

## 연성벽체 투수기를 이용한 흡세척 실험시 벽막을 통한 확산량 산정

박준범 · 김지상\*

서울대학교 공과대학 토목공학과

\*한국통신 선로기술연구소

## Membrane Diffusion through Flexible-Wall Permeameter for Soil Flushing Tests

Junboum Park · Jee-Sang Kim\*

*Department of Civil Engineering, Seoul National University*

*\*Korea Telecom Outside Plant Technology Laboratory*

### ABSTRACT

Solvent extraction using aqueous solutions is presumed as one of the most effective methods applicable to in situ conditions without excavation of contaminated soils. Laboratory permeameter soil flushing test is performed to describe the process of solvent extraction of contaminants absorbed on soil particles. When the permeameter tests conducted, diffusion of contaminants through the permeameter flexible-wall was considered for adjusting the remediation percentage. Input and output balance for concentration was well matched in the permeameter tests. Nitrobenzene diffused so excessively (approximately 75%) that it was not suitable for the permeameter desorption tests. No biodegradation was detected in the soil samples.

Key word : Permeameter, Membrane Diffusion, Soil Contamination, Organic Compounds

### 요 약 문

유기화합물로 오염된 지반을 정화하는 방법 가운데 화학약액을 주입하는 흡세척 방법은 매우 효과적인 것으로 알려져 있다. 이를 실험실에서 재현하는 경우에는 일반적으로 연성벽체의 주상실험을 실시하게 된다. 이때 유기화합물로 오염된 시편을 화학약액으로 세척하는 과정 중에서 일부의 유기화합

물은 연성벽체를 통하여 확산되고, 확산된 양은 화학약액에 의한 세척효율 산정시 반드시 고려하여야 할 것으로 나타났다. 연성벽막을 통한 확산량을 조사하고자 다섯가지의 유기화합물(페놀, 아닐린, 나이트로벤젠, 퀴놀린, 및 2나프톨)을 이용하여 breakthrough 시험을 실시하였다. 나이트로벤젠은 75% 이상이 벽막을 통하여 확산되었다. 나머지의 유기화합물은 25%이하의 확산량을 보였다. 실험중 생분해 효과는 관찰되지 않았다.

**주제어** : 투수기, 벽막확산, 흙의 오염, 유기화합물

## 1. INTRODUCTION

Since late 1970's, various remediation techniques have been developed and tested for the hazardous waste contaminated sites for cleanup. In most remediation process, physical removal or cutoff of the contaminant source is done initially for the preventing further contamination. Once the contamination source is successfully controlled, the next step of the process is to clean up the contamination plume or reduce the concentration of the contaminants by implementing various types of remediation techniques available for organic compounds. These techniques include: pump-and-treat technology<sup>1)2)3)4)</sup>, biodegradation<sup>5)6)7)</sup>, soil venting<sup>6)8)</sup>, soil excavation<sup>9)</sup>, and solvent extraction. But each treatment method has its own inherent disadvantages and limits; thus, the appropriate method should be carefully chosen depending on the geological conditions of the site and the characteristics of the contaminants. This paper focuses mainly on the in situ remediation of contaminated soils by soil flushing (or called 'aqueous solution extraction') thus investigating the feasibility of in situ treatment of soil to pro-

mote desorption of hazardous wastes, such that desorbed contaminants can be transported by induced hydraulic gradient and captured for wastewater treatment processing.

Desorption of contaminants from the soil for recovery and treatment can be archived through soil flushing. The contaminated soil is permeated or flooded with appropriate flushing solutions. The effluent solution is collected, treated, and recycled back into the soil. For the recovery of contaminated soil, a number of studies of the effectiveness of various aqueous solutions as decontaminants have been performed. The flushing aqueous solutions may include water, acidic or basic solutions<sup>10)11)12)</sup>, oxidizing compounds such as  $H_2O_2$ <sup>13)14)</sup> and surfactants (surface-active agents)<sup>15)16)17)</sup>. The principle of the removal technique through soil flushing with aqueous solutions relies on altering, in situ, either the surface chemistry of the soil particle or the nature of the sorbed organic compounds so that compounds will have been desorbed, transported through the liquid phase, and available for treatment. The effectiveness of soil flushing depends on the strength of the physico-chemical bonds between the soil and con-

taminant and the ability of the leaching solutions to break the bonds<sup>18)</sup>.

Laboratory modeling for the in situ remediation by soil flushing can be successfully achieved using permeameter column tests<sup>19)</sup>. Those tests were performed to evaluate the cleanup potential of each decontaminant solution. Although both fixed- and flexible-wall permeameters were constructed and tested, the flexible-wall permeameter described schematically in Fig. 1 was the most appropriate. The flexible-wall permeameter is preferred over the fixed-wall permeameter because it models effectively the in situ state of stress by applying confining pressure through the flexible membrane, which also minimizes side wall flow effects during the test. That volume of the decontaminant solution that flows along side wall channels may not effectively contact the contaminants in the soil sample and consequently cannot remediate the contaminated soil. The flexible wall permeameter allows for the application of mean effective stress within the soil mass that replicate those that would exist at a known depth in situ, provides for the control of the hydraulic gra-

dient within the sample, and is efficient in preventing leakage of fluid around the sample. Although the flexible wall permeameter can replicate the in situ condition it also has some problems. Diffusion through the flexible wall (the membrane) can affect the test results. The diffused amount should be measured and calculated for adjusting the test results. In this paper, the method to evaluate the amount of diffused contaminants was presented. Tests using flexible wall for permeameters should be adjusted depending upon the amount of diffused organics.

## 2. TEST MATERIALS

When in situ conditions are modeled in the laboratory, flexible wall membrane is commonly used to simulate the soil element subjected to confining pressure and soil stresses. Sometimes these membranes diffuse organic compounds, thus affect the remediation efficiency. Membrane diffusion amount should be properly estimated when solvent extraction remediation is modeled in the laboratory. Natural silty clay was prepared to blend with uniform, fine siliceous sand to make 65% sand, 20% silt, and 15% clay mixture, called test soil. Organic content of the test soil is 1.2%. The hydraulic conductivity of test samples is approximately  $10^{-6}$  -  $10^{-7}$  cm/sec. To exclude the effect of biodegradation, sodium azide (strong bactericide) was added to the test soil. Phenol, aniline, nitrobenzene, quinoline, and 2-naphthol were permeated into test soil. Those contaminants are listed on the US EPA toxic chemicals and

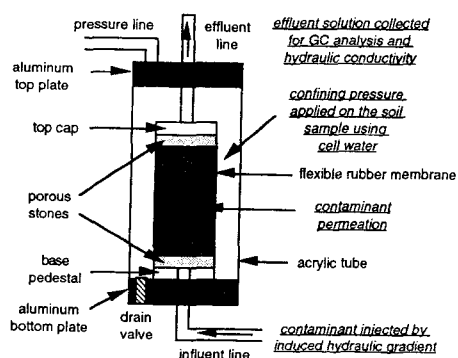


Fig. 1. Schematic Drawing...

found in many superfund sites. Phenols are single-ring compounds with a hydroxyl group directly bonded to an aromatic ring, Ar-OH. Aniline is weakly basic with an amine group ( $\text{NH}_2$ ) attached to an aromatic ring. Nitrobenzene is representative of nitro compounds, in which the aromatic compounds contain nitrogen as a derivative of nitric acid.  $\text{NO}_2$  attaches to an aromatic ring. Quinoline is a fused ring heterocyclic amine that contain both a benzene ring and a heterocyclic aromatic ring. 2-naphthol is a double ring structure phenol compound which includes hydroquinone, aminonaphthols, and bromonaphthols. The hydroxyl group attaches to the 2nd position of the two-benzene-ring structure.

### 3. MEMBRANE DIFFUSION TESTS

Effects other than desorption could cause the measured reductions in concentration of the contaminant in the soil. These effects are diffusion through the membrane and active biodegradation during permeation. The biodegradation effect was effectively eliminated by using sodium azide, but the effect of diffusion through the permeameter membrane could not be prevented. The effect of diffusion was investigated by balancing input and output concentrations. The following approximate procedure was used in this investigation.

Permeameter tests were conducted with the contaminant, at the standard concentrations of 50 mg/L and 100 mg/L, as the permeant. Compacted test soil samples were tested at 16% initial deionized water content at the level of

mean effective stress as was used in decontamination tests using hydraulic gradients in the range of 80 to 120. The weight of the input contaminant was estimated by multiplying the cumulative volume of collected effluent solution by the influent concentration of 50 mg/L or 100 mg/L. The weight of the output contaminant was divided into three categories, in which individual and independent weight estimates were made :

(1) Weight of contaminant in the effluent, estimated by the summation of each effluent volume multiplied by the concentration of the contaminant in mg/L in that volume of effluent solution.

(2) Weight of contaminant diffused through the sample membrane, determined by measuring the concentration of contaminant in the cell water at the conclusion of a test and multiplying by the volume of the cell water.

(3) Weight of contaminant remaining sorbed on the soil, estimated based on the Freundlich isotherm for each contaminant.

Summation of weights in each of the above three categories, which provides the output weight, can be compared with the initial input weights, or the weights can be converted to concentrations by dividing by the total volume of flow to yield  $C_0$ , the input concentration, and  $C$ , the output concentration, at any time during the test. Any appreciable difference in  $C$  and  $C_0$  was interpreted as being caused either by transient or steady state adsorption onto the soil, by biodegradation during the permeation process or by diffusion through the membrane.

Biodegradation was independently in-

investigated and shown to have essentially no effect by comparing results of effluent concentrations from permeameter tests in which sodium azide ( $\text{NaN}_3$ ) in the concentration of 0.5% by weight was added to the contaminating solution prior to permeation. Sodium azide is very effective in killing bacteria in the soil environment.

### 3.1 Phenol

The results for phenol are given in Fig 2. After flushing the test soil with 380 mL of phenol solution, relative concentration ( $C/C_0$ ) was still at about 0.75. That means phenol was being biodegraded or phenol was being adsorbed onto the test soil. However, the results with or without sodium azide remained virtually the same. Thus, it can be concluded that the soil was under going steady-state adsorption of phenol and/ or the permeant was diffusing through the membrane.

It can be seen in Fig. 2 that about 78% of the input phenol came out in the effluent after the permeation of 120mL of the contaminant. After the permeation of an additional 260mL, for a total permeation of 380mL (0.38L), the relative concentration remained the same. At that point the concentration of contaminant in the cell fluid was measured and found to be 10% (based on total volume of flow, not cell fluid volume). Since no biodegradation was indicated from the sodium azide test, the remaining 12% of the input existed in pore space of the soil or was adsorbed onto the soil particles. This is a total of  $(0.12) \times (50 \text{ mg/L}) \times (0.38\text{L}) = 2.28 \text{ mg}$  of phenol adsorbed. Based on the Freundlich

isotherm for phenol, the maximum adsorption is  $120 \text{ g} \times 0.02 \text{ mg/g} = 2.40 \text{ mg}$  (X/M value is about 0.02 g/g 50 mg/L). Hence, steady state adsorption was still underway after permeation of 380 mL. No adsorption was detected on the test equipment including influent and effluent tubing.

The implication of this result relating the permeameter tests is that the remediation percentage for each contamination should be adjusted according to the amount of diffused concentration measured during the tests. In the case of the permeameter desorption test for phenol, 5% (one-half of the diffusion in the permeameter tests) was reasonably assumed because (1) the 10% diffusion in this permeameter test was measured in a permeameter adsorption test in which fresh contaminant solution was being supplied at a constant concentration so that the diffusion is more active than in permeameter desorption tests, (2) most of the contaminants are in the pores in the diffusion adsorption test, and these contaminants moving in the pores are more easily diffused than the contaminants adsorbed onto soil particles for desorption tests, and (3) the average diffusion

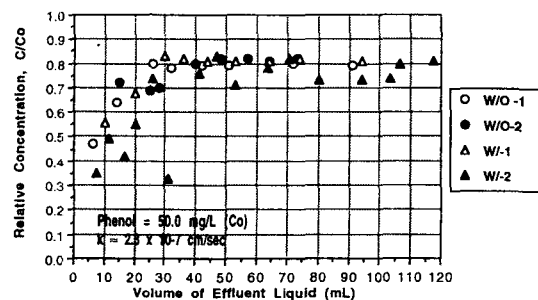


Fig. 2. Permeameter Adsorption Tests on Phenol, With (W/) or Without (W/O) Sodium Azide

percentage of the phenol-statistical check was 3.2%, and the largest diffusion percentage found in the tests was 4.8%, thus 5% is a safe assumption value for phenol diffusion. For the other contaminants, one-half of the diffusion adsorption results was also used for the diffusion of the desorption permeameter tests.

### 3.2 Aniline

The results for aniline are given in Fig. 3. About 80% of the input came out as effluent concentration, and 15% diffused through the mem-

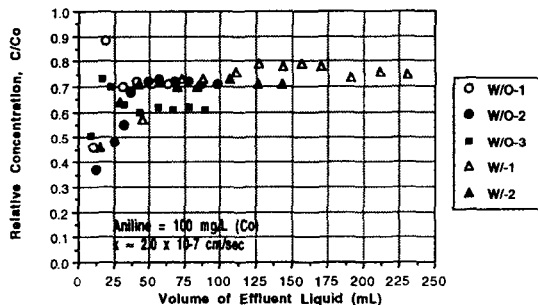


Fig. 3. Permeameter Adsorption Tests on Aniline, With (W) or Without (W/O) Sodium Azide

brane. No biodegradation is implied in Fig. 3. Only about 5% was adsorbed onto the test soil after 230mL of effluent solution. The adsorbed amount is  $0.05 \times 100 \text{ mg/L} \times 0.23 \text{ L} = 1.15 \text{ mg}$ , which is still smaller than the maximum possible adsorption amount inferred from the Freundlich isotherm. Steady state adsorption was still occurring after permeation of 230mL. Diffusion of 7% is considered appropriate for the permeameter desorption tests.

### 3.3 Nitrobenzene

Results of the tests on nitrobenzene are given in Fig. 4. Diffusion of nitrobenzene was found to be much higher than the other contaminants. About 75% of the initial concentration was de-

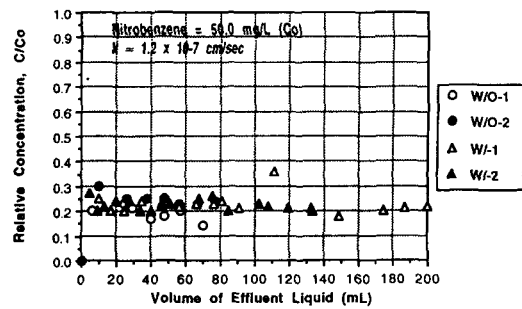


Fig. 4. Permeameter Adsorption Tests on Nitrobenzene, With (W) or Without (W/O) Sodium Azide

tected in the confining water after passage of 200 mL of effluent liquid. 20% was found in the effluent liquid. Only 5% was loaded onto the test soil, or 0.5 mg. The maximum possible absorption amount is 4.8 mg, based on the Freundlich isotherm data. Thus, nitrobenzene was still being adsorbed when 200 mL of the nitrobenzene solution had passed. Since the

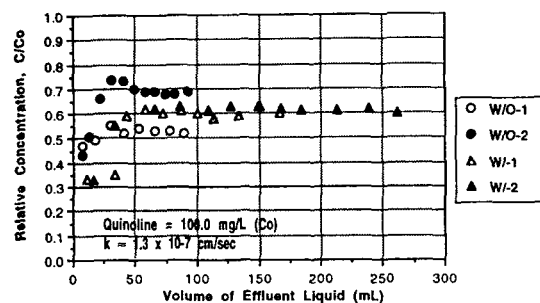


Fig. 5. Permeameter Adsorption Tests on Quinoline, With (W) or Without (W/O) Sodium Azide

amount of diffusion was excessive, nitrobenzene was not suitable for the permeameter desorption tests, even through biodegradation is not likely to happen.

### 3.4 Quinoline

The results for quinoline are shown in Fig. 5. The distortion of input concentration was 60% to effluent liquid concentration, 25% to diffusion, and 15% to steady state adsorption after 260 mL of effluent liquid flushing. Again, no biodegradation was detected. Quinoline has a relatively high diffusion value, hence remediation percentage for quinoline permeameter test should be corrected for diffusion of 12%.

### 3.5 2-Naphthol

The results for 2-naphthol are shown in Fig. 6. The accumulated amount of 2-naphthol in the confining water was only 2%, the effluent liquid had about 23%, and the adsorbed amount was 75% after flushing with 110 mL. The actual amount adsorbed on the soil is  $0.75 \times 100$

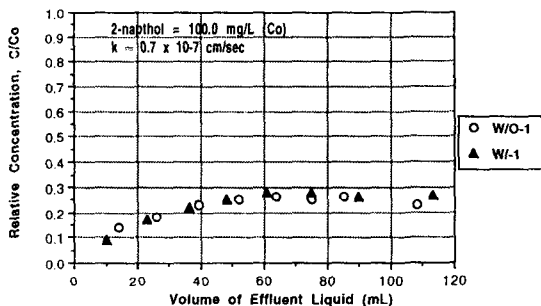


Fig. 6. Permeameter Adsorption Tests on 2-Naphthol, With (W/) or Without (W/O) Sodium Azide

mL  $\times$  0.11 L = 8.25 mg. The maximum possible loading amount with 100 mg/L solution is  $120 \text{ g} \times 70 \text{ g/g} = 8400 \text{ g} = 8.40 \text{ mg}$ . Thus, the sample was close to breakthrough. Once the soil is fully loaded with the contaminant (exhaustion), the effluent concentration increases substantially, a condition called breakthrough. For some contaminants, it takes a very long period of time to reach breakthrough, and breakthrough was not reached in any of these tests. In these tests, only the balance of input and output, diffusion effect, and biodegradation of the contaminants were investigated. For 2-naphthol, only 1% is considered for diffusion.

## 4. CONCLUSION

In this paper, the method to evaluate the amount of diffused contaminants was presented. Tests using flexible wall for permeameters should be adjusted depending upon the amount of organic compounds that diffused through the flexible wall of the permeameter. Diffusion of the contaminants through the flexible-wall in the permeameter was measurable and should be considered for adjusting the remediation percentage. Diffusion of 10%, 15%, 75%, 25% and 2% are considered appropriate for phenol, aniline, nitrobenzene, quinoline, and 2-naphthol, respectively, in the permeameter adsorption tests. Nitrobenzene diffused so excessively that it was not suitable for the further permeameter soil flushing tests. In the case of the permeameter desorption test for each contaminant, one-half of the diffusion amount obtained in the permeameter adsorption test was reasonably as-

sumed. Input and output balance for concentration was well matched in the permeameter tests. No biodegradation was detected in the soil samples.

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