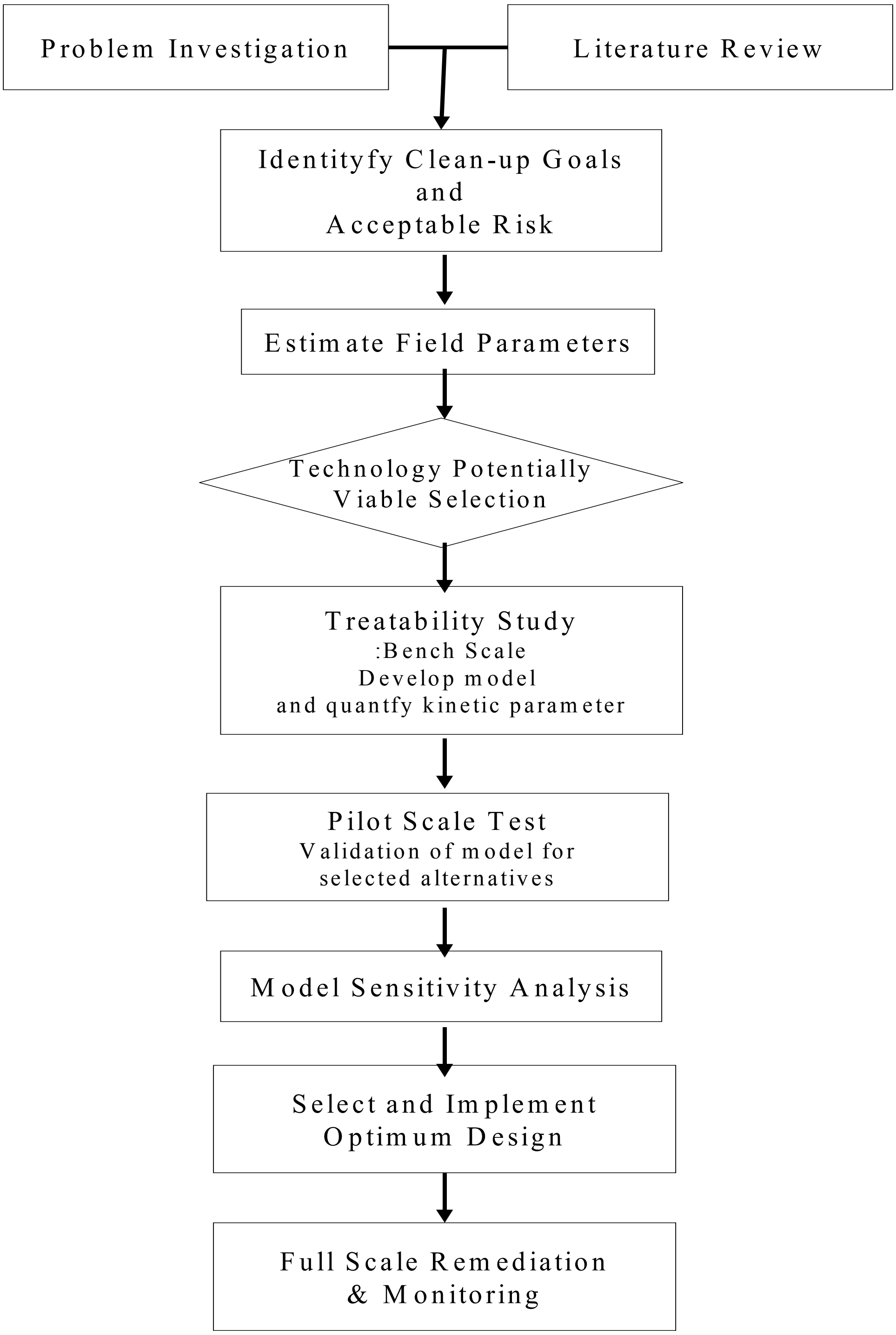
Geoenvironment Engrg. Ⅱ

Remediation Technology Selection Process



1. In-situ Bioremediation

- True in-situ technique

→ Actual reactions occur below ground

(destruction of OC)

$$\text{Xenobiotics}\quad \underset{\substack{\text{substrate}\\ \text{e donor}}}{\underline{HC}} + \underset{\substack{\text{Terminal}\\ \text{election}\\ \text{acceptor}}}{\underline{O_2}} + \text{Nutrients} \xrightarrow[\substack{\text{native}\\ \text{bacteria}}]{} CO_2 + H_2O + \text{More Bacteria}$$

> " You don't bring remediation to a site
> Laboratory controlled bacteria"
> "You only enhance the natural reactions that are already occuring"

▣ Three Main Topics

① Biochemical Reactions
② Natural Remediation (Attenuation)
③ Enhanced Bioremediation
(Oxygen + Nutrients) acceleration of biodegradation

1) Biochemical Reactions

① Microorganisms (MO_s)

; bacteria, fungi, algae, protoza and metazoa, virus.

→ bacteria + fungi for B.R.
원핵세포 진핵세포

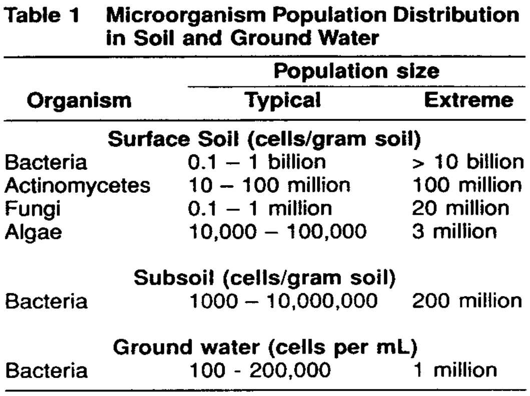


Table 1 Microorganism Population Distribution in Soil and Ground Water

Organism	Population size Typical	 Extreme
	Surface Soil (cells/gram soil)	
Bacteria	0.1 – 1 billion	> 10 billion
Actinomycetes	10 – 100 million	100 million
Fungi	0.1 – 1 million	20 million
Algae	10,000 – 100,000	3 million
	Subsoil (cells/gram soil)	
Bacteria	1000 – 10,000,000	200 million
	Ground water (cells per mL)	
Bacteria	100 - 200,000	1 million

Counting Methods

① direct count → 죽은 세포도 셀 수 있다.

② viable count (agar plate count)   ① > ②

colony forming

Biomass 추정

① 전환계수 적용법

$(0.847 \sim 8.6) \times 10^{-13}$ gC/㎛^{3}

Soil sample C를 측정

→ 전환계수 이용, 세균부피 구함

→ ex) 구균 $V = \frac{\pi}{6} D^3$

간균 $V = \frac{\pi}{6} W^2 \left(L - \frac{W}{3} \right)$

② 단백질 양 조사

③ ATP의 양

④ DNA의 양

⑤ 생리학적 분석

- 미생물의 호흡결과 발생하는 CO_2의 양을 측정 → 개체수

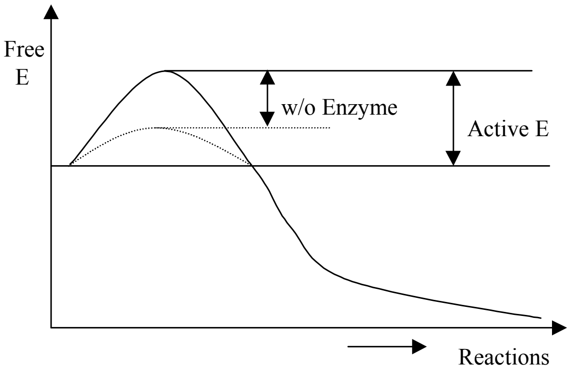
Substrate + TEA + ATP → Oxidized substrate + Reduced TEA + More ATP

| ATP : Adenosine Triphosphate

| (에너지원 energy currency of the cell)

└ ⇒ Enzymes (효소, 생체촉매)

: 생체내에서 여러 생화학 반응을 적절한 온도/pH/산소의 조건에서 일어나게 하는 물질.



B.R
- Aerobic Biod. 호기성 — O_2 ← more efficient rate faster
- Anaerobic Biod. 혐기성 생분해 — NO_3^- , SO_4^{2-} , CO_3^{2-}

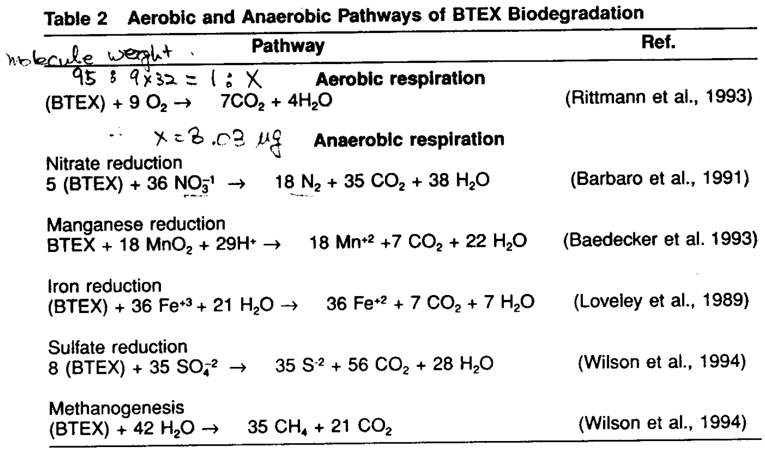


Table 2 Aerobic and Anaerobic Pathways of BTEX Biodegradation

molecule weight ·
95 : 9×32 = 1 : X
∴ x = 3.03 μg

Pathway	Ref.
Aerobic respiration	
(BTEX) + 9 $O_2 \rightarrow$ 7CO_2 + 4H_2O	(Rittmann et al., 1993)
Anaerobic respiration	
Nitrate reduction 5 (BTEX) + 36 $NO_3^{-1} \rightarrow$ 18 N_2 + 35 CO_2 + 38 H_2O	(Barbaro et al., 1991)
Manganese reduction BTEX + 18 MnO_2 + 29$H^+ \rightarrow$ 18 Mn^{+2} +7 CO_2 + 22 H_2O	(Baedecker et al. 1993)
Iron reduction (BTEX) + 36 Fe^{+3} + 21 $H_2O \rightarrow$ 36 Fe^{+2} + 7 CO_2 + 7 H_2O	(Loveley et al., 1989)
Sulfate reduction 8 (BTEX) + 35 $SO_4^{-2} \rightarrow$ 35 S^{-2} + 56 CO_2 + 28 H_2O	(Wilson et al., 1994)
Methanogenesis (BTEX) + 42 $H_2O \rightarrow$ 35 CH_4 + 21 CO_2	(Wilson et al., 1994)

O_2 NO_3^- Fe^{3+} SO_4^{2-} CO_3^{2-}

←

Faster / energy efficient

Metabolic Products	CO_2 / H_2O	CO_2 / N_2	CO_2 / Fe^{2+}	CO_2 / H_2S	CO_2 / CH_4

Environmental Factors.

- Temperature : T↑ - R↓
- Soil

함수비 w = 30% ~ 90% optimal condition

pH 6.5 ~ 7.5

Mixed communities have grater capacity to biodegrade Xenobiotics due to the grater diversity of the MO population.
(∵Complete mineralization of Xenobiotics may rely on enzyme systems produce by multiple species)

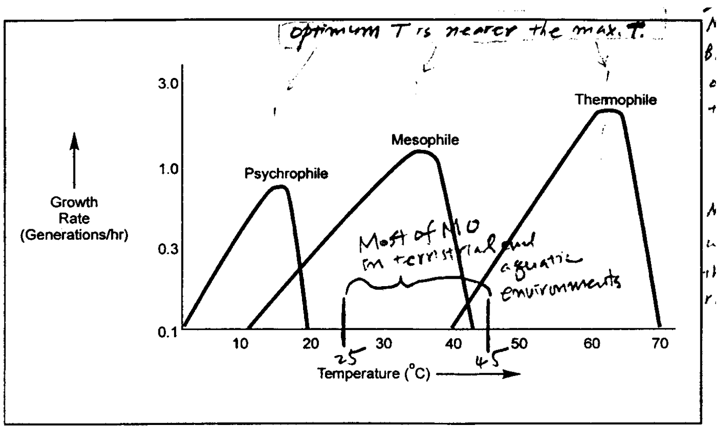


Figure 3 Temperature effect on growth rate. (From Brock, T.D., *Biology of Microorganisms*, Englewood Cliffs, NJ: Prentice-Hall, 1979. With permission.)

※ Enhanced Bioremediation

add oxygen(or nitrogen) + Nutrients

Anaerobic Biodegradation	+	cometabolities	+	aerobic → anaerobic
$\bar{e}$ acceptors rather then oxygen.		in order to produce enzymes that degrade target compounds.		env.

- aerobic

; add sugar

Bacteria using sugar will deplete all oxygen and nitrate available and lower redox potential where dehalogenation reaction occur.

"Do nothing technique"
= Natural attenuation or Intrinsic Biodegradation.

※ cometabolities
; Bacteria uses methane, benzene ring compounds for degradation of chlorinated hydrocarbons.
Reactions occur under aerobic cond.
→ secondary contaminant
→ Priority
→ under study

"Oxygen delivery"

①	air	5 - 10 mg/L
②	oxygen	20 - 40 mg/L
③	H_2O_2	50 - 100 mg/L

※ Kinetics of Biodegradation
Bacteria의 성장/소멸 과정
Microbial growth and decay stages during bioremediation.
(cell mass conc. vs time)

in a Limited Environment (limited supply of nutrients carbon and $\overline{e}$ acceptor)

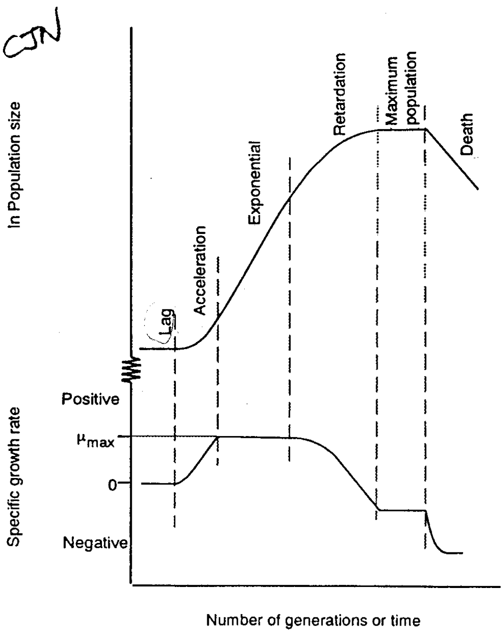


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Figure 8.2 Phases of growth occurring during a closed culture growth cycle in a limited environment, showing the changes in the organism's specific growth rate. Source: Bull, 1974

- Lag phase : where MOs are initially exposed to a chemical it takes them some time lag to get used to the environment in which the chemical is present.
- Acceleration phase : starting to propagate, the MOs synthesize enzymes required for the degradation.
- Exponential phase : cell mass conc. - time curve depicts an exponential function.

  cell growth occurs by cell division called binary fission.

  미분법

※ exponential function

$$\frac{dx}{dt} = \mu X \qquad (1)$$

X : Microbial population size

μ : specific growth rate

$X = C\ e^{\mu t}$

$X = X_0\ e^{\mu t}$ (initial cond. $t=0$; $X=X_0$)

For binary fission

$X = X_0\ 2^m$ (m : division times)

$$\begin{aligned}\log X &= \log X_0 + m \log 2 \\ &= \log X_0 + \frac{t}{k} \log 2\end{aligned}$$

Differentiating w. r. t. t gives

$$\frac{1}{X}\frac{dX}{dt} = \frac{\log 2}{k} = \mu \qquad \therefore k = \frac{\log 2}{\mu}$$

t : total time elaped since the begining of the division.

k : time required for one cell division.

- Retardation phase (Declining)

The growth starts to retard mainly due to the fact that chemical used for growth has been depleted.

- Stationary phase

Cell propagation is balanced by cell decay

- Decay (Exponential death) phase

The number of living cells decreases exponentially, when cell growth has ceased completely.

- Lynch & poole (1979)

begining of the exp. phase through the max. pop.

$$\frac{dX}{dt} = \mu_{\max} X\left(1 - \frac{X}{X_F}\right)$$

X : population size

$\mu_{\max}$: max growth rate

X_F : max population size

When X is small

$$\frac{dX}{dt} \rightarrow \mu_{\max} X$$

→ basic exp. growth.

→ at the end of retardation phase

→ max. pp.

· Biofouling → pumping injection no more available

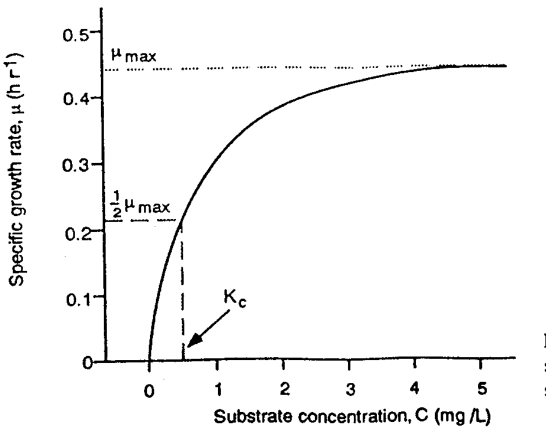


Figure 8.3 Relationship between specific growth rate and growth-limiting substrate concentration. Source: Lynch and Poole, 1979.

※ 3 main Expressions for modeling B.D Kinetics. (For GW aquifer)

① Monod Kinetics

For aerobic B.D. and assuming that oxygen and contaminants are the only substates required for growth, the changes in cont. and oxygen due to B.D is given by

$$\Delta C = M_t \mu_{\max} \frac{C}{K_c + C} \frac{O}{K_0 + O} \Delta t$$

$$\Delta O = M_t \mu_{\max} F \frac{C}{K_c + C} \frac{O}{K_0 + O} \Delta t$$

where, M_t : Biomass conc. (mg/L)

K_c : conc. of the growth-limiting substrate at 1/2 M_{max} (mg/L)

C : conc. of the growth-limiting substrate (mg/L)

F : $\frac{\text{Oxygen consumed}}{\text{Cont. consumed}}$; yield ratio

ex) $C_6H_6 + 15/2\ O_2 \rightarrow 6CO_2 + 3H_2O$

12×6+6 7.5×32

= 78 = 240

$$\rightarrow F = \frac{240}{78} \simeq 3$$

Advection - Dispersion Eq.에 대입하면

$$\frac{\partial C}{\partial t} = \nabla \cdot (D\nabla C - vC) - M_t \mu_{max} \frac{C}{K_c + C} \frac{O}{K_0 + O}$$

$$\frac{\partial O}{\partial t} = \nabla \cdot (D\nabla O - vO) - M_t \mu_{max} \frac{C}{K_c + C} \frac{O}{K_0 + O}$$

② <u>First order decay</u> Kinetics

unlimited cond. → (unlimited amount of cont. + oxygen)

$$C = C_0 e^{-kt}$$

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

③ Instantaneous Model

Assumes that the rate of utilization of the cont. and oxgen consumed by MOs is very quick → instantaneous

$$\triangle C_R = -\frac{O}{F}$$

ΔC_R : change in cont. conc. due to B.D.

O : oxygen conc.

ex) $C_{benzene}$ = 12.0 mg/L

O = 8.0 mg/L for 10 days

ⅰ) Monod Kinetics

K_0 = 0.1 mg/L (borden et al 1986)

K_c = 22.16 mg/L , μ_{max} = 93 day^{-1} (Tabak et al 1990)

M_t = 0.05 mg/L

$$\Delta C = 9.3 \times \frac{12C}{12 + 22.16} \frac{8}{8 + 0.1} \times 10 \times 0.05 = 1.59\ mg/L$$

Resulting Benzene conc. = 12 - 1.59 = 10.4 mg/L

most conservative.

ii) First order decay Kinetics

t_t = 5 days (Howard et al. 1991)

$$k = \frac{0.653}{5} = 0.1386\ day^{-1}$$

$$\therefore \text{ Resulting Conc.} = C_0 e^{-kt} = 12e^{-0.1386 \times 10} = 3.0 \text{ mg/L}$$

iii) Instantaneous Model

$1C_6H_6 : 7.5O_2$

$$F = \frac{240}{78} \approx 3$$

$$\Delta C_R = \frac{O}{F} = \frac{8}{3} = 2.67 \text{ mg/L}$$

∴ Resulting C = 12 - 2.67 = 9.33 mg/L

For 1-D Adv.-Disp.

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - \overline{v_x} \frac{\partial C}{\partial x} - \underline{R_c}$$

Biological decay

unlimited cond. $R_c = \mu C = \frac{\partial C}{\partial t}$ *C: substate conc.*

limited cond. $R_c = \mu_{max} \left(\frac{C}{K_c + C} \right) M_t$

Instantaneous (slug) source

without Biodegradation.

$$C(x, t) = \frac{M}{2\sqrt{\pi t D_x}} \exp\left[\frac{-(x - vt)^2}{4tD_x} \right]$$

with Biodegradation.

$$C(x,\ t) = \frac{M}{2\sqrt{\pi\, t D_x}} \exp\left[-\mu t - \frac{-(x - vt)^2}{4\, t D_x} \right]$$

ex) $M = 100\ \mathrm{g/ft^2}$

$x = 100\ \mathrm{ft}$, $t = 100\ \mathrm{days}$

$v = 1\ \mathrm{ft/day}$, $D_x = 10^{-4}\ \mathrm{ft^2/day}$

$\mu = 0.05\ \mathrm{day^{-1}}$

$C(100,\ 100) = \underline{28.2\ \mathrm{g/ft^3}}$ without Biod.

$C(100,\ 100) = \underline{2.0\ \mathrm{g/ft^3}}$ with Biod.

Continuous source

without Biod.

$$C(x,\ t) = \frac{1}{2} C_0\, erfc\left[\frac{x - vt}{2\sqrt{D_x t}} \right]$$

with Biod.

$$C(x,\ t) = \frac{1}{2} C_0 \exp\left\{ \left(\frac{x}{2\alpha_x} \right) \left(1 - \sqrt{1 + \frac{4\mu\alpha_x}{v}} \right) \right\} \times erfc\left[\frac{x - vt\left(1 + \frac{4\mu\alpha_x}{v}\right)^{1/2}}{2(\alpha_x v\, t)^{1/2}} \right]$$

2. Vapor Extraction and Bioventing

Inducing air flow in the subsurface using an above ground vacuum pump/blower system.

◆ Soil Vapor Extraction (SVE)

- Definition :

SVE removes volatile and some semi-volatile contaminants from the vados zone through the application of a vacuum using a system of well vents placed in the unsaturated zone. The gas removed from the soil may be then discharged directly to the air or more likely, to an off-gas treatment process. Vacuum pumps induce a pneumatic pressure gradient in the subsurface, resulting in an air flow field about an extraction well.

- Mechanism :

Gas-phase contaminants are removed via advective air flow entering extraction wells. Removal of gas-phase contaminants results in pore-scale concentration grade. This induces volatilization and contaminant diffusive transport into the advective air flow. Higher vapor pressure component are removed first. The residual soil concentration gradually becomes richer in the less volatile compounds. Consequently, as a result of compositional changes, the vapor concentration of the contaminants and mass removal rates decrease with time.

- Compounds Removed by SVE

Contaminants with vapor pressures greater than 0.5 mmHg. This includes VOCs and some semi-volatiles such as diesel fuel, kerosene and heavy naphthas. (Grasso pp. 4-6)

1 atm = 760 mmHg = 101.325 KPa

물	20℃	17.5 mmHg	0.023 atm
	100℃	760 mmHg	1 atm

1. Vapor pressure > 0.00066 atm (0.05 mmHg)
2. k > 10^{-4} cm/s

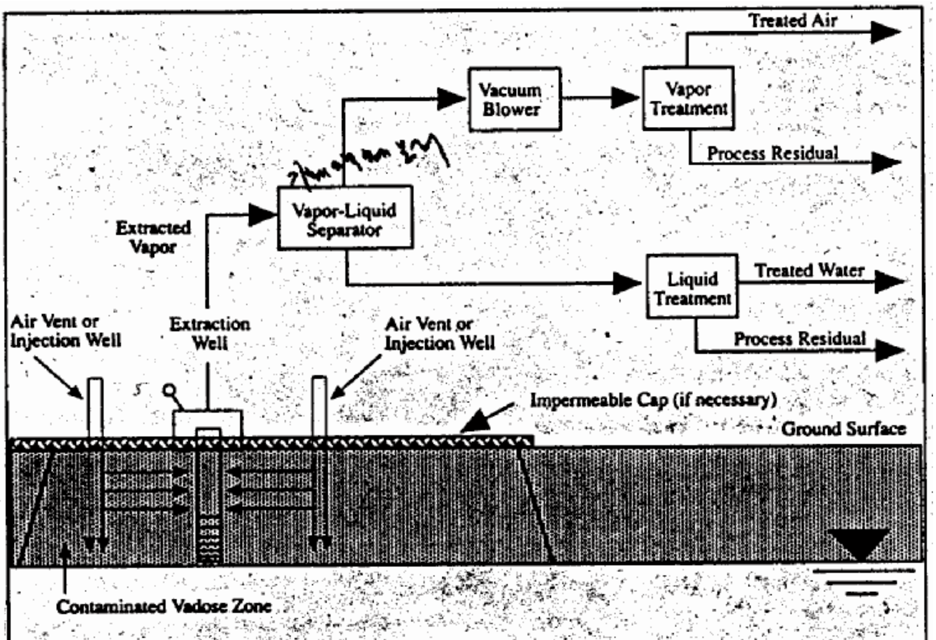


FIGURE 1.3
Generic Soil Vapor Extraction System
Soil Vapor Extraction

1.2 Compounds Removed by SVE

With the SVE process, it is feasible to treat contaminants with vapor pressures greater than 0.5 mm Hg[2]. This includes volatile organic compounds (VOCs) and some semi-volatile compounds, such as diesel fuel, kerosene, and heavy naphthas.

Volatiles

- Toluene
- Ethylbenzene
- Chloroform
- Tetrachloroethylene(PCE)
- Dichloroethylene(DCE)
- Cyclohexane
- Methyl isobutyl ketone(MIBK)
- Acetone
- Tetrahydrofuran
- Carbon tetrachloride
- Tichloroethane(TCE)
- Benzene
- Xylenes
- Hexane
- Methylene chloride
- Trichloroethylene(TCE)
- Ethyl acetate
- Methyl ethyl ketone(MEK)
- Methanol
- Pyridine
- Dimethylfuran
- Chlorobenzene

Semivolatiles

- Dichlorobenzene(DCB)
- Chlorobenzene
- Trichloropropane

Hydrocabons

- Jet fule
- Diesel
- Kerosene
- Gasoline
- Stoddard solvent
- Heavy naphthas

Table 1.1. Selected Gasoline Components and Their Chemical Properties

Compound	M_w* (g/mole)	T_b (1 atm)** (C)	P_v^o 20 C† (atm)	C_{est}†† (mg/L)
n-pentane	72.2	36	0.57	1700
n-hexane	86.2	69	0.16	560
trichloroethane	133.4	75	0.132	720
benzene	78.1	80	0.10	320
cyclohexane	84.2	81	0.10	340
trichloroethylene	131.5	87	0.026	140
n-heptane	100.2	98	0.046	190
toluene	92.1	111	0.029	110
tetrachloroethylene	166	121	0.018	130
n-octane	114.2	126	0.014	65
chlorobenzene	113	132	0.012	55
P-xylene	106.2	138	0.0086	37
ethylbenzene	106.2	138	0.0092	40
m-xylene	106.2	139	0.0080	35
o-xylene	106.2	144	0.0066	29
styrene	104.1	145	0.0066	28
n-nonane	128.3	151	0.0042	22.0
n-propylbenzene	120.2	159	0.0033	16
1,2,4 trimethylbenzene	120.2	169	0.0019	9.3
n-decane	142.3	173	0.0013	7.6
DBCP	263	196	0.0011	11
n-undecane	156.3	196	0.0006	3.8
n-dodecane	170.3	216	0.00015	1.1
naphtalene	128.2	218	0.00014	0.73
tetraethyllead	323	dec.@200C	0.0002	2.6
gasoline[1]	95		0.34	1300
weathered gasoline[2]	111		0.049	220

[1] Corresponds to "fresh gasoline" defined in reference 1

[2] Corresponds to "weathered" gasoline defined in reference 1

* M_w - molecular weight

** T_b(1 atm) - compound boiling point at 1 atm absolute pressure

† C_{est} - equilibrium vapor concentration - see equation 52

†† P_v^o 20 C - vapor pressure measured at 20 C

(1) Contaminant Partitioning in the Subsurface

Subsurface Distribution of released contaminants.
(by their physical properties and soil conditions)
In pore water 용해 liquid
In vapor 기체 gas ⇒ termed "Partitioning"
adsorbed to soil
In pure NAPL (Non-Aqueous Phase Liquid) → or Free Form

Transfer of the contaminants b/w phases is affected by the relative affinity of the contaminant to each phase can be evaluated using the partition coefficients to the various phase equilibrium concentration ratio of the cont. in each phase.
The most effective remediation will create the subsurface conditions that will drive the interphase transfer fowards the phases that allow for the most efficient mass removal.

→ SVE : Driving the contaminants to the vapor phase most effective mass removal phase.

Under most soil conditions, contaminant partitioning is the vadose zone (w/o residual NAPL) is shown below.

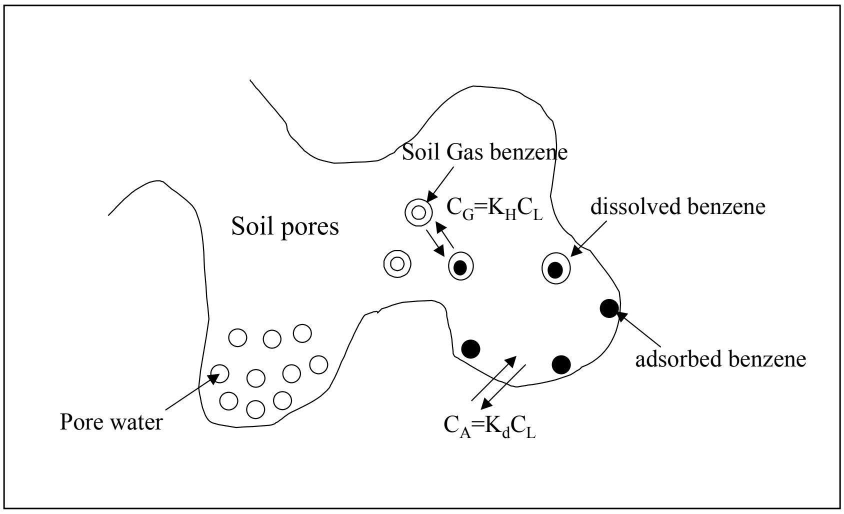


Figure 3 Equation schematic

$$C_T = P_b C_A + \Theta_L C_L + \Theta_G C_G \qquad (1)$$

C_T : 흙의 단위 부피에 존재하는 양

$P_b C_A$: 흙에 흡착된 양 (solid phase)

$\Theta_L C_L$: 물에 녹아있는 양 (dissolved, liquid phase)

$\Theta_G C_G$: 기체상으로 존재하는 양 (gas phase)

(1), (2), (3) → (4) and express in terms of gas phase only

$$C_G = K_H \cdot C_L$$

$$C_A = K_d \cdot C_L = K_d \cdot \frac{C_G}{K_H}$$

$$\therefore\ \Theta_G \frac{\partial C_G}{\partial t} + \frac{\Theta_L}{K_H}\frac{\partial C_G}{\partial t} + P_b \frac{K_d}{K_H}\frac{\partial C_G}{\partial t} = \Theta_G D_{ij}\frac{\partial}{\partial x_i}\frac{(\partial C_G)}{(\partial x_j)} - \Theta_G v_i \frac{\partial C_G}{\partial x_i}$$

Basic Governing Eq.

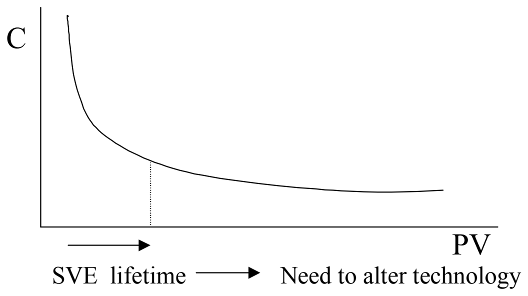
$$\boxed{R\Theta_G \frac{\partial C_G}{\partial t} = \Theta_G D_{ij}\frac{\partial}{\partial x_i}\frac{(\partial C_G)}{(\partial x_j)} - \Theta_G v_i \frac{\partial C_G}{\partial x_i}} \qquad (5)$$

↓

where, $R = 1 + \frac{\Theta_L}{\Theta_G K_H} + \frac{P_b K_d}{\Theta_G K_H}$ $\qquad (K_d = f_{oc} \cdot K_{oc})$

Mathematical Advective-Dispersive Model for SVE

⇒ but not account for the long tailing effect that is observed in field application



Air flow capability ← by solving Jacob's method.

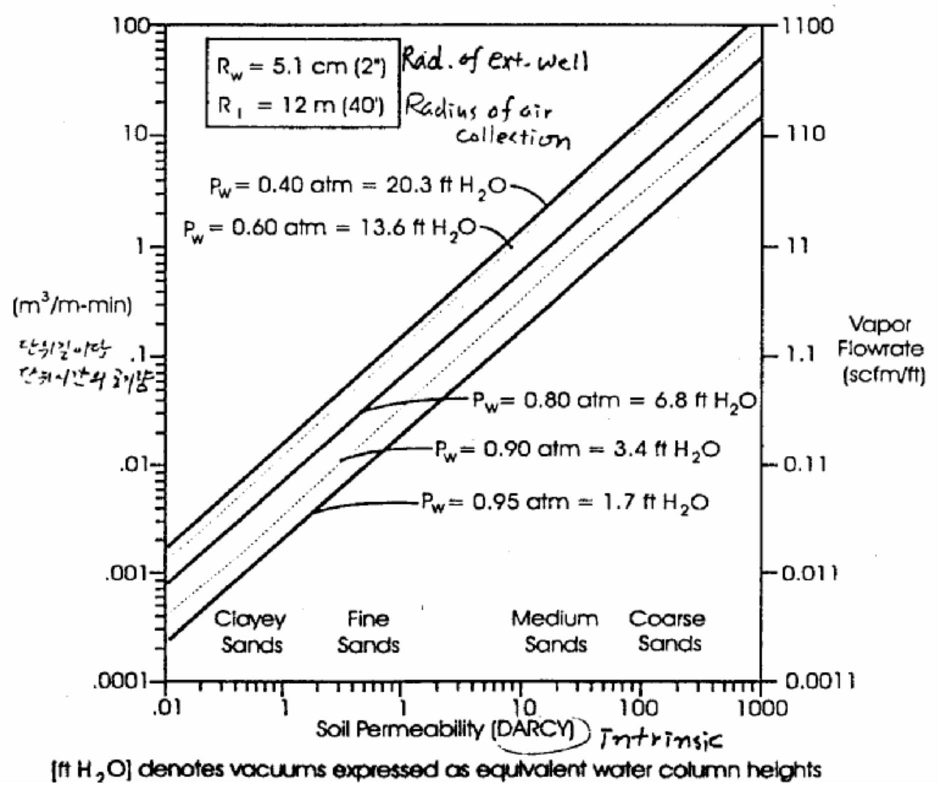


Figure 5 Air flow generation plot.

(2) Conditions for SVE

contaminants ...... vapor pressure, solubility, Henry's Law const
other molecular structure properties

soil .... porosity, soil moisture, adsorption, topography, site homogeneity, permeability(air)

*** contaminant Properties**

① Vapor Pressure

- used to estimate the tendency of a compound to volatilze and partition into the gaseous state
- defined as the pressure exerted by the vapor at equilibrium with the liquid phase(NAPL) of the compound in the system at a given temperature (mm Hg)
- The higher the vapor pressure, the more it is amenable to vapor extraction
  If it is less volatile(lower vapor pressure), it will have the greater seliance on Bioventing.
- For mixtures of compound(i.e. gassoline),

$$Pi^{*} = Xi \cdot Ai \cdot Pi^{0}$$

where, Pi^{*} = equilibrium partial pressure of i in the organic mixture
Xi = mole fraction of component i in the organic mixture (%)
Ai = activity coefficient of i in the organic mixture
(dilute sol. $M<10^{-3}M$ → $Ai = 1$, 하지만 농도증가하면 $Ai < 1$)
Pi^{0} = vapor pressure of i as a pure compound

② Solubility

- Partitioning is a important factor → remediation과 직결
- defined as the maximum amount of a constituent that will dissolve in pure

water at a specified temperature

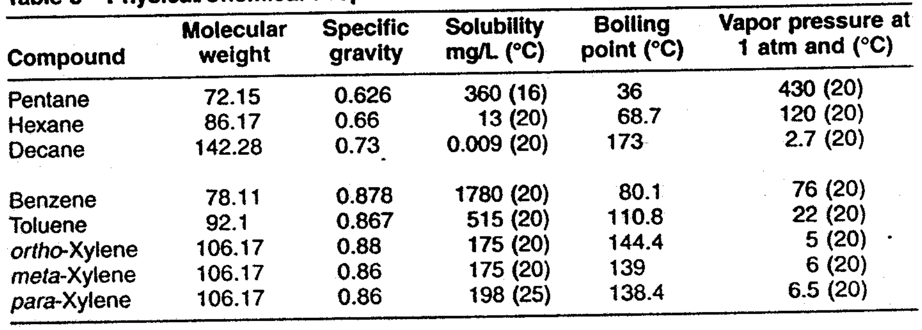
- For mixtures(gasoline),

$$Ci^{*} = Xi \cdot Ai \cdot Ci^{0}$$

Ci^{*} : equilibrium conc. of i in the org. mixture

Ci^{0} : equilibrium solute conc. of i as pure compound

Table 3 Physical/Chemical Properties of Selected Petroleum Hydrocarbons



Compound	Molecular weight	Specific gravity	Solubility mg/L (°C)	Boiling point (°C)	Vapor pressure at 1 atm and (°C)
Pentane	72.15	0.626	360 (16)	36	430 (20)
Hexane	86.17	0.66	13 (20)	68.7	120 (20)
Decane	142.28	0.73	0.009 (20)	173	2.7 (20)
Benzene	78.11	0.878	1780 (20)	80.1	76 (20)
Toluene	92.1	0.867	515 (20)	110.8	22 (20)
ortho-Xylene	106.17	0.88	175 (20)	144.4	5 (20)
meta-Xylene	106.17	0.86	175 (20)	139	6 (20)
para-Xylene	106.17	0.86	198 (25)	138.4	6.5 (20)

Note: Compiled from various sources.

- under most vapor extraction scenarios, the vadore soils is relatively moist(10~14% by cot.) and contaminants are generally dissolved in the soil pore water.

③ Henry's Law

- describe solubility of gas in a liquid at equilibrium

$$P_g = H\ C_L$$

where, P_g : (vapor) partial pressure of the gas (atm)

H : Henry's const.

C_L : concentration of chemical in the liquid(solubility) or

$$H = C_{sq} \ / \ C_{si}$$

C_{sq} : compound conc. in the vapor phase at the water/vapor interphase

C_{si} : compund conc. in the water phase at the water/vapor interphase

ex. Acetone → very volatile, but very soluble in water
→ mostly dissolved in pore water
→ not well remediated by SVE but by Bioventing
(Figure7 : Henry's Law constant 참조)

※ Temperature

Higher temperatures in the vadose zone enhance volatilization, which improves operation of SVE. Increased Temp. also enhances biodegradation, the rate of desorption by weakening the adsorption bonding.

※ Larger, bulkier (branched chains) molecules travel more slowly within soil micopores and tend to adsorb more strongly to soil surfaces.

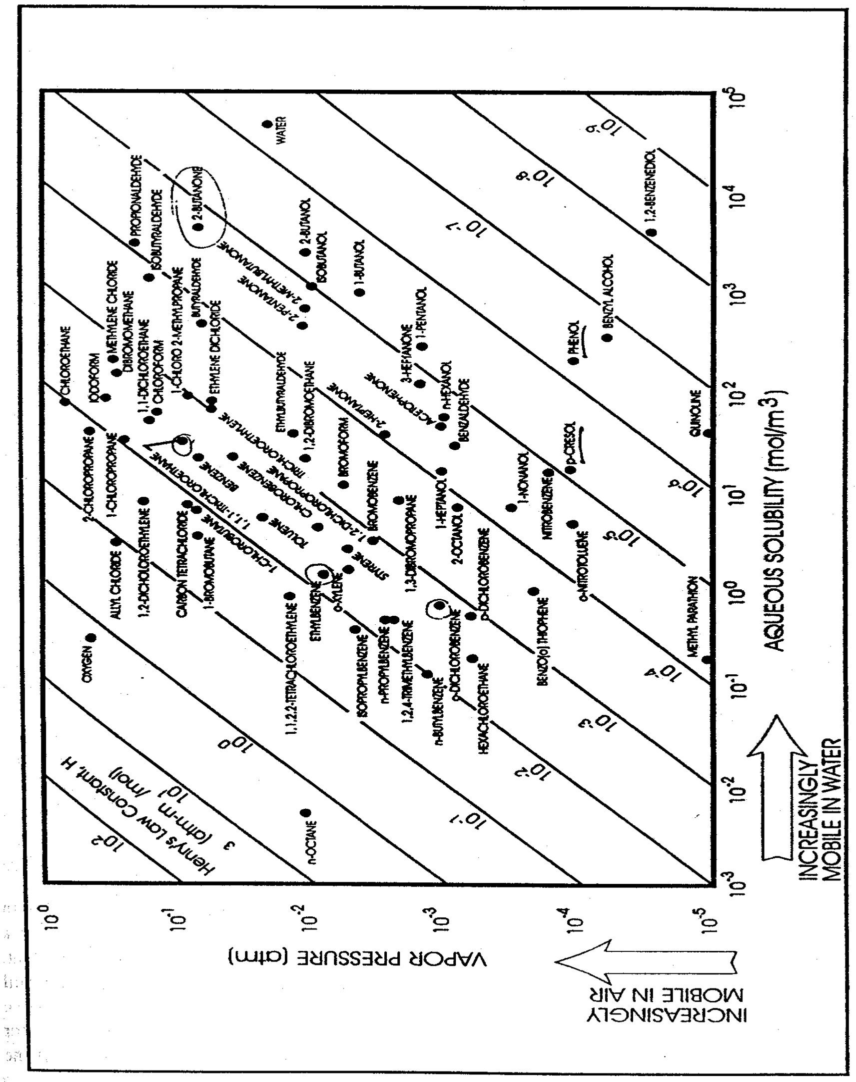


Figure 7 Henry's Law constant as a function of vapor pressure and solubility. (After Lyman et al., 1982).

* **Properties of Soil**

Soil-Air Permeability → key characteristic parameter

① Soil Porosity

Decreasing soil porosity → soil-air permeability decreasing

→ reducing the efficiency of SVE

(SVE can be employed when the soil has its s-a permeability)

② Soil Adsorption (on clay or Natural organic matter)

natural organics
Organic compounds on to
mineral clay surface sites

→ increase the immobile fraction of the consts.
→ reducing the efficiency of SVE

Clays, net negatively charged surface, are excellent adsorbent of positively charged cations or very polar organic cations.

Most organic contaminants are more easily adsorbed to the soil than they are desorbed. It therefore takes much longer and requires more energy to remove the contaminants from the subsurface than it does to spill them.
→ slow down the SVE process than would be predicted by simple adsorption isotherm data.

③ Soil Moisture (Moisture content or Deg. of saturation)

Drier soils ahve greater availability of pore area, which permits higher airflow(desirable). [하지만, 너무 dry 하여지면, soil-cont. bonding이 강하여진다. SVE 효과 감소 (말라 붙는 상황). 이때의 함수비를 critical moisture content (monolayer coating이 가능한 양의 물)]

High soil moisture content limits air advection travel rate pathways by occupying void space. Movement of VOCs in gas phase is much faster than in liquid phase.
→ Dewatering (Demoisturing) will be helpful for increasing the efficiency of SVE.

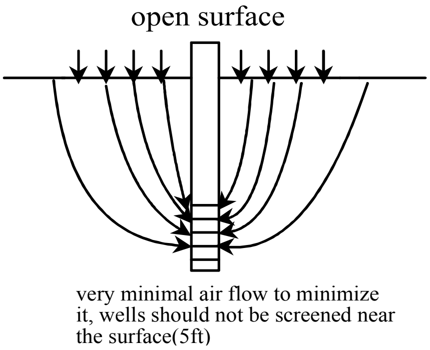
④ Site Surface Topography

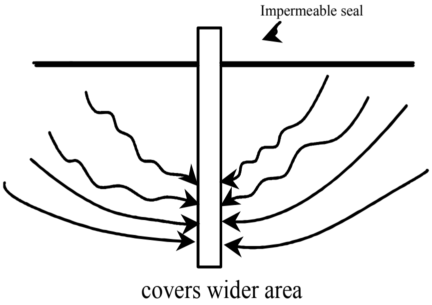
Impermeable surface (Pavement or concrete, Buildings plastic membranes.....)

First zone → minimize the infiltration of raincoater to the vadose zone

some control over soil moisture.

Second, eliminates the possiblity of extraction well short circuiting.



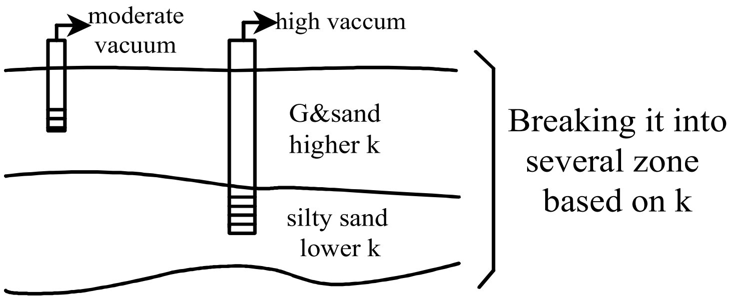


⑤ Site Homogeneity

The air carrier must flow past the contaminants if they are to be removed.

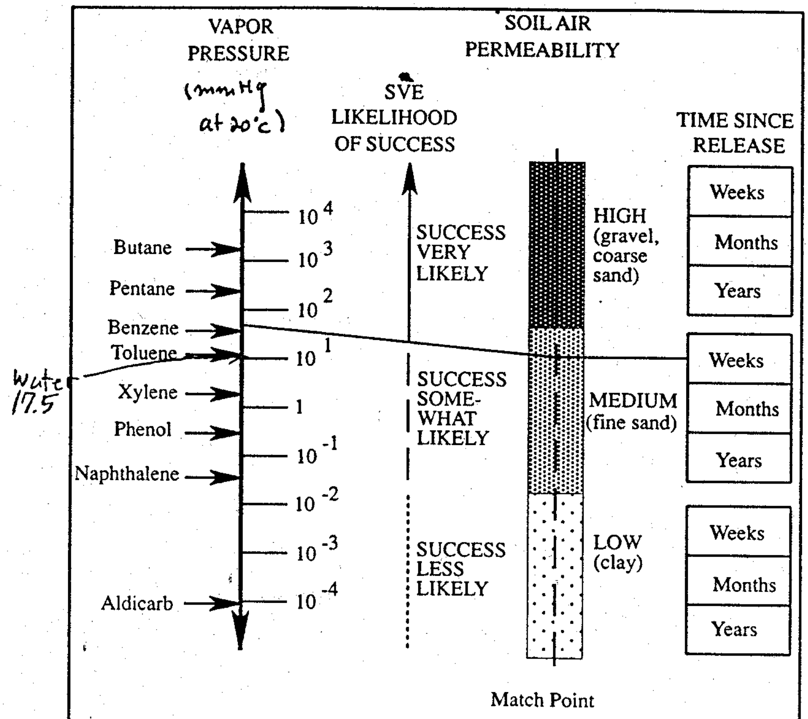
In low k zone .... fully opening wells

In high k zone .... closing others



하나만 사용하면 모든 airflow는 higher k zone에서만 발생

soil/cont. parameter 중에서 가장 중요한 항목으로 SVE의 성공여부 판단 가능



Domestic [illegible] F-30 page

FIGURE 5.1
SVE Applicability Nomograph
Soil Vapor Extraction

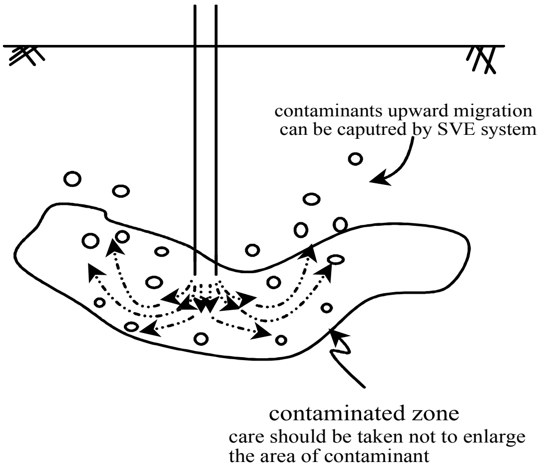
* SVE systems may be enhanced through the addition of alternative options / enhancement

① GW extraction pumps → lower GW table to enlarge the vadose zone

② Placing on inpermeable barrier over the surface to minimize short-circuiting of air flow→ increase the radius of influence up to 90m(compared with 6～45m without blankets)

③ Installing air blower(recharge wells) around the zone of contamination for enhancing movement of soil gases

④ Air sparging



◎ Volatilization of stagnant contaminant at surface (지표에 오염물질이 spill 되었을 때 증발하는데 걸리는 시간)

→ Hartly method for estimating the volatilization of chemicals from soil based on the heat balance b/w the contaminant and air.

$$J=\frac{A_{sat}\frac{1-h}{\delta}}{\frac{1}{D}+\frac{\lambda^2(A_{sat})M}{kRT^2}}$$

where,

J = flux (g/cm^2 · sec)

A_{sat} = saturation concentration in air (at temperature of outer air(g/cm^3)

h = relative humidity ($0< h <1$)

δ = thickness of stagnant boundary layer(cm)

D = diffusion coefficient in air(cm^2/sec)

λ= latent heat of vaporization (cal/g)

M = molecular weight(g/mol)

k = thermal conductivity of air (61×10^{-6}cal/sec · cm · k)

R = universal gas constant(1.987 cal/mol · k)

T = temperature (in K)

(3) Design Considerations

○ SVE's primary benefit is as in situ remediation tool for removal of VOCs from soils in the vadose zone

○ But SVE is not very applicable to sites with low hydraulic permeability ($k < 10^{-4}cm/s$), with low vapor pressure ($V \cdot P < 0.5mm.Hg$) and low values of Henry's constant (Henry's constant : 표 참조) under moist conditions(like vadose zone 물이 없으면 V・P가 감소 with some water content). henry's const is the key parameter because it considers the Aqueous solubility, too.

[ex) 2-Butanone은 V・P는 아주 높으나(very volatile) 물에 아주 잘 녹으므로 SVE 가 쉽지 않다.]

and with high GW table → 그러면 Extraction well의 깊이가 얕아지고, 그렇게 되면 air의 short-circuiting이 발생한다.

*** Process Description**

A typical SVE system consists of the following components

Infrasturcture :

○ one or more vapor extraction wells

○ Piping connecting extraction well with vacuum source

○ vacuum monitoring wells

○ vacuum gages and flow control valves at each wells

○ impermeable cover over the system site to minimize the downward infiltration of air (for short-circuiting) and water

○ one or more air injection (vent) wells to enhance air movement through the vadose zone

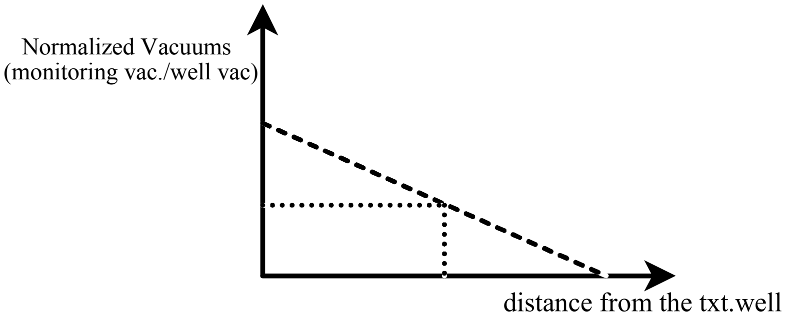
Extraction Equipment :

○ vaccum / blower unit

○ moisture knockout drum (to remove water)

○ off-gas treatment

실제 디자인전에 먼저 pilot test를 거쳐서 각 vacuum 앞에 대한 nomalized vacuum value of 0.01 되는 점의 distance를 찾는다.



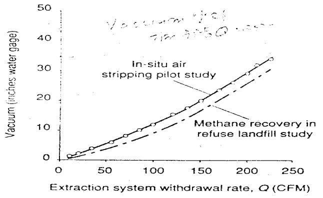


FIGURE 9-10
Twin Cities army ammunition plant ratio of withdrawal rate vs. vacuum head.[36]

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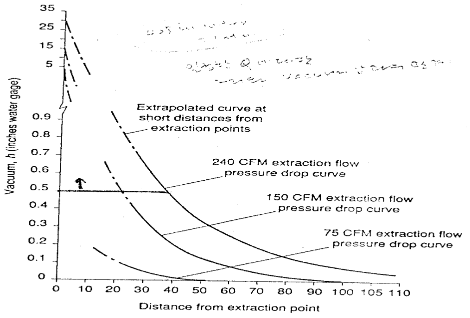


Note: Soil conditions consist of sandy materials with traces of silt or gravel and occasional gravelly layers.

FIGURE 9-11
Twin Cities army ammunition plant vapor pressure drop vs. distance.[37]

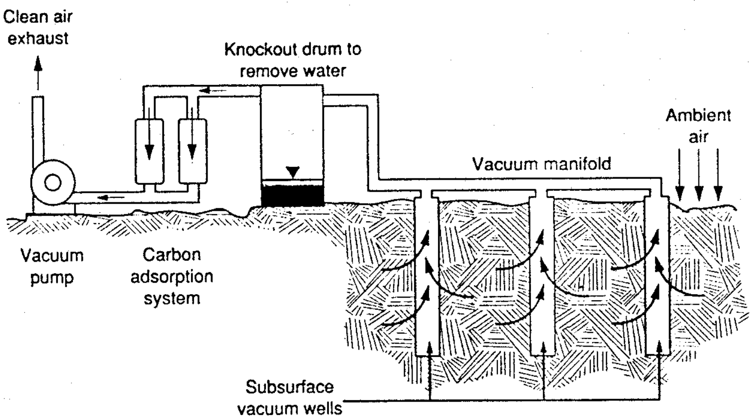


FIGURE 9-6
Schematic of SVE system.

(4) Bioventing (air as oxygen source)

Oxygen supply to vadose zone contaminantion by pumping air (similar to SVE)

→ optimize natural aerobic biodegradation

→ soil gases at monitoring locations (O_2, CO_2, CH_4) generally are monitored to ensure the presence of aerobic conditions

→ Not like SVE, moisture and nutrients addition is considered to enhance system performance

→ Generally SVE is followed by Bioventing for non-volatile organic treatment (as long as the compounds are biodegradable)

→ The minimum ratio of air pumped to the contaminantsis approximately 13lb of air / pound of typical petroleum contamination

→ For Bioremediation of GW, need to deliver over 1000g of GW to deliver the same amount of oxygen(13lb) to the contamination. This is because oxygen saturation in water is roughly 8mg/L, where as air is 20% oxygen.

→ Use air-injection mode, rather than vacuum in SVE because high vacuum rate can affect microbial growth

* **Permeable Reactive Wall**

○ Another " True in-situ Tech"

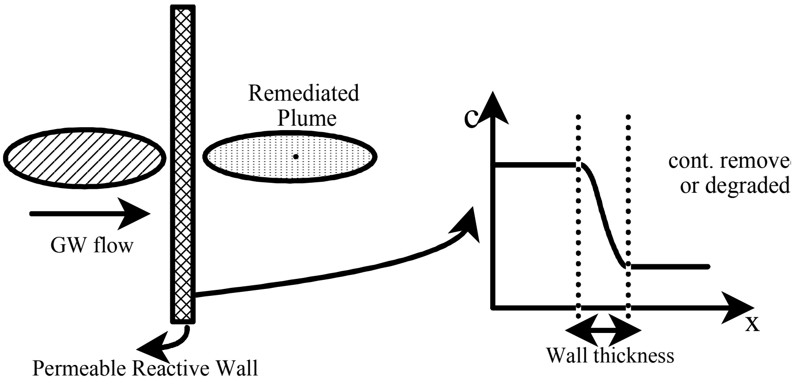
○ Abandoned-landfill contaminant system + clean up

○ wider contaminated area

○ cost effective

attempt to eliminate or at least minimize mechanical system, thus site dose not need a continuous input of energy and manpower.

" Contaminated Groundwater is remediated while passing through the permeable reactive wall"



; basically a permeable wall containing the appropriate reactive material is placed across the path of contaminant plume, allowing GW to continue its natural course through the flow system. (Waterloo Center for GW Research)

○ To successfully remediate a plume, a PRW will must be large enough to remediate the entire plume. For large or deep plume, Funnel-and-Gate system is prefered.

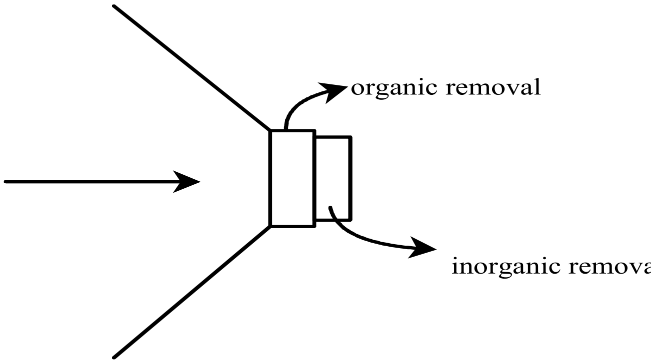
* **Design focus**

○ Ratio of funnel to gate area to achieve remedial objective at least cost

○ Residence time (for sufficient Retention time to remove contaminants while maintaining natural flow rate)

○ For mixture Contaminants (ex. organics + inorganics)

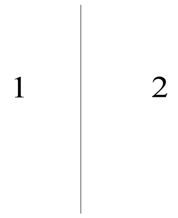
→ use serial PRW



○ Use wall cassette (retrievable wall) for change gate material (sufficient strength to maintain structural integrity GAC(활성탄) during placement and removal)

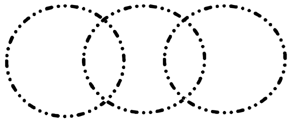
* **Installation**

1) sheet pile method



① sheet pile installed
② excavation
③ backfill with PR material

2) Overlapping caissons (up to 100')



① Caisson driven
② excavation and backfilling
③ Caisson withdraw

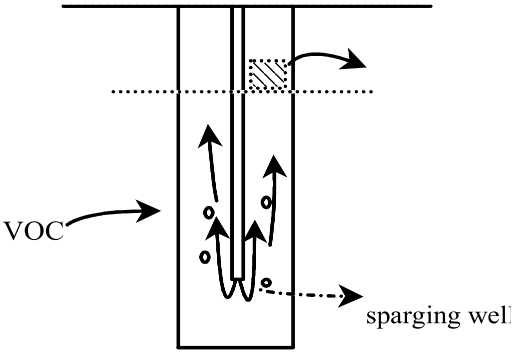
* **Types of In-situ Reactors**

○ Transformation Processes

Fe^0 (zero-valent iron) metals to promote transformation of various chlorinated organic compound. (reductive dehalogenation) - Cu, Al, Zn, etc.

[Fe^0 → most effective, costless, availability]

○ Physical Removal



If plume contains VOCs, the PRW could be a air sparging point.

○ Modify pH

mainly for metal removal

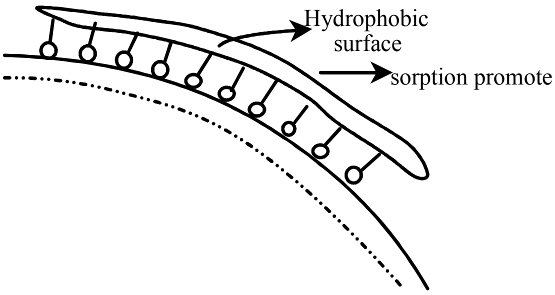
Abandoned mine site, pH is mostly less than 3.0 with very high conc. of Cu, Zn, etc.

The PRW is installed to increase pH of GW by conveying through a limestone bed to precipitate metal hydroxide

○ Sorption or Ion Exchange

use Granulated Activated Carbon(GAC) or Cationic Surfactants → organic compounds

(Cationic Surfactants → 살균력이 좋다 → Biological activity reduce)



○ Biological Degradation (organic compound available)

- surface area가 큰 clay

  bacteria need the proper amound of soil surface area in order to interact with plume

- oxygen ; air sparging

  briqutte(조개껍데기 같은 것)

*** For degradation process**

→ 1st order decay (안전측)

the retention time necessaring is given as

$$C_{eff} = C_{in} \left(\frac{1}{2}\right)^{N_{\frac{1}{2}}}$$

$N_{\frac{1}{2}}$: number of half-life required

C_{eff} : conc. of the desired effluent

C_{in} : conc. of the influent

$$\rightarrow \ N_{\frac{1}{2}} = \frac{\ln(C_{eff}/C_{in})}{\ln\left(\frac{1}{2}\right)}$$

ex) TCE $t_{\frac{1}{2}} = 13.6hr$, $C_{eff\ req} = 5ppb,$ $C_{in} = 1000ppb$

$$\rightarrow \quad N_{\frac{1}{2}} = \frac{\ln\left(\frac{5}{1000}\right)}{\ln\left(\frac{1}{2}\right)} = 7.64$$

Total residence Time

$$T_{req} = t_{\frac{1}{2}} \times N_{\frac{1}{2}} = 13.6 \times 7.64 = 103.45hr = 4.3\ days$$

4. Containment

* Introduction

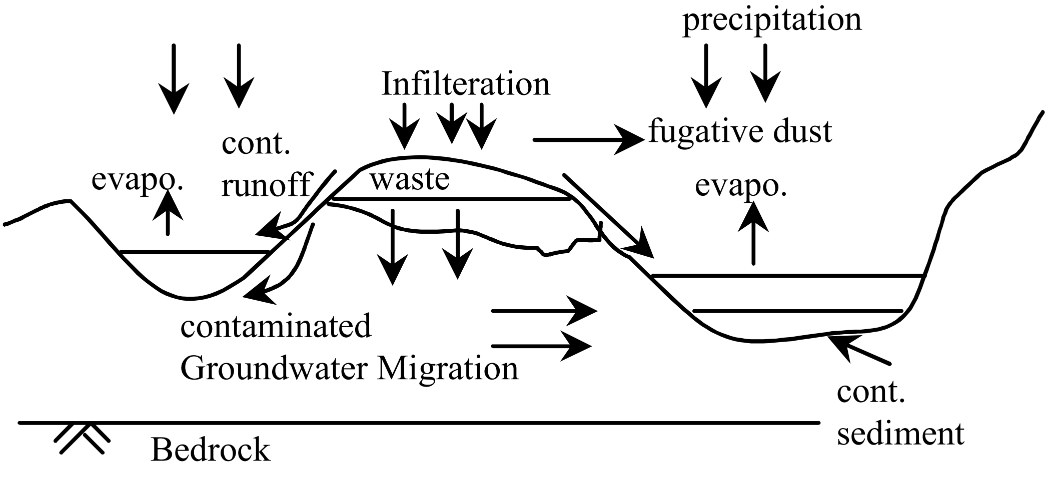
- Source Control (not remediation) ∴ Passive Method

- It is necessary to minimize the rate of offsite contaminant migration employing containment technologies to reduce risk to public health and the environment
- Containment technologies may be associated with other technologies (such as in-situ remedial alternatives) to implement a long-term clean up strategy for the site

Containment technique -> active remediation followed
(pump & treat, Biorem...)

- remedial alternatives
  · removal (by excavation) and treat (for OCs, thermal, Biorem., washing..)
  · in-situ (without containment)
  · containment -> very site specific

- eventually to decrease the containment transfer rates
- Pathways for contamination



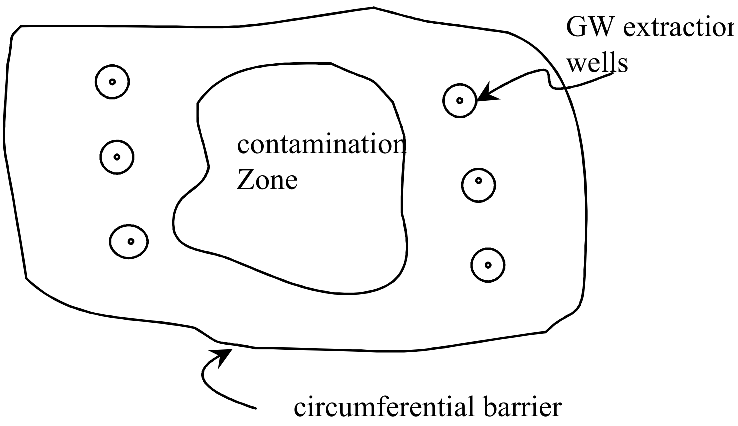
Containment controls the hydrogeologic pathways for contaminant migration

- Surface water control : Covers / Caps

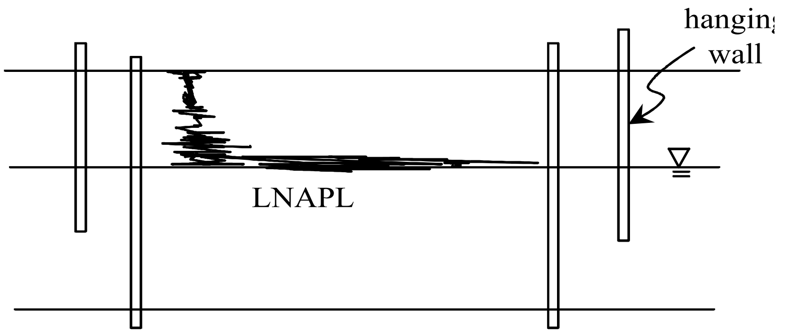
reduce infiltration and eliminates the problems of direct contact by run off and fugitive dust

* Groundwater control

- Subsurface vertical barriers for containing contaminants and to redirect GW flow.
- Barriers including slurry trench cutoff walls (made of soil-bentonite. cement-bentonite etc.) , grout curtains (made of cement-based of chemical grouts), and steel sheet piling. With the installation of a vertical barrier, clear regional GW is prevented from entering the site
- Vertical barriers are commonly used in conjuction with GW extraction and treatment system



- Vertical barriers are typically embedded or keyed into the bedrock or low k zone, but not necessary for LNAPL



- $k < 1\times10^{-7}$ cm/s typically, but k can be up to $10^{-5} cm/s$

ex)

· 3ft thickness circumferential wall

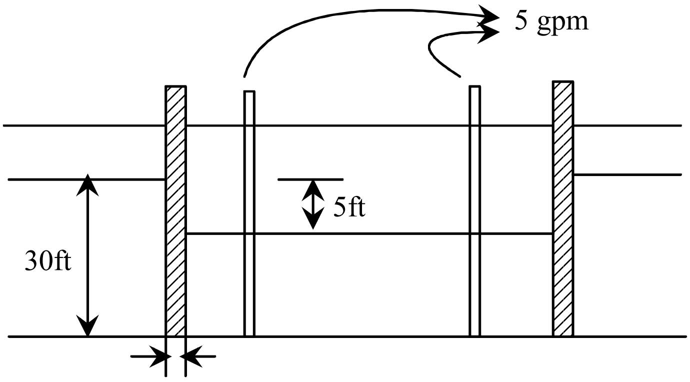
· effective treatment plant capacity, $5\ gpm$

· perimeter 3000 ft

· aquifer thickness 30 ft

· in-outer water table difference 5ft maintained

· $k = ?$



sol) $q = kiA$ (Darcy's law)

$$q = 5gpm \qquad i = \frac{5}{3} = 1.67 \qquad A = 30ft \times 3000ft = 90,000ft$$

$$\therefore k = \frac{5}{1.67 \times 90,000 \times 7.48} = 4.5 \times 10^{-6} ft/\min = 2.3 \times 10^{-6}\ cm/s$$

-> considers advective flow only no consideration for differential transport

* Soil - Bentonite slurry trench Cut-off walls

- Construction

-> Fig 16-6 (OHP, HWM pp 974)

First process water/Bentonite mixture

95% water + 5% bentonite by wt -> water-bento mixture

Na - bentonite (우리나라는 Ca-bentonite)

Trench collapse is controlled by the fluied pressure of the slurry opposing the active earth pressure to maintain the trench stabilital, and vertical excavations to depths of more than 100ft

bentonite(Gs=2.77) 100lb per 200 gallons of water

Bentonite contant by wt.

% bentonite = 100 lb / $(200gal/7.48gal/ft^3 \times 62.4lb/ft^3)$ = 6%

Fluid const. wt

$$Gs = \frac{W_s}{\gamma_s \gamma_w} \quad \gamma_s = \frac{W_s}{Vs}, \qquad V_s = \frac{W_s}{G\gamma_w} = \frac{100}{2.77 \times 62.4} = 0.58ft^3$$

Vol of water V_W

$$V_w = 200gal \times \frac{1}{7.48gal/ft^3} = 26.74ft^3$$

wt. of water W_w

$$W_w = V_w \times \gamma_w = 26.74ft^3 \times 62.4lb/ft^3 = 1668lb$$

Fluid unit wt. $\gamma_f = \frac{W_T}{V_T} = \frac{W_w + W_b}{V_w + V_s} = \frac{1668+100}{26.74+0.58} = 64.7lb/ft^3$

- Trench stablility

Active Earth pressure (Driving force) ↔ fluid pressure exert by the bentonite-water slurry (resisting force)

Literatures ; ① Xanthakos, " Slurry walls" McGraw-Hill, NY, !974

② Spooner, Philip, et al " slurry trench construction for pollution migration control" EPA-540/2-84-00 u.s EPA, Feb, 1984

③ Nash, K,L "Stability of trenches filled with fluid ASCE, J. of Const.

Div. V.100 No4 pp 533-543

For Clays

$$F.S = \frac{R.F}{D.F} = \frac{4Su}{H(\gamma_s - \gamma_f)}$$

S_u : undrained shear strength (cohesion)

H : depth of wall

γ_s : total unit wt. of soil

γ_f : unit wt. of bentonite-water slurry

ϕ : angle of internal friction

For Sands

$$F.S = 2\sqrt{(\gamma_s \cdot \gamma_f)} \times \tan\phi \,/(\gamma_s - \gamma_f)$$

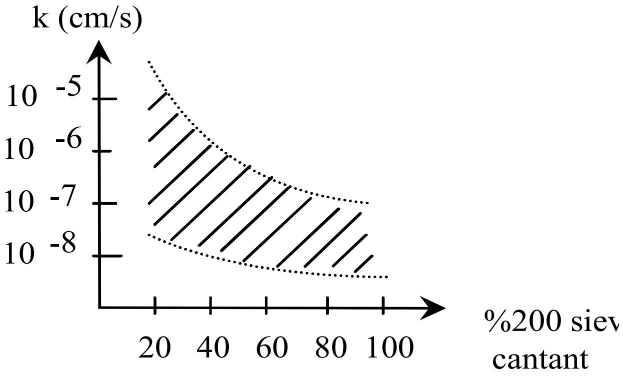
ex) F.S H = 30 ft sand soil ϕ = 30

$\gamma_f = 64.7\,lb/ft^3$ $\gamma_s = 130\,lb/ft^3$

$$F.S = 2\sqrt{(\gamma_s \cdot \gamma_f)} \times \tan\phi \,/(\gamma_s - \gamma_f) = 2\sqrt{130 \times 62.4} \times \tan 30/(130 - 64.7) = 1.62$$

- Placing Soil-bent backfill is the second part of the process of constructing a soil-bent slurry wall. After the treat excavation is completed to the entire depth. Water-bent slurry is the displaced with soil-bent backfill.

Soil + water + bent -> $k = \approx 10^{-7} \sim 10^{-8}$



- Backfill Design

Requirements

① Chemical Compatibility (against leachate attracts)
② Low k
③ Low compressibility
④ Moderate Strenth

- Backfill Defects

① improper mixing, unmixing soil

② inadequate excavation (flow beneath the soil)

③ cycle of freezing and thawing (increase k)

④ cycle of wetting and drying (increase k)

⑤ chemical imcompatibility (k↑)

Cement-Bentonite Slurry wall

→ one step process as the mixture (cement/soil/bent/water) is left to harden in a trench

→ the wall is more prone to increase is k in response to the contaminant fluids

∴ not recommanded for hazadous waste contaminant applications

5. Landfills

A Landfill is defined as that system designed and constructed to contain discarded waste as to minimize releases of contaminants to the environment.

From the top to the bottom,
* Daily cover ; placed at the close of each operational day, consisting of soil I think. It minimize odor, air borne transport of contaminants, and potential for direct contact, and maximize aesthetic (장점)
But is both expensive and uses up valuable landfill space creates a highly anisotropic environment (seepage often exits along the relatively permeable daily cover layers and through the side slopes. (단점)

* The landfill materials interact with moistures received from rainfall or snow to form or snow to form a liquid called "Leachate" (침출수). It is the main source of GW contamination. It is important that leachate be properly contained in all landfill

* Landfill Liners
- Until 1982 the predominant liner material used was clay (< $10^{-7} cm/s$)
- 1984 U.S EPA all new landfills should have double liners and systems for leachate collection and removal (clay soil + geomembrane / geonets)

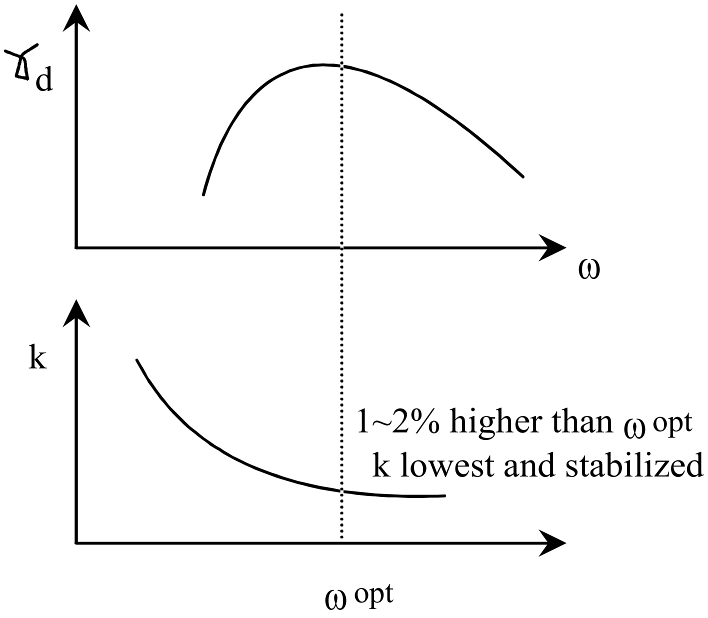
(1) Clay
To have k less than $10^{-7} cm/s$
Soil should meet the following criteria (EPA, 1989)

① Soil should have at least 20% fines (silts/ clay-size particles)
② 10 < PI < 30 (workability)
③ Soil should not have more than 10% gravel size particles (D> 4.75)
④ Soil should not contain any particles or chunks of rock that are

- In many cases, the soil found at the construction site may be somewhat non-plastic. Such soil may be blended with imported clay mineral like Na-bentonite to achieve the designed properties as a clay liner

- Factors affecting k of a compacted clay

① Moisture content and Dry unit of compaction



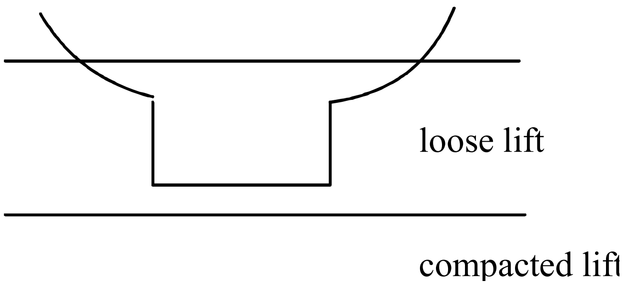
② Lift thickness

Sheepfoot roller should penetrate the full thickness of the lift

→ large shear strain during compaction

→ more dispersed structure

→ lower k



③ size of clay clods

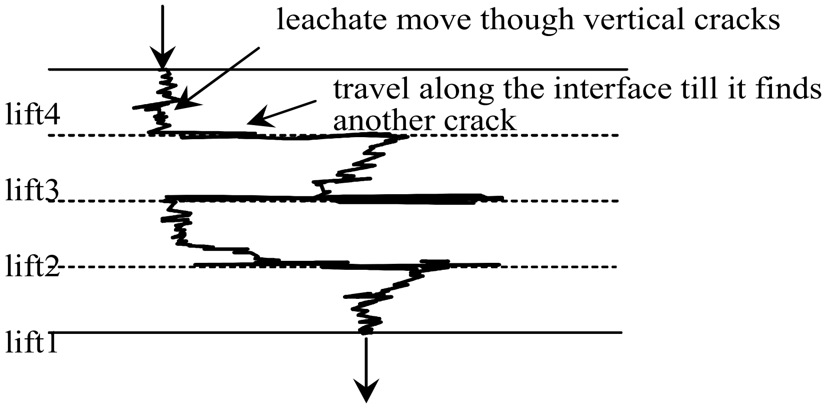
clay clods affect k

larger clod size can increace k by several orders of ___ the degree of increase in k decreases with the increase in w

→ clods should be brocken down mechanically as small as possible

→ heavy roller needed

④ Bonding between lifts



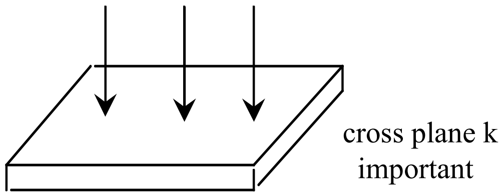
(2) Geosynthetics

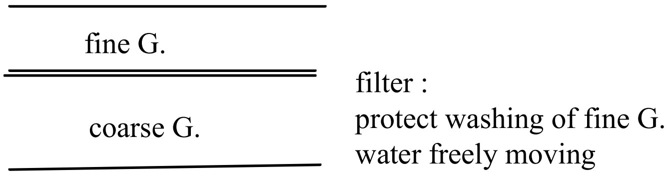
- fabric like material made from polymers such as polyester polyelthylene, polvunyl chloride, nylon etc.
- geotextiles, geomembranes, geonets etc
- major functions
  - · separation
  - · reinforcement
  - · filteration
  - · drainage

① Geotextiles

Polyester, polyethylene, and polypropylene, and fiberglasses → durable

major function → filteration





Thickness of geotextile changes depending on the effective normal stress → k changes

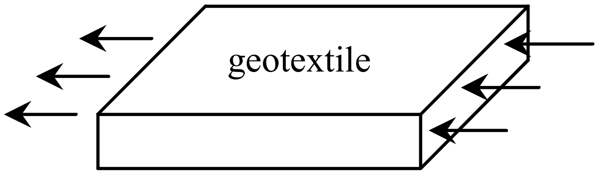
Permitivity P $[T^{-1}]$

$$P = \frac{k_n}{t}$$

k_n : k for cross-plane flow

t : thickness of the geotextile.

In-plane flow for Drainage, Transmissivity T introduced



$$T = k_p \cdot t \qquad \left[\frac{m^3/\sec}{m}, \frac{V_o 1/T}{L}\right]$$

k_p : k for in-plane flow

Typical values

k_n : $1\times10^{-3}\sim2.5\times10^{-1}cm/s$

P: $2\times1-^{-2}\sim2.0\sec^{-1}$

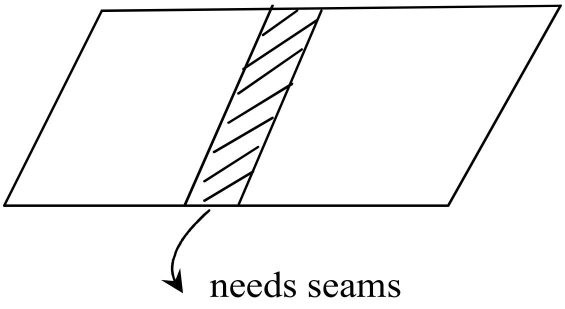
k_p: $10^{-3}\sim5\times10^{-2}cm/s$

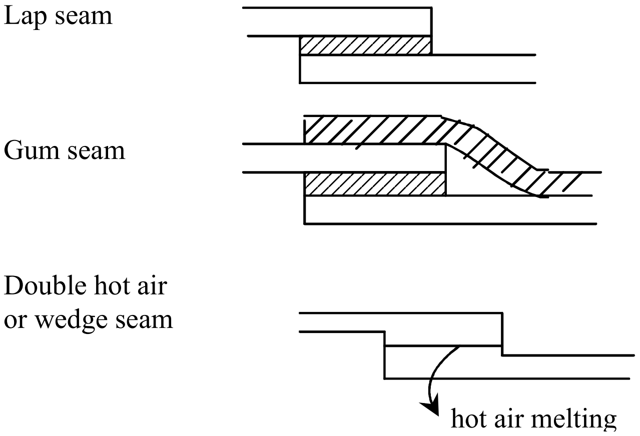
T: $2\times10^{-9}\sim2\times10^{-6}m^3\sec/m$

② Geomembranes

- Polyvinyl chloride (PVC) , polyethlene, polyamide
- impermeable barriers ($10^{-10} \sim 10^{-13} cm/s$)
- single sheet (0.25~0.4mm)

  single sheet of geomembrane can be laminated together to make thicker sheets
- seaming very important



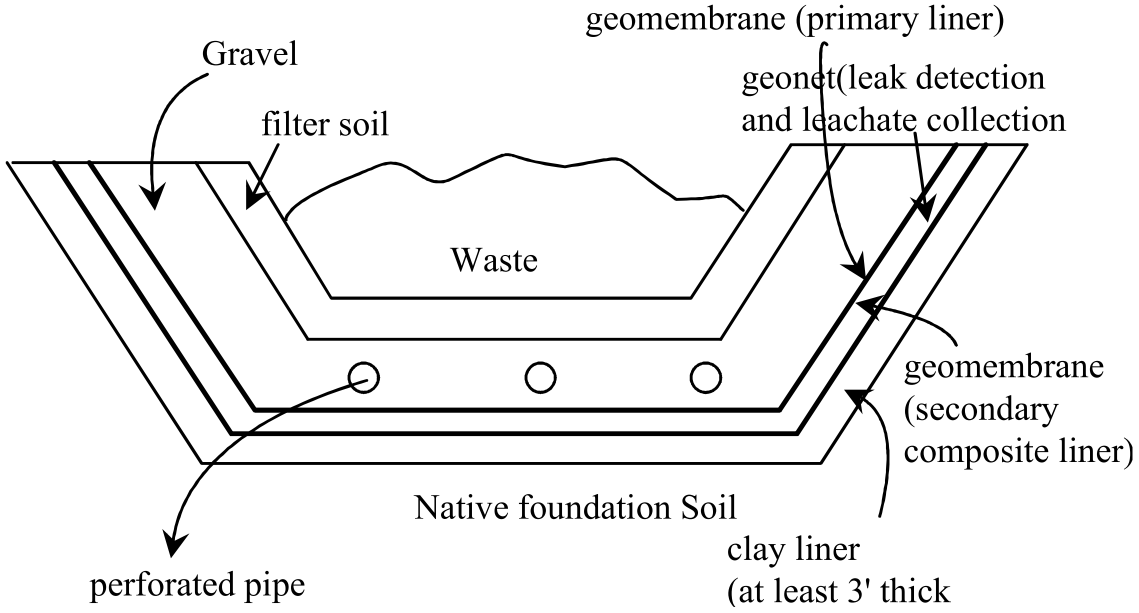


③ Geonets

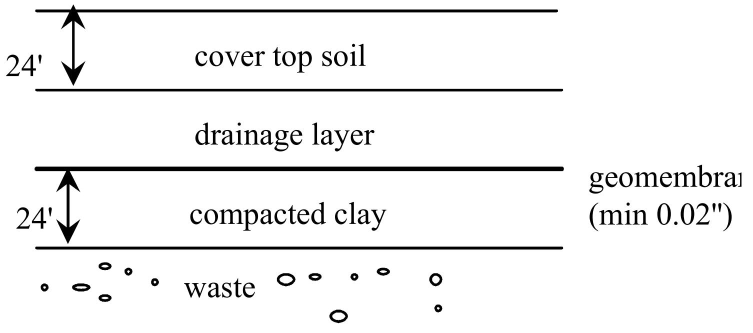
For filteration

Seaming : Staples, wires, threaded loops

* Double Linear Systems



* Landfill cap (Cover) for landfill closure



* Contaminant Transport through Landfill Barriers

① Transport through Liners

- By hydraulic gradient (advection) + molecular diffusion (concentration gradient)
- Ficks low for molecular Diffusion (through clay liners)

$$\frac{\partial c}{\partial t} = \frac{D^*}{R}\frac{\partial^2 C}{\partial x^2}$$

c : conc. of solute (mg/㎤)

t : time (sec)

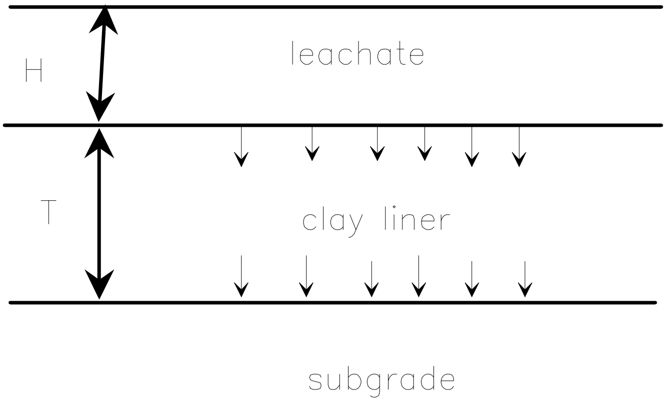
D^* : effective diffusion coeff. (㎠ /sec)

R : net factor → $1+(\frac{\rho}{\eta})k_d$

ρ : bulk density η : porosity

x : distance of diffusion (cm)

- Advection (through clay liners)

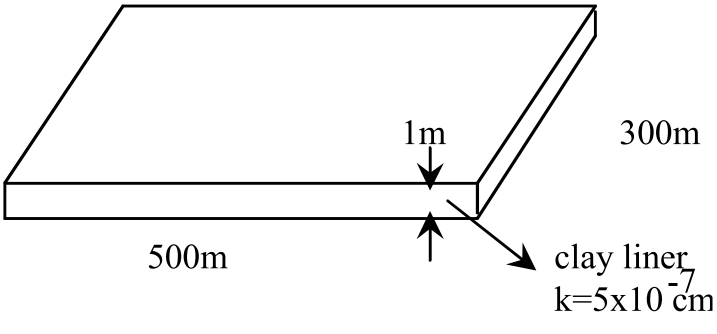


Hydraulic gradient $i = \frac{\Delta h}{L} = \frac{H+T}{T}$

$v = ki$

$q = kiA$ (Darcy's flux)

$Q = kiAt$ (influx vol.)



avg. leachate head = 0.5

conc. $C = 1.0mg/L$ (OCl_4) of leachate indicater

q= ?

일년에 이양으로 지하수를 얼마나 오염시킬수 있는가? 매분 0.005mg/L

$$i = \frac{H+T}{T} = \frac{0.5+1}{1} = 1.5m/m$$

$$v = ki = 5\times10^{-7}cm/s\times1.5m/m = 7.5\times10^{-9}m/s$$

influx vol. $Q = kiAt = vAt = 7.5\times10^{-9}m/s\times300m\times500m\times3.16\times10^{7}\sec/yr$

$$=3.6\times10^{4}m^{3}/yr$$

Loading amount of CCl_4 per yr

$$3.6\times10^{4}m^{3/yr}\times1.0mg/L\times1000L/m^{3} = 3.6\times10^{7}mg/yr$$

→ 3,6 times 10^4 g/yr → 36 kg/yr

이양으로 지하수는 얼마나 오염시킬수 있는가? (1년에)

$$\frac{36kg}{0.0005mg/L} = \frac{36\times10^{6}mg}{0.005mg/L} = 7.2\times10^{9}L$$

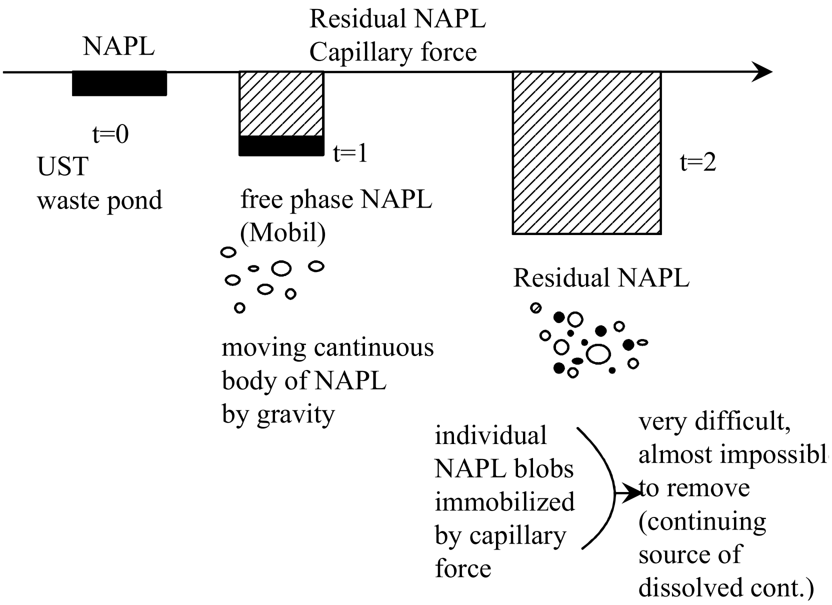
$\simeq$ 7 billion liters per yr. form 36 kg CCl_4

* NAPLs (Non-Aqueous Phase Liquids)

· NAPLs are hydrocarbons that do not dissolve in water, using, separate oily phase. Migration is governed by gravity, buoyancy capillary force.
↔ dissolved cont. (advection - dispersion eq.)

· After moving downward through the vadose zone
LNAPLs ($\rho_{Ln} < \rho_w$) float and move on top of water table.
while DNAPLs ($\rho_{Ln} > \rho_w$) penetrate into the saturated zone.

ex.



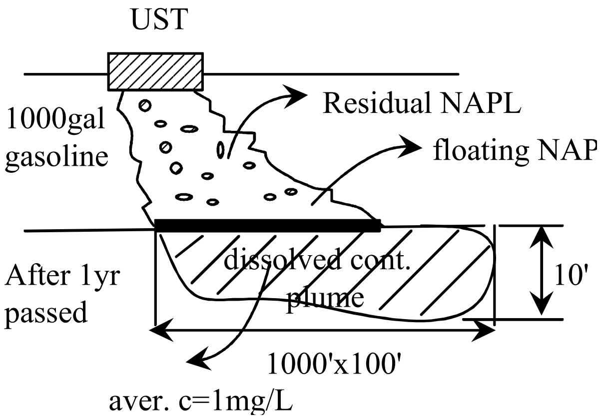
* Key Concepts

① Single vs Multiple NAPLs
TCE gasoling ↘ bebavior move complex to predict
② Saturation & Residual Sat.
(Handout Fig 11.3)

· Relative Mass of Hydrocarbons in Dissolved Phase vs NAPLs
Generally, NAPL mass >> dissolved phase

(%) (ppm/ppb)

ex)



$n = 0.3$

$\rho_{ngasoline} = 0.9 g/mL$

Total : 1000 gal = 3402 kg

Vol. of Cont. GW = 1000' x 100' x 10' x 0.3 x 28.3 L/ft^3

= $8.49 \times 10^6 L$

Mass of Dis. HC = 8.49 x 10^6 x 1mg/L x $kg/10^6 mg$

= 8.5kg

Comparisons

Total : 3402 kg

Dissolved HC : 8.5 kg (0.2%)

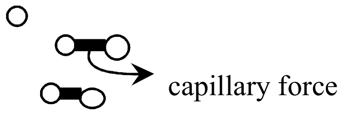
NAPL : 3393.5 kg (99.8%)

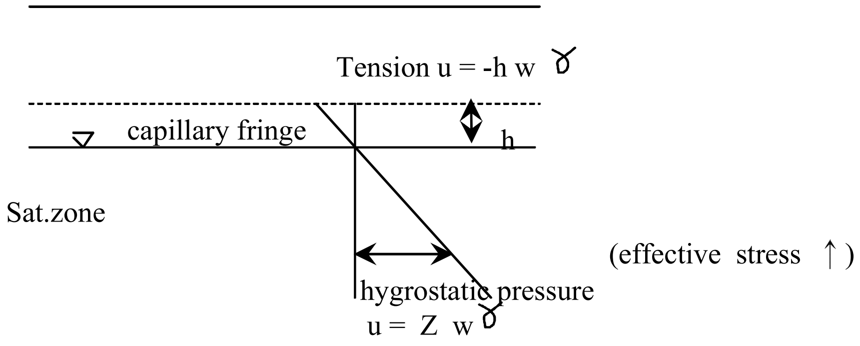
⇒ Removing even a few gal. of NAPL may prevent possible contamination of Millions of gal. of GW

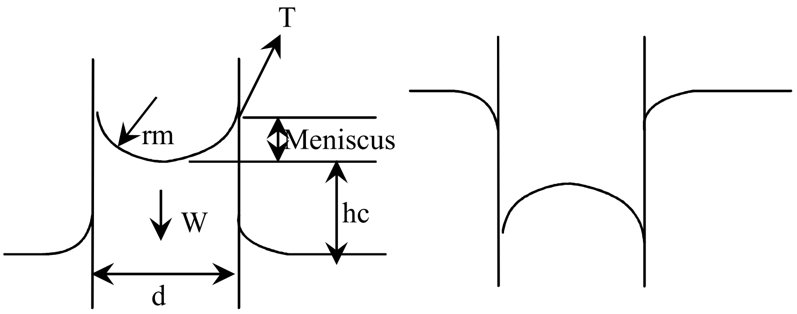
⇒ NAPL Removal ; very important.

· DIfficulty in Removing Trapped Residual NAPLs.

why ? - Capillary force







adhesion > cohesion	adhesion < cohesion
wetting material	nonwetting material

For Force Equilibrium

$$\Sigma F_{down} = W = vol \cdot \gamma_w = (h_c \frac{\pi}{4} d^2)\gamma_w$$

$$\Sigma F_{up} = T\cos\alpha(\pi d)$$

$$\therefore\ \Sigma F_{down} = \Sigma F_{up}$$

$$h_c = \frac{4T}{\gamma_w d}\cos\alpha$$

For glass tube, soil particle, pure water $\alpha \rightarrow 0$

$$\Rightarrow h_c = \frac{4T}{\gamma_w d}$$

20℃에서 T = 73 dynes/cm = $73\times10^{-3} N/m$

$$h_c = \frac{-4\times73\times10^{-3}N/m}{9800N/m^3 \cdot d} \simeq \frac{3\times10^{5}m^2}{d(m)}$$

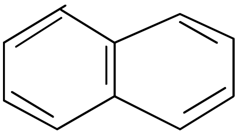
d = $D_{10} \cdot (0.2)$ ← soil에서

$$\therefore\ h_c = \frac{3\times10^{-5}(m^{2)}}{0.2D_{10}(m)}$$

* Types of NAPLs

- **LNAPL**

- gasoline, kerosene, diesel.
  → Typical chemicals - BTEX + Naphthalene



- relatively biodegradable

▶ LNAPL conceptual Models

①

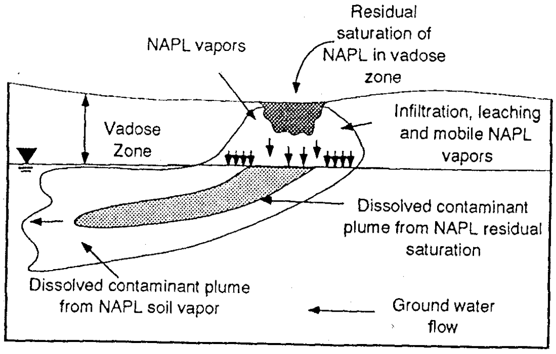


Figure 11.8 LNAPL release to vadose zone only. Source: Waterloo Centre for Ground Water Research, 1991.

②

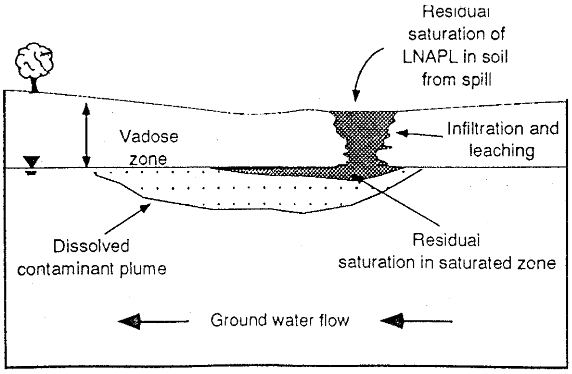


Figure 11.4 Typical LNAPL release.

③

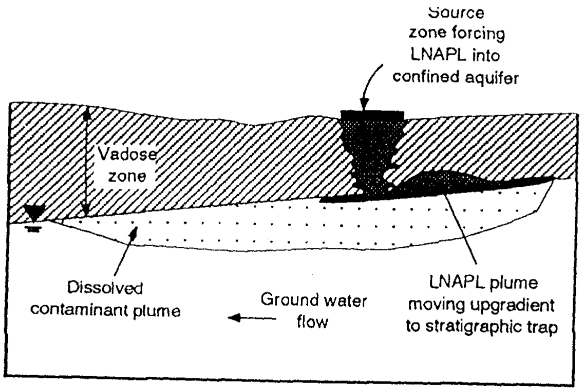


Figure 11.10 LNAPL accumulating in stratigraphic trap in confined aquifer.

To increase the recovery of LNAPL recovery wells should be screened near the confining unit-aquifer boundary

④

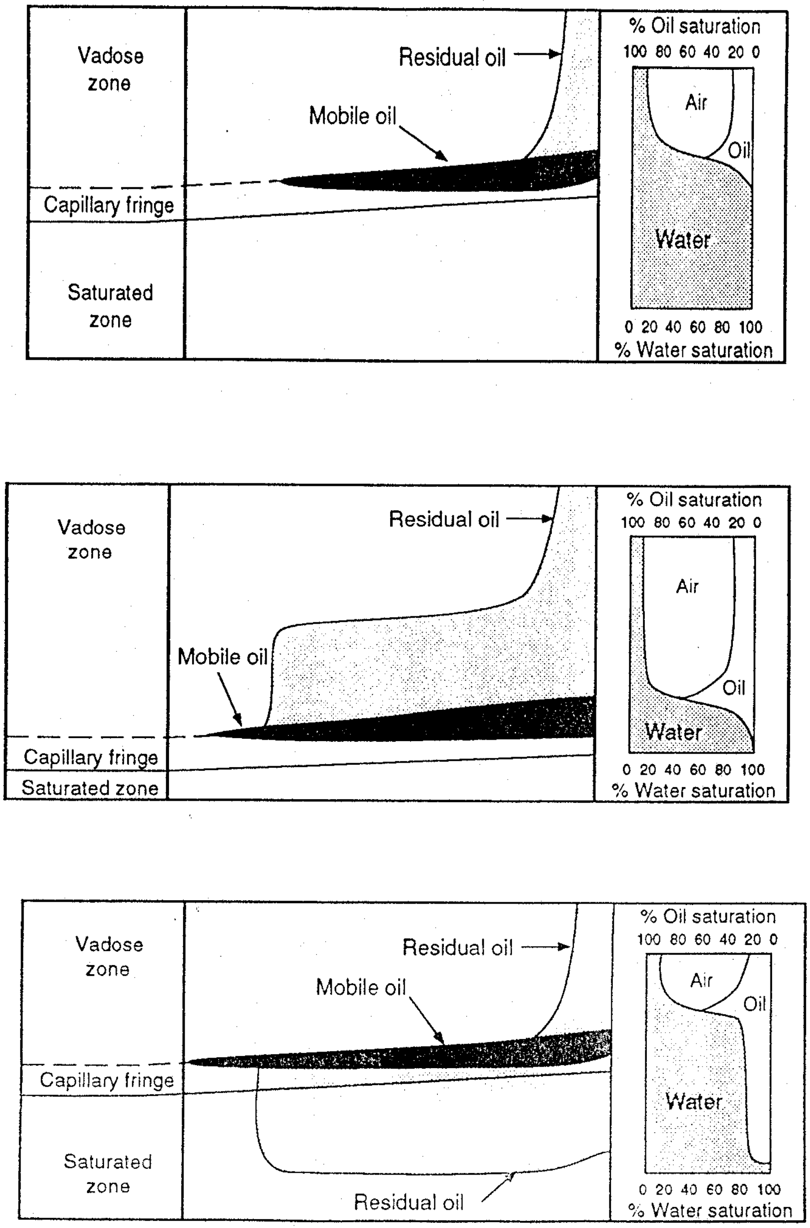


Figure 11.9 Effect of a falling and rising water table on the distribution of mobile and residual phases of an LNAPL. Source: Fetter, 1993. © 1993 by Macmillan College Publishing Company. Reprinted with permission.

Increase the 3 one containing residual hydrocarbons, thereby increasing the concentration of dissolved organics in GW.

· **DNAPL**

- Halogenated Volitile / semi Vol, OCs.
(TCE/PCE) (Pentachlorophenol)

- Nonhalogenated Semi Volitils.
(Cresol / phenol)

- More recalcitrant (formidable) for biodegradation.

why? ① chemically, chlorinated compounds, toxic
do not biodegrade and persist for a long period of time
② $\rho_n > \rho_w$ → sink deep into aquifer
→ less oxygen found
→ difficult condition for aerobic bio.
③ Chlorinated comp. (very low viscosity) bio.
→ penetrate through fractures (as small as 20㎛)

▶ DNAPL conceptual Models

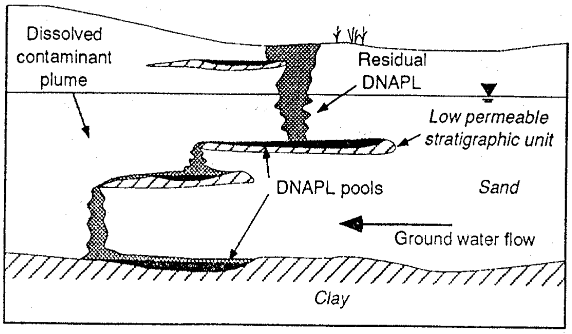


Figure 11.5 Typical DNAPL release. Source: Waterloo Centre for Ground Water Research, 1991.

Move down until converted into a residual state or until low-perm zone are encountered that create DNAPL pools

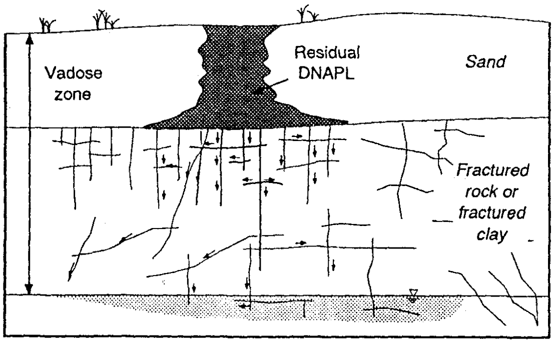


Figure 11.11 Fractured rock or fractured clay system. Source: Waterloo Centre

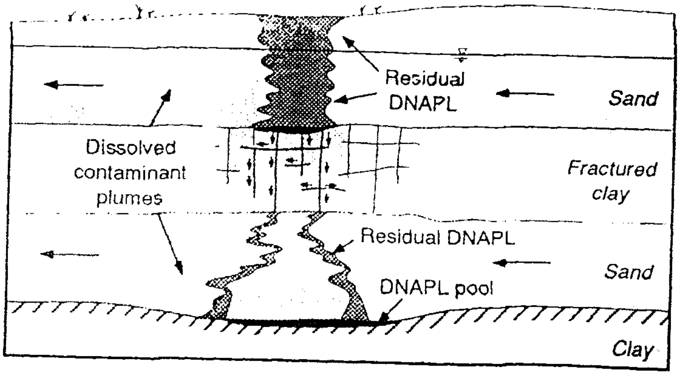


Figure 11.12 Composite DNAPL site. Source: Waterloo Centre for Ground Water Research, 1991.

*** NAPL transport ; General process**

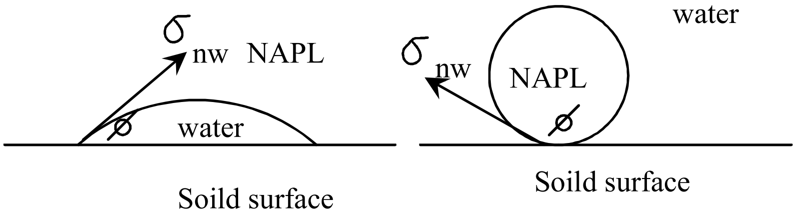
· At the pore level.

Free phase NAPL movement requires <u>pressure</u> to pass through a small pore thoat, displacing air and/or water occupied the pore.

depends on the <u>capillary force</u> acting on the fluids on either side of the pore throat.

The way that capillary force act on NAPL/water is explained by "wettability"

Wettability - the tendency of one fluid to preferentially spread over a solid surface in favor of the second fluid. This property is measured by observing the contact angle (ϕ) of a test fluid on a surface when surrounded by a larger volume of a background fluid.



⇒ water : wetting material.

NAPL : nonwetting material

ϕ<70° 이면 test fluid ; wetting
back fluid ; nonwetting

ϕ>110° 이면 test fluid ; nonwetting
back fluid ; wetting

70°<ϕ<110° 이면 ; neutral wetting system

System	Wetting fluid	Nonwetting fluid
air, water	water	air
air, NAPL	NAPL	air
water, NAPL	water	NAPL
air, water, NAPL	water > NAPL	air

· Downward Migration of DNAPLs in Sat. zone

Solid / water / DNAPL

"wetting" "nonwetting"

· DNAPLs must overcome capillary forces to squeeze though the pore throat

(entry pressure)

· Driving Force (gravity) > entry pressure

⇒ DNAPL move down.

If not, DNAPL will split apart into blobs and locate mostly in the pores in the aquifer

Residual NAPL

· NAPL in Vadose Zone.

Air / Solid particles / NAPL

Downward Migration of NAPL is relatively easy. because the pores are filled largely with air.

If sufficient NAPL is available, it continuous to move downward from the source area. by forming (1) films between the gas and the water phase. (2) blobs of NAPL that replace gas in the pores.

(or water)

$S_{r.sat} = (2 \sim 5) S_{r.unsat.}$

why? Drainage in vadose zone is much better but NAPLs are nonwetting fluid in the Sat. zone and so are trapped in the pores.

NAPL Transport

▶ Very difficult to predict → General methods (pore level, site level)

① Pore level

· Capillary Pressure

$$P_c = P_{nw} - P_w$$

P_c ; capillary pressure

P_{nw} ; pressure of NW(non-wetting) fluid (such as NAPL)

P_w ; pressure of W(wetting) fluid (such as water)

As the diameter of the soil pores get smaller, Pc required to force NAPL into or get out of the pore, increases Clay silt → more difficult for NAPL to move through

NAPL head > Capillary height

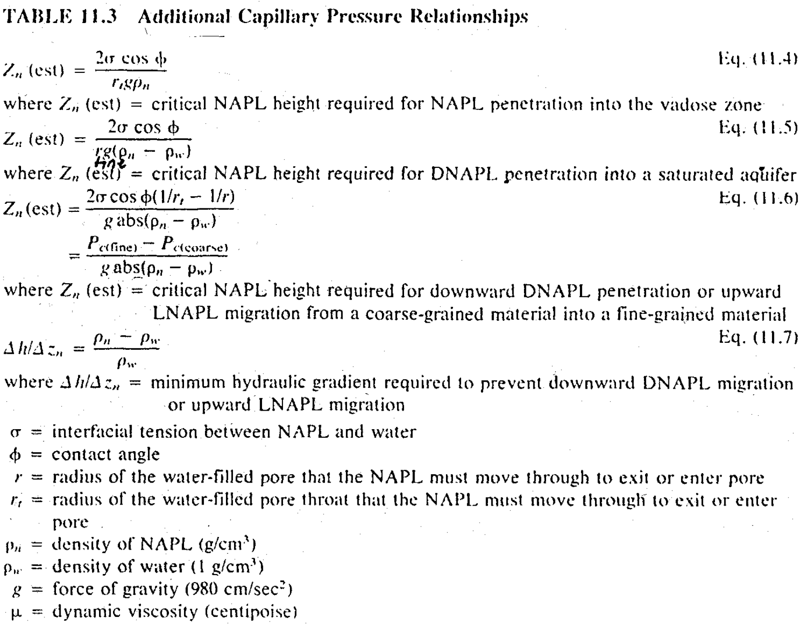


TABLE 11.3 Additional Capillary Pressure Relationships

$$Z_n\,(\text{est}) = \frac{2\sigma \cos \phi}{r_t g \rho_n} \qquad \text{Eq. (11.4)}$$

where Z_n (est) = critical NAPL height required for NAPL penetration into the vadose zone

$$Z_n\,(\text{est}) = \frac{2\sigma \cos \phi}{r g(\rho_n - \rho_w)} \qquad \text{Eq. (11.5)}$$

where Z_n (est) = critical NAPL height required for DNAPL penetration into a saturated aquifer

$$Z_n(\text{est}) = \frac{2\sigma \cos \phi(1/r_t - 1/r)}{g\,\text{abs}(\rho_n - \rho_w)} = \frac{P_{c(\text{fine})} - P_{c(\text{coarse})}}{g\,\text{abs}(\rho_n - \rho_w)} \qquad \text{Eq. (11.6)}$$

where Z_n (est) = critical NAPL height required for downward DNAPL penetration or upward LNAPL migration from a coarse-grained material into a fine-grained material

$$\Delta h/\Delta z_n = \frac{\rho_n - \rho_w}{\rho_w} \qquad \text{Eq. (11.7)}$$

where $\Delta h/\Delta z_n$ = minimum hydraulic gradient required to prevent downward DNAPL migration or upward LNAPL migration

σ = interfacial tension between NAPL and water
ϕ = contact angle
r = radius of the water-filled pore that the NAPL must move through to exit or enter pore
r_t = radius of the water-filled pore throat that the NAPL must move through to exit or enter pore
ρ_n = density of NAPL (g/cm^3)
ρ_w = density of water (1 g/cm^3)
g = force of gravity (980 cm/sec^2)
μ = dynamic viscosity (centipoise)

· Darcy's law

If all or almost of the open pore space is filled with continuous free-phase NAPL mass, Darcy's eq. can be applied to NAPL movement. Use intrinsic permeability(k) to account for the different hydraulic characteristics related to the NAPL fluid.

$$N = -\frac{k\rho g}{\mu}\frac{dh}{dl}$$

· Related Permeability

Multiphase flow occurs when two different fluids flow through a porous media, compete for available pore spaces, and there by reduce the mobility of both fluids.

This reduction is explained by 'Relative Permeability' $\left(\frac{k_{\text{mixed}}}{k_{\text{sat, with the fluid}}}\right)$

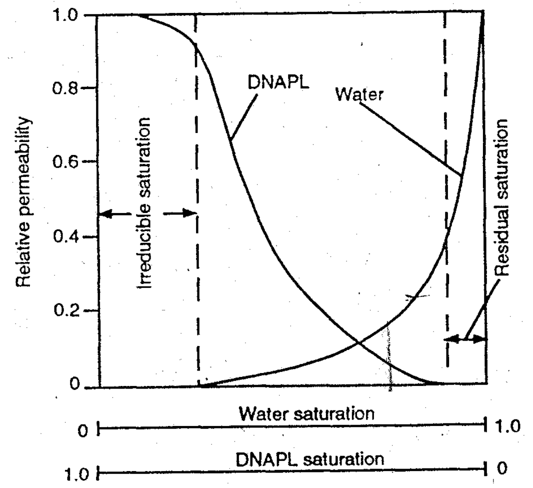


Figure 11.13 Residual saturation curve. Source: Schwille, 1988. © 1988 by Lewis Publishers, a subsidiary of CRC Press, Boca Raton, FL. Reprinted with permission.

Sir.avg.of NAPL = 0.2 (Swr = 0.8) ┌ R.P. of water = 0.2 [1]
└ R.P. of NAPL = 0.02

R.P. of water & NAPL ?

⇒ movement slow down significant where oil & water mixed together.

To minimize the removal of a free-phase NAPL, the NAPL pool should be maintained for as long as possible to avoid the interference caused by pumping.

---

[1] water flows through the current mixture of sand & trapped NAPL at only 20% of the rate that water would flow through sand alone.

② NAPL Computation at the site level

while the capillary forces that hold residual NAPL in pores are relative strong. They can be overcome by gravity forces associated with buoyancy-density forces or by viscous forces associated with groundwater flow.

Bond Number $(N_b) = \frac{k\Delta p g}{\sigma}$ (Δp : fluid-fluid density difference)

Capillary Number $(N_c) = \frac{-k\rho g\delta h}{\sigma\,\Delta l}$

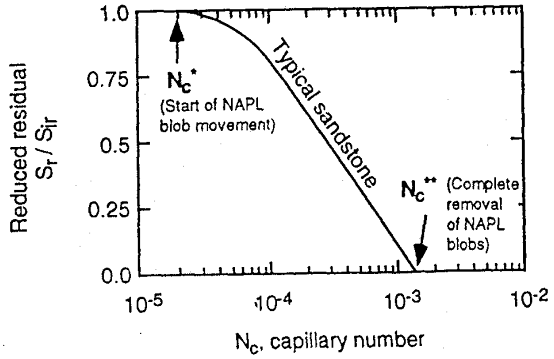


Figure 11.15 Residual hydrocarbon saturation ratio, relating final residual saturation S_r to initial residual saturation S_{ir} as a function of capillary number N_c. Source: Wilson and Conrad, 1984.

As N_c increases (by increase of GW velocity or a reduction in interfacial Tension2)) the amount of residual saturation decrease, Capillary Number can be used to estimate the potential efficiency of a hydrocarbon removal employing either high I or reduced interfacial tension or both.

Wilson & Conrad(1984) ; with the emperical data from the sandstone, they showed the I to mobilize NAPL blobs under various conditions.

From the Fig. 11.16, complete mobilization of residual NAPLs is very difficult or impossible to achieve in most aquifers using hydraulic gradient alone.

The required i's are so high for most aquifer(greater than 1) that no reasonable configuration of pumping and injection wells could be designed to sweep all the required residual NAPL trapped in the pores of the aquifer.

→Addition of Surfactants → Increase N_c by reducing σ

---

2) surfactant washing

＊ Fate of NAPL in the Subsurface.

- Volatilization (transferred to the air)
- Chemical and/or biodegradation
- Dissolution (transferred to water)

(1) Volatilization

Volatilization can occur when NAPL comes in contact with air. For a single-component NAPL, the vapor pressure defines the equilibrium between NAPL and air : the vapor pressure found in chemical reference book is equal to the concentration. of the vapor in the air that is in equilibrium with the single-comp. NAPL.
For NAPL mixture, use Raoult's law.

$$P_a = X_a \cdot P_o^a$$

P_a ; vapor pressure of the NAPL mixture (atm)
X_a ; mole fraction of HC a in NAPL mixture (if single comp. $X_a=1.0$; $P_a=P_o^a$)
P_o^a ; vapor pressure of the HC a as a pure-phase comp.

Ex) benzene NAPL-unsat zone.
ⓐ theoretical conc. of benzene in air stream?
ⓑ ⓐ와 동일. if the NAPL is composed of only 20% of mole fraction of NAPL and 80% non-volatile organics?

<sol>
ⓐ $P_a = X_a \cdot P_o^a = 1.0 \times 0.1 = 0.1$ atm
$C = P_a \times 1{,}000{,}000 = 100{,}000$ ppmv[3]

$$C\ (\mathrm{mg/L}) = \frac{X_a \cdot P_o^a \cdot MW}{RT} = \frac{0.1\mathrm{atm} \times 78.1\mathrm{g/mol} \times 1000\ \mathrm{mg/g}}{0.082 \times \frac{1-\mathrm{atm}}{\mathrm{mol}_\circ\ \mathrm{K}}\ (293_\circ\ \mathrm{K})}$$
$$= 325.1\,\mathrm{mg/Lair}\ @\ 20\,℃$$

ⓑ only 20%
$P_a = 0.2 \times 0.1 = 0.02$ atm (@ 20℃)

---

[3] health based standard

C = 20,000 ppmv

$$C = \frac{0.2\times0.1\times78.1\times1000}{0.082\times293} = 65.1\text{mg/Lair}\ (@20℃)$$

② Chemical & Biological Degradation

· Hydrolysis → mainly the outsied of NAPL mass actually contacts water.

$R\text{-}X \Rightarrow R \cdot OH + X^- + H^+$

X ; Halogen, Carbon, Phosphorous

· In-situ Biodegradation

Instantaneous reaction

Monod Kinetics

Exponential decay

Ex) Instantaneous Reaction

How long does it take to naturally biodegrade 100gal(250kg) of gasoline spill in the saturated zone?

Cond> ① Depth of LNAPL in sat. zone = 2m

② Width of LNAPL in sat. zone = 10m

③ Darcy's velocity of HW = 1m/day

④ Background conc. of oxygen= 5mg/L

⑤ Oxygen-HC consumption ratio = 2mg oxygen/1mgHC

Total oxygen required = 500kg oxygen

∴ Total GW needed

5mg : 1L= 500kg : X(L)

∴ $X=10^8$ L

Time to have 10^8L of GW for 2m×10m NAPL with 1m/day

$10^8\text{L} = 2\text{m}\times10\text{m}\times1\text{m/day}\times10^3\text{L/m}^3\times t$

∴ t = 5000 days → 14years(Bio. only)

⇒Vol. Chem. dissolution should be more rapid.

③ Dissolution

Immiscible NAPL → Water

Factors controlling dissolution rate are the saturation of the NAPL and the effective solubility of NAPL.

For mixed components,

Effective Solubility

$S_i^e = X_i S_i \gamma_i$

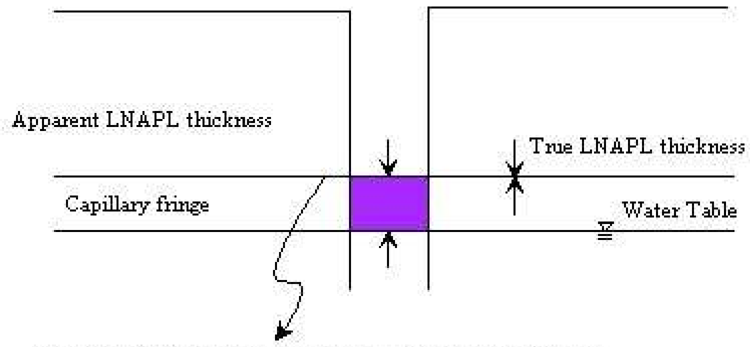
S_i^e : eff. solubility of I in the water phase (mg/L)

X_i : mole fraction of I in multiple NAPL

S_i : Solubility of i in water (mg/L)

γ_i : Correction factor to adjust for contaminant concentration observed in the field(0.1$\sim$0.5). (In soluble organics in the water will reduce the effective soil)

<LNAPL thickness Problem>



LNAPL is floating on the top of the capillary fringe while the NAPL in the well floats on top of the actual water table

If $\rho_n < \rho_w$

it will accumulate on the top of the capillary fringe[4] and eventually flow in the sheets after a certain minimum thickness is achieved.

If the LNAPL flow rate through the vadose zone is fast enough capillary fringe will collapse and LNAPL will float on water table.

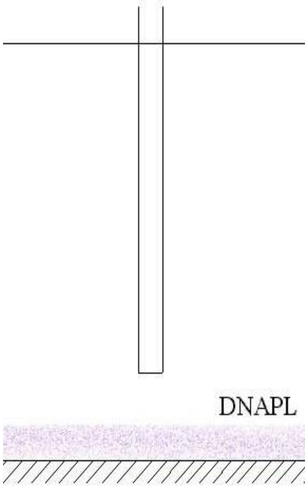
$$h_f = \frac{h_f(\rho_{water} - \rho_{LNAPL})}{\rho_{LNAPL}}$$ (Hampton & Miller, 1988)

h_f : thickness of LNAPL in formation

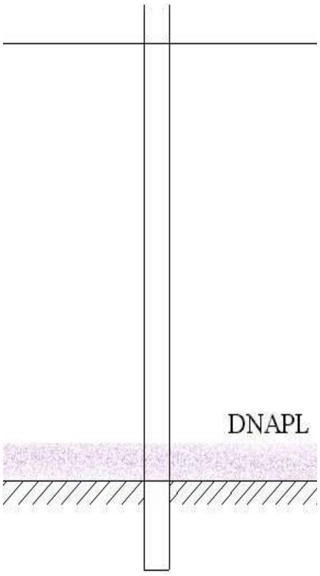
---

[4] water(wetting), LNAPL(non wetting) movement is repelled by capillary fringe.

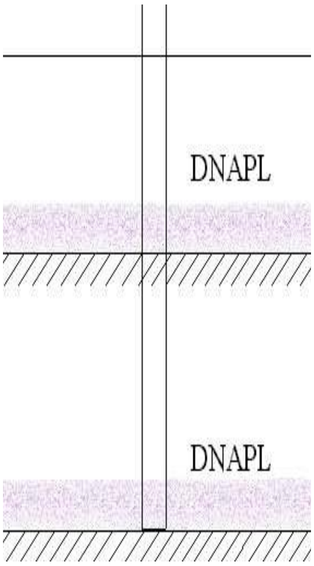
h_w : thickness of LNAPL in well



Screen too high above conf. unit



Screen too deep below conf. unit too much accumulation



Screen penetrates conf. unit Accumulation in wrong place

Hydrophobic dye (Sudan IV)

GW Concentration and Distribution
except Concentration of Dissolved Chemicals in NAPL zones would be near the solution of the chemicals
→ Not! → Why? ① effective sol. interference
② 10'-20' long screen intersects clean flow→dilution

If C_{NAPL} is greater than 1% NAPL presents
(Waterloo Center for GW Research)

If the theoretical pore-water Concentration is greater than the effective solubility of the organic compounds, NAPL may be present at the site.

ⅰ) Calculate S_i^e (effective solubility of the organic compound)

ⅱ) K_{oc}, $K_{oc} = f_n (K_{ow})$

ex) $\log K_{oc} = 1.0 \log K_{ow} - 0.21$

ⅲ) f_{oc}

ⅳ) ρ_b (bulk density), n (porosity)

ⅴ) $K_d = K_{oc} f_{oc}$

ⅵ) measure C_t(measure concentration of organic compound in Saturated soil, mg/kg)

ⅶ) $C_w = \frac{C_t \rho_b}{K_d \rho_b + n}$ (theoretical pore water Concentration)

ⅷ) Compare C_w and S_i^e

$C_w < S_i^e$; possible absence of DNAPL

$C_w > S_i^e$; possible presence of DNAPL

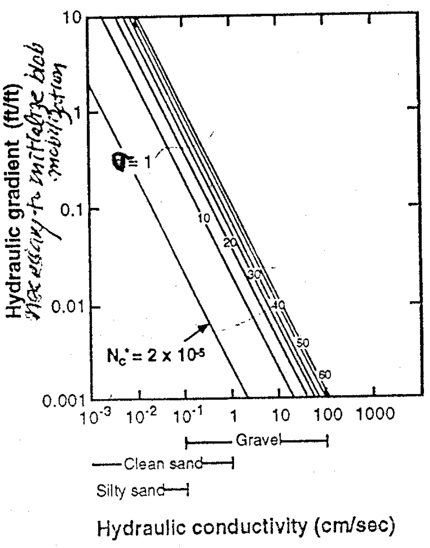


Figure 11.16 Hydraulic gradient necessary to initialize blob mobilization (at N_c^*) in soils of various permeabilities. for hydrocarbons of various interfacial tensions, σ. Source: Wilson and Conrad, 1984.

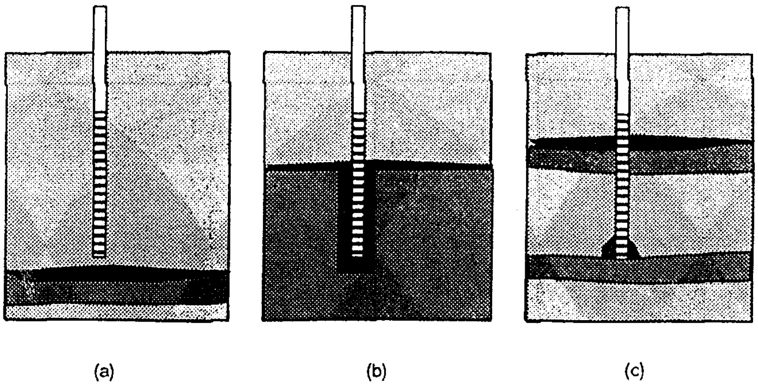


Figure 11.19 Problems with measuring DNAPL in monitoring wells. (a) Screen too high above confining unit. No accumulation. (b) Screen too deep below confining unit. Too much accumulation. (c) Screen penetrates confining unit. Accumulation in wrong place.

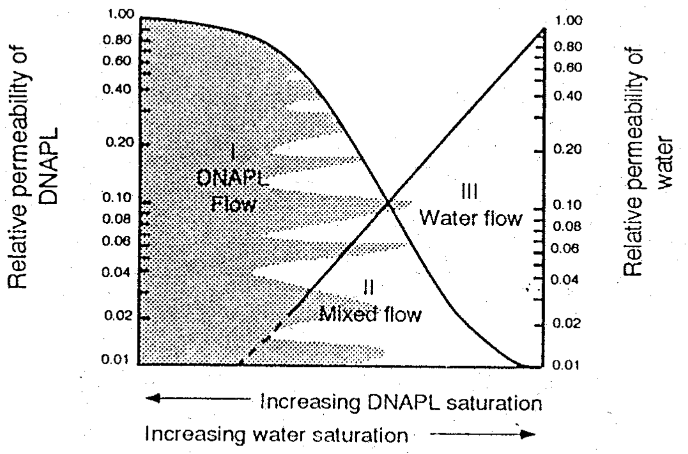


Figure 11.14 Different flow regimes in NAPL–water system. Source: Williams and Wilder, 1971.

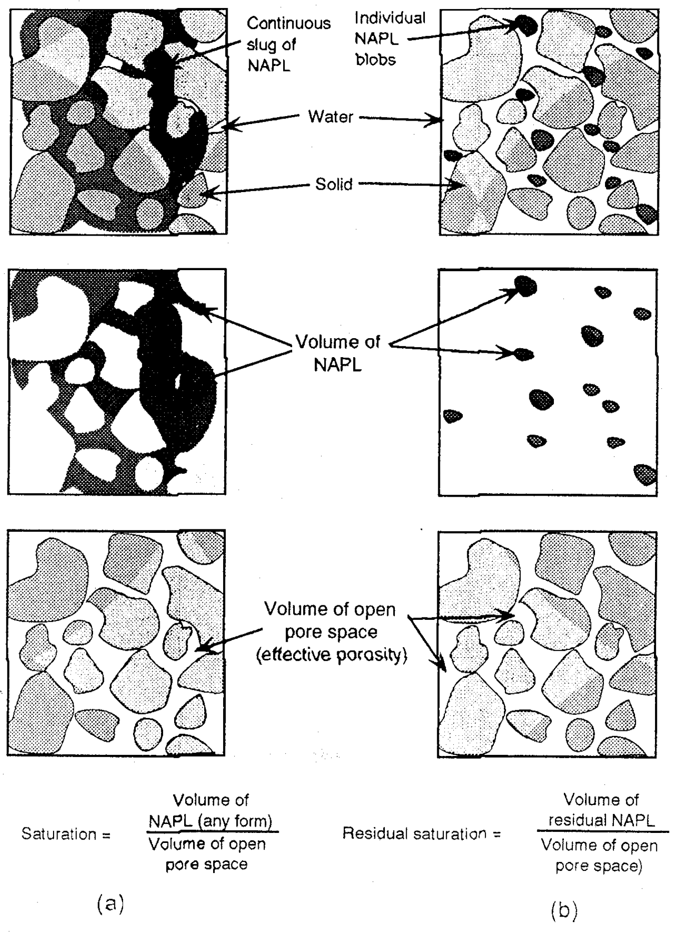


Figure 11.3 Saturation and residual saturation. (a) Free-phase DNAPL. (b) Residual NAPL.

② Clay aquitards that same as effective confining units in the context of GW flow may not serve as effective barriers to migration of some NAPLs. Some Low-viscosity DNAPLs can penetrate and migrate through fractures as small as 20㎛ ??

DRASTIC

1. DRASTIC Mehotd 정의 및 필요성

- ▸ Simple Risk Assessment Method for Raing the Subsurface (specifically, Groundwater) Contamination Potential of Any Area
- ▸ DRASTIC is designed to be used as a Planning Screening or Prioritizing Tool.
- ▸ D: Depth to water
  R: Recharge
  A: Aquifer media
  S: Soil media
  T: Topography
  I: Impact of the vadose zone
  C: Conductivity of aquifer (hydraulic)
- ▸ 환경영향평가와 더불어, DRASTIC과 같은 Rating 기법을 활용하여 매립지 부지 선정시 해당 부지의 지반오염 위해도 가능성과 부지의 선정타당성을 객관, 정량화 한다.

2. DRASTIC FACTORS

(1) Depth to Water

· Confined Aquifer: Surface to the top of the aquifer(having Piezometric surface)
· Unconfined Aquifer: Surface to the water table(having atmosphere surface)

“지하수가 지표로부터 깊을수록 낮은 점수(rating)” 왜냐하면 지표에서 지하수까지의 깊이가 깊을수록 오염물질의 이동거리가 길어지고 이동시간이 지체되어 오염물질이 이동중 attenuation될 확률이 높다.

(2) Recharge

Recharge is the amount of water per unit area of land which penetrates the surface and reaches the water table-수문학적 자료

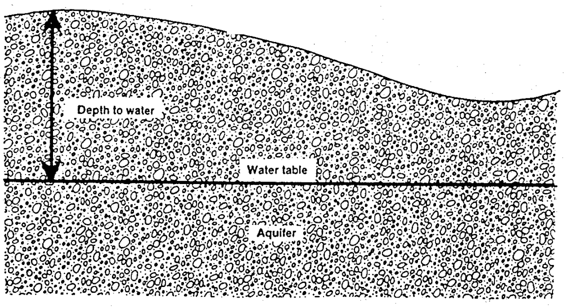
“Recharge가 많을수록 오염물질을 더욱 쉽게 이동시키어 지반의 오염가능성을 높인다.
(except. dilution less than GW pollution potential). Recharge가 적을수록 낮은 점수“

참고: Recharge and Discharge Area by Hydraulic gradient.

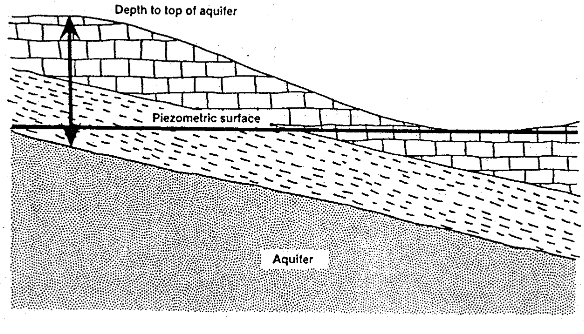
(3) Aquifer Media

"In general, the larger the grain size and the more fractures within the aquifer, the higher the permeability and the lower the attenuation capacity of the aquifer media."

Rating: Limestone > Sand and Gravel > Silt and Clay Mixtures > Metamorphic/Igneous Rock > Massive Shale (least contamination potential, lowest rating)



A. Determining depth to water in an unconfined aquifer.



B. Determining depth to water in a confined aquifer.

Figure 19. Diagrams showing how to determine depth to water.

(4) Soil Media

대략 0'-6' 사이의 표층흙.

“The less the clay shrinks and swells and the smaller the grain size, the less the pollution potential."

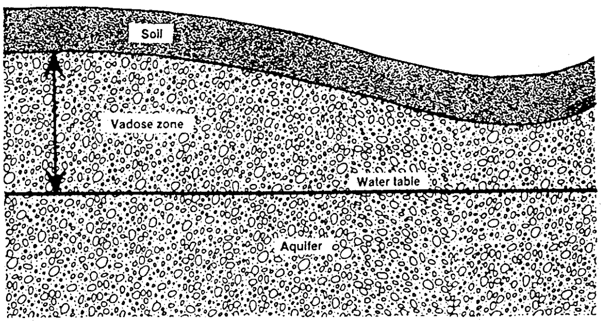
Rating: Gravel > Sand > Silt > Clay (lowest pollution potential)

(5) Topography

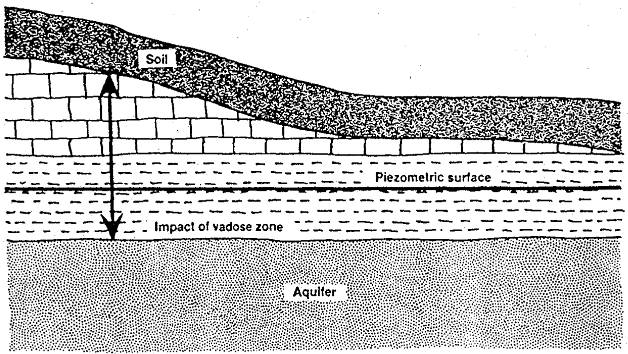
지표의 경사/굴곡 상태
“경사가 급할수록 낮은 점수. Runoff에 의하여 지반으로 infiltration하지 않고 흘러지나간다. 보통 2% 이하의 경사로 된 지역은 오염가능성이 가장 높고, 18% 이상의 경사지는 오염물질의 지표유입 가능성이 적어 가장 낮은 점수.”

(6) Impact of Vadose Zone

Bottom of the Soil Layer(0'-6') down to Water Table(Unconf.) or to the top of the aquifer (Conf.)
Vadose zone 이 어떠한 물질인가에 따라 rating 결정. Gravel, sand, silt, clay의 순으로 pollution potential 감소, 낮은 점수.



A. Determining the impact of the vadose zone media in an unconfined aquifer.



B. Determining the impact of the vadose zone media in a confined aquifer.

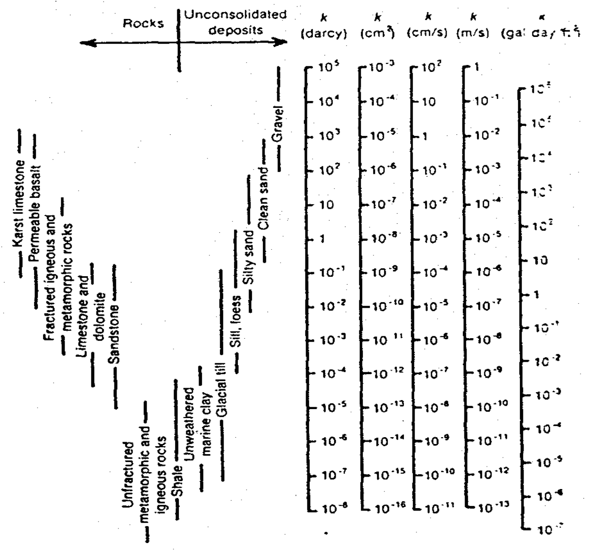
Figure 21. Diagrams showing how to determine the impact of the vadose zone media.

(7) Conductivity

Hydraulic conductivity of the aquifer.

k값이 작을수록 낮은 점수.
Rating: Gravel > Sand > Silt > Clay (낮은 점수)
"It is evident that all of the DRASTIC parameters are interacting, dependent variables."

TABLE 12. RANGE OF VALUES OF HYDRAULIC CONDUCTIVITY AND PERMEABILITY (FREEZE AND CHERRY,1979)



3. DRASTIC에 의한 Risk Assessment

▸ How to Use DRASTIC?

(1) Identify the Region

(2) Select Settings that Best Matches Your Area

(3) Adjust DRASTIC Ratings if Necessary

▸ DRASTIC Index = Weight × Rating

(Examples : Glacial Till / Alternating SS, LS, and SH - Thin Soil)

GLACIATED CENTRAL

(7Aa) Glacial Till Over Bedded Sedimentary Rocks

This hydrogeologic setting is characterized by low topography and relatively flat-lying, fractured sedimentary rocks consisting of sandstone, shale and limestone which are covered by varying thicknesses of glacial till. The till is chiefly unsorted deposits which may be interbedded with loess or localized deposits of sand and gravel. Although ground water occurs in both the glacial deposits and in the intersecting bedrock fractures, the bedrock is the principal aquifer. The glacial till serves as a source of recharge to the underlying bedrock. Although precipitation is abundant in most of the region, recharge is moderate because of the glacial till and soils which are typically clay loams. Depth to water is extremely variable depending in part on the thickness of the glacial till, but tends to average around 30 feet.

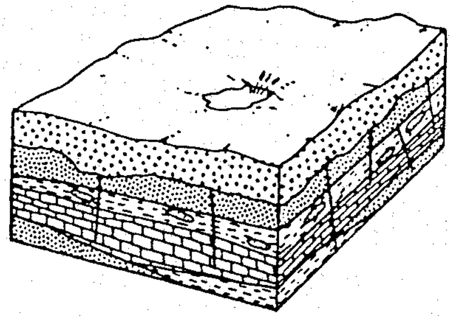


Figure 22. Description and illustration for setting 7Aa—glacial till over bedded sedimentary rocks.

NON-GLACIATED CENTRAL

(6Da) Alternating SS, LS, and SH - Thin Soil

This hydrogeologic setting is characterized by low to moderate topographic relief, relatively thin loamy soils overlying horizontal or slightly dipping alternating layers of fractured consolidated sedimentary rocks. Ground water is obtained primarily from fractures along bedding planes or intersecting vertical fractures. Precipitation varies widely in the region, but recharge is moderate where precipitation is adequate. Water levels are extremely variable but on the average moderately shallow. Shale or clayey layers often form aquitards, and where sufficient relief is present, perched ground water zones of local domestic importance are often developed.

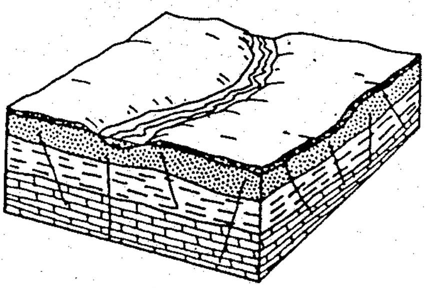


Figure 23. Description and illustration for setting 6Da—alternating sandstone, limestone and shale-thin soil.

TABLE 14. DRASTIC AND PESTICIDE DRASTIC CHARTS FOR SETTING 7Aa — GLACIAL TILL OVER BEDDED SEDIMENTARY ROCKS

Setting 7Aa Glacial Till Over Bedded Sedimentary Rock		General		
Feature	Range	Weight	Rating	Number
Depth to water	30-50	5	5	25
Net recharge	4-7	4	6	24
Aquifer media	Bedded SS, LS, SH sequences	3	6	18
Soil media	Clay loam	2	3	6
Topography	2-6%	1	9	9
Impact vadose zone	Silt/Clay	5	3	15
Hydraulic conductivity	100-300	3	2	6
			Drastic Index	103

Setting 7Aa Glacial Till Over Bedded Sedimentary Rock		Pesticide		
Feature	Range	Weight	Rating	Number
Depth to water	30-50	5	5	25
Net recharge	4-7	4	6	24
Aquifer media	Bedded SS, LS, SH sequences	3	6	18
Soil media	Clay loam	5	3	15
Topography	2-6%	3	9	27
Impact vadose zone	Silt/Clay	4	3	12
Hydraulic conductivity	100-300	2	2	4
			Pesticide Drastic Index	125

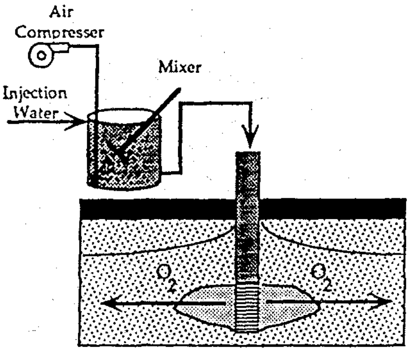
TABLE 15. DRASTIC AND PESTICIDE DRASTIC CHARTS FOR SETTING 6Da — ALTERNATING SANDSTONE, LIMESTONE AND SHALE — THIN SOIL

Setting 6Da Alternating Sandstone, Limestone and Shale — Thin Soil		General		
Feature	Range	Weight	Rating	Number
Depth to water table	15-30 ft	5	7	35
Net recharge	4-7 in	4	6	24
Aquifer media	Thin bedded SS, LS, SH sequences	3	6	18
Soil media	Loam	2	5	10
Topography	2-6%	1	9	9
Impact vadose zone	Bedded LS, SS, SH	5	6	30
Hydraulic conductivity	1-100 gpd/ft^2	3	1	3
			Drastic Index	129

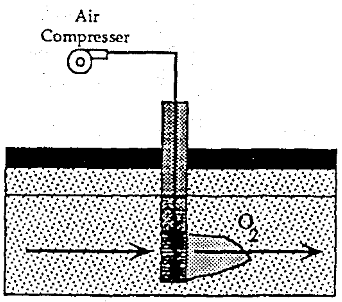
Setting 6Da Alternating Sandstone, Limestone and Shale — Thin Soil		Pesticide		
Feature	Range	Weight	Rating	Number
Depth to water table	15-30	5	7	35
Net recharge	4-7	4	6	24
Aquifer media	Thin bedded SS, LS, SH sequences	3	6	18
Soil media	Loam	5	5	25
Topography	2-6%	3	9	27
Impact vadose zone	Bedded LS, SS, SH	4	6	24
Hydraulic conductivity	1-100	2	1	2
		Pesticide Drastic Index		155

Methods of Supplying Oxygen to Grounwater:

1. Air Sparging



Sparging With Injection



Sparging Directly Into Well

Maximum oxygen concentration: 5-10㎎/l

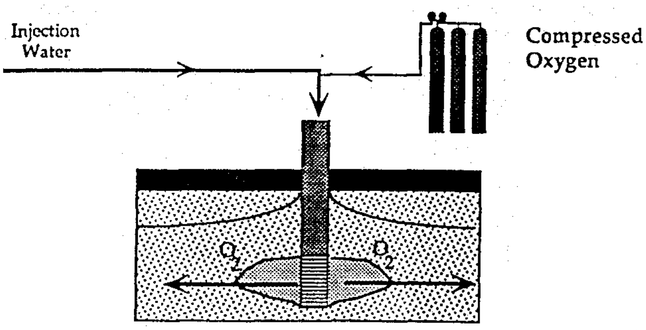
Advantages:

- Inexpensive.
- Easy to operate.

Disadvantage:

- Low oxygen delivery rate;slow.
- Possible water chemistry problems.

2. Compressed Oxygen



Maximum oxygen concentration: 20-40㎎/l

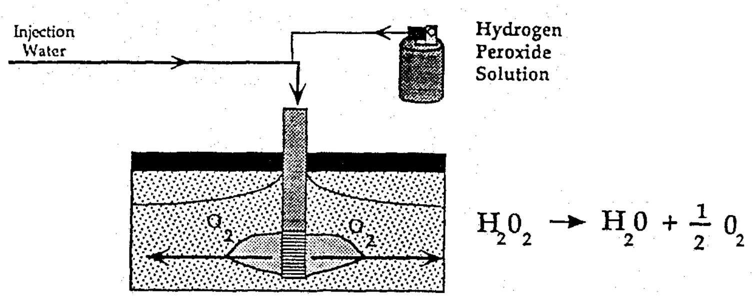
Advantages:

- Higher oxygen concentration than sparging.
- Reliable.

Disadvantage:

- Management of O_2 supply
- Higher operating cost.

3. Hydrogen Peroxide



$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$$

Maximum oxygen concentration: 50-100㎎/l

Advantage:

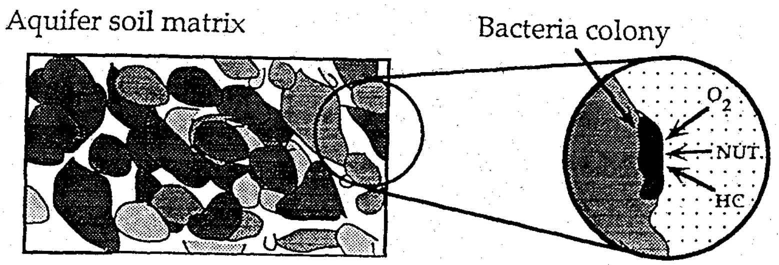
- Easy to handle.
- Provides very high oxygen concentrations.

Disadvantage:

- Peroxide stability problems.
- Can sterilize aquifer if overapplied.
- Expensive.

Overview of In-Situ Biodegradation

- Research performed by EPA and Rice University.
- Uses native bacteria in aquifer.
- Degradation hydrocarbons to CO_2 and H_2O
- Can be used for dissolved constituents and residual hydrocarbons.
- Engineering application: add oxygen and nutrients.



Where

C_r = total quantity of chemical per unit soil volume.

C_A = adsorbed chemical concentration.

C_L = dissolved chemical concentration.

C_G = vapor concentration.

p_b = soil bulk density.

Θ_L = volumetric water content.

Θ_G = volumetric air content.

The equilibrium relationship b/w vapor concentration (C_G) and the associated pure water concentration(C_L) is given by Henry's Law.

$C_G = K_H \cdot C_L$ (2)

K_H : Henry's law constant → Air stripping에 가장 중요한 factor

Likewise, the relationship between equilibrium solution conc. and adsorbed conc. is given by;
$C_A = K_d \cdot C_L$ (3)

K_d is the distribution coefficient (L^3/M) expressed as $K_d = f_{oc}\ K_{oc}$ where f_{oc} is the organic constant and K_{oc} is the organic carbon partition coeff. Eq(3) is valid for soils with $f_{oc} > 0.1\%$

Mathematical Model for SVE

The above eq's have defined partitioning of conts. in the subsurface without air movement. Partitioning without advective air movement occurs via diffusion.
Under SVE operating conditions, both diffusive and advective transport are occurring.

$$\Theta_G \frac{\partial C_G}{\partial t} + \Theta_L \frac{\partial C_L}{\partial t} + P_b \frac{\partial C_A}{\partial t} = \Theta_G D_{ij} \frac{\partial}{\partial X_i} \frac{(\partial C_G)}{(\partial X_j)} - \Theta_G V_i \frac{\partial C_G}{\partial X_i}$$

D_{ij} : dispersion coeff tensor
V_i : air velocity from Darcy's law