMs with different Pd/Fe loading rate (SC and WC in the legend refer to the solution chamber and water chamber, respectively).

**Table 3**  
Comparison of the reactivity of Pd/Fe powder and Pd/Fe RGM.

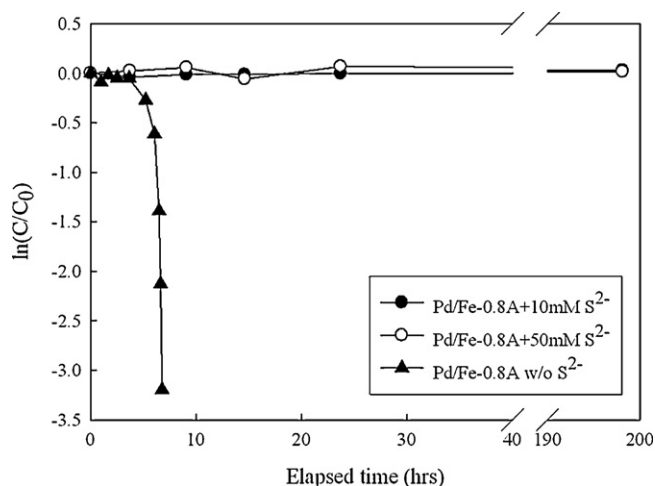
Test method	Type of Pd/Fe RGM (or Pd/Fe)	<A> Pd/Fe amount (on RGM) (g)	<B> Volume of TCE solution (L)	<A/B> Mass concentration of Pd/Fe (g/L)	Observed reaction rate constant ( $\text{h}^{-1}$ )	$k_{SA} \times a_s$ ( $\text{Lg}^{-1} \text{h}^{-1}$ )
Batch test	Pd/Fe-0.05N	1.000	0.04	25.000	(1) $1.821 \times 10^0$ (2) $2.090 \times 10^0$	$7.8 \times 10^{-2}$ (average)
CDCA test	Pd/Fe	0.335 <sup>a</sup>	2.58	0.130	$1.0 \times 10^{-4}$	$7.7 \times 10^{-4}$
	RGM-0.05N-1.842	3.216 <sup>a</sup>	2.58	1.246	$1.0 \times 10^{-3}$	$8.0 \times 10^{-4}$

<sup>a</sup> Pd/Fe loading rate ( $\text{mg}/\text{cm}^2$ )  $\times$  14 cm  $\times$  13 cm  $\times$  0.001 g/mg.

### 3.3. Effect of sulfide ion on reactivity of Pd/Fe

It is known that sulfide ion reacts with palladium and changes the chemical state of palladium from 0 to +2 valences [23]. Also, palladium of Pd/Fe is damaged permanently as the catalyst which can reduce CVOCs. Sulfur-reducing bacteria (SRB) can reduce sulfate ion ( $\text{SO}_4^{2-}$ ) to sulfide ion ( $\text{S}^{2-}$ ) in a sulfate-rich subsurface environment. Therefore, batch tests at sulfide ion concentrations of 0, 10, and 50 mM were conducted to evaluate the effect of sulfide ion on the reactivity of Pd/Fe-0.8A. Dechlorination of TCE by Pd/Fe under different sulfide ion concentrations is shown in Fig. 11. Over the eight days, TCE was not dechlorinated at the presence of 10 and 50 mM of sulfide ion and the palladium of Pd/Fe was deactivated completely. A surface analysis of Pd/Fe was conducted to determine the change of the chemical state of palladium by X-ray photoelectron spectroscopy. In accordance with the increment of sulfide ion concentration, the amount of sulfur deposited on the surface increased (Fig. 12). Also, the sulfur reacted with the palladium and changed the chemical state of the palladium. In Fig. 12, the peak shifts of Pd 3d orbitals meant that the chemical state of palladium changed from  $\text{Pd}^0$  to  $\text{Pd}^{2+}$ , which could no longer be used as a catalyst.

Two CDCA tests were conducted to verify the effect of sulfide on Pd/Fe RGM. In one test, Pd/Fe RGM was installed without sulfide ion and in the other test, Pd/Fe RGM was installed with 10 mM sulfide solution and the mass transfers of TCE through Pd/Fe RGM are shown in Fig. 13. Curve fitting was conducted by numerical analysis to obtain the observed reaction rate constant of Pd/Fe RGM. RGM without sulfide showed that the mass transfer of TCE was mitigated and the observed reaction rate constant was  $0.008 \text{ h}^{-1}$ . On the other hand, in the case of Pd/Fe RGM with 10 mM sulfide, any obvious dechlorination of TCE was not observed. Even though

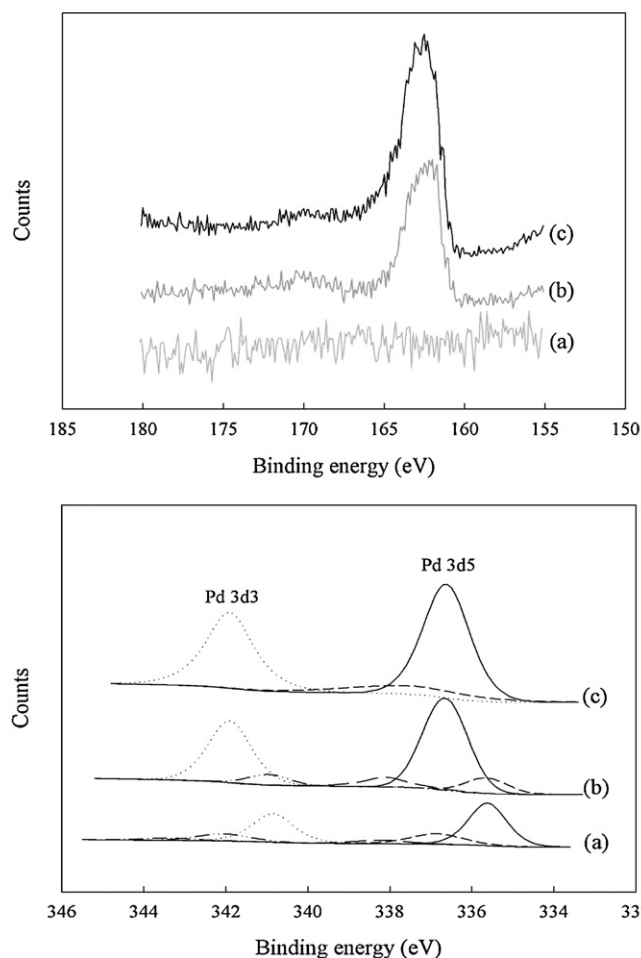


**Fig. 11.** TCE dechlorination by Pd/Fe-0.8A at different sulfide ion concentrations in the batch test.

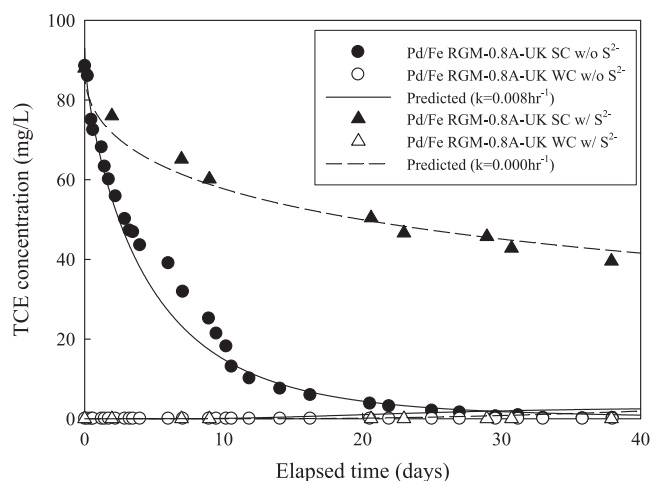
the exact range of sulfide or other reduced ions to deactivate Pd/Fe dechlorination was not clarified in this study, it was clear that the reactivity of Pd/Fe may be deactivated at a certain range of sulfide ion concentration, e.g., 10 mM. Sulfate is one of the most abundant ions in groundwater and leachate and it can be easily transformed naturally to sulfide. Therefore, sulfide and sulfate ion should be monitored to guarantee the containment of chlorinated volatile organic contaminants when Pd/Fe RGM is installed in a subsurface environment.

### 3.4. Effect of aging on reactivity of Pd/Fe RGM

It is also known that palladium does not react with oxygen in air at room temperature and does not tarnish in the air [24]. However, iron can react easily with water and oxygen in the air. If iron



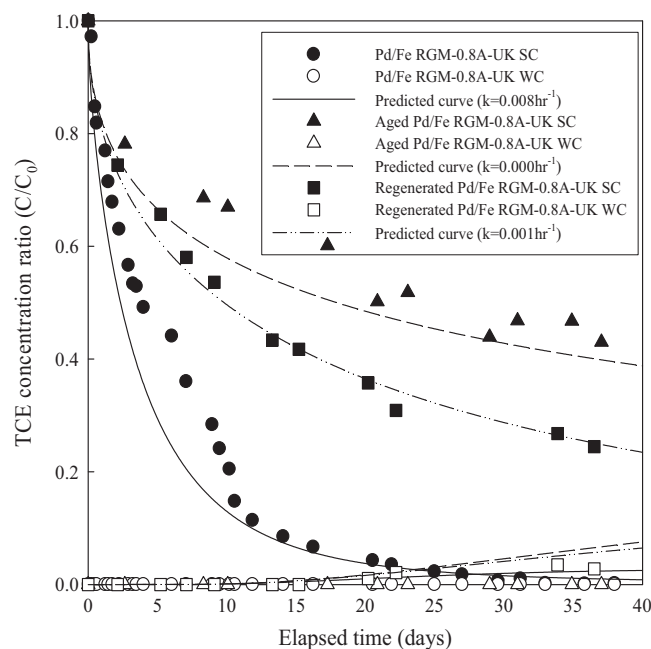
**Fig. 12.** Photoelectron spectra of Pd/Fe at (a) 0 mM  $\text{S}^{2-}$ , (b) 10 mM  $\text{S}^{2-}$  and (c) 50 mM  $\text{S}^{2-}$  (top: sulfur 2p orbital, bottom: palladium 3d orbital).



**Fig. 13.** Effect of sulfide ion (10 mM) on the mass transfer of TCE through Pd/Fe RGM (SC and WC in the legend refer to the solution chamber and water chamber, respectively).

oxide film formed during long-term storage or if shipping blocks the surface of the palladium catalyst against TCE, the reactivity of Pd/Fe RGM can be decreased. Therefore, two CDCA tests were conducted to verify the effect of long-term aging on Pd/Fe RGM. In order to age Pd/Fe RGM, it was stored at an atmosphere of 20 °C in a thermostatic room for three years. Compared to the result of fresh RGM, aged RGM lost its mitigation ability (Fig. 14). Permeation of TCE through aged RGM from the solution chamber to the water chamber occurred after 20 days, and the concentration in the water chamber reached 3 mg/L after 37 days elapsed. Meanwhile, fresh RGM dechlorinated all of the TCE in the solution chamber and the mass transfer of TCE from the solution chamber to the water chamber did not occur until 37 days. Oxidation for three years could damage the reactivity of Pd/Fe RGM significantly.

A CDCA test was also conducted with regenerated RGM which was prepared by immersing aged RGM in 2 N HCl solution for



**Fig. 14.** Effect of long-term aging and regeneration by acid treatment on the mass transfer of TCE through Pd/Fe RGM-0.8A-UK (SC and WC in the legend refer to the solution chamber and water chamber, respectively).

5–10 s. Iron oxide film formed on the surface of the palladium caused by aging was removed by acid. However, reactivity was partially, though not completely, recovered. The observed reaction rate constant of regenerated RGM was  $0.001 \text{ h}^{-1}$ , which was higher than aged RGM ( $k = 0.000 \text{ h}^{-1}$ ), and lower than fresh RGM ( $k = 0.008 \text{ h}^{-1}$ ). This result demonstrated that iron oxide film on palladium caused a decrease in the reactivity of RGM. However, the possible loss of Pd/Fe particles during acid treatment may be another reason why the reactivity of regenerated RGM is lower than that of fresh RGM.

#### 4. Conclusions

A batch immersion test using toluene and a student's *t*-test results to understand the mass transfer of CVOCs through Pd/Fe RGM proved that the effect of Pd/Fe coating on mass transfer parameters such as partition and diffusion coefficients is not significant. Therefore, it is available that the partition and diffusion coefficients evaluated from NGM are applied to mathematical model instead of the partition and the diffusion coefficients evaluated from RGM.

There are two feasible methods for increasing the CVOC mitigation ability of Pd/Fe RGM. One method involves applying Pd/Fe particles that have high Pd content and the other method involves increasing the Pd/Fe loading rate on RGM. According to batch tests, the latter is a better approach because the reactivity of Pd/Fe was not significantly enhanced as the Pd content increased and palladium was very expensive, while iron was relatively cheap. Furthermore, the reactivity of Pd/Fe coated on the surface of the geomembrane was smaller than that of the Pd/Fe powder by a factor of one hundred. Therefore, the amount of Pd/Fe required may be 100 times more than that expected through the batch test when Pd/Fe RGM was designed for field application.

It was verified that a sulfide ion concentration of more than 10 mM significantly deactivated Pd/Fe particles and immediately deprived Pd/Fe RGM of the mitigation ability. Since the reaction between Pd/Fe and sulfide ion is very rapid, the monitoring of sulfate ion and sulfide ion and other reductive agents should be conducted during the period of service to guarantee the performance of Pd/Fe RGM. Exposure to the atmosphere and oxygen for three years also deprived Pd/Fe RGM of the mitigation ability. The reactivity of aged Pd/Fe RGM can be regenerated to some extent by acid treatment, although it cannot be regenerated completely. Therefore, the protection of Pd/Fe RGM from oxidation should be provided during storage and shipping.

#### Acknowledgments

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (KRF-2008-314-D00239). The authors wish to thank the Engineering Research Institute and the Integrated Research Institute of Construction and Environmental Engineering at Seoul National University for their technical assistance.

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