

ESTIMATION OF MASS TRANSFER COEFFICIENTS USING AIR-LIQUID INTERFACIAL AREA IN POROUS MEDIA

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ABSTRACT

Accidental spillages or leakages of organic compound within the environment, released as non-aqueous phase liquid (NAPL), result a widespread contamination of subsurface soils and groundwater. In such multi-phase flow system in porous media, interphase mass transfer mainly governs the overall transport processes that occur in the interface between the two fluid phases. Air-liquid interfacial area plays a significant role in mass transfer during the remediation of contaminated soil in unsaturated zone. Usually interphase mass transfer coefficient is expressed as a lumped parameter together with the specific interfacial area. In this paper, interphase mass transfer coefficients are estimated separately using the air-liquid interfacial area based on soil characteristics curve. A series of NAPL volatilization experiments was carried out for different NAPL saturation (13.8%~71%) and pore gas velocities (0.1~2 cm/sec) for different porous media. Three uniform size glass beads ($d_{50}=0.25\text{mm}$, 0.50mm, 0.75mm) and a medium grain silica sand ($d_{50}=1.4\text{mm}$) were selected as the porous media and Toluene was chosen as single component NAPL. The results revealed that the mass transfer coefficient increases with pore gas velocities and grain sizes. Dependency of mass transfer on pore gas velocity was found to be linear. Mass transfer coefficient was gradually decreased with saturation for uniform size glass beads but sharply decreased in case of silica sand for NAPL saturation of 40-50%.

Key Words : Mass transfer, Interfacial area, NAPL, Soil, Volatilization

INTRODUCTION

Increased production of chemicals during the past several decades has led to numerous accidental spills and leakage of organic compounds within the environment and this has resulted a widespread contamination of subsurface soils and groundwater. These chemicals are released as non-aqueous phase liquids (NAPLs) and are slightly soluble in

water. They are migrated downward through the tortuous path of the subsurface soil in the unsaturated zone. Before reaching to groundwater some portion of these chemicals are entrapped in unsaturated zone due to capillary action of the pores and distributes according to the pore sizes. This capillary force is inversely related to pore diameter. At first, NAPL will be entrapped in the smallest

pores with highest capillary rise which is referred to residual saturation. Largest pores will be filled up by NAPL with lowest capillary rise which is referred to capillary fringe. There is a variation of saturation in between these two zones. This variably saturated zone is sometimes called as funicular or transition zone. However, these NAPLs entrapped in unsaturated zone may persist as long time contamination of subsurface soil and groundwater.

Many of these chemicals are found to be volatile organic compounds (VOCs). The transport and the fate of these VOCs in the subsurface is a problem of great importance. It is increasing to propose innovative strategies for subsurface remediation of VOCs. Among them, soil vapor extraction (SVE), also known as soil venting, vapor stripping, or in situ volatilization, is an accepted and cost-effective technique for the removal of VOCs from the contaminated soils¹⁻⁵. During SVE, advective vapor phase flow is induced within the subsurface to enhance the volatilization of NAPL entrapped in unsaturated zone. This technique has led to an interest in vapor-phase mass transport processes. For VOCs that readily partition into the vapor phase, this technique may be the economical methods for subsurface restoration. Interphase mass transfer is important processes that occur during the application of remediation technique in contaminated soil or groundwater. In multi-phase flow system mass transfer mainly govern the overall transport processes that occur in the interface between the two fluid phases. In order to clean-up the sub-surface soil and groundwater by SVE system it is necessary to understand the NAPL-vapour phase mass transfer process.

To date, the role of NAPL-vapour phase mass transfer in residual saturation zone was described⁶ and the mass transfer in variably

saturated zone was quantified⁷. Researchers usually expressed the interphase mass transfer as a lumped parameter with specific interfacial area^{6,8-11} because of inaccessibility to this parameter in air-liquid interface for a long time. Many efforts have been made to quantify the air-liquid interfacial area both by theoretical¹²⁻¹⁶ and experimental method¹⁷⁻²¹. Anwar et al.⁷ was the first to express the actual mass transfer coefficient during NAPL volatilization in porous media. In their study, the mass transfer coefficient was separated using interfacial area calculated from the surfactant mass balance²⁰.

In this paper, actual mass transfer coefficient is estimated⁷. Only difference is that the air-liquid interfacial area used here is estimated from soil characteristics curve instead of surfactant mass balance which is readily available or easily obtainable for any types of porous media. First, NAPL volatilization experiments were carried out in different porous media for heavy contaminated zone and lumped vapor phase mass transfer coefficient was estimated under steady state condition for different flowing phase velocity. Second, actual interphase mass transfer coefficient was estimated using corresponding air-liquid interfacial area. The air-liquid interfacial area can be calculated using soil characteristics curve²².

MATERIAL AND METHODS

A single component contaminant, Toluene (purity>99%; supplied by Yoneyama yakuhin kogyo co. ltd., Japan) was selected as NAPL for the volatilization experiments because of its common presence in subsurface environment with a relatively high vapor pressure. It has a density less than water and hence it is called LNAPL (light non-aqueous phase liquid). Three different sizes of glass beads and one silica sands were chosen as the porous media for experiments because of their high air permeability. The

properties of the porous media are shown in **Table 1**. A peristaltic pump was used to induce advective airflow in the system. All the tubings were made of Teflon.

Table 1 : Properties of the porous media used.

Porous medium	Average diameter d_{50} (mm)	Bulk density ρ_b (g/cm ³)	Porosity ϕ_t	Saturated hydraulic conductivity K_h (cm/sec)
Glass bead	0.25	1.55	0.387	0.019
Glass bead	0.50	1.53	0.373	0.023
Glass bead	0.75	1.51	0.368	0.026
Silica sand	1.4	1.47	0.39	0.034

NAPL Volatilization Experiments

A series of one-dimensional volatilization experiments were carried out in a horizontal Teflon column of 20 cm long and 1.6 cm diameter as shown in **Fig. 1**. The column was kept horizontal in order to get the uniform distribution of NAPL inside the porous media during the experiments. Two brass tubes of same diameter were attached at two ends keeping an outlet and inlet for gas phase flow. Column was packed with porous medium in small increments and was tapped each time. This procedure ensured the uniform packing of the glass beads in the column. In order to induce advective airflow at the influent end of the column, a peristaltic pump was calibrated ($r^2=0.99$) for each porous medium. Based on the targeted saturation, a predetermined volume of NAPL was added to the medium by a syringe and was shaken to get uniform distribution of NAPL inside the porous medium. The column was horizontally kept on a weigh meter to evaluate the NAPL mass removed during the volatilization process gravimetrically. The influent end was connected with the air pump and effluent end was connected to exhaust hood by Teflon tube via a sampling port prepared by septum. A gas tight syringe was used to collect the gas phase effluent sample. Gas sample of

2ml was immediately injected to a gas chromatograph (GC-14B, Shimadzu Corporation, Kyoto, Japan) equipped with a packed column (SBS-120, 12% Shincarbon A 80-100; manufactured by Shinwa-kako co. ltd., Japan) and a flame ionization detector (FID) for analysis. Chromatogram results were standardized with vapor phase concentration of NAPL at the NAPL-vapor interface taken as the saturated vapor concentration.

NAPL saturation was varied from 13.8%~71%. For each NAPL saturation experiment, pore gas velocity was varied between 0.1~2 cm/sec as pore gas velocity is found to be less than 2cm/sec in a typical SVE system²³. Each experiment with one NAPL saturation and different pore gas velocities were run for 42~62 minutes. All experiments were carried out under steady state conditions at a constant room temperature of $25 \pm 1^\circ\text{C}$. The amount of NAPL volatilized during each experiment was determined both gravimetrically and through the integration of chromatogram results as a function of flow rate and time. It was confirmed from the analysis that only 1.5~7% of NAPL was removed during steady state volatilization. Here steady state condition refers to the early achievement of a uniform effluent concentration during the

volatilization process prior to significant contaminant removal and alteration of the entrapped NAPL distribution. So it was reasonable to assume that NAPL saturation remain constant for one experiment and

small removal of NAPL in steady state volatilization did not substantially alter the specific interfacial area between NAPL and vapour phase over the course of the experiments.

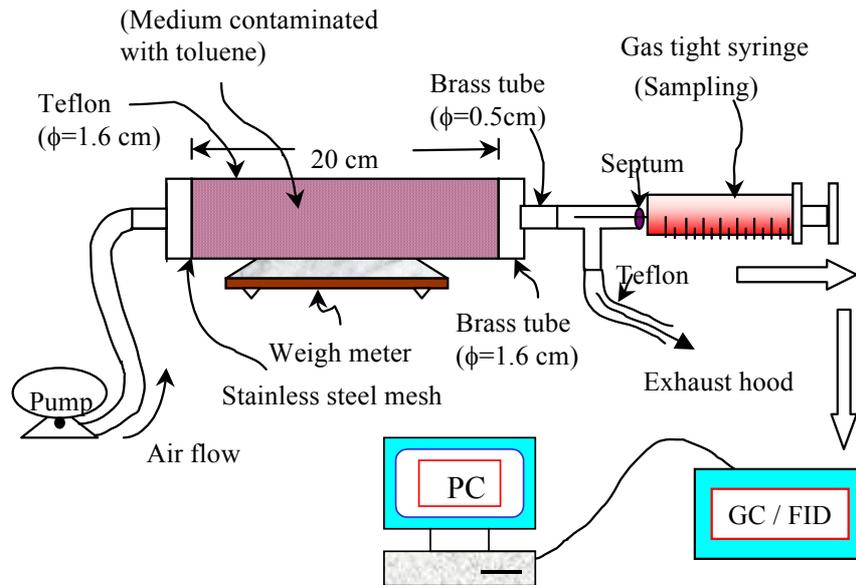


Fig. 1 : Experimental setup for NAPL volatilization in porous medium.

Estimation of air-liquid interfacial area

Air-liquid interfacial area (a_i) is an important parameter in the subsurface hydrology that describes the pore scale distribution of air and liquid inside the porous media. In order to quantify this parameter, a theoretical model using soil characteristics curve was developed introducing a term "hydraulic radius" for the pores inside the medium²². This term diminishes the effect of any shape factors for the pores. The derivation becomes a simple expression which needs only drainage soil characteristics curve. The air-liquid interfacial area (a_0) can be calculated by:

$$a_0 = \frac{\rho g}{\gamma} \int_0^{\theta_g} \psi(\theta_g) d\theta_g \quad (1)$$

where ψ is the suction head of liquid (cm) and function of volumetric gas content θ_g

(cm^3/cm^3), γ is the surface tension of the liquid (N/m). The soil characteristics curve (ψ - θ) was developed for all the porous media. A column composed of several PVC rings (each 5cm long and 10cm diameter) were packed with porous media under water saturated condition and water was allowed to drain out maintaining a constant water table for 24 hrs. The suction head (ψ) was measured as the distance from the water table and moisture content (θ) in each ring was measured gravimetrically.

RESULTS AND DISCUSSION

Air-liquid interfacial area

The soil characteristics curves developed for different porous media are shown in Fig. 2. At first, ψ - θ curve was subdivided into small gas content increments of $d\theta_g=0.005\text{cm}^3/\text{cm}^3$ and corresponding

suction head ($d\psi$) was located in the curve. Air-water interfacial area was estimated for different water content using equation (1) and shown in **Fig. 3** for different porous media. Most of the pressure saturation relationships only describe the region where both fluids are continuous. It does not give any information below the residual saturation. Thus the interfacial area calculated using equation (1) is strictly valid only for variable region of liquid saturation. The interfacial area must pass through a maximum and return to zero as liquid saturation tends to zero. It may be explained as the saturation

increases from zero, interfacial area should also start from zero and pass through a maximum value and return to zero at the saturated condition. But interfacial area below this residual saturation has not yet been studied. Moreover, for a particular porous medium in real case, residual saturation also remains constant for a specific liquid, as soil characteristics curve is unique for that porous medium. But in this study, we are interested to estimate the mass transfer coefficient in variable saturated zone where interfacial areas are also varies with saturation.

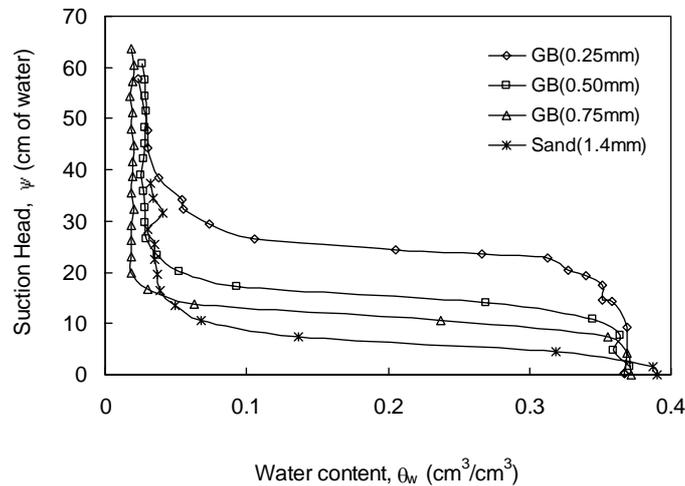


Fig. 2 : Measured ψ - θ curves for different porous media.

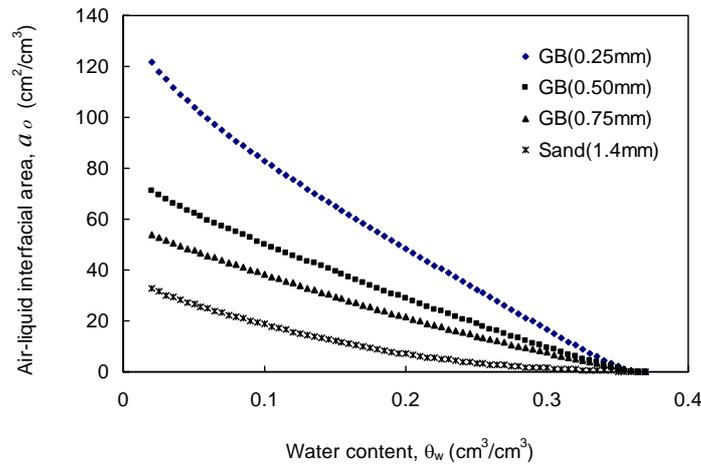


Fig. 3 : Estimated air (or gas)-liquid interfacial area using equation (1)

Estimation of interphase mass transfer coefficients

Measurements from each volatilization experiment consisted of effluent concentrations, NAPL saturation and pore gas velocity. In order to characterize NAPL-vapor phase mass transfer first, normalized vapor phase effluent concentration (C_g/C_i) was plotted with pore gas velocity and NAPL saturation. These results are presented in **Fig. 4** and **Fig. 5** respectively for 0.25mm glass beads medium. Results revealed that C_g/C_i has significant deviation from unity, which represents the departure from local equilibrium assumption (LEA). This indicates that the NAPL-vapour phase mass transfer is a rate-limited process. Similar situation was also observed by Wilkins et al.⁶ where they found that NAPL-vapour phase mass transfer was highly dependent on pore gas velocity with significant deviation from local equilibrium assumption. Kearl et al.²⁵ also observed these deviations from unity and reported that rate-limited mass transfer was found to be occurred only for extremely high gas flow rates, corresponding to pore gas velocities greater than 2cm/sec. This pore gas velocity is commonly unusual in field soil vapor extraction system²³. However, they used NAPL saturation in their investigation as the residual one. Here it is extended for higher NAPL saturation range and mass transfer process showed much more deviation from LEA, which provides an opportunity to assume non-equilibrium NAPL volatilization in unsaturated porous media for the experimental conditions used here.

Assuming that linear driving force model can adequately represent interphase mass

transfer in unsaturated porous media⁶⁻⁷, this expression can be incorporated in one-dimensional mass balance equation for the transport of organic component in the vapor phase. The one-dimensional advective-dispersive-reactive equation used for the analyses of column effluent data is as follows⁶⁻⁷:

$$\phi_g \frac{\partial C_g}{\partial t} = \phi_g D_g \frac{\partial^2 C_g}{\partial x^2} - \phi_g v_g \frac{\partial C_g}{\partial x} + k_0 (C_i - C_g) \quad (2)$$

where, D_g is the hydrodynamic dispersion or effective gaseous molecular diffusion coefficient, v_g is the interstitial or pore velocity of the gas phase, k_0 is the lumped mass transfer coefficient and ϕ_g is the gas filled porosity. Mass transfer coefficient k_f is lumped together with the specific interfacial area and presented as lumped parameter ($k_0 = a_0 k_f$). For low gas velocities, usually found in SVE, gas dispersion in soil is primarily due to gas diffusion through the porous media. Hence, it appears that diffusion predominates over mechanical dispersion for gas phase transport at low velocity. Models using Fick's law to describe gas phase diffusion have been used successfully to simulate gas phase advective transport of solute in soil columns²⁶. The diffusion rate through a porous medium is less than that through free air because of the reduced cross sectional area available for movement and the increased path length brought about by the tortuosity of the pore channels. Many correlations exist for determining tortuosity of air filled pores in porous media. In this study, modified form of Millington's model was used for the calculation of tortuosity factor²⁶.

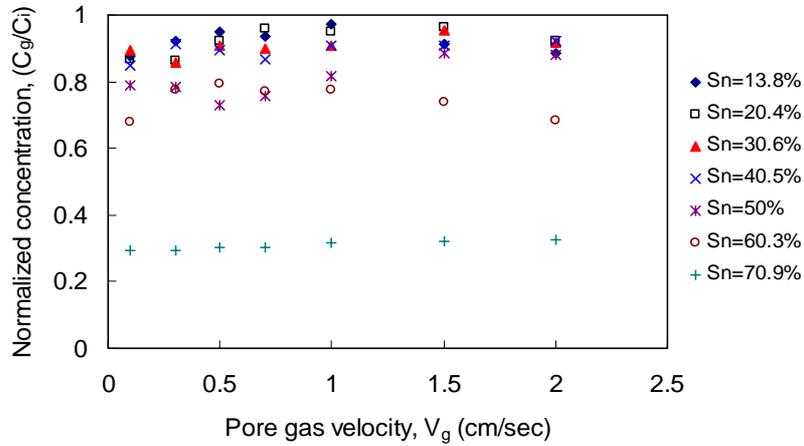


Fig. 4 : Characterization of normalized vapor phase concentration with pore gas velocity for 0.25mm glass beads.

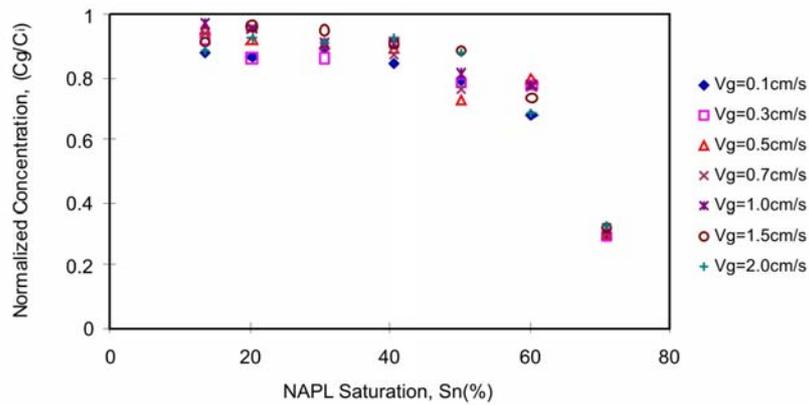


Fig. 5 : Trend of normalized vapor phase concentration with NAPL saturation.

Under the steady-state experimental conditions ($\partial C_g/\partial t=0$) and boundary conditions $\{C_g(0)=0 \text{ and } \partial C_g/\partial x (x=L) = 0\}$, the solution of equation (2) is as follows²⁷:

$$\frac{C_g(x)}{C_i} = 1 - \exp\left[\left(\frac{x}{2D_g}\right)\left(v_g - \sqrt{v_g^2 + (4D_g k_0 / \phi_g)}\right)\right] \tag{3}$$

Equation (3) was used to estimate lumped mass transfer coefficient, k_0 from the effluent vapor phase concentration. The mass transfer coefficient was then calculated from k_0 and the corresponding air-liquid interfacial area (Fig. 3). Here, air-liquid interfacial area was calculated from the soil characteristic curve

which was developed using water as fluid. It was assumed that the interfacial areas between the NAPL and gas phases were the same in different liquid-gas systems having identical liquid saturations⁷. Clearly, this assumption is valid only when the contact angles of NAPL-solid-air and water-solid-air systems are the same for two different liquid-gas systems. This situation could be established when the solid phase is strongly NAPL-wet or water-wet. Drainage soil characteristics curves were developed from saturated condition so the solid phase can be assumed as strongly water-wet. In the case of NAPL volatilization experiments, the solid

phase was made partially saturated with toluene from dry conditions. Those solid grains contacted with toluene to make the system unsaturated were also strongly toluene-wet. Thus, it may be considered that the air-liquid interfacial areas are similar in both systems for the same liquid saturations.

Results on mass transfer coefficients revealed that it depends on the flow velocity, geometry of the porous medium and the properties of fluid. The actual mass transfer coefficient k_f was plotted with pore gas velocity v_g for different NAPL saturation for different porous media. **Fig. 6** shows the variation of mass transfer coefficient with pore gas velocities for different porous media for NAPL saturation of 40%. These results indicate that the mass transfer increases with velocities and grain sizes. Mass transfer mainly occurs in the interfaces between the fluid phases. The velocity component parallel to the interface does not contribute to the mass transfer. Only the velocity component perpendicular to the interface is responsible for mass transfer. Dependency of mass transfer on velocity was found to be linear.

Mass transfer coefficients again are plotted with saturation for different porous media and shown in **Fig 7**. Mass transfer

coefficient was found to be gradually decreased with saturation for uniform size glass beads. In case of uniform glass beads the specific area available for transferring mass from NAPL to vapor phase also decreased gradually with saturation. But in case of natural sand (medium), mass transfer coefficients were found to be sharply decreased between the NAPL saturation of 40-50%. From ψ - θ curve, it was observed that residual saturation increased with decreasing grain size for uniform glass beads which is consistent with capillary theory. But significantly higher residual saturation was observed in the case of silica sand. This can be explained by the presence of more irregular particle shapes and higher porosity of the natural sand. Increased particle irregularity and porosity may provide more available surface area and pore space. Again, it may have several types of pore shape and the particle itself may have many crevices and grooves. The sharp decrease in mass transfer may be attributed to this surface area. Most of the crevices and grooves may be filled up with NAPL in this saturation of 40-50% and sharply decreased the available area for transferring mass and hence decrease the mass transfer coefficient sharply.

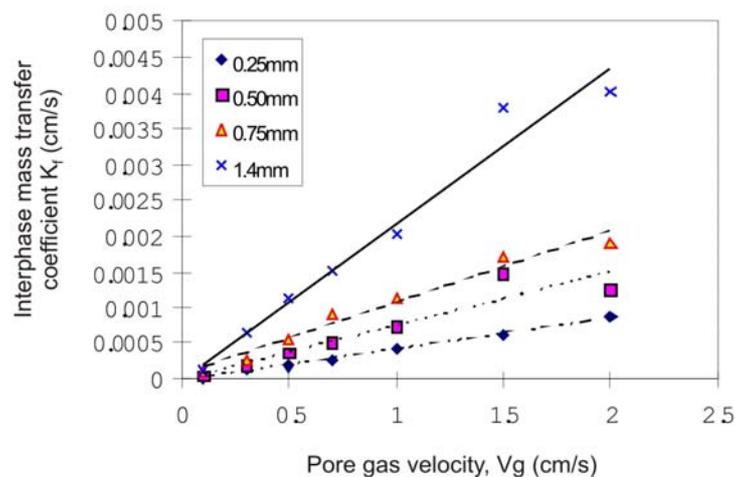


Fig. 6 : Interphase mass transfer coefficient varies with pore gas velocities

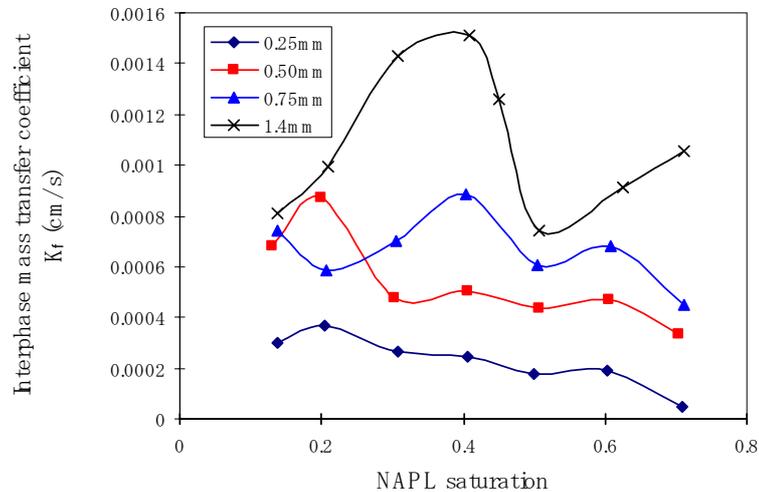


Fig. 7 : Interphase mass transfer coefficient varies with NAPL saturation

CONCLUSION

A series of NAPL volatilization experiments was carried out for different porous media and the actual interphase mass transfer coefficients were evaluated using corresponding air-liquid interface area. Specific air-liquid interfacial area was calculated from soil characteristics curve. Results revealed that the mass transfer coefficients depend on the flow velocity, geometry of the porous medium and the properties of fluid. These results indicate that the mass transfer increases with velocity and grain size and it shows linear relationship with pore gas velocities. Mass transfer coefficient was also found to be gradually decreased with saturation for uniform size glass beads but sharply decreased in case of silica sand for the NAPL saturation of 40-50%.

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