EnvSE 408

Contaminant Hydrology

TABLE 1.1 Ground-water usage in the United States, 1985.

Category	Ground-water Use (million gallons/day)	Percent of Total Use Supplied by Ground Water
Public water supply	14,600	40.0
Domestic, self-supplied	3,250	97.9
Commercial, self-supplied	746	60.7
Irrigation	45,700	33.4
Livestock	3,020	67.6
Industrial (fresh)	3,930	17.6
Industrial (saline)	26	0.7
Mining (fresh)	1,410	52.8
Mining (saline)	626	81.9
Power plant cooling	608	0.5

Source: Solley, Merk, and Pierce, 1988.

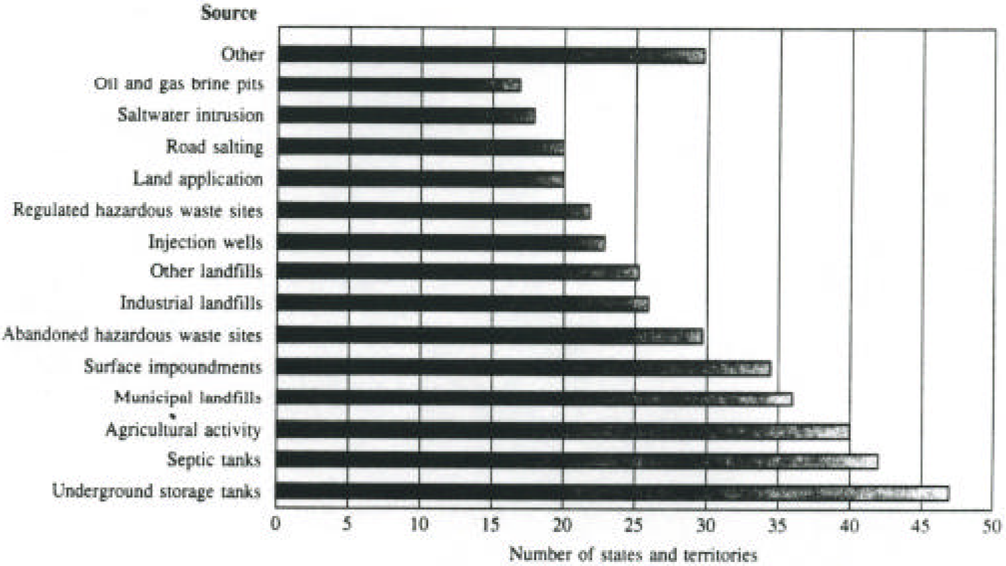


FIGURE 1.2 Frequency of various contamination sources considered by states and territories of the United States to be major threats to ground-water quality. *Source:* National Water Quality Inventory, 1988 Report to Congress, Environmental Protection Agency, 1990.

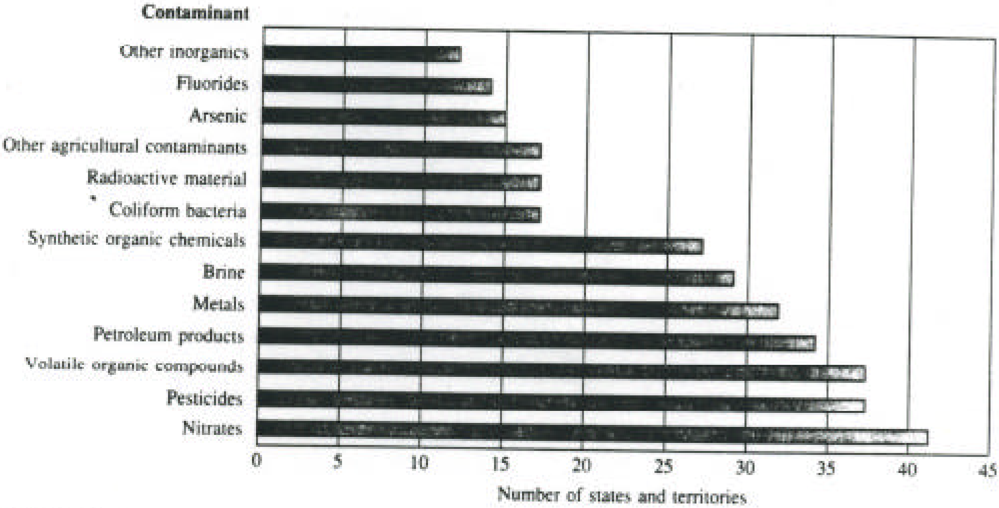
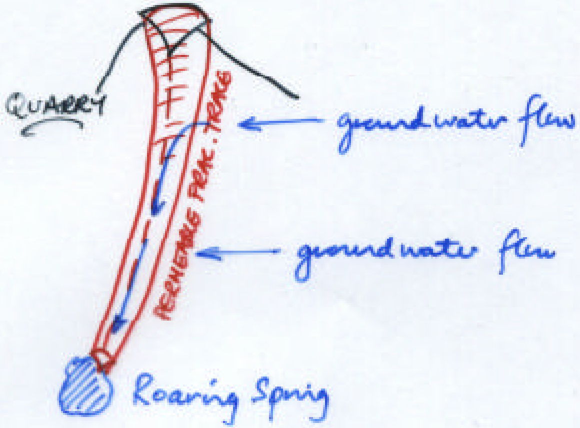


FIGURE 1.5 Frequency of various contaminants considered by states and territories of the United States to be a major threat to ground-water quality. *Source:* National Water Quality Inventory, 1988 Report to Congress, Environmental Protection Agency, 1990.

WATER RESOURCE PROTECTION

New Enterprise Stone & Lime (Huntingdon, PA).

- Expand quarry by deepening -
- What effect on g/w resources?



Uses: Appleton Paper 500,000 gal/day

Roaring Spring Bottling: 30,000 gal/da

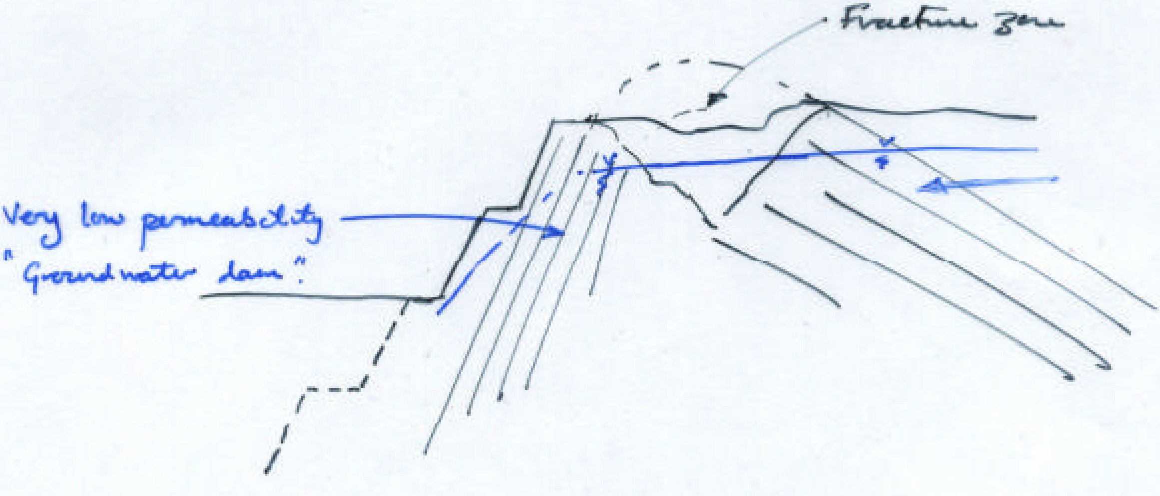


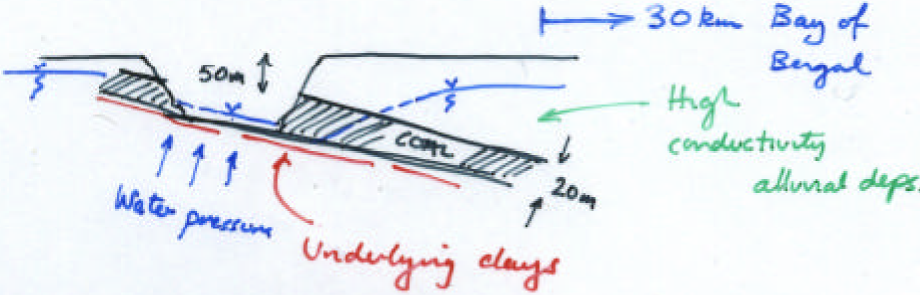
Figure 4-2
Regional Geologic Map
From: U.S.G.S. 7.5 min. Roaring Spring
and Martinsburg quads.
Scale: 1" - 5208.33'

MEISER & EARL, INC. / Hydrogeologists

1512 W. COLLEGE AVE.
STATE COLLEGE, PA 16801

GROUNDWATER PROTECTION

Neyvelli, India.



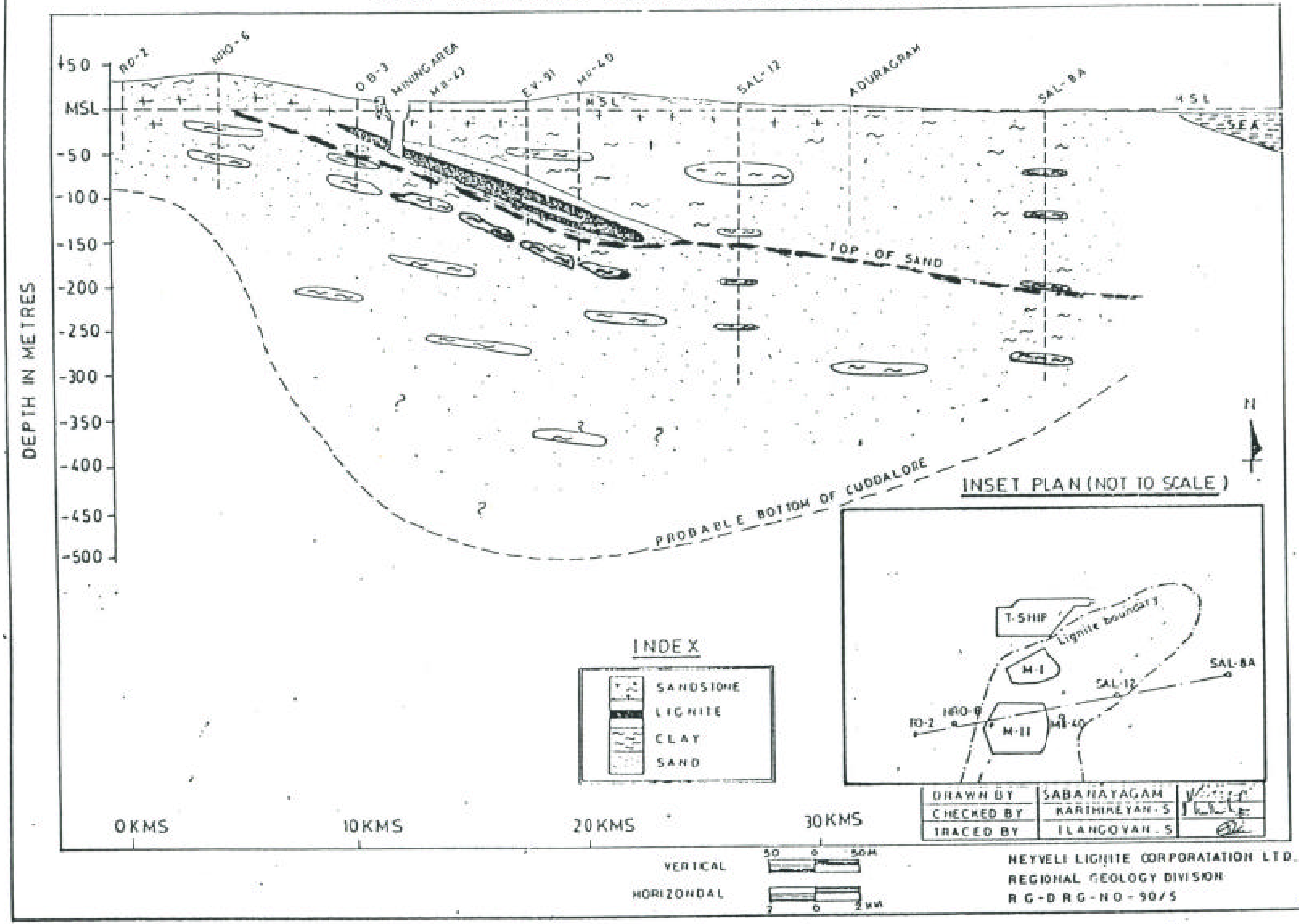
Purpose: • Dewater coals prior to mining – not possible

• Depressurize coals to prevent uplift/rupture

Problems:
- 80 – 160 m below ground level
- Groundwater flow 450,000 tons/day
- Monsoons

Benefits: Excess water
- Consumed by power plants (600 MW).
- 30 M gallons/yr used for agriculture.

WEST EAST CROSS SECTION ACROSS SECOND MINE



DRAWN BY	SABANAYAGAM	
CHECKED BY	KARTHIKEYAN. S	
TRACED BY	ILANGOVAN. S	

NEYVELI LIGNITE CORPORATATION LTD.
REGIONAL GEOLOGY DIVISION
R G-D R G-N O-90/5

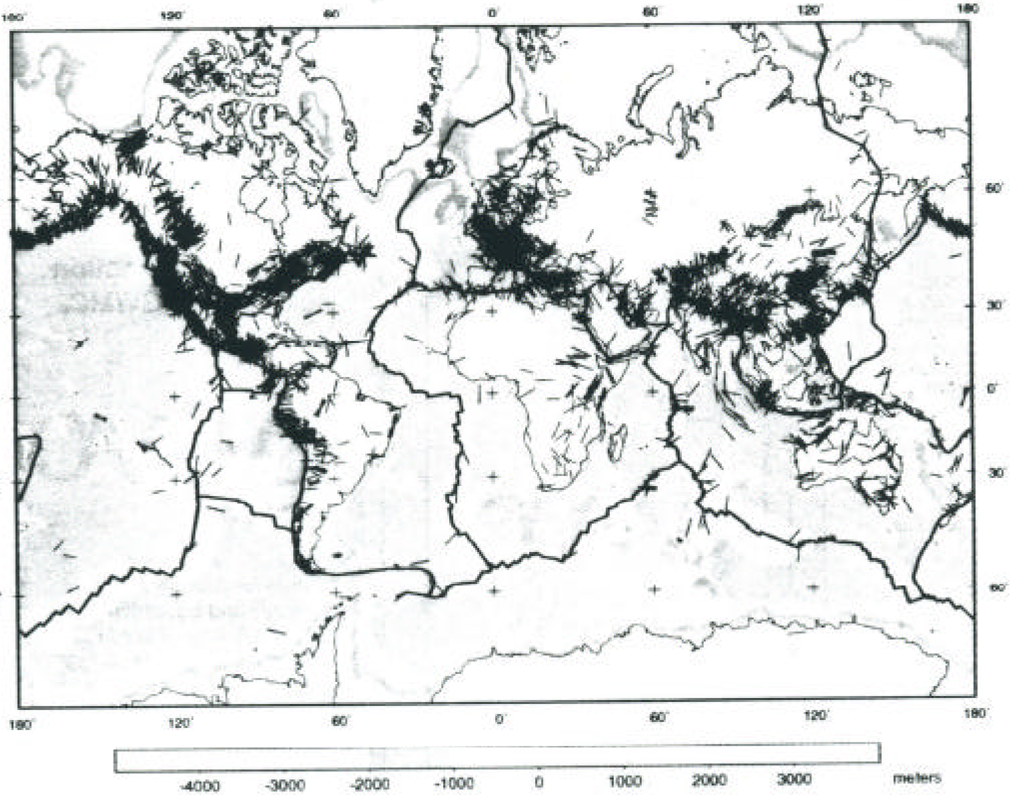


Fig. 1. World stress map, with S_{Hmax} orientations plotted on a base of average topography. Line lengths of data are proportional to quality. Red data indicate a normal faulting stress regime, green data indicate a strike-slip faulting stress regime, purple data indicate a thrust faulting stress regime, and black data indicate an unknown stress regime.

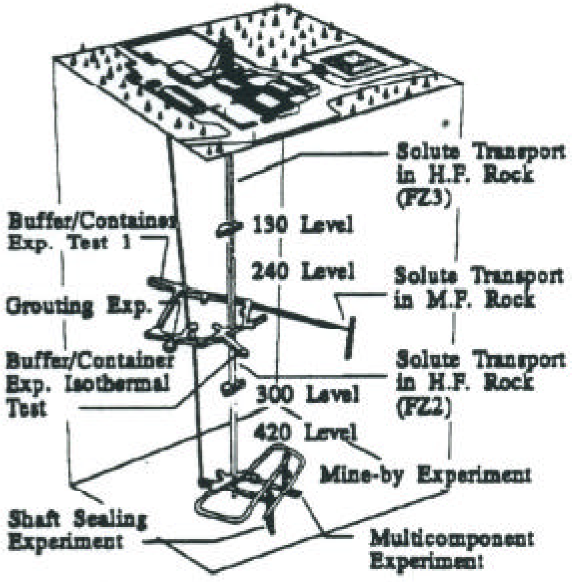
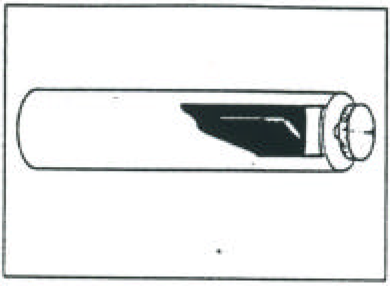


Figure 1 The location of AECL's experiments in the URL

Safety barrier system for high-level waste

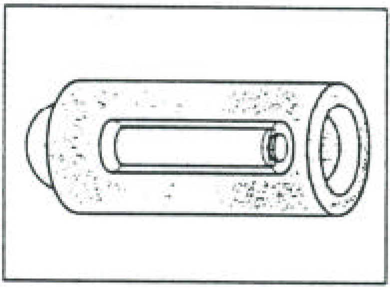
Glass matrix (in steel mould)

- Low corrosion rate of glass
- High resistance to radiation damage
- Homogeneous radionuclide distribution



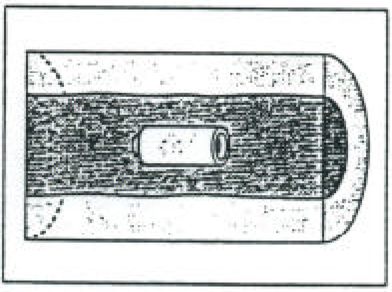
Steel container

- Completely isolates waste for > 1000 years
- Corrosion products act as a chemical buffer
- Corrosion products take up radionuclides



Bentonite backfill

- Long resaturation time
- Low solute transfer rates (Diffusion)
- Retardation of radionuclide transport (Sorption)
- Chemical buffer
- Low radionuclide solubility in leachate
- Colloid filter
- Plasticity (self-healing following physical disturbance)



Geological barriers

Repository zone:

- Low water flux
- Favourable hydrochemistry
- Mechanical stability

Geosphere:

- Retardation of radionuclides (sorption, matrix diffusion)
- Reduction of radionuclide concentration (dilution, radioactive decay)
- Physical protection of the engineered barriers (e.g. from glacial erosion)

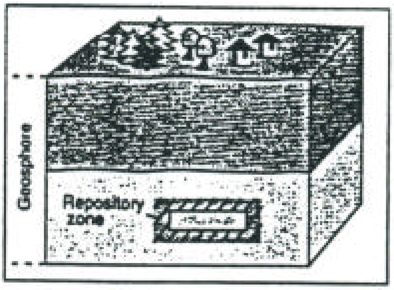


Fig. 2 The safety barrier system for disposal of high-level waste.

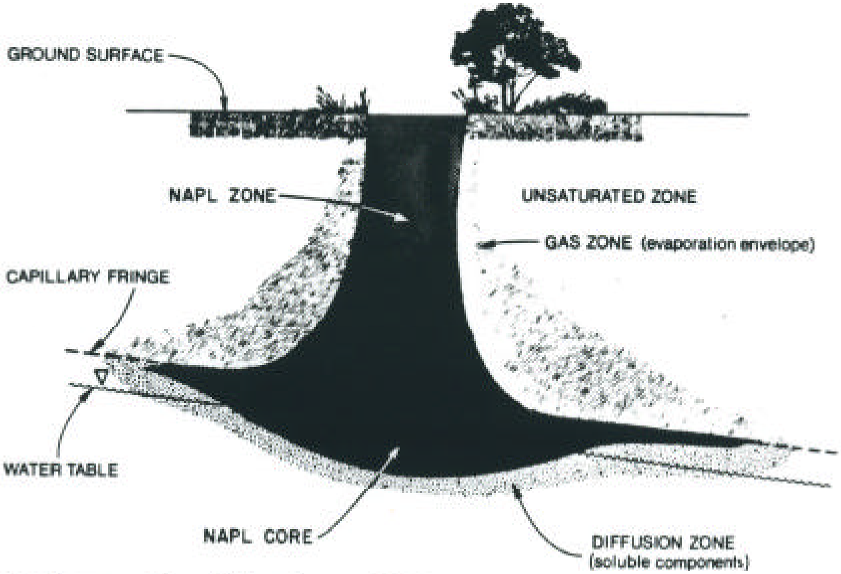


Fig. 1. Schematic representation of lighter than water NAPL movement through the unsaturated and into the saturated zone [after *Abriola and Pinder*, 1985*a*].

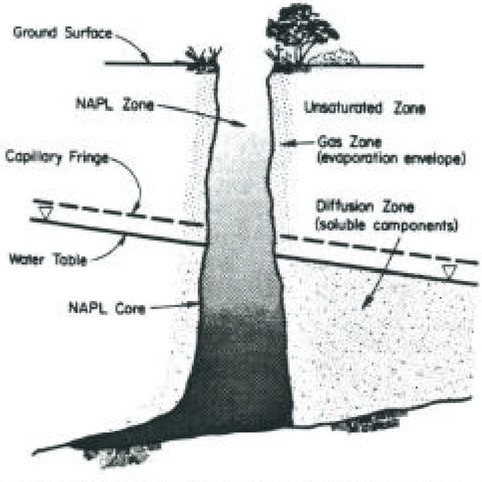


Fig. 2. Schematic representation of heavier than water NAPL movement through the saturated and unsaturated zones.

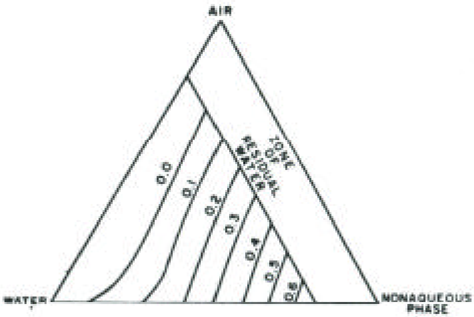
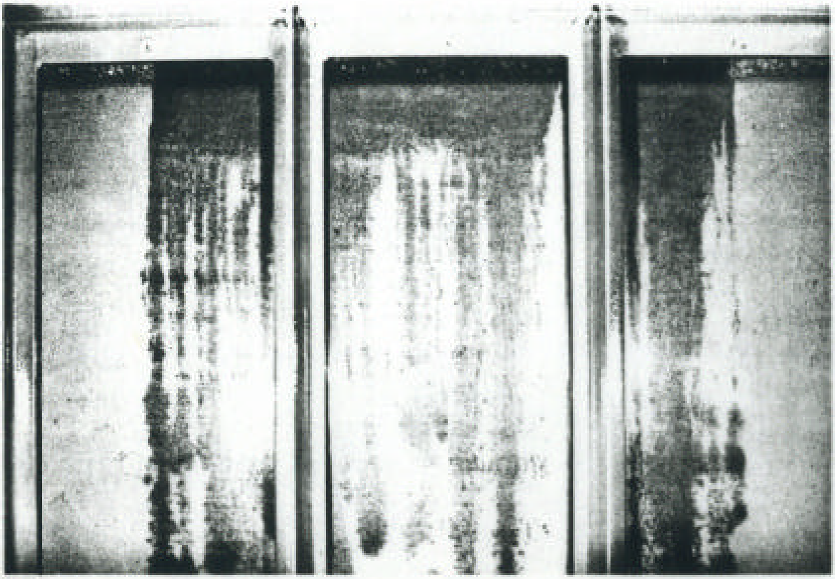


Fig. 3. Ternary diagram showing the relative permeability of the nonaqueous phase as a function of phase saturations [after *Faust*, 1985].

X.a.



X.b.

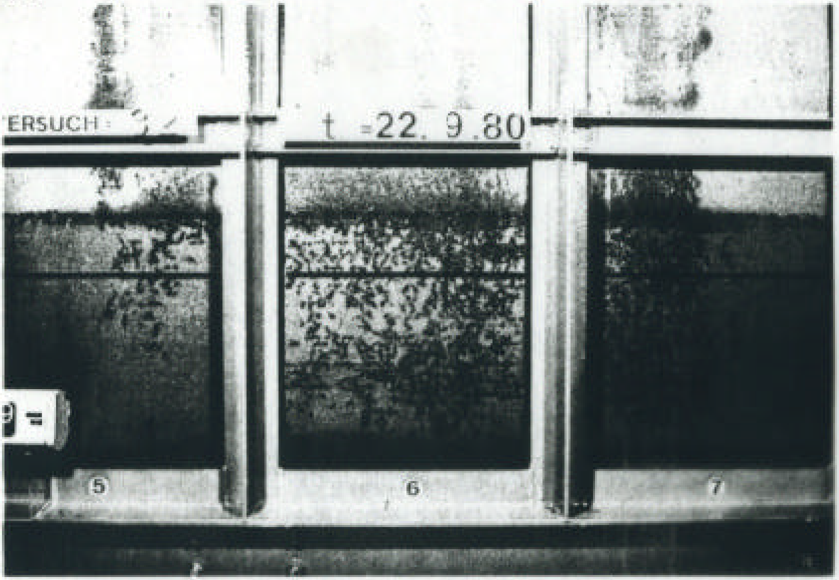


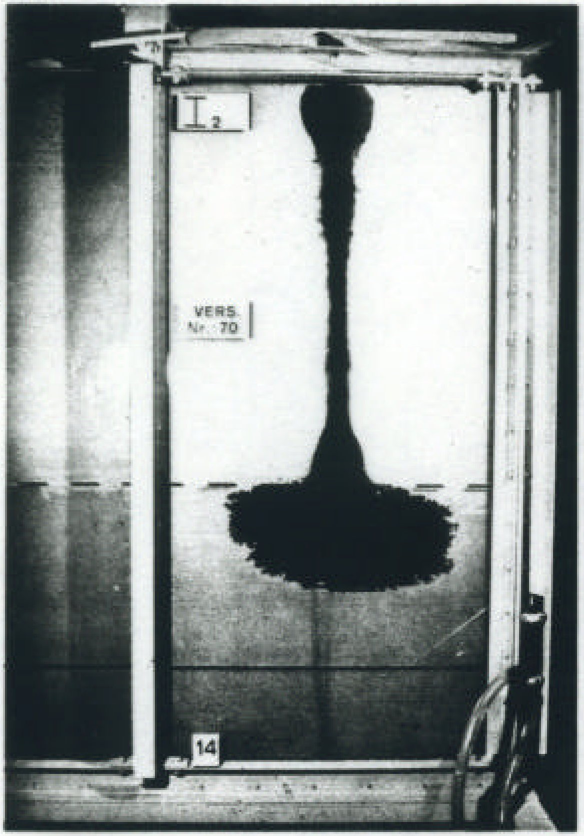
Figure X.a. Sheet-like spill of 36.3 L of PER. View of spill above the capillary fringe.

Figure X.b. Sheet-like spill of 36.3 L of PER. View of spill below the capillary fringe. Time = ~10 min.

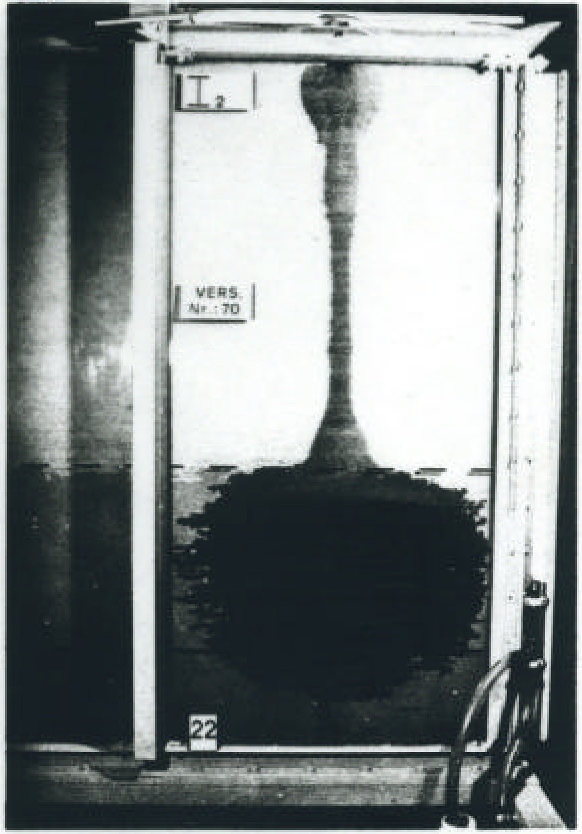
I.a.
PER. Kinematic
= 0.54 mm^2/s.
~1 h.

I.b.
PER. Later
spill depicted in
I.a. Kinematic
= 0.54 mm^2/s.

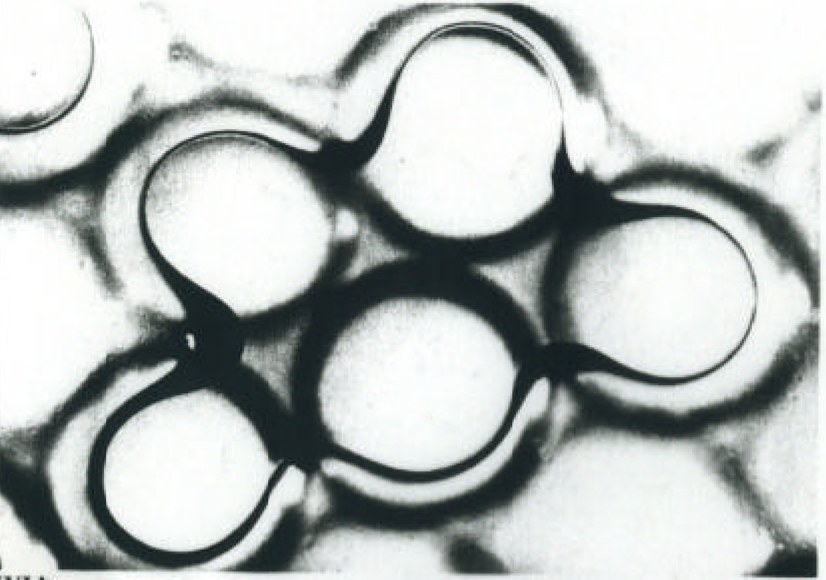
XI.a.



XI.b.



XVI.a.

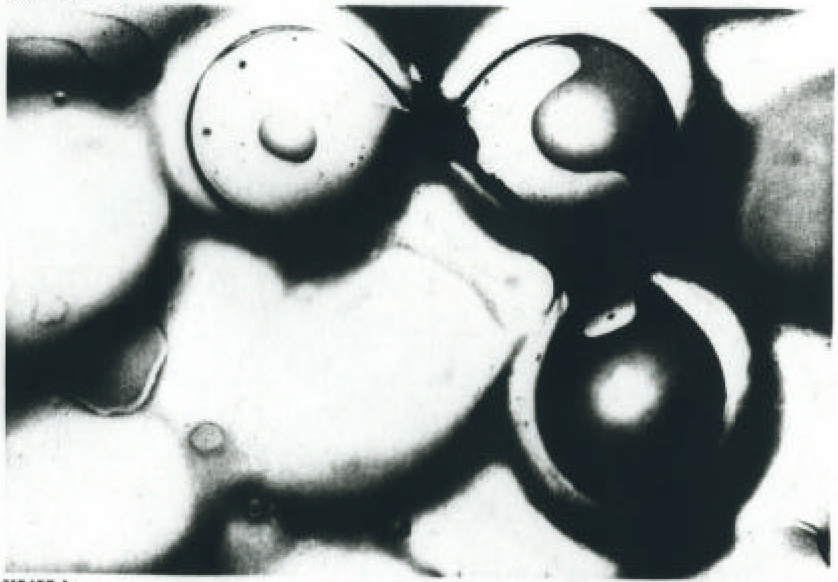


XVI.b.

Figure XVI.a. Beads initially moist; diameter range = 0.85 - 1.23 mm. PER then dripped in from above. The PER accumulated as a sheath around a zone of high water content.

Figure XVI.b. Beads initially saturated with water; diameter range

XVII.a.



XVII.b.

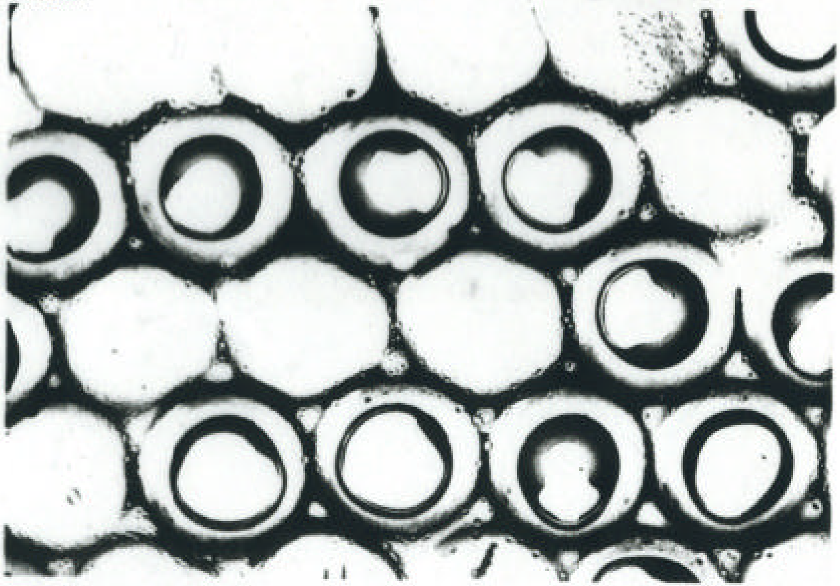
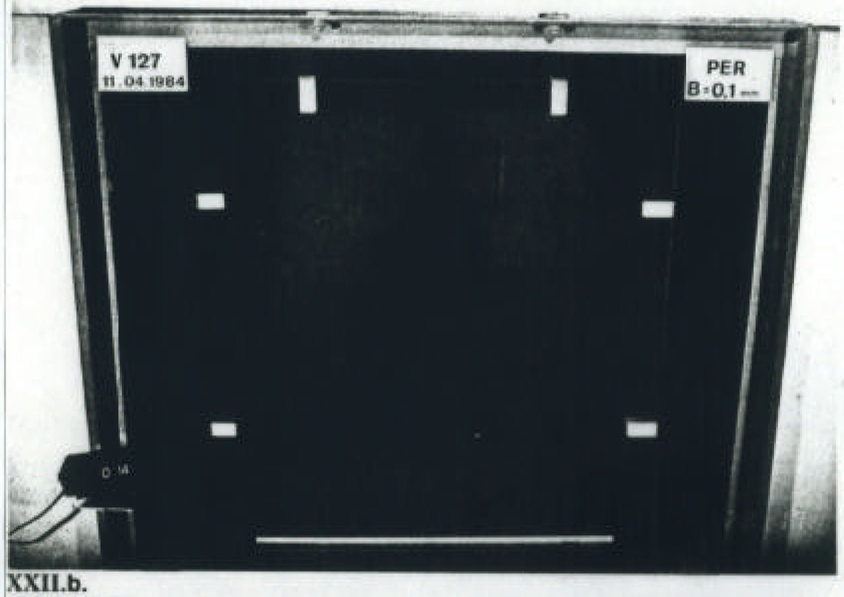


Figure XVII.a. Beads initially dry; diameter range = 0.85 - 1.23 mm. PER first applied from above. Water then applied from above. Infiltrating water drove PER from the bead surfaces.

Figure XVII.b. Later stage of process depicted in Figure XVII.a.

XXII.a.



XXII.b.

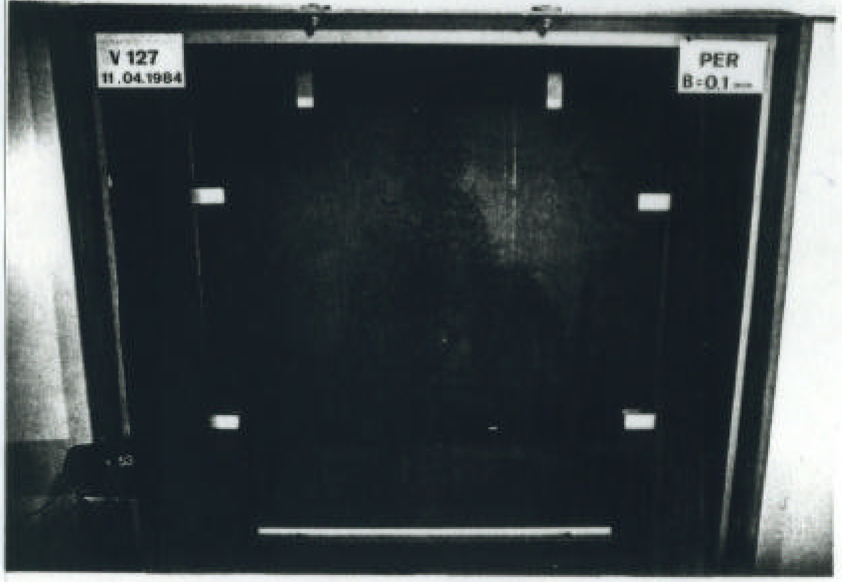
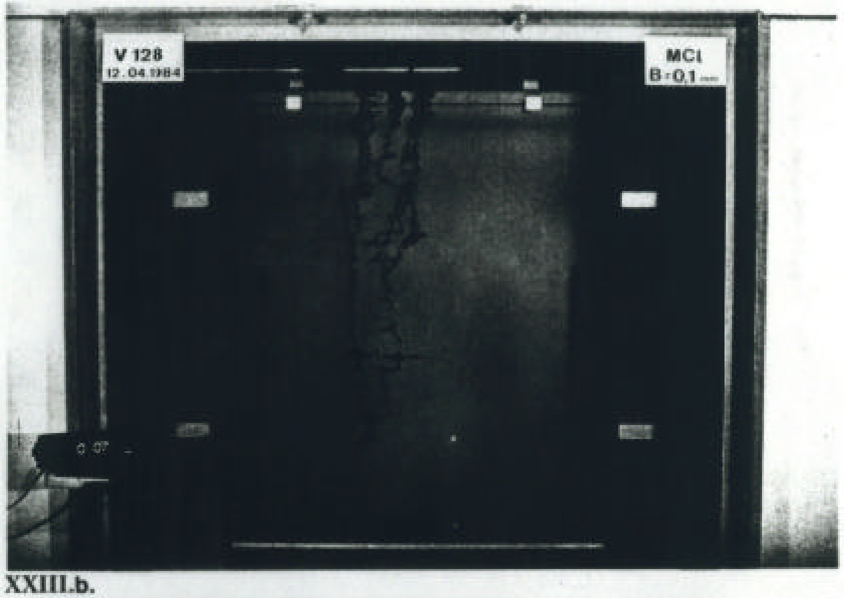


Figure XXII.a. Fracture with an aperture of 0.1 mm, and rough walls initially saturated with water. Water level then lowered. PER then applied at 1.3 mL/min. Water remaining on fracture walls affected distribution of PER.

Figure XXII.b. Same system as in Figure XXII.a., but at 1.5 h after discontinuation of the application of PER. All PER shown is in a stable state.

XXIII.a.



XXIII.b.

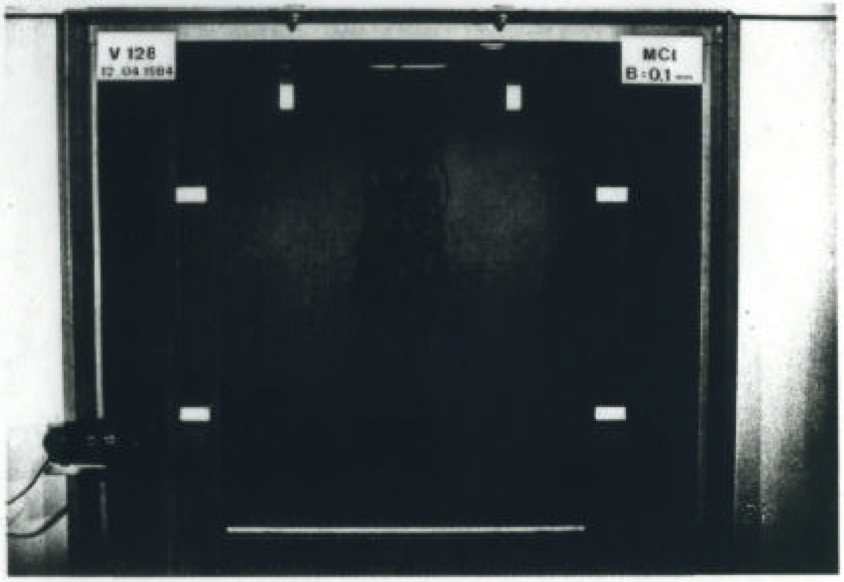
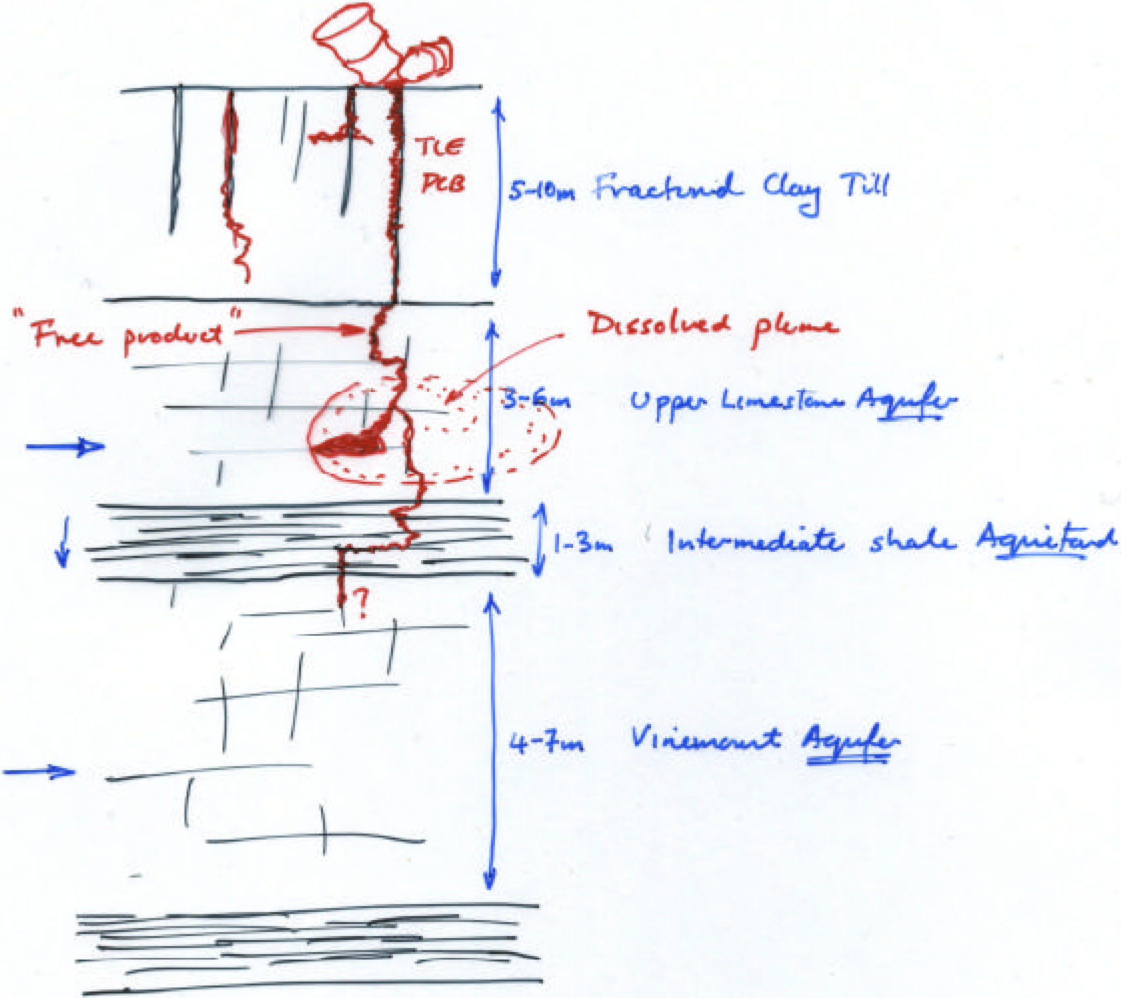
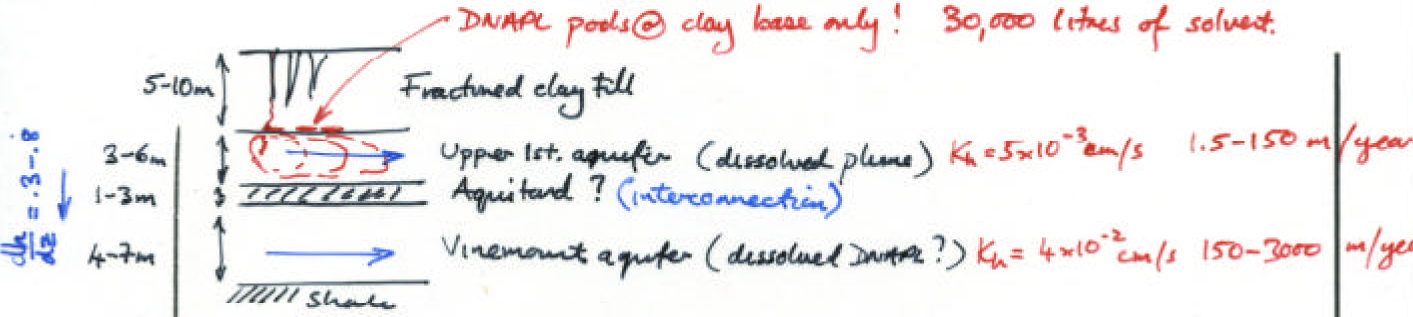


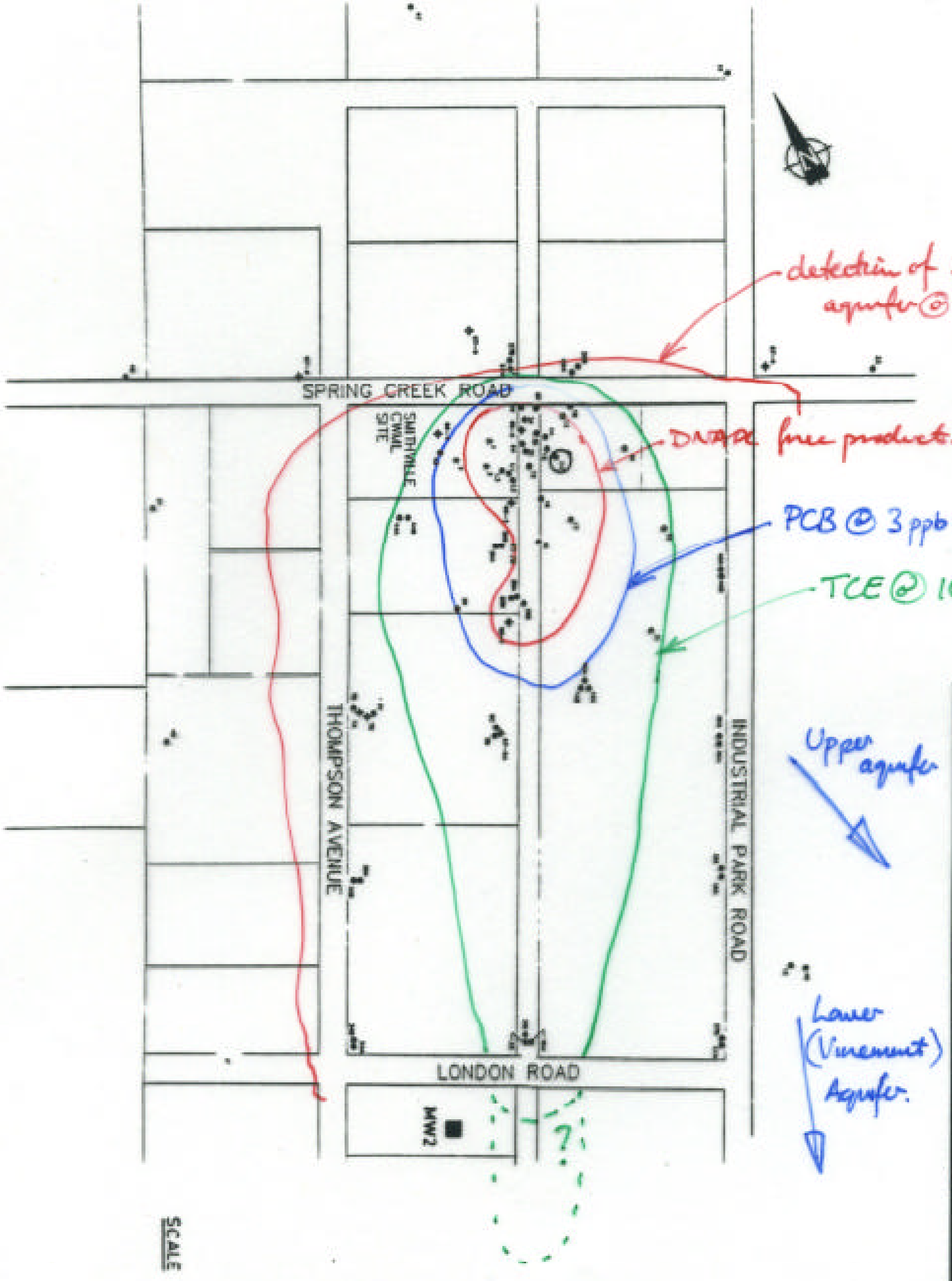
Figure XXIII.a. Infiltration of DCM into a fully saturated fracture with an aperture of 0.1 mm, and rough walls. DCM appled at 1.4 mL/min. Results similar to those for PER in Figure XXI.b.

Figure XXIII.b. Continuation of Figure XXIII.a. experiment. 45 min after ending the DCM application, the water level was lowered. Little DCM

SMITHVILLE SITE







WELL LOCATION PLAN

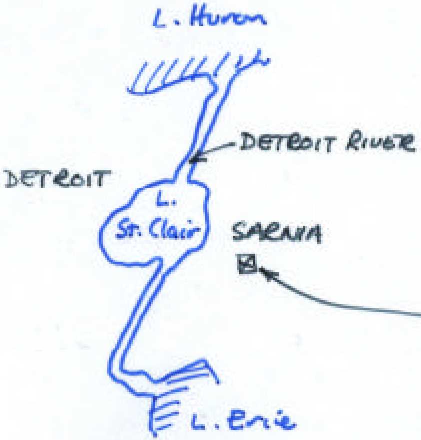
FIGURE 4

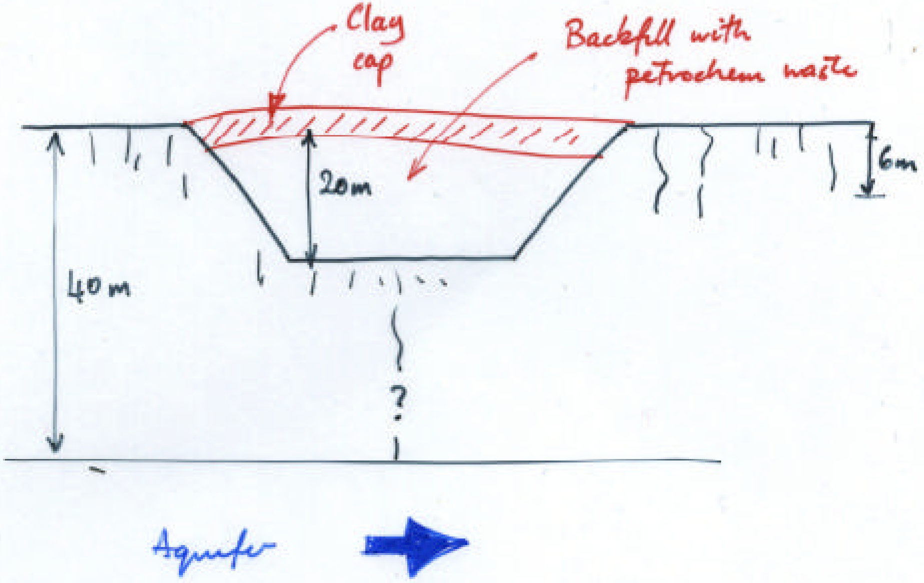
Golder Associates

SCALE 1:3100

Date ....
Project 881-1505M
Drawn ....
Chkd ....

HYDROLOGY OF AQUICLUDES





SCIENTIFIC ISSUES

Most insidious/penetrative contaminants are NAPLs.

1. How to determine location of free product:
   - what hydrologic controls (multiphase flow)
   - how far will it migrate
     - influence of unsaturated zone; fractures; g/w flow
   - once arrested, will it remobilize? can it?

2. Characterization of travel/retardation times:
   - What are the dissolution rates
   - How quickly and at what concentration will the plume develop?
   - How long will it endure?

3. Methods of removal/isolation: (Economics)
   - What methods will work?
   - How much will each method cost?
   - Do we need to isolate/remediate?

Historical perspective: $\begin{cases}\text{1930s – 1970s — Resource exploitati}\\ \text{1970s + Resource protection.}\end{cases}$

2. PHYSICAL HYDROLOGY

REVIEW

What do we know? → what do we need to know?

Category

Specifics

Uncertainties

UNDERLYING PRINCIPLES

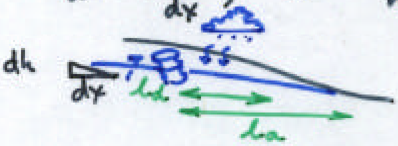
1. Hydrologic cycle and budgets

SCIENTIFIC PRINCIPLES

2. Darcy's law $q = -AK\frac{dh}{dx}$

DISCRETE PA

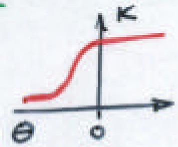
$v_d = -K\frac{dh}{dx}$; $v_a = -\frac{K}{n}\frac{dh}{dx}$



$l_d = v_d t$

$l_a = v_a t$ ✓

Unsaturated flow :



UNSATURATED

QUANTIFICATION

3. Continuity: $\frac{dq_i}{dx_i} = S_s\frac{dh}{dt} \Rightarrow \frac{\partial}{\partial x}K\frac{\partial h}{\partial x} = S_s\frac{\partial h}{\partial t}$

Evaluate: q, v_d, v_a

CHARACTERIZATION

4. Drilling & Geophysics

Theim ; Theis ; Unconfined; Leaky

$T = Kb$; T and $S = S_s b$

LOCATE PATHWA

EVALUATE PARAMS

PROJECT BEHAVIOR

5. Mathematical models

Flow / Transport / Non-aqueous flow

Geochemical transformation

DATA POOR

REMEDIATION

6. —

WHAT METHODS

DISCRETE PATHS

A. Discrete pathway flows — Rootholes
- Fractures — Alberta till 50m
- Lovisianna clays — 160'
  free product DNAP
- Radwaste — fracture zon

UNSATURATED

B. Unsaturated/partial saturation zones (All fluids transit zone)
1. Trap immiscible fluids (abstraction)
2. Reservoir for immiscible fluids (dissolution)

LOCATE PATHWAYS

A. Locate pathways / pathway depth to determine free product / migration location

B. Fast pathways for advection & dissolution
Large surface area for retardation

EVALUATE PARAMETERS

A. Evaluate — dispersion
— retardation

DATA POOR

- Models well understood but data poor
- Sensitivity approach

WHAT METHODS

- What methods are <u>economic</u>

Throughout → Economics

FLOW – REFRESHER

Permeability (L^2)

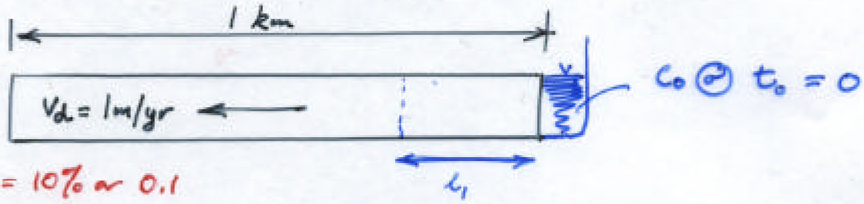
Hydraulic conductivity (LT^{-1})

$$\frac{k}{\mu} = \frac{K}{\rho g}$$

$$Q = -AK\frac{dh}{dx} \quad ; \quad v_d = -K\frac{dh}{dx}$$

$$v_a = \frac{v_d}{n}$$

RTD (Residence Time Distribution) or "Breakthrough" Curves

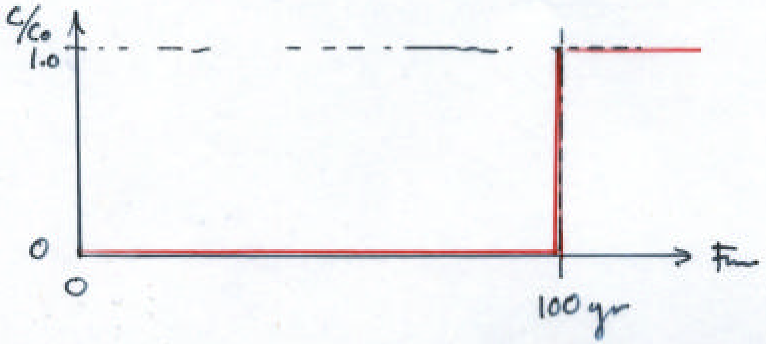


Porosity, n = 10% or 0.1

Darcy Velocity: $v_d = 1 \text{ m/yr} = \frac{1}{1000} \text{ km/yr}$

Advection velocity: $v_a = \frac{v_d}{n} = \frac{10^{-3}}{0.1} = 10^{-2} \text{ km/yr}$

Breakthrough time: $v_a = \frac{l}{t} \quad \therefore \quad t = l/v_a = \frac{1 \text{ km}}{10^{-2} \text{ km/yr}} = 100 \text{yr}$



2

Physical Hydrology

[2:1] Capillary Behavior

Overview – LNAPL DNAPL

Immiscible Transport – Overview

Generalities of Interfacial Behavior

- On Surfaces
- In Porous media

Capillary response

- Single capillary tube
- Contacting Grains
- Fracture

LNAPL Idealized behavior

eg. Gasoline, kerosene.

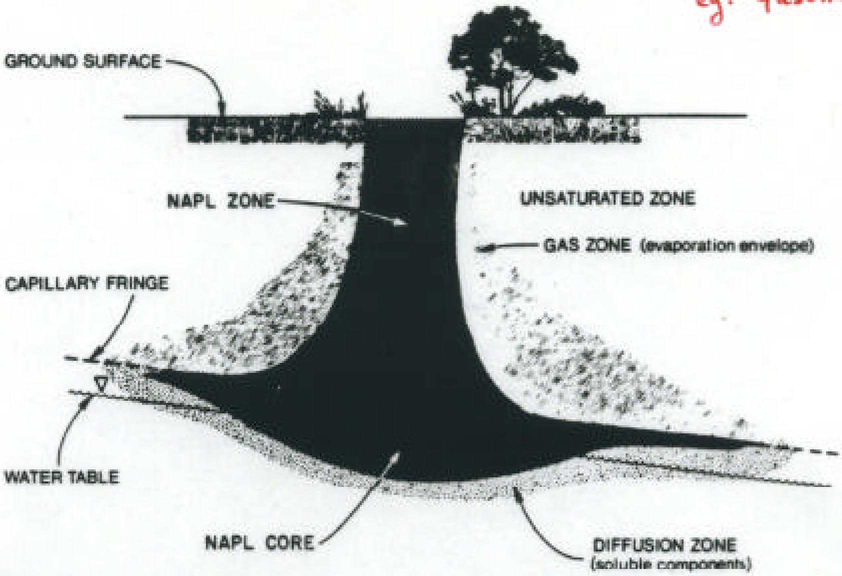


Fig. 1. Schematic representation of lighter than water NAPL movement through the unsaturated and into the saturated zone [after *Abriola and Pinder*, 1985*a*].

DNAPL eg. Dry cleaning solvents, TCE, PERC.

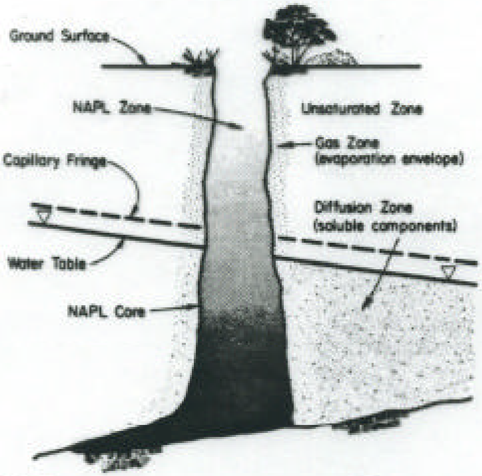


Fig. 2. Schematic representation of heavier than water NAPL movement through the saturated and unsaturated zones.

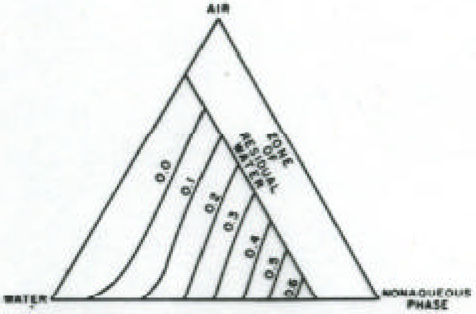
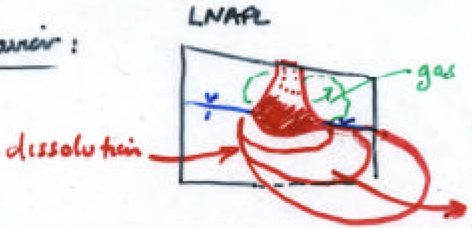
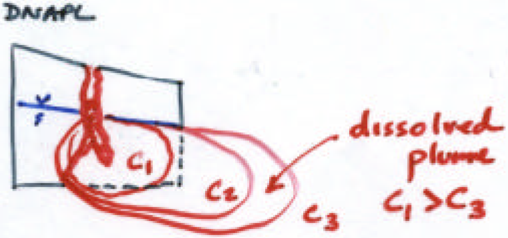


Fig. 3. Ternary diagram showing the relative permeability of the nonaqueous phase as a function of phase saturations [after *Faust*, 1985].

Immiscible Transport

Idealized behavior:





If contaminants are immiscible then these processes are important

---

True behavior:

1. Fingering results
2. Erratic and unpredictable distribution
3. DNAPLs "very" penetrative { low viscosity
   high density
   low interfacial tension

Questions:

☐ How far will they migrate

☐ What are the controls on penetration

clay -vs- sand aquitards

fractured -vs- unfractured

☐ How do they dissolve / bind / retard

☐ How may they be:

○ Remobilized

○ Chemically immobilized

○ Physically isolated.

FLOW OF IMMISCIBLE FLUIDS

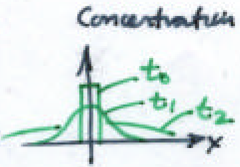
Bear, J., Dynamics of Fluids in Porous Media,
Chapter 9., 1988.

1. Types of Fluid Flows:

Miscible displacement: Two fluids completely soluble

No interface ∴ no interfacial tension

Hydrodynamic dispersion / diffusion



eg. NaCl, Ca

Immiscible displacement: Simultaneous flow of two fluids

Capillary pressure difference. eg. Air-water

oil-water (gas)

Some mixing at interface is possible but likely small.

2. Interfacial Tension and Capillary Pressure:

2.1 Saturation and Fluid Content:

$$S_\alpha = \frac{\text{volume of fluid } \alpha \text{ within REV}}{\text{volume of voids within REV}} \; ; \; \sum_\alpha S_\alpha = 1$$

$$S = V_f / V_v$$

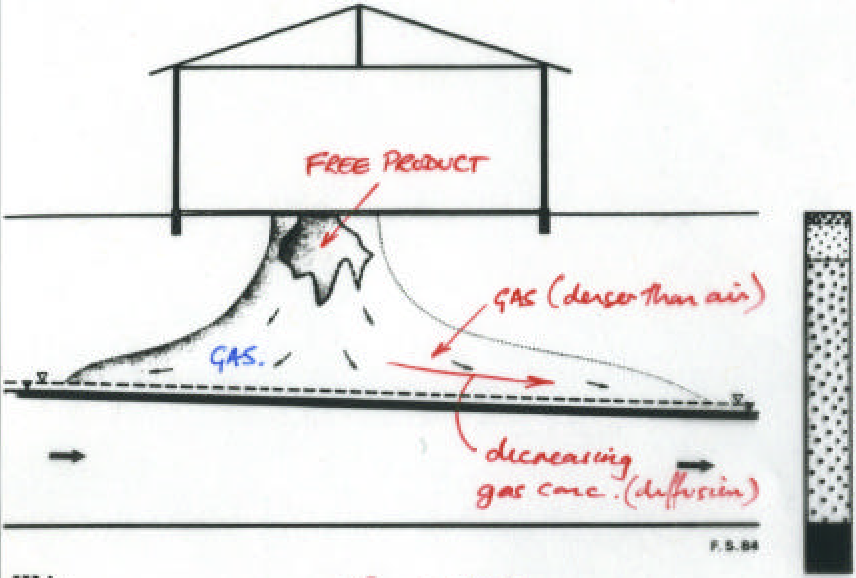
Unsaturated flow; volumetric moisture content, θ : $\theta = \frac{\text{vol. water in REV}}{\text{bulk vol. of REV}} \neq 1$

$$\theta = V_w / V_T \; ; \; V_T = V_v + V_s$$

Note that moisture content in soil mechanics is by weight, not volume. i.e.

$$m/c = \frac{W_w}{W_s}$$

III.a.



III.b.

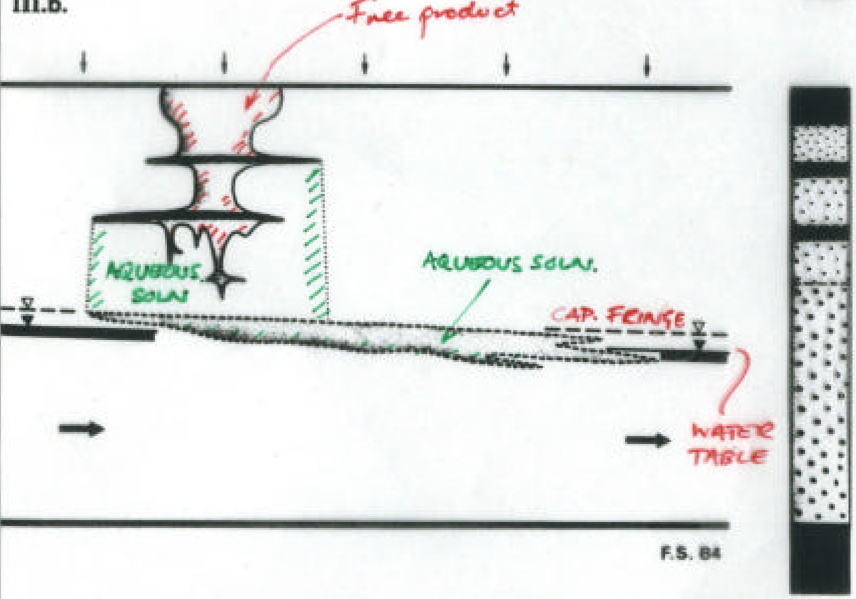


Figure III.a. Schematic of a small spill in a permeable unsaturated zone with a resulting mound of CHC gas. Concentration decreases with distance from spill. Grainsize shown at right.

Figure III.b. Larger spill than in III.a., but still not large enough to exceed the retention capacity of the unsaturated zone; no liquid CHC reaches the

XVI.a. INITIALLY UNSAT (MOIST)

XVI.b. SATURATED

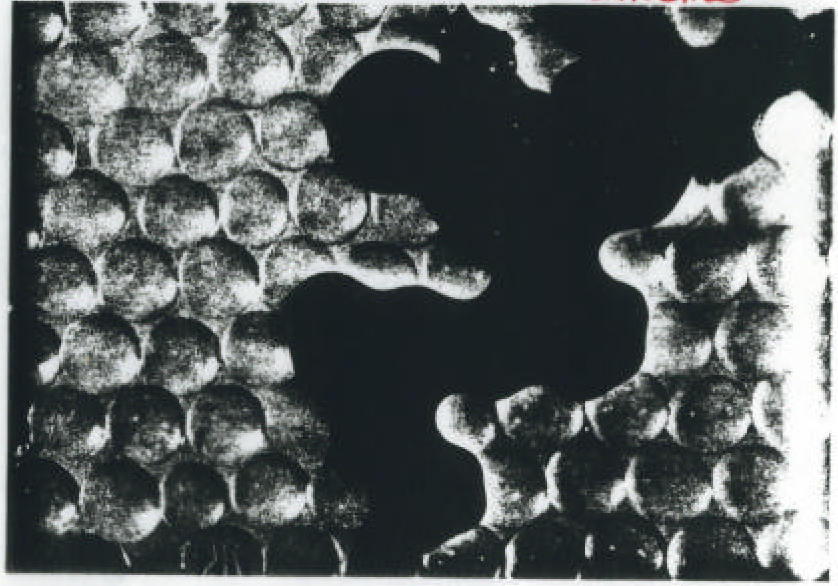
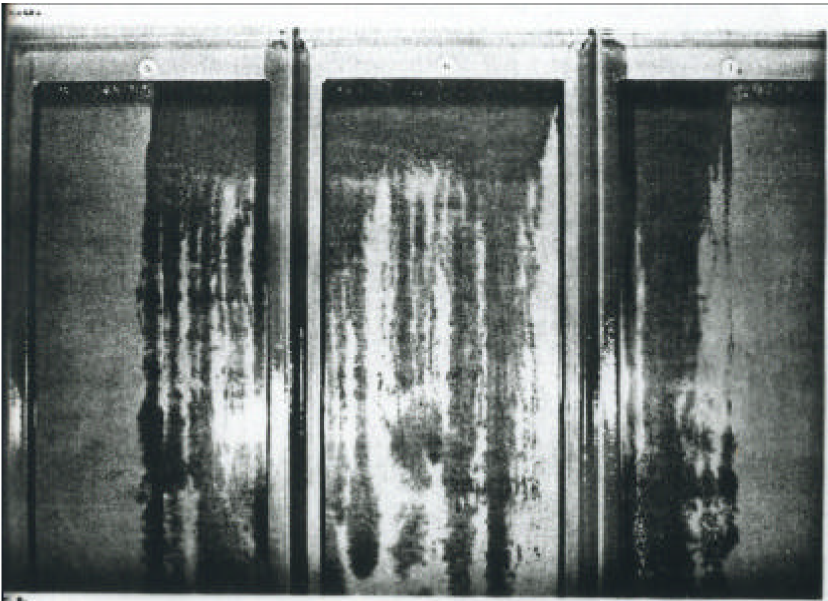


Figure XVI.a. Beads initially moist; diameter range = 0.85 - 1.23 mm. PER then dripped in from above. The PER accumulated as a sheath around a zone of high water content.

Figure XVI.b. Beads initially saturated with water; diameter range = 0.49 - 0.70 mm. PER then applied from above. When the flow of PER was discontinued, the front portion of the PER stream broke off and halted



.b.

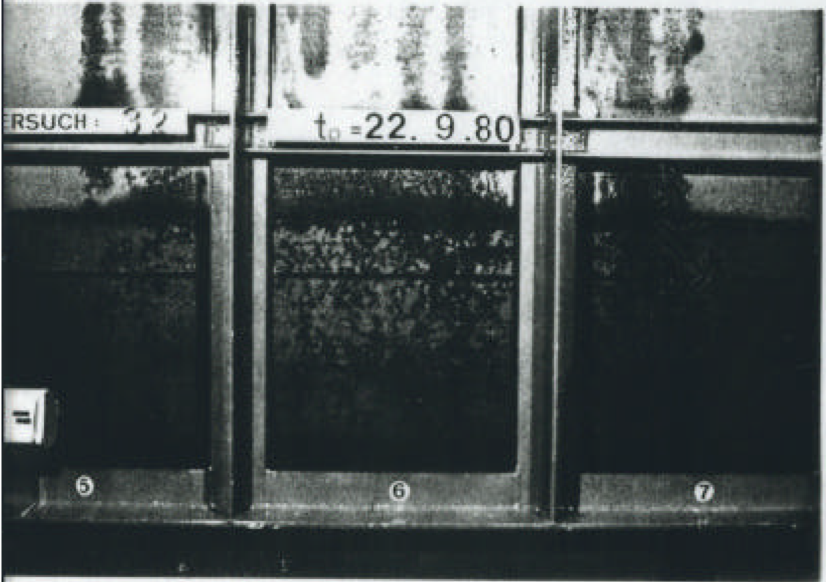


Figure X.a. Sheet-like spill of 36.3 L of PER. View of spill above the capillary fringe.

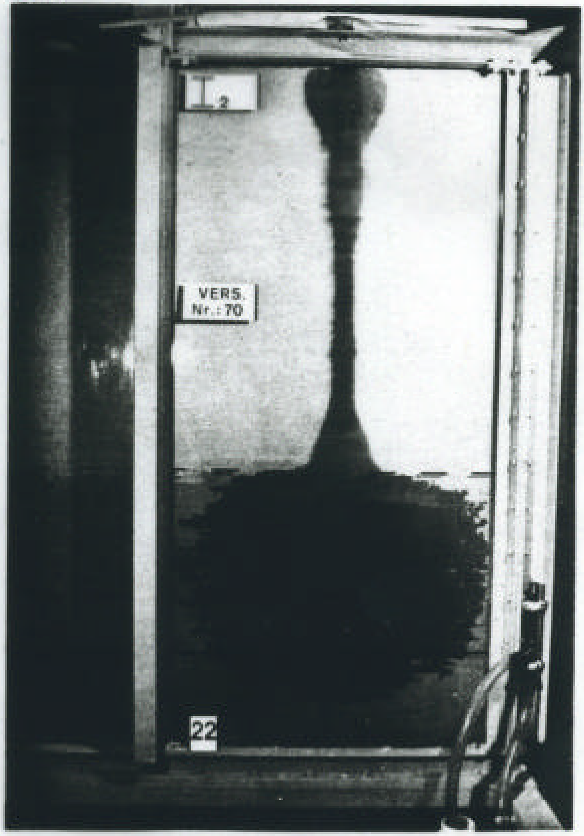
Figure X.b. Sheet-like spill of 36.3 L of PER. View of spill below the capillary fringe. Time = ~10 min.

re XI.a.
of PER. Kinematic
sity = 0.54 mm²/s.
= ~1 h.

re XI.b.
of PER. Later
of spill depicted in
re XI.a. Kinematic
sity = 0.54 mm²/s.

XI.a. AFTER 1 HOUR

XI.b.



2.2 Interfacial Tension and Wettability

Interfacial tension due to mollecular attraction – different in two fluids

Interfacial tension, σ_{ik}, between two fluids i and k.

σ_{ik} is temperature dependent $\therefore$ Capillary pressure $= f(T)$.

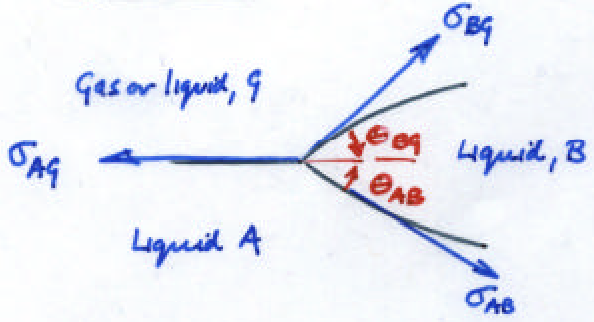
Dupré's formula $W_{ik} = \sigma_i + \sigma_k - \sigma_{ik}$ ⇒ work to separate into substanc
i and k with vapor interface

σ_i = surface tension

σ_{ik} = interfacial tension

σ_i = surface tension of fluid with its own vapor.

Equilibrium



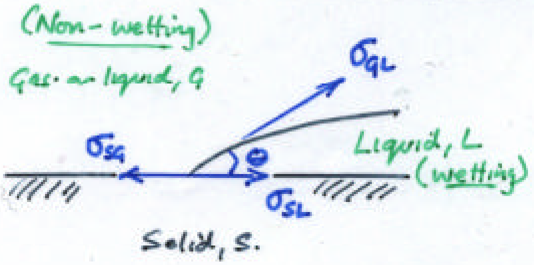
Equilibrium: $\sigma_{AG} = \sigma_{AB}\cos\theta_{AB} + \sigma_{BG}\cos\theta_{BG}$

Only satisfied if $\sigma_{AG} < (\sigma_{AB} + \sigma_{BG})$

$\therefore$ lense of B formed.

If $\sigma_{AG} > (\sigma_{AB} + \sigma_{BG})$

then B spreads between A and G.



By convention, θ measured in denser fluid

Equilibrium: $\sigma_{GL}\cos\theta = \sigma_{SG} - \sigma_{SL}$

$$\cos\theta = (\sigma_{SG} - \sigma_{SL})/\sigma_{GL}$$

$\therefore$ May determine interface angle for known σ (contact angle, θ).

– influenced by surface roughness.

If $(\sigma_{SG} - \sigma_{SL})/\sigma_{GL} > 1$ ⟹ No equilibrium

Liquid flows over solid → wettability

Wettability Defined by θ

$\theta < 90°$ eg Fluid, L wets the solid; wetting fluid

$\theta > 90°$ eg Fluid G, is non wetting fluid

$\theta = 90°$ Zero adhesion tension since equal affinity.

Wettability is controlled by: a) Chemical composition of fluids

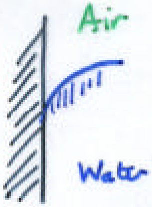
eg. adding dopant

b) Sequence of wetting

eg. Advancing or receding.

∴ hysteresis – wetting or draining

Water wets solid



Water non-wets solid

Most geologic systems are water wet.

petroleum/water

air/water

NAPL/water.

IMPORTANT ASPECTS OF WETTING

Water Wet

a) Pendular rings @ grain contacts

- no continuous water phase
- except mono-molecular coating of H_2O

b) ↑ wetting phase saturation →

- continuous water (wetting) phase
- equilibrium saturation = when phase (wetting) is continuous

Implication: wetting phase may be removed.

c) Above critical saturation (equilibrium) funicular saturation

- Now non-wet phase non-continuous.
- Can only remove non-wetting phase if large pressure gradient to squeeze through pore throat.

Funicular saturation critical in remediation!

Remediation @ residual saturations:

Grains

Important since difficult to remove last few % of saturation.

Pools

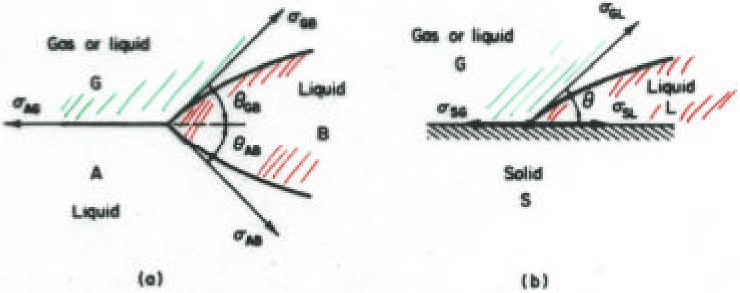


FIG. 9.2.1. Interfacial tensions.

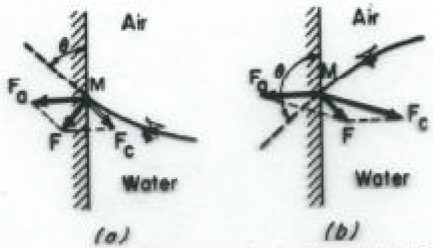


FIG. 9.2.2. Contact angle between a water-air interface and a solid. (a) Water wetting the solid. (b) Water nonwetting the solid.

Usual oil reservoir

Possible also.

Non-wetting phase removed (oil)

Continuous oil phase ∴ produce oil

Wetting phase removed (water)

Continuous water phase ∴ pump water

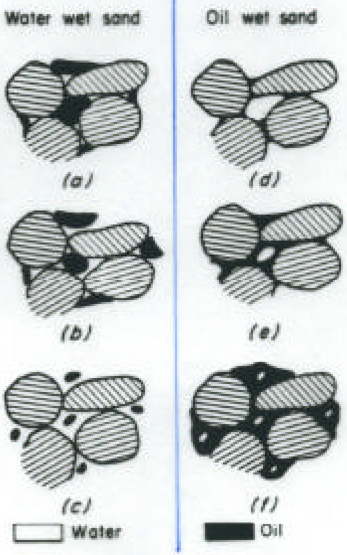


FIG. 9.2.3. Possible fluid saturation states.

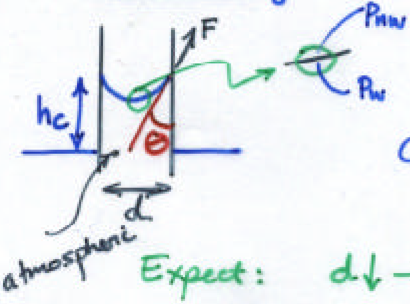
2.3 Capillary Pressure

Important: Controls penetration of immiscible fluids

Note (a) $p_x = p_y = p_z$ within any phase for static conditions

(b) p_w depends on surface curvature

Water-wet system



Capillary rise, h_c: $\gamma h_c \pi \frac{d^2}{4} = \sigma_{12} \pi d \cancelto{1}{\cos\theta}$ $\therefore h_c = \frac{4\sigma_{12}}{d \gamma_w}$

Expect: $d\downarrow \rightarrow h_c\uparrow$

d = pore throat or fracture aperture

Capillary pressure, p_c: $p_c = p_{nw} - p_w \Rightarrow \frac{p_c}{\gamma_w} = \frac{1}{\gamma_w}(p_{nw} - p_w) = h$

In the capillary pressure relationship, $h_c = \frac{4\sigma_{12}}{d\gamma_w}$ the assumption that $\theta \rightarrow 0$ is made for clean glass.

Not good for soils/rocks

Most important deduction: $p_c = h_c \gamma_w \propto \frac{\sigma_{12}}{d}$

Capillary pressure inversely proportional to pore dia, d.

Smaller d, requires larger p_c to penetrate.

Since many potential pore throat diameters exist, a capillary model may be replaced by a grain-grain contact model.

CAPILLARY PRESSURES - POROUS MEDIA

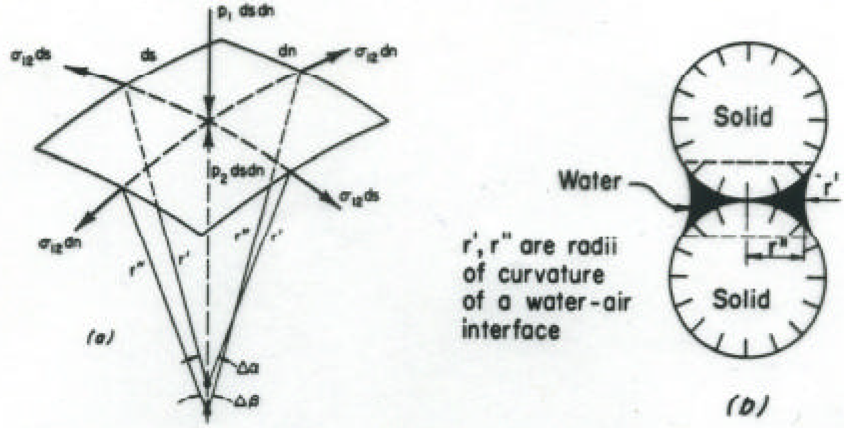


FIG. 9.2.4. Equilibrium at a curved interface between two immiscible fluids.

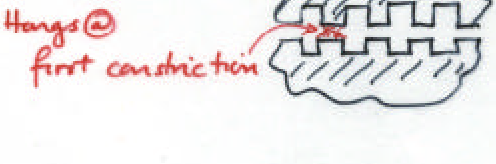
Soil suction or tensi

$$\Delta p = p_c = p_2 - p_1 = \sigma_{12}\left(\frac{1}{r'} + \frac{1}{r''}\right) = \boxed{\frac{2\sigma_{12}}{r^*} = p_c}$$

r^* = mean radius => $\frac{2}{r^*} = \left(\frac{1}{r'} + \frac{1}{r''}\right)$ (Laplace eqn.).

PROBLEM: r^* is difficult to determine

- ☐ Multiple grain sizes (and pore throat sizes)
- ☐ Distribution of pore sizes



or

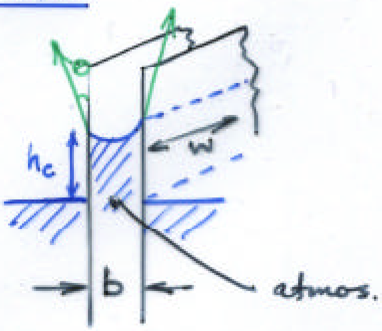
- ☐ Pore geometry
- ☐ Fluids (σ_{12}) and contact angles ($\cos\theta$)

∴ Use a statistical average => Determine $p_c = p(S_w)$ Lab ok

Field be

CAPILLARY RISE IN FRACTURES

IDEALIZED



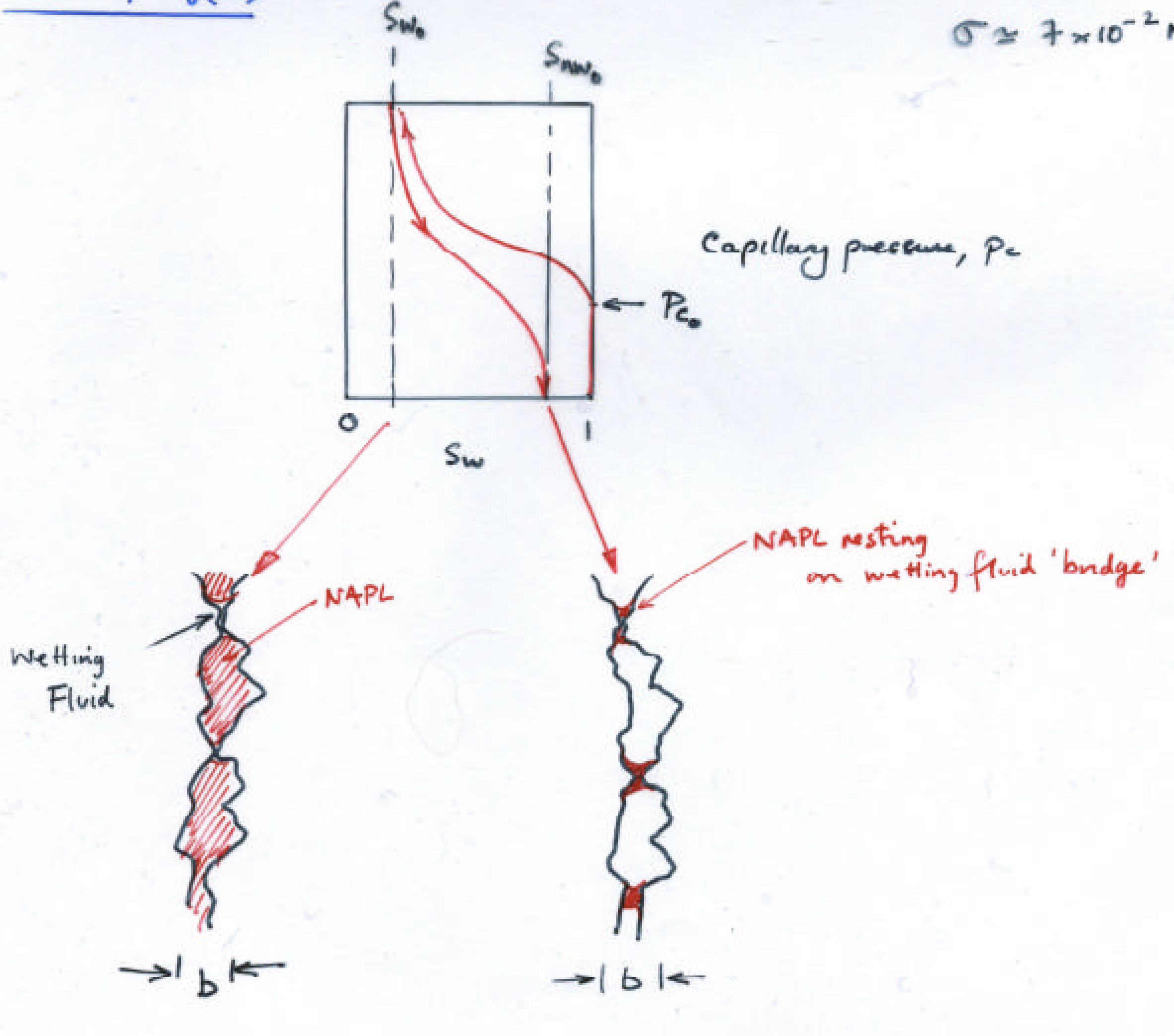
$$\underbrace{w \cdot b \cdot h_c}\gamma_w = 2w\sigma \cancelto{1}{\cos\theta}$$

$$h_c = \frac{2\sigma}{\gamma_w b}$$

$$P_{c_0} = \frac{2\sigma}{b} \qquad P_{c_0} \propto \frac{\sigma}{b}$$

REAL $P_c = f(S_w)$

$\sigma \simeq 7\times10^{-2}$ N/m.



[2:2] Capillary Behavior

Recap

Capilary Pressure –vs- Saturation curves

- Leverett
- Brooks-Corey

Drainage and Imbibition

Penetration of NAPLs – How deep?

Experimental Determination of Pc vs-Sw curves

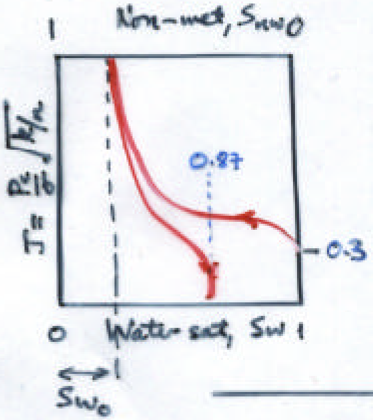
HOW TO DETERMINE $\underline{P_c} = \underline{P_c(S_w)}$

For capillary tube of radius, r.

$$P_c = \frac{2\sigma_{12}}{r}\cos\theta$$

Semi-empirical approach, Leverett (1941). Dimensional analysis gives:

$$J = J(S_w) = \left(\frac{P_c}{\sigma}\right)\sqrt{k/n} \quad ; \qquad P_c = P_c(S_w)$$



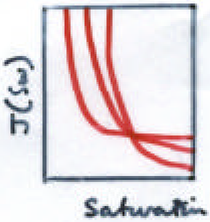
J = Leverett function reduces to a common curve for different materials

k = permeability (L^2)
n = porosity

$\left.\begin{matrix} k \\ n \end{matrix}\right\} \sqrt{k/n} \propto$ to mean pore diameter

---

May also be influenced by $\cos\theta$ (factors influencing contact angle).



$$J = J(S_w) = \left(\frac{P_c}{\sigma\cos\theta}\right)\sqrt{k/n}$$

∴ Dependent on formation type

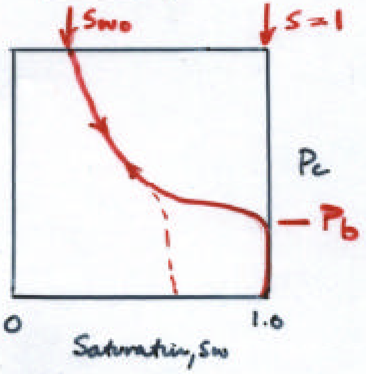
Brooks & Corey (1964) $\quad P_c = P_c(S_e) \qquad S_e = \frac{(S_w - S_{w0})}{(1 - S_{w0})}$

S_e = effective saturation
S_{w0} = irreducible wetting fluid saturation

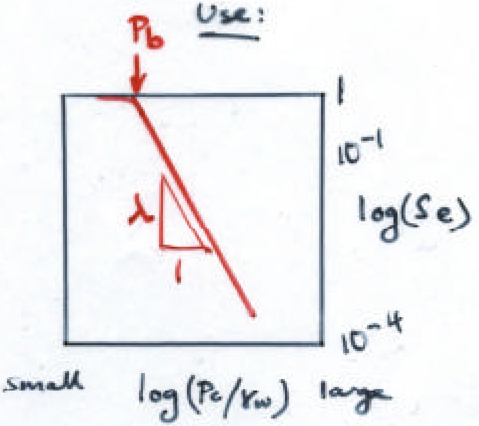
Gives a straight line relationship in log-log S_e versus P/γ_w space except close to S_e = 100%

BROOKS – COREY CURVES

Instead of:



Use:



$$S_e = \frac{(S_w - S_{wo})}{(\underset{\uparrow\, S=1}{1} - S_{wo})}$$

S_e = effective saturation

S_{wo} = irreducible wetting fluid saturation

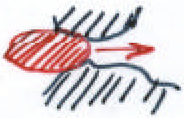
Curve defined by two parameters:

λ = -ve slope of curve (pore size distribution)

P_b = intercept of line and $S_e = 100\%$

also termed "bubbling pressure"

Pressure needed to force a "bubble" of fluid through the pore throat



REPRESENTED AS:

$$S = (1 - S_{wo})\left(\frac{P_c}{P_b}\right)^{-\lambda} + S_{wo}$$

or $$S_e = \frac{(S - S_{wo})}{(1 - S_{wo})} = \left(\frac{P_c}{P_b}\right)^{-\lambda}$$ i.e. $\log(S_e) = -\lambda \log\left(\frac{P_c}{P_b}\right)$

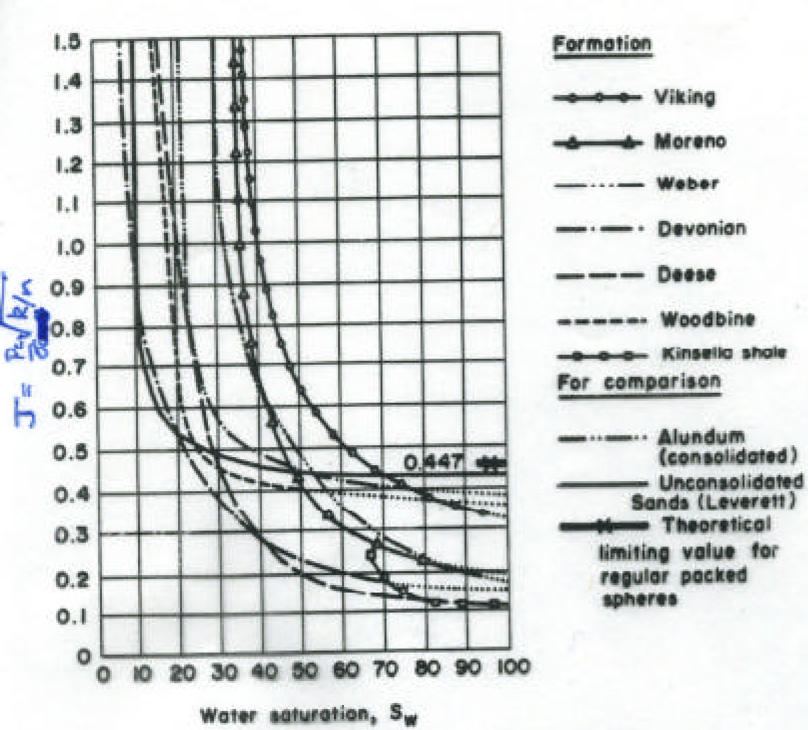


FIG. 9.2.6. Leverett function for various formations (Rose and Bruce, 1949).

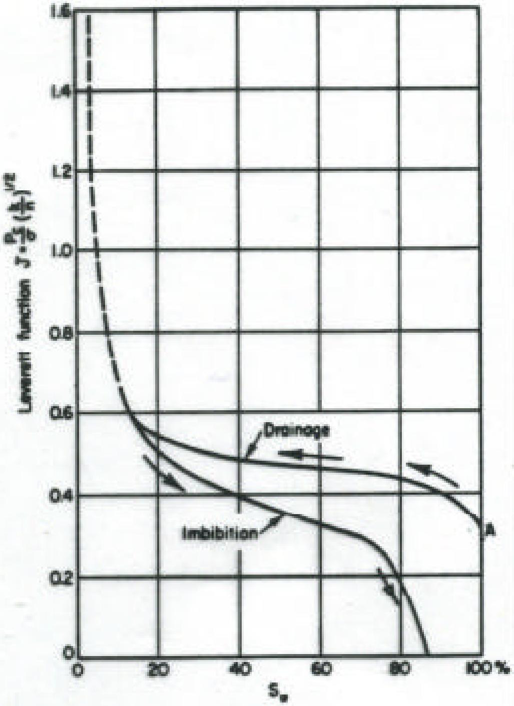


FIG. 9.2.5. Typical Leverett functions for sand (Leverett, 194

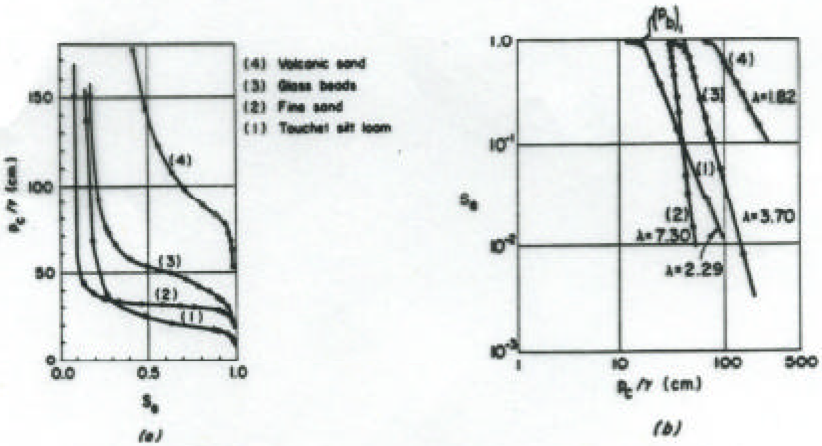
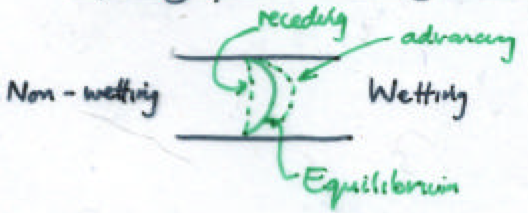


FIG. 9.2.7. Capillary pressure head as a function of effective saturation for porous materials of various pore-size distributions (Brooks and Corey, 1964).

2.4 DRAINAGE AND IMBIBITION

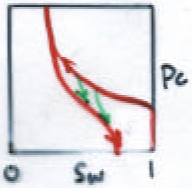
Capillary pressure is hysteretic

θ changes with direction of displ.



⇐ For two fluids (liquids)

For Fluid-gas



∴ Not a unique function of Sw, but depends on path.

∴ conclude that we cannot determine Pc from Sw, alone

Drainage – Saturated with wetting fluid initially – displace with non-wetting

Imbibition – Saturated with non-wetting fluid initially – place wetting fluid on surface → "spontaneous" imbibition to equilibrium condition where capillary forces equal those due to gravity.

Unsaturated flows – Water = wetting ; air = non-wetting

S_{nw_0} = entrapped air in sample

$S_{nw} \leq S_{nw_0}$ the non-wetting fluid is non continuous ∴ does not flow.

Drying and wetting scanning curves are hysteretic.

FIG. 9.2.8. Contact angle (θ) in a capillary tube in a stationary state, in a displacement of a nonwetting liquid by a wetting one (θ_1) and in a displacement of a wetting liquid by a nonwetting one (θ_2).

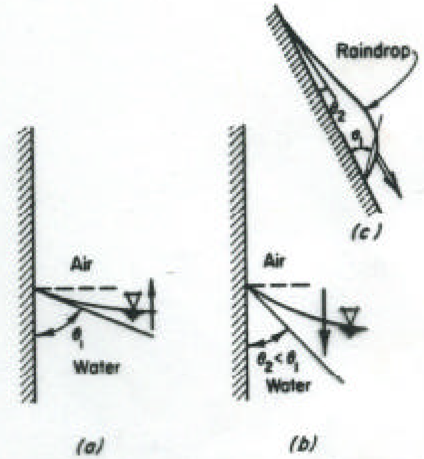


FIG. 9.2.9. Hysteresis in contact angle (rain drop effect).

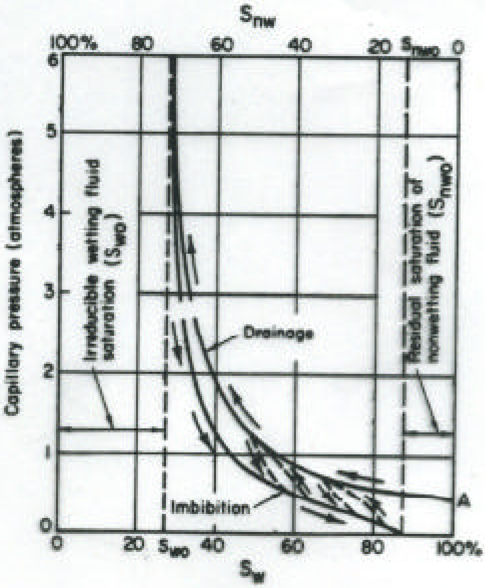


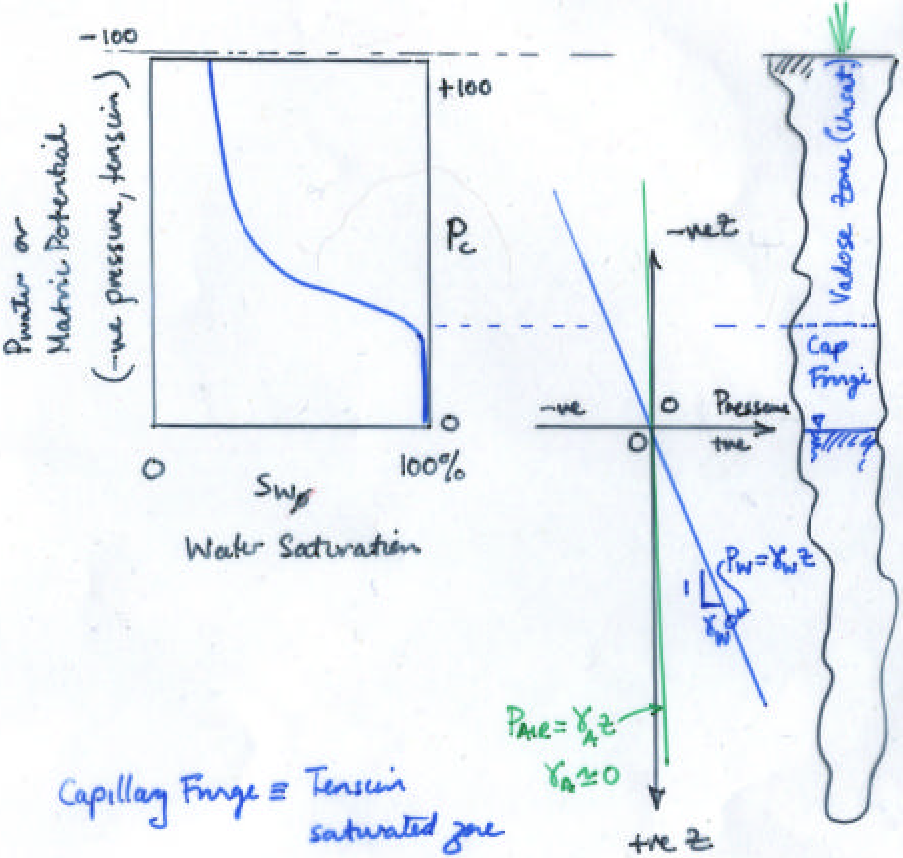
FIG. 9.2.10. Typical capillary pressure—wetting fluid saturation curves illustrating hysteresis.

STATIC SYSTEMS

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

Vadose zone

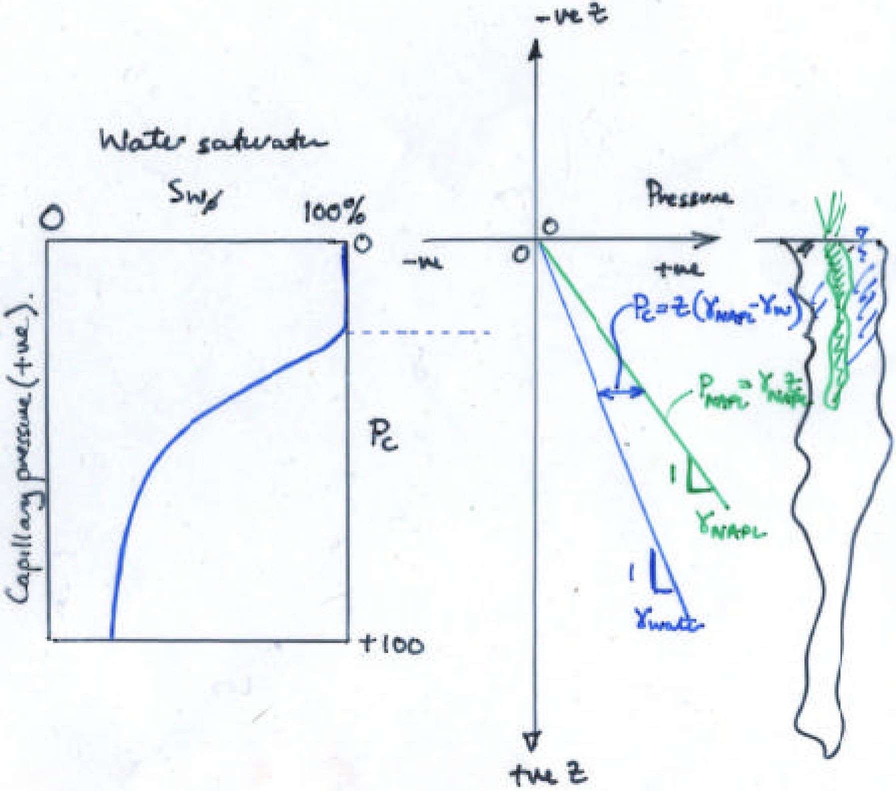
$$P_c = \underline{P}_{air} - P_{water}$$



Capillary Fringe ≡ Tension saturated zone

NAPL in Groundwater

$$P_c = \underline{P}_{NAPL} - P_{WATER}$$



[2:3] Capillary Behavior

Recap

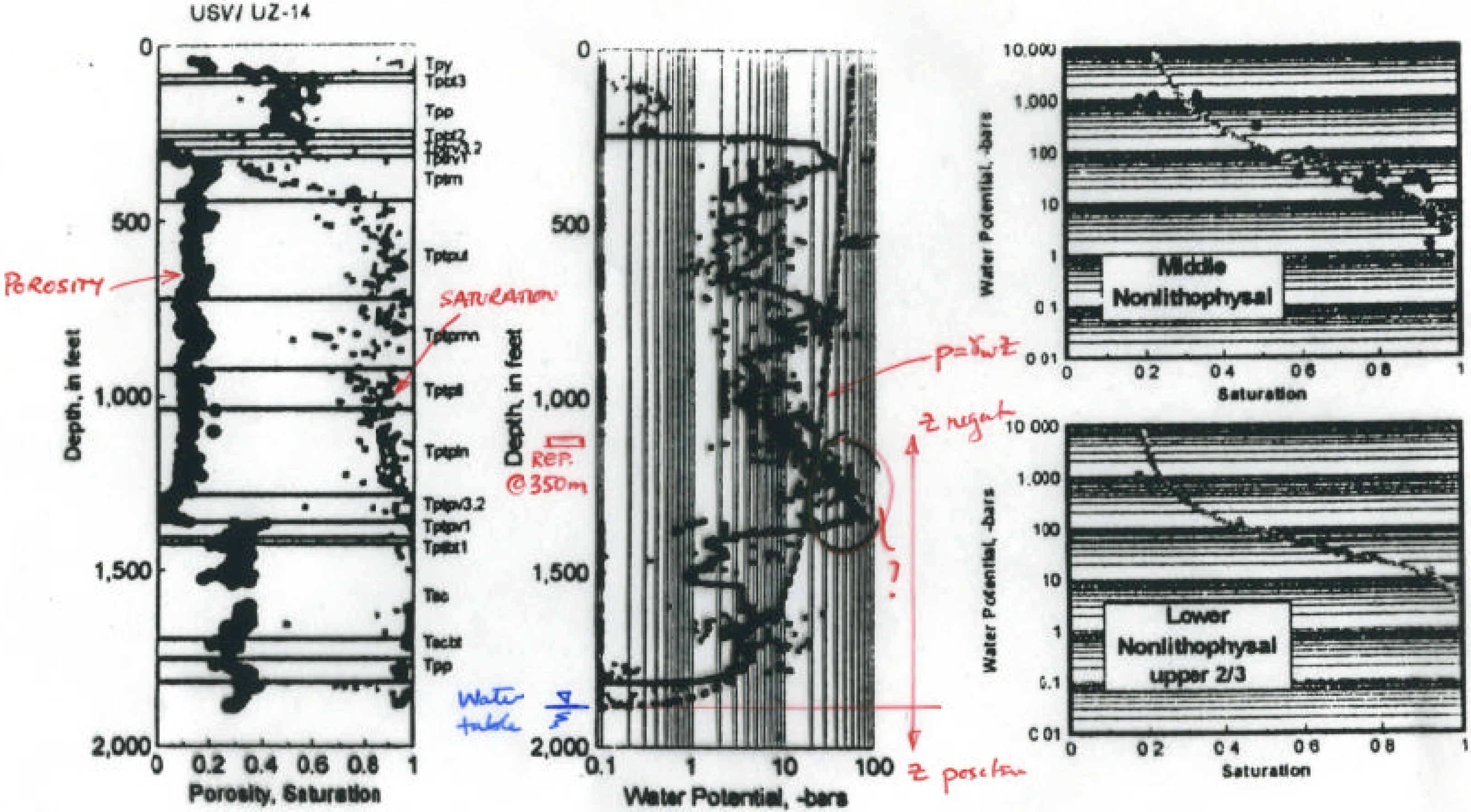
Penetration of NAPLs – How deep?

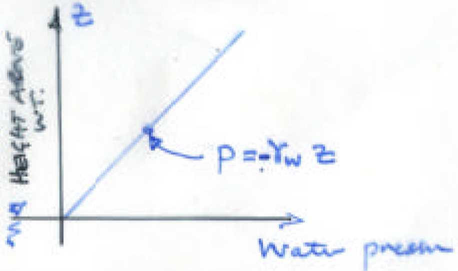
Experimental Determination of Pc vs-Sw curves

Examples

- Vinometer
- Invasion
- S_{nw}-depth distribution

YUCCA MTN - UZ-14





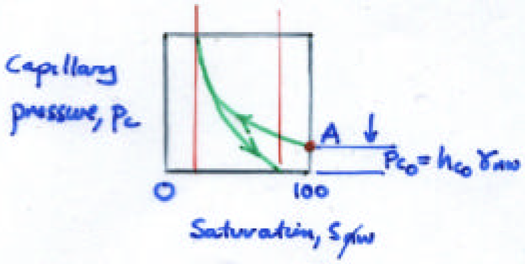
1 bar = 100 kN/m²

≃ 10 m of water

2.5 Non-Aqueous Fluid Penetration (Static groundwater field)

Question: How deep will a DNAPL penetrate?; Will it arrest?

Experience/evidence shows insidious penetration.

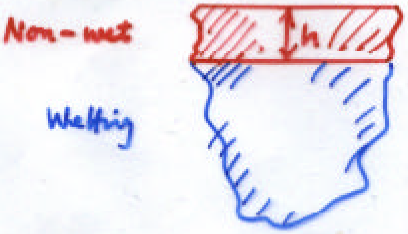


P_{c_0} = entry pressure

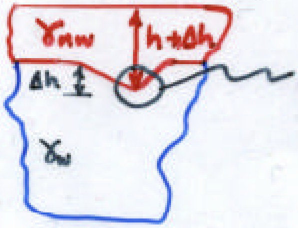
Note – wish to penetrate at minimum saturation, not to saturate.

i.e. Penetrate @ low saturation

Consider without porous medium



No penetration unless instability develops



$P_{nw} = \gamma_{nw}(h+\Delta h)$

$P_w = \gamma_{nw} h + \gamma_w \Delta h$

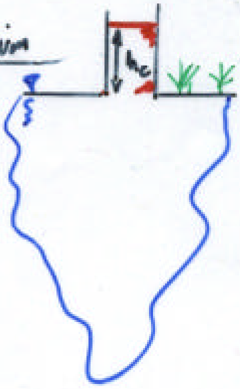
If $\gamma_w < \gamma_{nw}$

then $p_w < p_{nw}$

∴ Instability develops and pressure difference builds as Δh increases

i.e. Accelerating instability

In porous medium

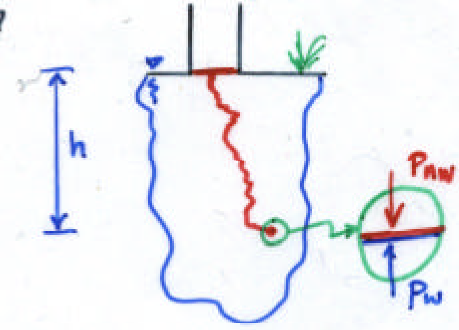


$P_{c_0} = h_c\gamma_{nw}$

Fluid will penetrate into porous medium. Two possibilities.

1) Flows until all large void space is filled, and stops?
2) Flows, but large void space is sufficiently connected to drain reservoir?

Can flow stop?



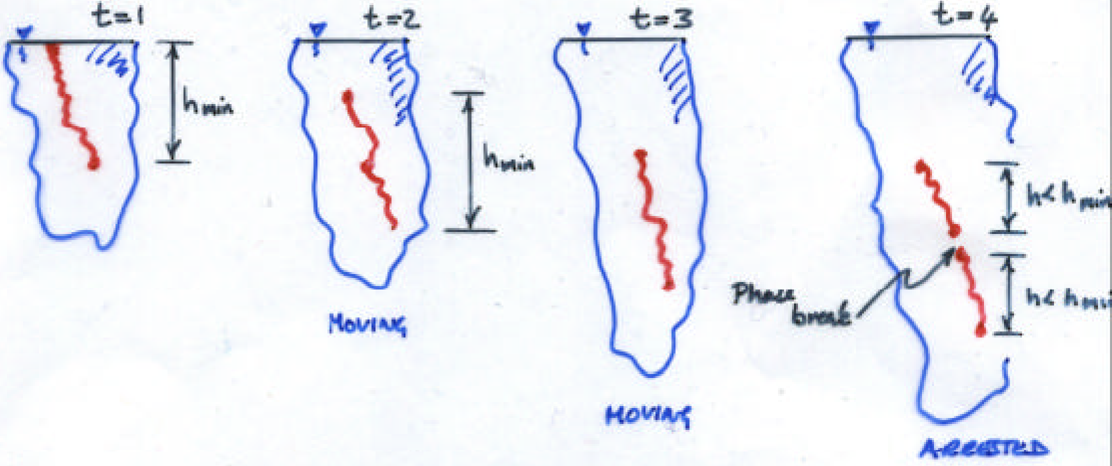
Will stop if $p_{nw} \le p_w + p_{co}$ (1)

$$h\gamma_{nw} \le h\gamma_w + h_c\gamma_{nw} \quad (2)$$

$$h\frac{\gamma_{nw}}{\gamma_w} - h = h_c\frac{\gamma_{nw}}{\gamma_w} \quad (3)$$

$$\boxed{h_{min} = \frac{h_c}{(1-\gamma_w/\gamma_{nw})}} = \frac{p_{co}/\gamma_{nw}}{(1-\gamma_w/\gamma_{nw})} \quad (4)$$

Only limitation is that "phase must be "continuous."



Equation (4) shows: • h_{min} largest if densities of fluids are close — as γ_{nw} becomes denser, then less high column of non-wetting fluid needed to generate p_{co}.

Practical Implications

1. Will only stop if (a) Fills "large voids" space and no connected "large void" space remains.
   (b) Flow "necks-down" and h_{min} is split
   (c) Fluid system is not "static". What is flow direction.

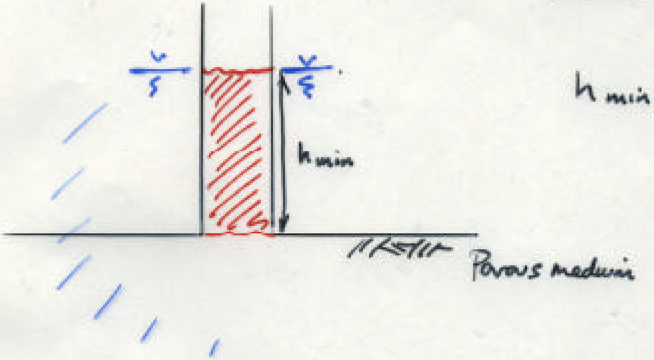
Important parameter is the connected pore space!!

This is difficult to evaluate with conventional test methods.

MAKE SURE YOU UNDERSTAND THE UNDERLYING ASSUMPTIONS

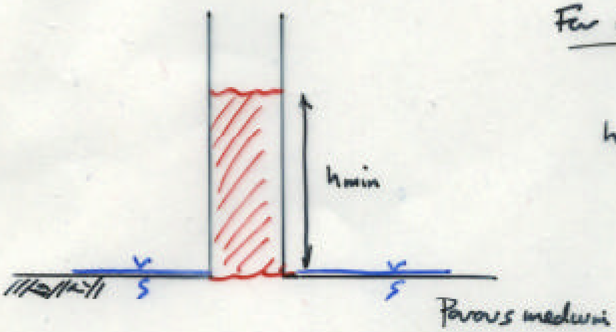
BEFORE YOU APPLY THESE

For invasion:



$$h_{min} = \frac{P_{co}/\gamma_{nw}}{(1 - \gamma_w/\gamma_{nw})} = \frac{h_c}{(1 - \gamma_w/\gamma_{nw})}$$

For invasion:



$$h_{min} = P_{co}/\gamma_{nw} = h_c$$

Table 4-2. Relationships between capillary pressure, gravity, and hydraulic forces useful for estimating conditions of DNAPL movement (from Kueper and McWhorter, 1991; WCGR, 1991; and Mercer and Cohen, 1990).

Condition	Equation
(a) Capillary pressure exerted on the surface of a nonwetting NAPL sphere	$P_c = P_{NAPL} - P_w = (2\sigma\cos\phi) / r$
(b) Capillary pressure exerted on the surface of NAPL in a fracture plane where b is the fracture aperture	$P_c = P_{NAPL} - P_w = (2\sigma\cos\phi) / b$
Hydrostatic Conditions	
(c) Critical height of DNAPL required for downward entry of DNAPL through the capillary fringe (the top of the saturated zone)	$z_n = (2\sigma\cos\phi) / (r\, g\, \rho_n)$
(d) Critical height of DNAPL required for downward entry of DNAPL into the water-saturated base of a lagoon where DNAPL is pooled beneath water; or, below the water table, for entry of DNAPL into a layer with smaller pore openings (assuming top of DNAPL body last existed under imbibition conditions)	$z_n = (2\sigma\cos\phi) / [rg(\rho_n - \rho_w)]$
(e) Critical height of DNAPL required for entry of DNAPL into a water-saturated fracture at the base of a lagoon where DNAPL is pooled beneath water; or, below the water table, for entry of DNAPL into a water-saturated fracture having an aperture, b, smaller than the host medium pore radii; or, below the water table, for entry of DNAPL into a water-saturated fracture segment having an aperture smaller than that of the overlying host fracture segment (assuming top of DNAPL body last existed under imbibition conditions)	$z_n = (2\sigma\cos\phi) / [bg(\rho_n - \rho_w)]$
(f) Critical height of DNAPL required below the water table, for entry of DNAPL into a layer with smaller pore openings where the top of the DNAPL body is under drainage conditions	$z_n = [P_{d(fine)} - P_{d(coarse)}] / [g(\rho_n - \rho_w)]$
(g) The stable DNAPL pool length, L_n, that can exist below the water table following initial DNAPL migration where θ is the dip [illegible] of the base of the host medium and L_n is measured parallel to the host medium base slope	$L_n = (2\sigma\cos\phi) / [rg(\rho_n - \rho_w)\sin\theta]$
(h) The stable DNAPL pool length, L_n, within a fracture that can exist below the water table following initial DNAPL migration where θ is the dip angle of the fracture, b is the maximum fracture aperture at the leading edge of the DNAPL pool, and L_n is measured parallel to the fracture slope	$L_n = (2\sigma\cos\phi) / [bg(\rho_n - \rho_w)\sin\theta]$
Hydrodynamic Conditions	
(i) Neglecting capillary pressure effects, the critical upward hydraulic gradient, i_c, required across a DNAPL body of height z_n to prevent downward DNAPL migration in a uniform porous medium	$i_c = \Delta h/\Delta z_n = (\rho_n - \rho_w) / \rho_w$
(j) Neglecting capillary pressure effects, the minimum hydraulic head difference between the bottom and top of a DNAPL body of height z_n to prevent downward DNAPL migration in a uniform porous medium	$\Delta h = i_c\, \Delta z_n = z_n(\rho_n - \rho_w) / \rho_w$
(k) Neglecting capillary pressure effects, the critical hydraulic gradient, i_c, required to prevent the downward movement of DNAPL along the top of a dipping (angle = θ) capillary barrier (i.e., in sloping fractures, bedding planes, or within a sloping coarse layer above a fine grained layer) with i_c measured parallel to the slope	$i_c = [(\rho_n - \rho_w)\sin\theta] / \rho_w$
(l) The critical horizontal hydraulic gradient, i_c, which must exist across a DNAPL pool of length L beneath the water table to overcome capillary resistance and mobilize DNAPL in the pool (to calculate i_c for a pool of DNAPL in a horizontal fracture, replace r with the fracture aperture, b)	$i_c = (2\sigma\cos\phi) / (r\rho_w g L)$
(m) The critical upward hydraulic gradient, i_c, required to arrest the downward migration of DNAPL through an aquitard of thickness, Δz, where ΔP_c is the capillary pressure of DNAPL pooled at the top of the aquitard minus the threshold entry (displacement) pressure of the aquitard	$i_c = \Delta h/\Delta z = [(\rho_n - \rho_w)/\rho_w] + [\Delta P_c/(\rho_w g \Delta z)]$

2.6 EVALUATION OF CAPILLARY PRESSURE CURVES

Theoretical evaluation – Difficult except for uniform rods/spheres

Use $P_c = (2\sigma/r)\cos\theta$

eg. Collins (1961) for packed rods

R = radius

Limited Sw range since result valid only until adjacent fluid interfaces contact.

Laboratory Methods $P_c = P_c(S_w)$

a) Displacement methods: Establish successive states of hydrostatic equil

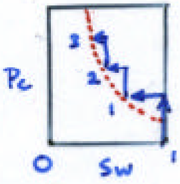
b) Dynamic methods: Establish successive states of hydraulic steady flow

Both with a wetting and non-wetting fluid.

Displacement methods

Porous diaphragm method:

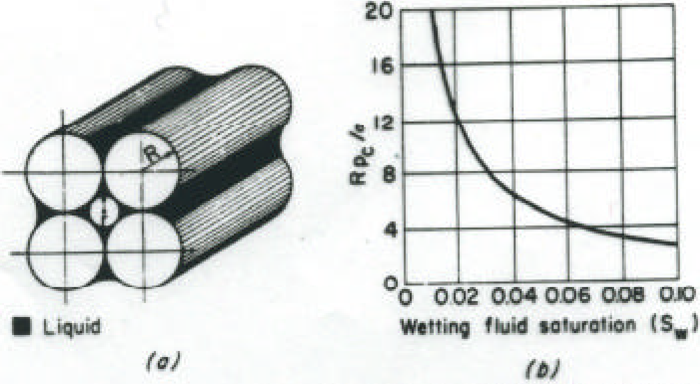
1. Wetted core inside non-wetting fluid.
   Underlain by diaphragm disc – permeable but not to the non-wetting fluid.
2. Increase pressure of non-wetting (displacing) fluid and wait for equilibrium (saturation)
   Trace curve with: 1., 2., 3, etc.



3. Determine saturation from displaced fluid or X-ray/CT scan.

Limitations: 1. Length of time for equilibrium. 10-20d per point?
2. Is all pore space being accessed? Does it matter?

Advantage: Uses 'real' fluids (of interest).



(a)

(b)

FIG. 9.2.13. Capillary pressure in a cubic packing of circular rods with liquid-air interfaces (after Collins, 1961).

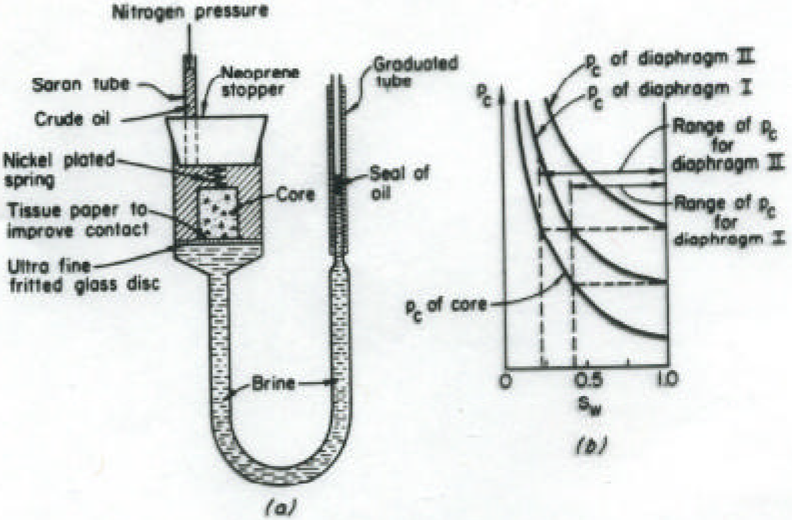
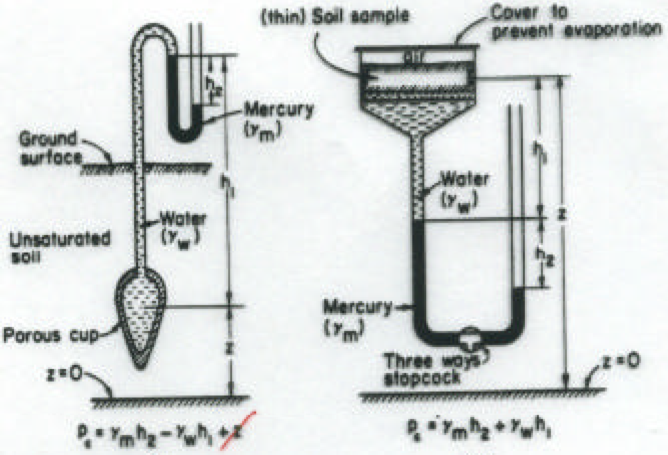


FIG. 9.2.14. Schematic diagram of a porous diaphragm device for capillary pressure determination (Welge and Bruce, 1947).



$p_c = \gamma_m h_2 - \gamma_w h_1 + \cancel{z}$

(a)

$p_c = \gamma_m h_2 + \gamma_w h_1$

(b)

FIG. 9.4.4. The use of mercury tensiometer manometers. (a) Measurement of capillary pressure in the field, (b) the Haines apparatus for determining $p_c = p_c(S_w)$.

[2:4] Multiphase Flow

Recap

Darcy’s law

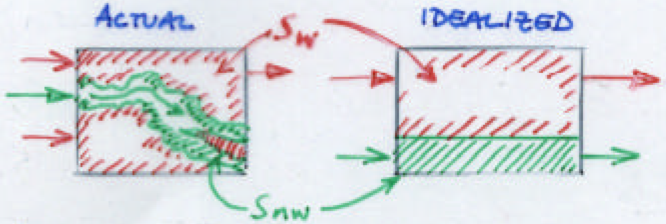
    Relative permeabilities

3. SIMULTANEOUS FLOW OF TWO IMMISCIBLE FLUIDS

☐ Capillarity and capillary pressures govern the "equilibrium" penetration of fluids — static behavior

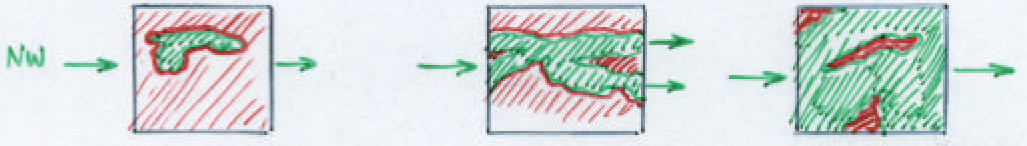
☐ Once penetrated, the individual phases may transfer and be transported

- Pure phase (free product)
- Dissolved form (later).



a) Note that flow within phase is not subject to capillarity (capillarity acts at fringes, only)

b) Each fluid establishes its own "tortuous" path → stable channels



No flow of NW (Discontinuous NW)

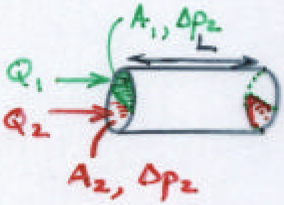
Both fluids flow

No flow of W (Discontinuous Wetting)

Increasing saturation of Non-Wetting →

3.1 MOTION EQUATIONS

Apply Darcy's Law



Establish steady flow at volumetric flow rates, Q_1 and Q_2.

$$\left.\begin{array}{ll} \square & q_1 = \left(\frac{k_1}{\mu_1}\right) \frac{\Delta p_1}{L} \\ & \\ \square & q_2 = \left(\frac{k_2}{\mu_2}\right) \frac{\Delta p_2}{L} \end{array}\right\} \quad q_\alpha = \left(\frac{k_\alpha}{\mu_\alpha}\right) \frac{\Delta p_\alpha}{L} \quad ; \quad q_\alpha = \frac{Q_\alpha}{A_\alpha}$$

Δp_α = effective pressure drop of α^{th} fluid
k_α = "effective" permeability of medium to fluid α.

k_α depends on: a) Porous medium (pore size & distribution and fractures).
b) Saturation, Sw and Snw.

"Relative" permeabilities

$$k_{r_1} = \frac{k_1}{k}(S_1) \quad ; \quad k_{r_2} = \frac{k_2}{k}(S_2)$$

- □ Relative to single phase permeability of a fully saturating fluid
- □ Determine from "equilibrium" laboratory flow tests under different saturations.

$$\overset{\text{Effective permeability}}{k_1} = \underset{\text{Relative permeability}}{k_{r_1}}\ \underset{\text{True permeability }(L^2)}{k}$$

FLUID MOTION EQUATION (DARCY'S LAW)

i = flow direction, x_1, x_2, x_3.

("z" is // to x_3)

$$q_{i_1} = -\frac{k_1}{\mu_1}\left(\frac{\partial p_1}{\partial x_j} + \rho_1 g \frac{\partial z}{\partial x_j}\right) = -k\frac{k_{r1}}{\mu_1}\left(\frac{\partial p_1}{\partial x_j} + \rho_1 g \frac{\partial z}{\partial x_j}\right)$$

$\frac{K_2}{\rho_2 g}$

$$q_{i_2} = -\frac{k_2}{\mu_2}\left(\frac{\partial p_2}{\partial x_j} + \rho_2 g \frac{\partial z}{\partial x_j}\right) = -k\frac{k_{r2}}{\mu_2}\left(\frac{\partial p_2}{\partial x_j} + \rho_2 g \frac{\partial z}{\partial x_j}\right)$$

May also use piezometric head, h, for constant ρ_1 and ρ_2, but must be defined separately for each fluid, h_α

$$h_\alpha = \frac{p_\alpha}{\rho_\alpha g} + z \quad ; \qquad \alpha = 1, 2$$

$$\boxed{\begin{aligned} q_{i_1} &= -k\frac{k_{r1}}{\mu_1}\rho_1 g \frac{\partial h_1}{\partial x_j} \\ q_{i_2} &= -k\frac{k_{r2}}{\mu_2}\rho_2 g \frac{\partial h_2}{\partial x_j} \end{aligned}}$$

Similarity between:

permeability (L^2)

$$q = -k\frac{\rho g}{\mu}\frac{dh}{dx_j}$$

$$= -K\frac{dh}{dx_j}$$

Hydraulic Conductivity (L/T)

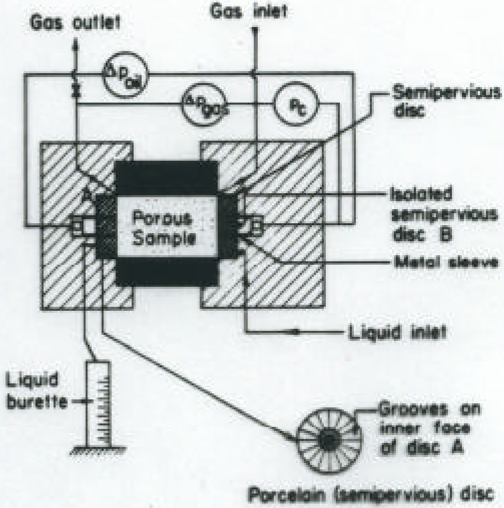


FIG. 9.2.15. Hassler's apparatus for relative permeability determination (after Osoba et al., 1951).

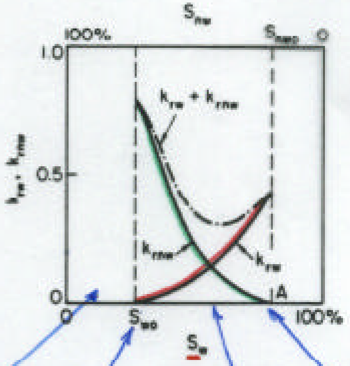


FIG. 9.3.1. Typical relative permeability curves (e.g., wetting fluid = water, nonwetting fluid = oil).

[2:5] Multiphase Flow

Recap

Permeability

- Permeability of fractures
- Linkage between perm-sat and Pc-sat
- Buckley-Leverett
- Flow calculation

3.2 RELATIVE PERMEABILITY

- $k_{r_{nw}} + k_{r_w} \neq 1 \Rightarrow k_{r_{nw}} + k_{r_w} < 1$.

  Most effective transmission is at 100% saturation (if accessible). Interference.

- Usually $k_{r_{nw}}$ closer to 1 than k_{r_w}
- Steep decline of k_{r_w} with increasing S_{nw} indicates larger pores occupied first by nonwetting phase.

  Nonwetting phase occupies larger pores preferentially due to capillary pressure arguments.

//

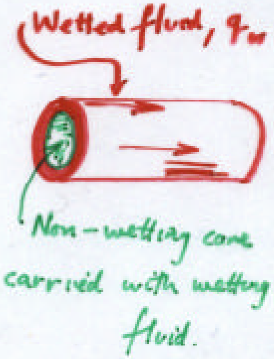
- k to wetting fluid is always *larger* for open pored unconsolidated material.

- k to *non*-wetting fluid is always *smaller* for open-pored unconsolidated material.

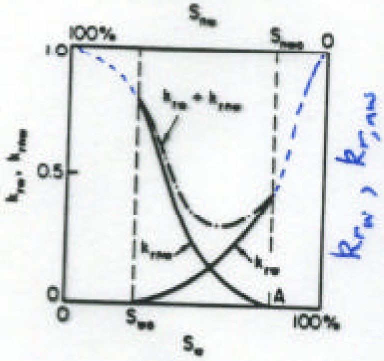
//

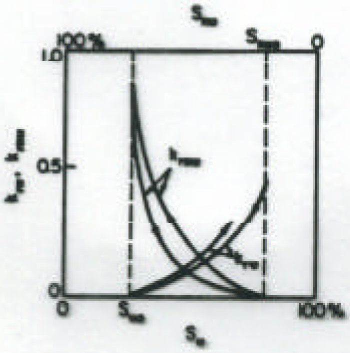
Hysteresis:

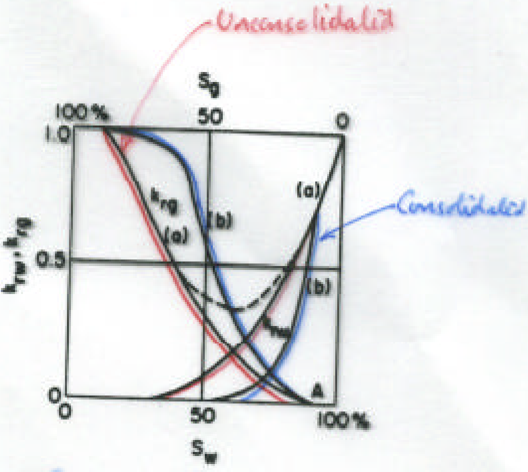
1. Wetting fluid surrounds grains and non-wetting fluid ∴ may move nw fluid even if no pressure gradient in nw fluid.



2. Since change in saturation requires change in wetted grain surface – wettability is hysteretic. ∴ permeabilities are hysteretic.



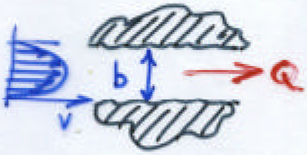




Curves switch over
– nw fluid saturates
largest pores first.

PERMABILITY/CONDUCTIVITY OF FRACTURES

Flow in fractures



$$\underset{\sim}{k}$$

$$\bar{v} = -\frac{gb^2}{12\nu}\frac{dh}{dx}$$

$\bar{v}$ = average velocity.

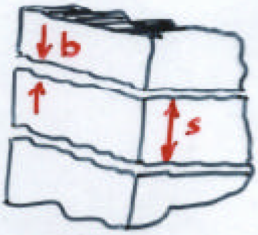
ν = kinematic viscosity of fluid

$\nu = \mu/\rho$

Equivalent flow rate per unit width: for single fracture

$$Q = b\,\frac{gb^2}{12\nu}\frac{dh}{dx}$$

Multiple fractures arranged in parallel:



Total of N fractures per unit height:

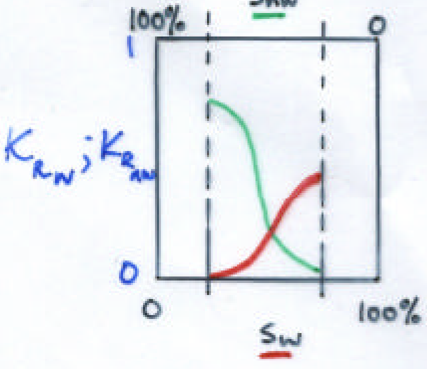
$N = 1/s$

$$Q = \underbrace{\frac{gb^3}{12\nu}\frac{1}{s}}_{K_b}\frac{dh}{dx}$$

Equivalent conductivity for multiple sets : $K_b = \frac{gb^3}{6\nu s}$

Enables b to be evaluated if K known (measured).

Relative permeability of fractures



- Similar behavior to porous medium
- Distribution of apertures 

  Large apertures saturate first

Capillary pressure or head $h_c = \frac{2\sigma}{b\gamma_w}$

FRACTURE PERMEABILITIES AND CAPILLARY PRESSURES

$$k = \frac{b^2}{12}$$ single fracture permeability (1)

$$k_b = \frac{b^3}{12s}$$ bulk permeability

Permeabilities and capillary pressures related.

$$h_c = \frac{2\sigma}{b\gamma_w} \quad \text{or} \quad h_c\gamma_w = \frac{2\sigma}{b} = P_{c_b} \qquad (2)$$

From (1) and (2) $$P_{c_b} = \frac{2\sigma}{\sqrt{12k}}$$

General relation for fractures and porous media

$$P_c \propto \sqrt{\frac{1}{k}}\,.$$

e.g. Leverett 'J' function –

$$J = \frac{P_c}{\sigma}\sqrt{\frac{k}{n}}$$

$$\therefore P_c = J\sigma\sqrt{\frac{n}{k}}$$

3.3 Mass Conservation in Multiphase Flow

Continuity equation: $\frac{\partial}{\partial t}(n S_\alpha \rho_\alpha) + \frac{\partial}{\partial x_i}(\rho_\alpha q_\alpha) = 0$ $\alpha = 1, 2$

or $\alpha = 1, 2, 3.$

For an incompressible fluid and medium $\frac{\partial}{\partial t}(n \text{ and } \rho) = 0$

Substitute q_α from relative permeability relation:
Results in 4 equations:

$$n \frac{\partial S_1}{\partial t} - \frac{\partial}{\partial x_i}\left[k \frac{k_{r1}}{\mu_1}\left(\frac{\partial p_1}{\partial x_j} + \rho_1 g \frac{\partial z}{\partial x_j}\right)\right] = 0$$

$$n \frac{\partial S_2}{\partial t} - \frac{\partial}{\partial x_i}\left[k \frac{k_{r2}}{\mu_2}\left(\frac{\partial p_2}{\partial x_j} + \rho_2 g \frac{\partial z}{\partial x_j}\right)\right] = 0$$

$$S_1 + S_2 = 1$$

$$p_2 - p_1 = p_c(S_1)$$

Solve for 4 unknowns: S_1, S_2, p_1, p_2

with $h_1 = z + \frac{p_1}{\rho_1 g}$; $h_2 = z + \frac{p_2}{\rho_2 g}$

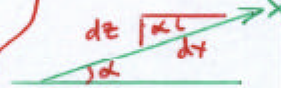
Solve using numerical techniques.

3.5 BUCKLEY – LEVERETT (1942) EQUATIONS

Assume: Neglect gravity, capillarity, liquid compressibility.

Homogeneous reservoir of thickness, b, inclined @ α°.

$dx \sin\alpha = dz$



$\sin x = \frac{dz}{dx}$

$$\left.\begin{aligned} q_w &= -(k_w/\mu_w)(\partial p_w/\partial x + \rho_w g \sin\alpha) \\ q_{nw} &= -(k_{nw}/\mu_{nw})(\partial p_{nw}/\partial x + \rho_{nw} g \sin\alpha) \end{aligned}\right\} \text{Relative permeability and Darcy's Law.}$$

$$\left.\begin{aligned} n\,\partial S_w/\partial t + \partial q_w/\partial x &= 0 \qquad (1) \\ n\,\partial S_{nw}/\partial t + \partial q_{nw}/\partial x &= 0 \qquad (2) \\ S_w + S_{nw} &= 1 \qquad (3) \\ p_c = p_{nw} - p_w & \qquad (4) \end{aligned}\right\} \text{4 equns for 4 unknowns.}$$

Initial and boundary conditions

Irreducible wetting saturation

$t \leq 0 \qquad 0 \leq x \leq L \qquad S_{nw} = 1 - S_{w_0}$

$t > 0 \qquad x = 0 \qquad q_w = \text{constant}; \quad q_{nw} = 0$

Wetting fluid injected to displace non-wetting fluid (oil) at irreducible wetting saturation $S_{nw} = 1 - S_{w_0}$

Injected @ constant rate at $x = 0$.

Unconsolidated → open pores

∴ high k to wetting fluid

low k to non-wetting

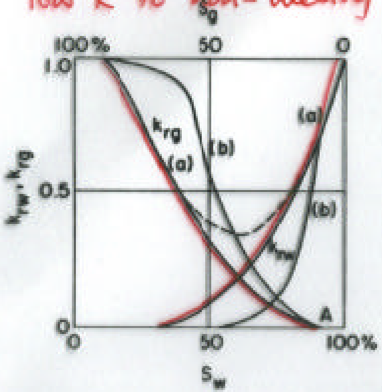


FIG. 9.3.2. Typical relative permeability to gas and water. (a) Unconsolidated sand. (b) Consolidated sand (Botset, 1940).

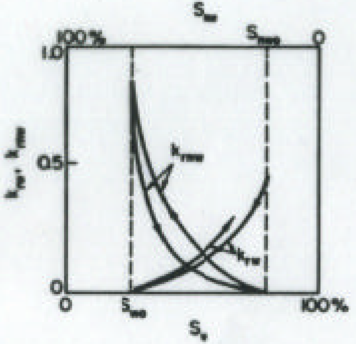


FIG. 9.3.3. Effect of hysteresis on relative permeability.

$dx \sin\alpha = dz \Rightarrow \frac{dz}{dx} = \sin\alpha$

Inject water @ $x=0$ $t=0$

Inject water as wetting fluid

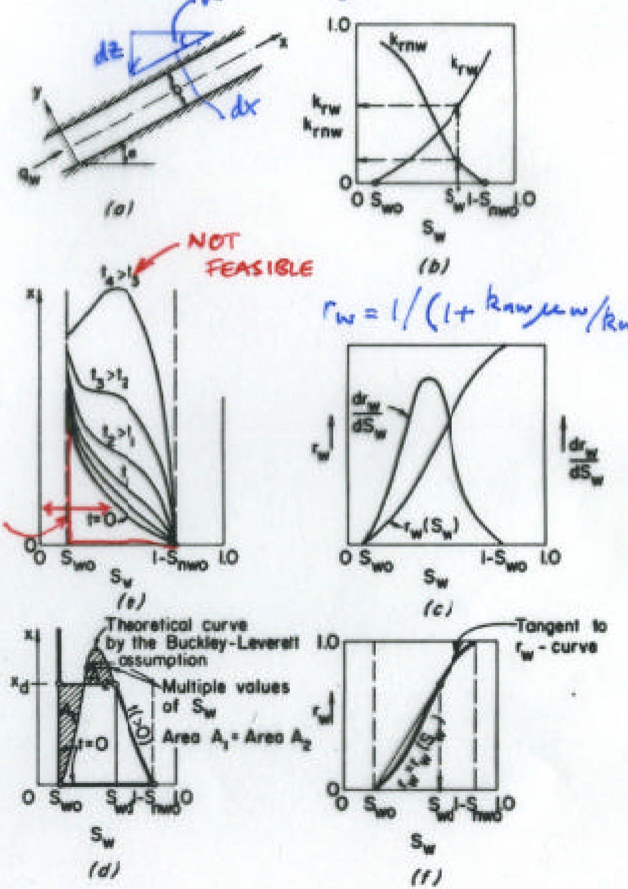


FIG. 9.3.4. The Buckley-Leverett solution for a linear immiscible displacement.

B-L Equations (cont'd)

Enables evaluation of front movement, see figure 9.3.4.(e)

$M = \frac{V_w}{V_{nw}}$

$$r_w = 1/(1+ k_{nw}\mu_w / k_w \mu_{nw}) = [1/(1 + 1/\text{Mobility ratio})]$$

Note since capillarity neglected @ t_4, two saturations exist.

∴ only applicable to high flow rates

– where capillary effects are masked

$$M = \frac{k_w \mu_{nw}}{k_{nw} \mu_w} = \frac{\bar{V}_w}{\bar{V}_{nw}}$$

General Comments

① Techniques developed for petroleum industry

Difficult interpretation for saturations less than irreducible saturation. This is perhaps most important region for groundwater contamination

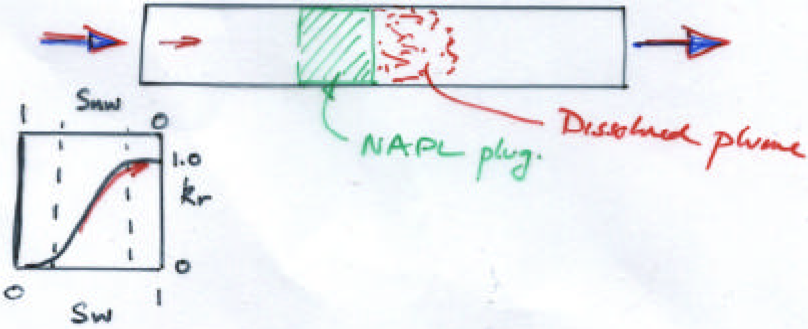
□ Need to incorporate:

Dissolution effect.

② For pump-and-treat need to understand two effects

a) Role of k_r in controlling water flow rates through NAPL plug. Plug does not move since funicular water saturation

b) Role of dissolution as S_{nw} ↓



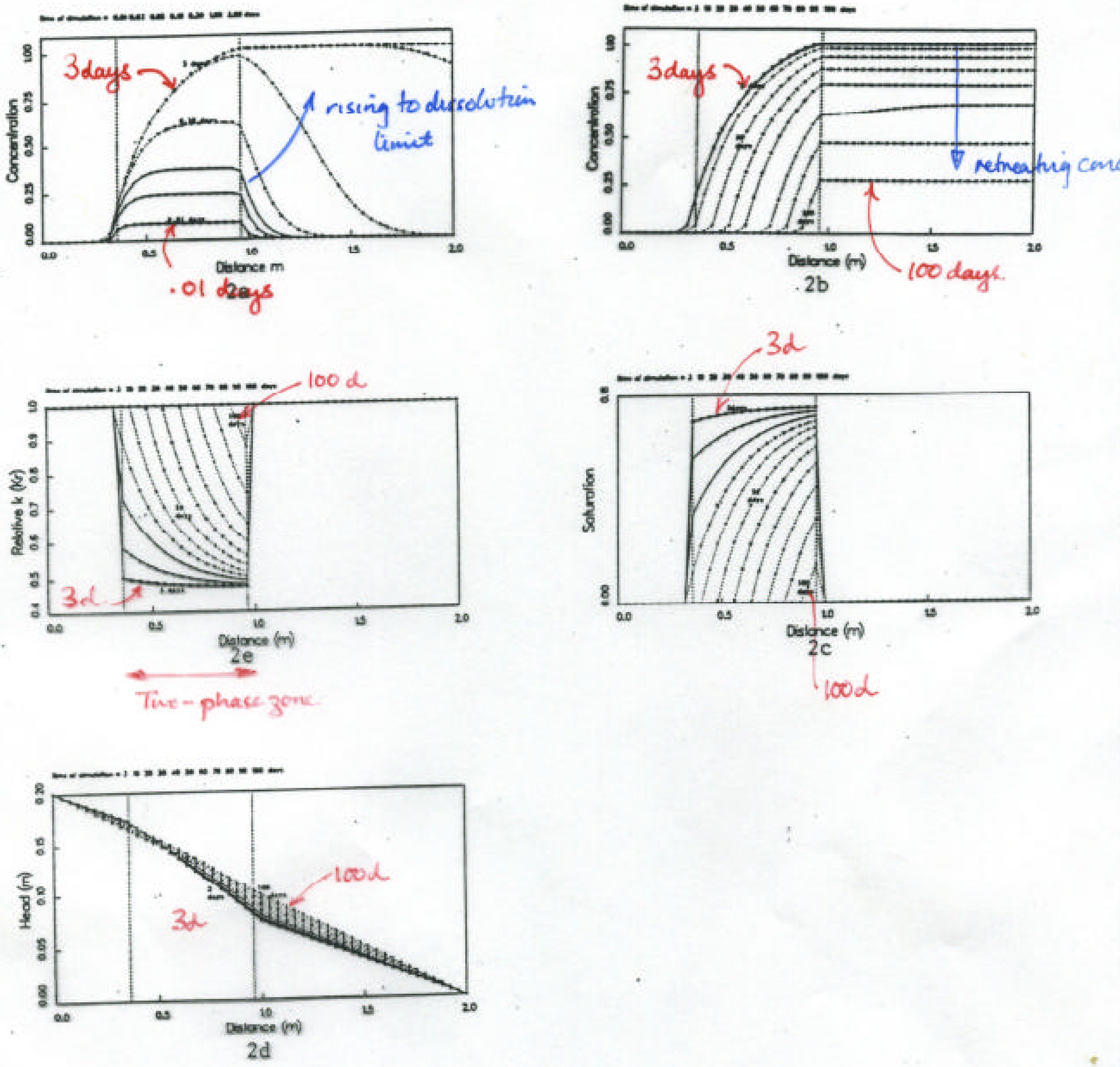
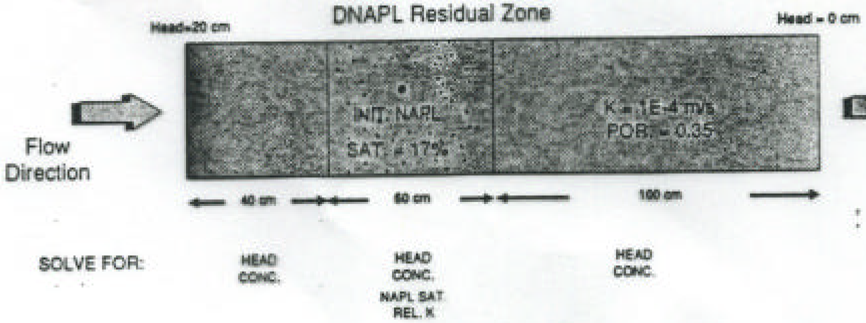


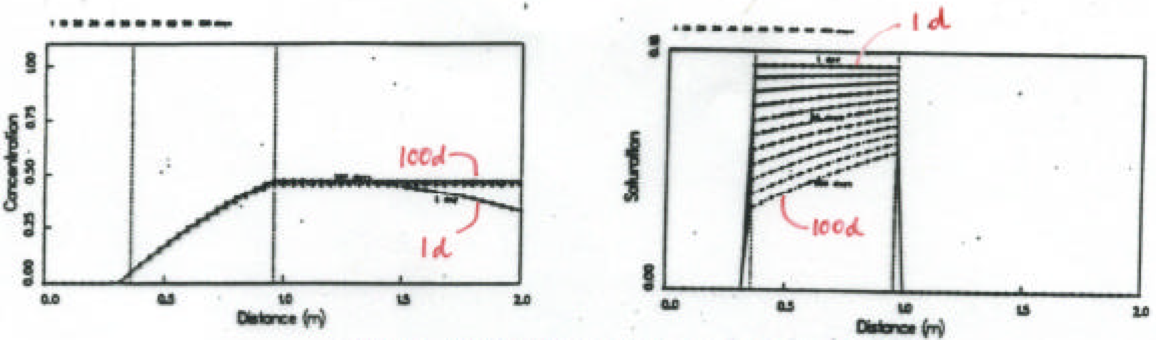
Fig. 2 - Results with Mass Transfer Coefficient = $1\text{x}10^{-4}$ $1/_s$ (a)Conc. at early times (b)Conc. at late times (c)DNAPL Saturation (d)Head distribution (e)Relative permeability.

COLUMN EXPERIMENT



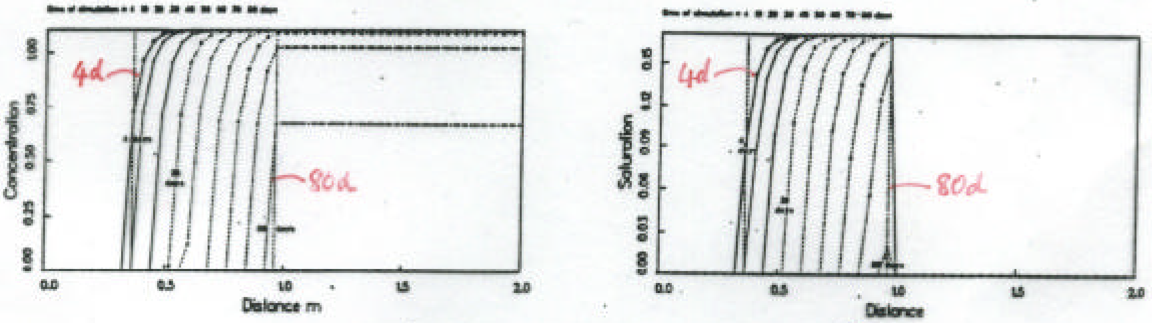
(BORDEN SAND)

$\frac{dh}{dx} = 0.1$



SMALL MASSTRANSFER COEFF. 1×10^{-5} 1/s

Fig. 3 - Results with Mass Transfer Coefficient = 1x10~~-3~~ $^{-5}$ 1/s



LARGE ~~SMALL~~ MASS TRANSFER COEFF. 1×10^{-3}

Fig. 4 - Results with Mass Transfer Coefficient = 2x10~~-5~~ $^{-3}$ 1/s

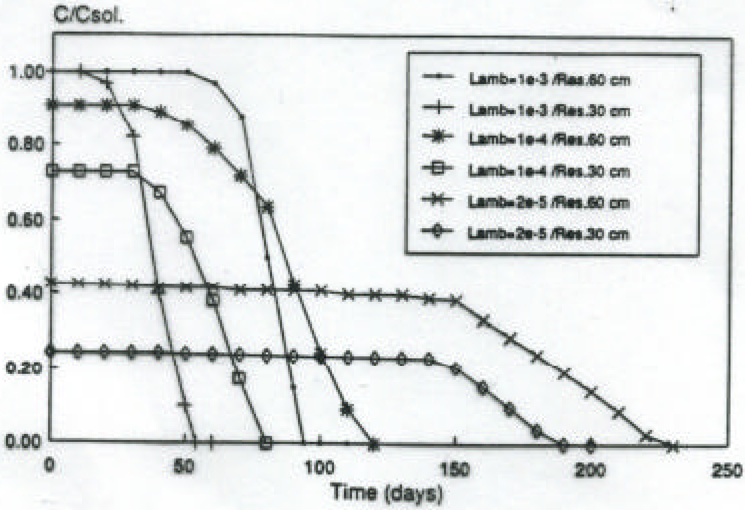


Fig. 5 - Concentration observed at the end of the residual saturation zone for different Mass Transfer Coefficients and lengths of the residual saturation zones

[2:6] Multiphase Flow

Recap

NAPLs – movement

- LNAPL
  - Saturation behavior
  - Thickness of floating product
- DNAPL
  - Saturation behavior
- Monitoring

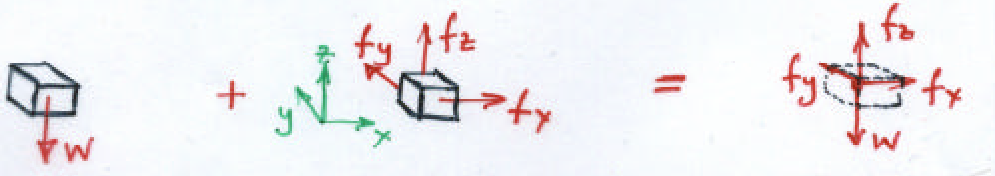
3.6 Non-Aqueous Fluid Penetration (Moving Groundwater)

Two situations: ① NAPL saturates medium → No capillary forces
② NAPL and water

3.6.1 NAPL Saturated

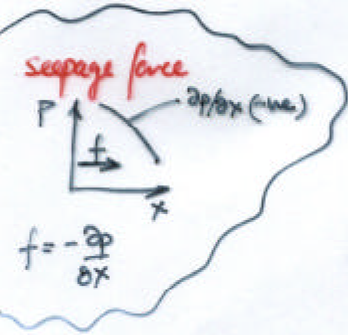
What pressure gradient to move fluid?
What direction of movement?

$dxdydz = dV$



BODY FORCE SEEPAGE FORCE RESULTANT

$$dV\rho g \begin{Bmatrix}0\\0\\-1\end{Bmatrix} + dV\begin{Bmatrix}-\partial/\partial x\\-\partial/\partial y\\-\partial/\partial z\end{Bmatrix} p = \underline{F}$$



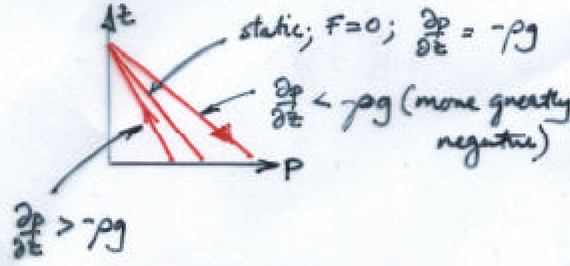
$$\left[\rho g\begin{Bmatrix}0\\0\\-1\end{Bmatrix} - p\begin{Bmatrix}\partial/\partial x\\ \partial/\partial y\\ \partial/\partial z\end{Bmatrix}\right]dV = \underline{F}$$

equilibrium @ $F=0$

$$\frac{\partial p}{\partial z} = -\rho g$$

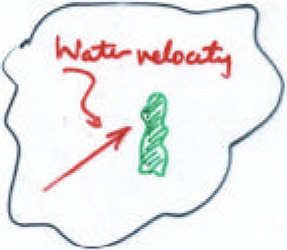
$\underline{F}$ is the resultant force vector. Force per unit volume.
Define the direction of force and ∴ direction of movement.

$F_z = 0$	$\partial p/\partial z = -\rho g$	static fluid
$F_z = +ve$	$\partial p/\partial z < -\rho g$	↑ flow
$F_z = -ve$	$\partial p/\partial z > -\rho g$	↓ flow



Also define lateral direction of flow.

3.6.2 NAPL and water



Will the gradient move the NAPL

Require to overcome capillary pressure, P_{co}

P_c acts uniformly in all directions
and must be overcome

Need to know size of NAPL pocket.

τ acts over length, L.

L is typically unknown

3.7 BEHAVIOR OF LNAPLS

3.7.1 Migration of LNAPLS

Surface spill: 1. Penetrate vadose zone under gravity with influence of capillary forces.

Vadose zone water wet.

NAPL is non-wetting.

Capillary Fringe: Holds water as continuous phase with residual air saturation

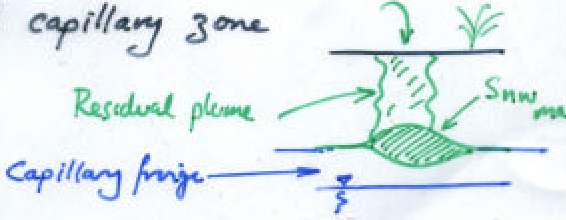
$h_c \uparrow$ with $\downarrow$ grain size $\rightarrow \downarrow$ pore size

$\left\{ \text{i.e. } h_c = \frac{4\sigma}{d\gamma} \right\}$

Example usual capillary rise

	Grain size (mm)	Rise (cm
Fine gravel	2-5	2.5
Medium sand	0.2-0.5	24.6
Fine silt	0.02-0.05	200+

LNAPL will penetrate down to top of capillary zone (if enough volume)



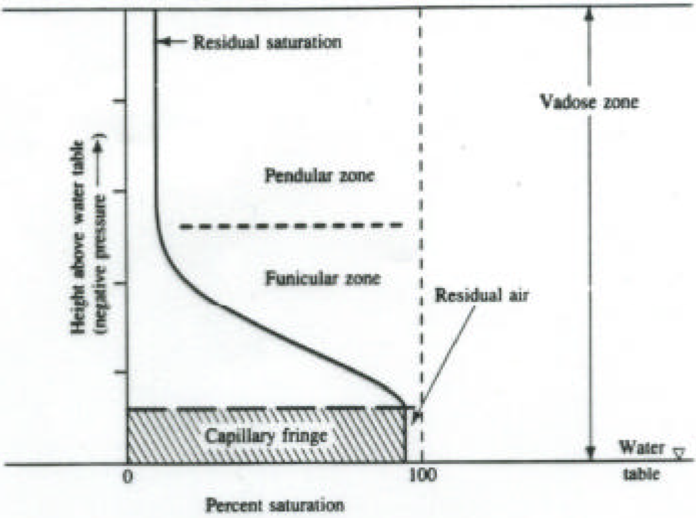


FIGURE 5.13 Vertical distribution of water in the vadose zone in the absence of nonaqueous phase liquids. *Source:* A. S. Abdul, *Ground Water Monitoring Review* 8, no. 4 (1988):73–81. Copyright © 1988 Water Well Journal Publishing Co.

TABLE 5.1 Visual capillary rise in unconsolidated materials (porosity of all samples is about 41%).

Material	Grain Size (mm)	Capillary Rise (cm)
Fine gravel	2–5	2.5
Very coarse sand	1–2	6.5
Coarse sand	0.5–1	13.5
Medium sand	0.2–0.5	24.6
Fine sand	0.1–0.2	42.8
Silt	0.05–0.1	105.5
Fine silt	0.02–0.05	200 +

Source: Lohman (1972).

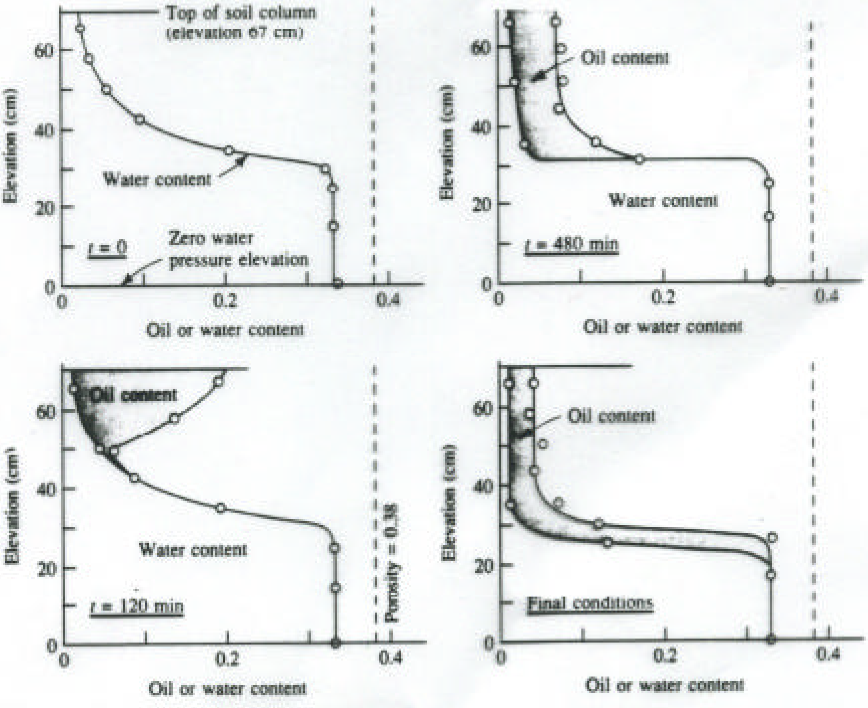


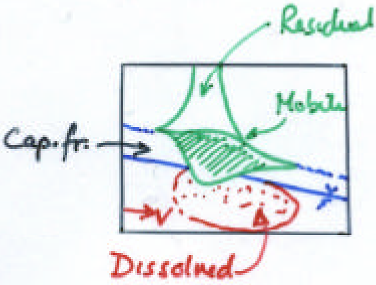
FIGURE 5.14 Changes in the vertical distribution of oil with time after a slug of oil is added to the top of a column of sand. Oil content and water content are expressed as a fraction of the total volume of the porous media. *Source:* D. K. Eckberg and D. K. Sunada, *Water Resources Research* 20, no. 12 (1984):1891–97. Copyright by the American Geophysical Union.

DEVELOPMENT OF AN OIL TABLE (Abdul, 1988)

Add oil incrementally to a) → b) develop oil fringe
b) → c) develop oil table
c) → d) remove capillary fringe and create oil table.

Mobile oil product may migrate "free" product

3 Components



☐ Residual column

- What is saturation? – Since free phase moved through zone, residual saturation must be greater than irreducible.
- Re-mobilized as rainfall from surface &

Partitioning → 1. Vapor phase → volatilization.
2. Dissolves in aqueous phase.

☐ "Free" product – May mobilize with rising / falling water table. May flow down steep water table

☐ Dissolution into groundwater

Gasoline → Benzene, Toluene, Ethylbenzene & Xylene (BTEX) soluble fractions.

Degree of partitioning depends on volatility of fractions

Which fractions will partition in → air } Henry's Law
→ water }

What is partitioning rate?

→ Transport processes (aqueous / gaseous).

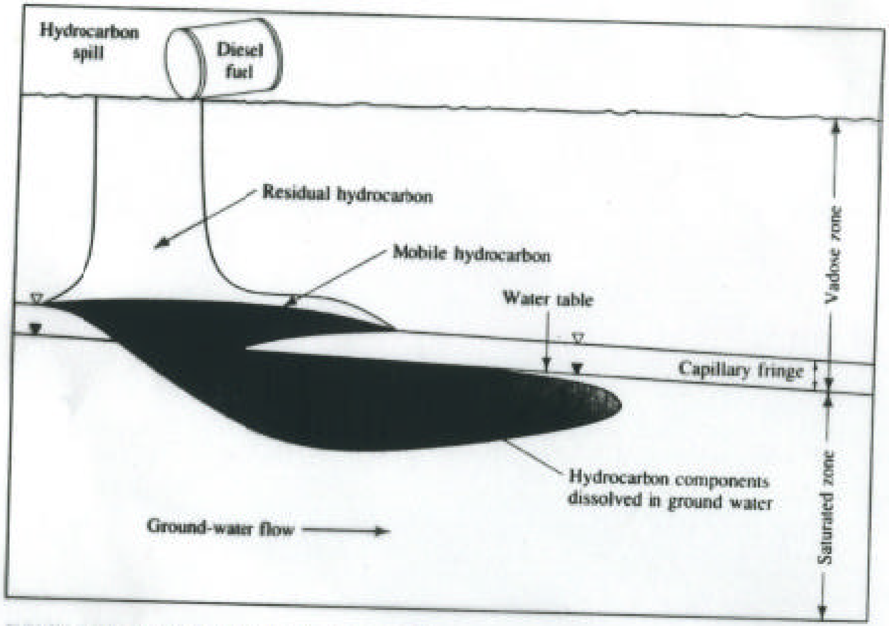


FIGURE 5.16 Subsurface distribution of an LNAPL spill.

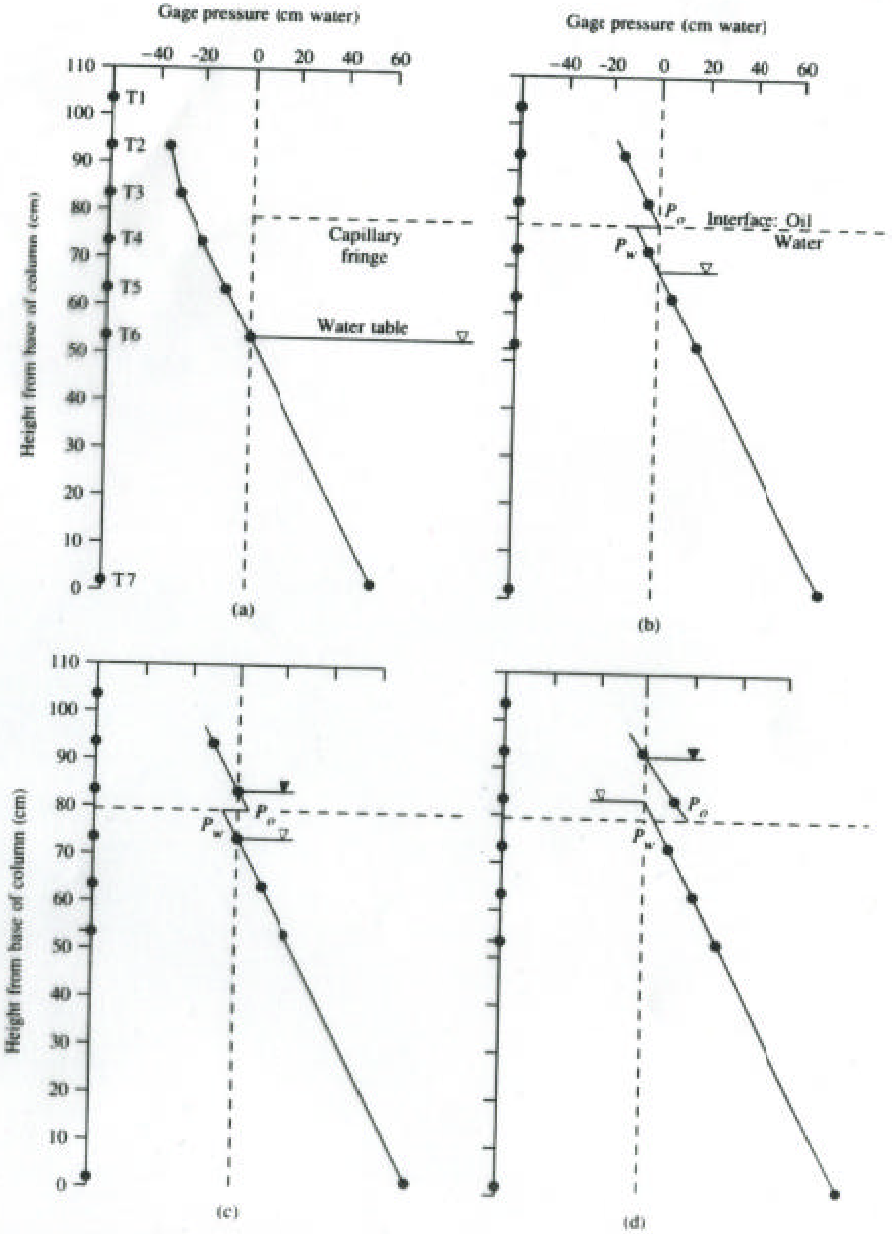


FIGURE 5.15 Hydrostatic pressure head/tension distribution in a sand column to which oil is being added to the top of the column. (a) Before the addition of the oil, (b) after addition of the oil showing the development of an oil fringe, (c) after addition of sufficient oil for an oil table to form, and (d) after sufficient mobile oil has accumulated to eliminate the water capillary fringe. *Source:* A. S. Abdul, *Ground Water Monitoring Review* 8, no. 4 (1988):73–81. Copyright © 1988 Water Well Journal Publishing Co. Used with permission.

Henry's Law

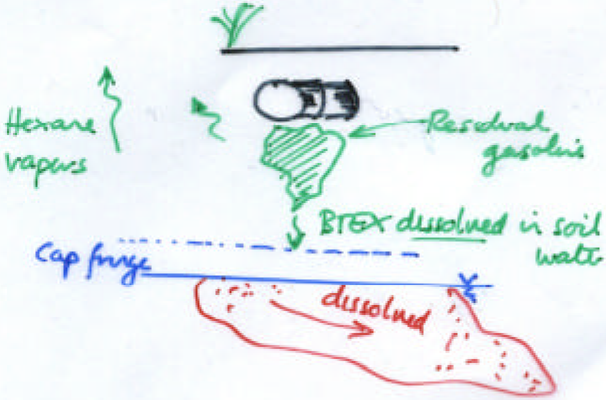
Linear relationship between vapor pressure of a solute and its aqueous solution and the concentration of the solution.

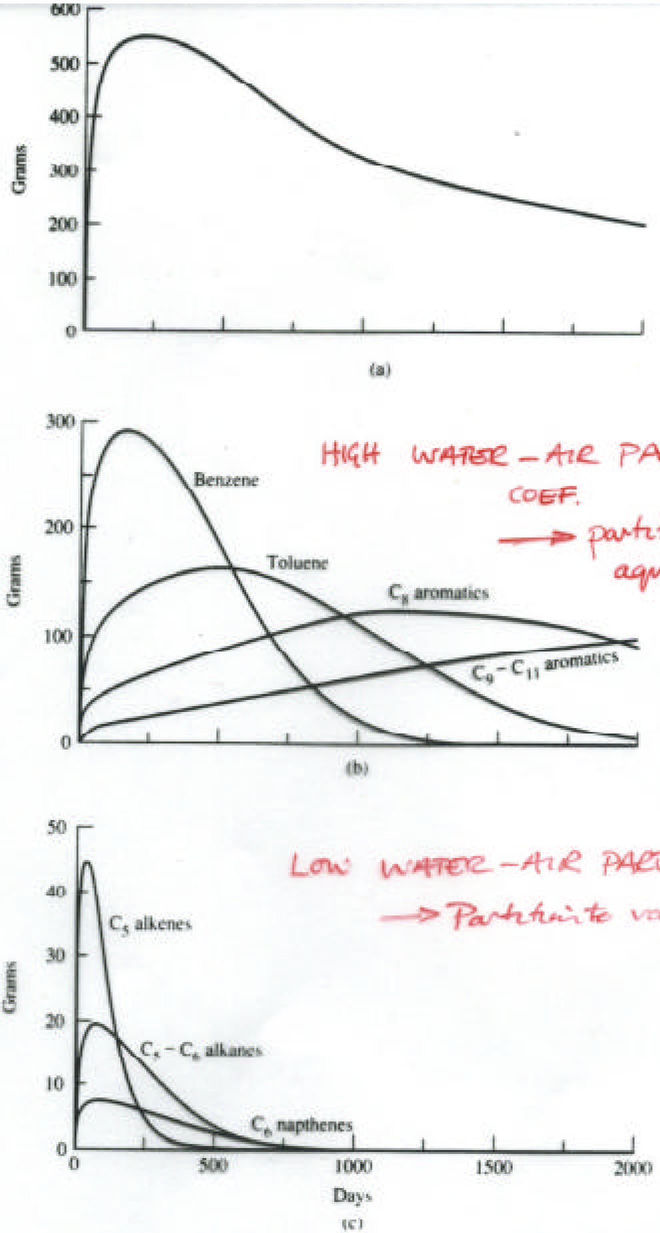
Proportionality coefficient ≡ Henry's Law constant.

Also applicable to partitioning in air.

Low water-air partition coefficients (alkanes) -> favor vapor phase
High water-air " " (benzene) -> favor aqueous phase

Different type of release for different materials:





HIGH WATER – AIR PARTITION COEF.
→ partition to aqueous phase

LOW WATER – AIR PART. COEF
→ Partition to vapor

FIGURE 5.17 Mass of residual hydrocarbon in vadose zone partitioning into capillary water as a function of time, with (a) total hydrocarbons, (b) aromatic constituents, and (c) nonaromatic constituents. *Source:* A. L. Baehr, *Water Resources Research* 23, no. 10 (1987): 1926–38. Copyright by the American Geophysical Union.

TABLE 5.2 Water-air partition coefficients for selected organic compounds.

Compound	Formula	Molecular Weight	Water-Air Partition Coefficient
Aromatics			
Benzene	C_6H_6	78	5.88
Toluene	C_7H_8	92	3.85
o-Xylene	C_8H_{10}	106	4.68
Ethylbenzene	C_8H_{10}	106	3.80
Nonaromatics			
Cyclohexane	C_6H_{12}	84	0.15
1-Hexene	C_6H_{12}	84	0.067
n-Hexane	C_6H_{14}	86	0.015
n-Octane	C_8H_{18}	114	0.0079

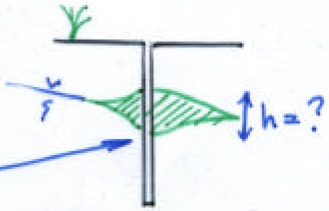
Source: A. L. Baehr. *Water Resources Research* 23, no. 10:1928. Published 1987 by American Geophysical Union. Used with permission.

3.7.2 Thickness of Floating Product

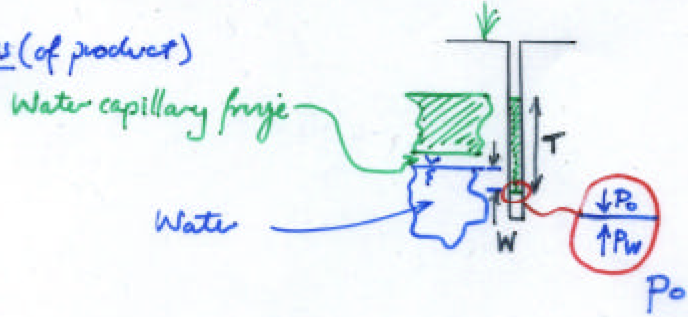
What is true depth/thickness of NAPL

Borehole will show artificial LNAPL depth

Artificial depth since.



Well thickness (of product)



$$P_o = P_w$$

$$P_o = \rho_o T g$$

$$P_w = \rho_w W g$$

Equating $\rho_o T = \rho_w W$ $\Rightarrow$ $\boxed{W = T\left(\frac{\rho_o}{\rho_w}\right)}$

Measure T, calculate W.

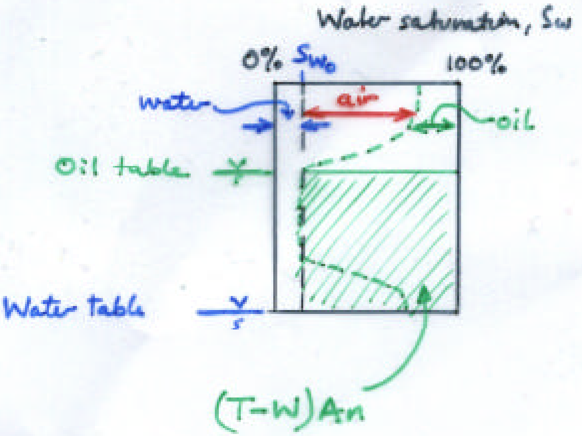
Volume of product $\Rightarrow$ Thickness $(T-W)$ (ignoring cap fringe height)

Volume of porespace $A(T-W)n$

Volume of product $\sim$ $A(T-W)n\underbrace{(1-S_{w_o})}_{S_{nw_o}}$

Not all is recoverable!!

Approx recoverable volume of product $\sim A(T-W)n(1-S_{w_o}-S_{nw_o})$

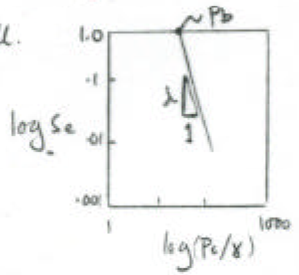


Recoverable Volume

Farr, Houghtalen, and McWhorter (1990) and Lenhard and Parker (1990) developed two methods to estimate the volume of recoverable LNAPL in an aquifer based on the thickness of the LNAPL floating in a monitoring well. These methods are based on the capillary soil properties. One of the two methods is based on the determination of soil properties as reported by Brooks and Corey (1966). We will look at this method in some detail using the derivation of Farr, Houghtalen, and McWhorter.

Brooks-Corey (1966) soil.

Recall.



Se = effective saturation

$$S_e = \frac{(S_w - S_{wo})}{(1 - S_{wo})}$$

T as shown in Figure 5.19 is the difference between the depth to the water-oil interface in the well, D_w^{ow} and the depth to the oil-air interface, D_w^{ao}. The values of the depth to the oil table in the aquifer, D_a^{ow}, and the depth to the top of the capillary fringe, D_a^{ao}, can be computed.

$$* \quad D_a^{ao} = D_w^{ao} - \frac{P_d^{ao}}{\rho_o g} \tag{5.29}$$

height of oil capillary fringe

$$* \quad D_a^{ow} = D_w^{ow} - \frac{P_d^{ow}}{(\rho_w - \rho_o)g} \tag{5.30}$$

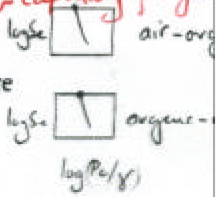
height of W + water capillary fringe

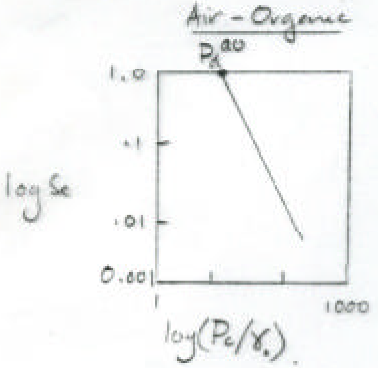
where

P_d^{ao} = the Brooks-Corey air-organic displacement pressure

P_d^{ow} = the Brooks-Corey organic-water displacement pressure

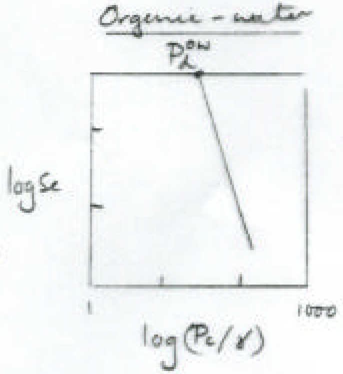
g = the acceleration of gravity





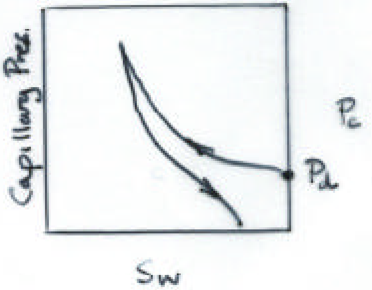
Wetting = organic

Non-wetting = air



Wetting = water

Non-wetting = organic



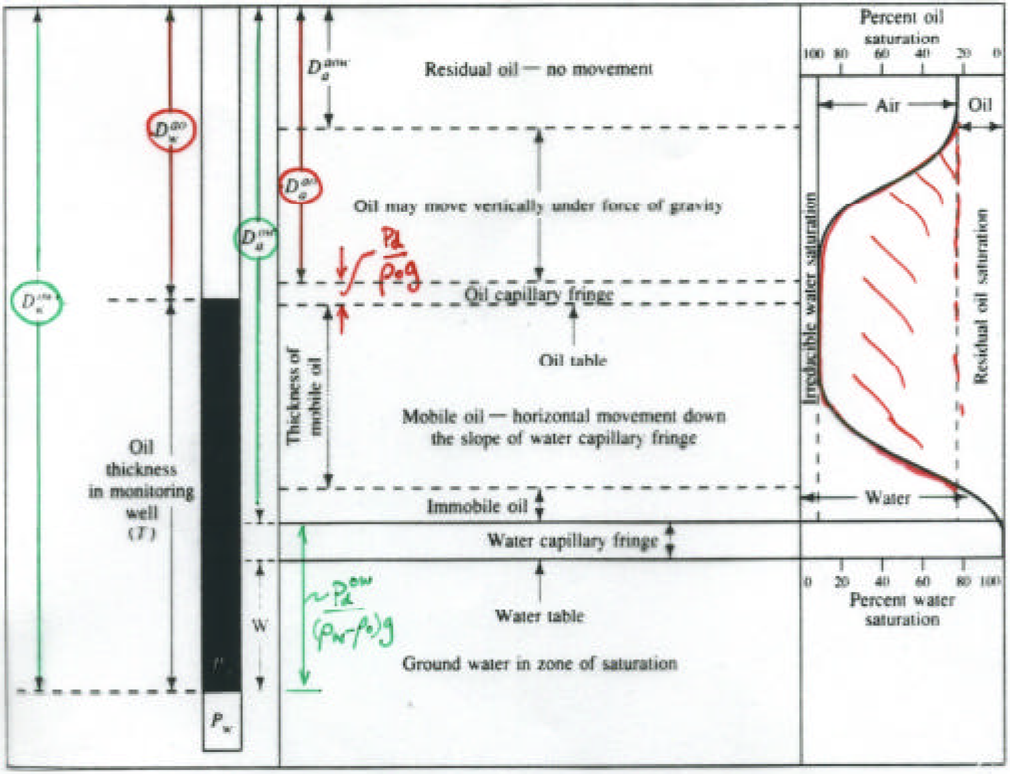


FIGURE 5.19 Comparison of distribution of mobile oil in an aquifer with the thickness of floating oil in a monitoring well for the case where a water capillary fringe exists below the zone of mobile oil.

TERMINOLOGY: D_W^{ow}

organic-water interface

Measured in the well

Since on figure $D_w^{ow} = D_w^{ao} + T$, then

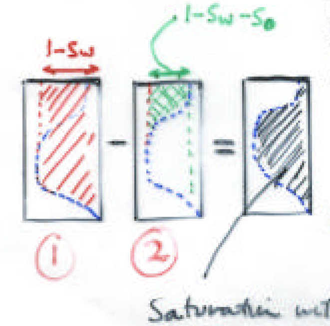
Equation 5.30 may be rewritten as

$$D_a^{ow} = \left(D_w^{ao} + T\right) - \frac{P_d^{ow}}{(\rho_w - \rho_o)g} \tag{5.31}$$

If any of the organic liquid exists at a positive pore pressure, then D_a^{ow} will be greater than D_w^{ao} and from Equation 5.31,

$$T \geq \frac{P_d^{ow}}{(\rho_w - \rho_o)g} \tag{5.32}$$

SUM OIL COMPONENTS



If the organic liquid is all under tension in the capillary zone, then there will be no mobile organic layer and no organic liquid will collect in the monitoring well. Under these conditions, Equations 5.29, 5.30, 5.31, and 5.32 are not applicable. However, as soon as free organic liquid appears in the aquifer, it will collect to a depth of at least $P_d^{ow}/(\rho_w - \rho_o)g$

The total volume of nonresidual organic liquid in the vadose zone is given by

$$V_o = n\left\{\underbrace{\int_{D_a^{owa}}^{D_a^{ow}} (1 - S_w)\,dz}_{\textcircled{1}} - \underbrace{\int_{D_a^{owa}}^{D_a^{ao}} [1 - (S_w + S_o)]\,dz}_{\textcircled{2}}\right\} \tag{5.33}$$

where

V_o = the volume of organic liquid per unit area
n = the porosity
S_w = the water-saturation ratio
S_o = the organic liquid saturation ratio
z = the vertical coordinate measured positively downward
D_a^{ow} = a value determined from Equation 5.30
D_a^{ao} = a value determined from Equation 5.29
D_a^{owa} = the top of the zone where nonresidual oil occurs

RELATE FLUID PRESSURES TO SATURATIONS

Based on work by Lenhard and Parker (1987, 1988), the fluid-content relations are

$$S_o - S_w = (1 - S_{wi})\left(\frac{P_c^{ao}}{P_d^{ao}}\right)^{-\lambda} + S_{wi}, \qquad P_c^{ao} > P_d^{ao} \tag{5.34a}$$

$$S_o + S_w = 1, \qquad P_c^{ao} < P_d^{ao} \tag{5.34b}$$

$$S_w = (1 - S_{wi})\left(\frac{P_c^{ow}}{P_d^{ow}}\right)^{-\lambda} + S_{wi}, \qquad P_c^{ow} > P_d^{ow} \tag{5.35a}$$

$$S_w = 1, \qquad P_c^{ow} < P_d^{ow} \tag{5.35b}$$

where

S_{wi} = the irreducible water saturation
λ = the Brooks-Corey pore-size distribution index

In addition,

$$P_c^{ao} = \rho_o g(D_w^{ao} - (P_d^{ao}/\rho_o g) - z) + P_d^{ao} \tag{5.36}$$

$$P_c^{ow} = g(\rho_w - \rho_o)\left[D_w^{ow} - \frac{P_d^{ow}}{(\rho_w - \rho_o)g} - z\right] + P_d^{ow} \tag{5.37}$$

Integration of Equation 5.33 for $D_a^{aow} > 0$, using Equations 5.34, 5.35, 5.36, and 5.37, yields the following. For λ not equal to 1,

VOLUMES IF
RESIDUAL
ZONE
PRESENT

$$V_o = \frac{\overset{n}{\phi}(1 - S_{wi})D}{1 - \lambda}\left[\lambda + (1 - \lambda)\left(\frac{T}{D}\right) - \left(\frac{T}{D}\right)^{1-\lambda}\right] \tag{5.38a}$$

For λ equal to 1,

$$V_o = n(1 - S_{wi})[1 - D(1 + \ln T)] \tag{5.38b}$$

where

$$D = \frac{P_d^{ow}}{(\rho_w - \rho_o)g} - \frac{P_d^{ao}}{\rho_o g}$$

$$T = D_w^{ow} - D_w^{ao} \geq \frac{P_d^{ow}}{(\rho_w - \rho_o)g}$$

If organic liquid above the residual saturation exists all the way to the land surface, then D_a^{aow} does not exist. Under this condition integration of Equation 5.33 yields the following. For λ not equal to 1,

VOLUMES IF
RESIDUAL
ZONE
ABSENT

$$V_o = n(1 - S_{wi})\left\{(T - D) - \frac{P_d^{ao}}{\rho_o g(1 - \lambda)}\left[1 - \left(\frac{\rho_o g D_w^{ao}}{P_d^{ao}}\right)^{1-\lambda}\right] + \frac{P_d^{ow}}{(\rho_w - \rho_o)g(1 - \lambda)}\left[1 - \left(\frac{(\rho_w - \rho_o)g D_w^{ow}}{P_d^{ow}}\right)^{1-\lambda}\right]\right\} \tag{5.39a}$$

For λ equal to 1,

$$V_o = n(1 - S_{wi})\left[(T - D) - \frac{P_d^{ow}}{(\rho_w - \rho_o)g}\ln D_w^{ow} + \frac{P_d^{ao}}{\rho_o g}\ln D_w^{ao}\right] \tag{5.39b}$$

Approx. volume (simple) = $V \simeq n(1 - S_{wo} - S_{nwo})(T - W)$

Reasons not to be able to recover free product:

1. Lenses of low conductivity

3.7.3. Rise and Fall of Water-Table

Fall of water table — "Free" product drops

Rise of water table — Residual LNAPL is trapped below water table and available → dissolution

Rate of movement controlled by:
- Darcy's law, $k_r k/\mu$
- Density (driving flow)
- Capillarity

Residual volumes controlled by soil retention capacity

$$\left.\begin{array}{l}\text{Gravel } 5\text{ L/m}^3\\ \text{Silty sand } 40\text{ L/m}^3\end{array}\right\}\text{ due to capillarity}$$

Say $n = 30\%$ $1\text{m}^3 = 1000\text{L}$

porosity @ 30% → 300L

$\therefore$ saturation $S_{nwo} = \frac{5}{300}$ to $\frac{40}{300}$

$S_{nw_0} = 1.6\%$ to 13%

- Free product may be drained by open wells and trenches
- Bound product must be removed by → volatilization/venting
  → dissolution

Note: cannot apply high fluid suction pressures due to short circuiting.

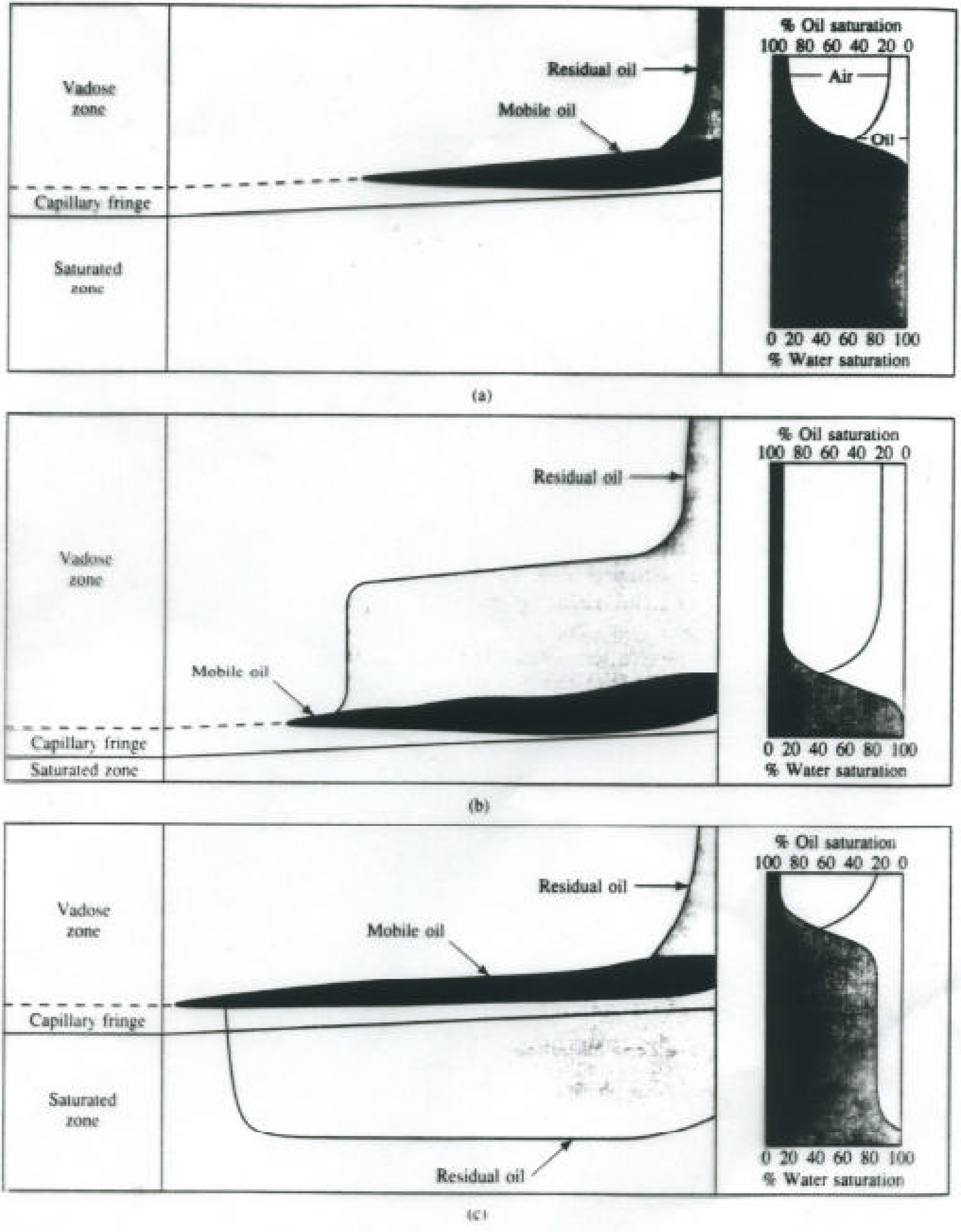


FIGURE 5.22 Effect of a falling and then rising water table on the distribution of mobile and residual phases of an LNAPL.

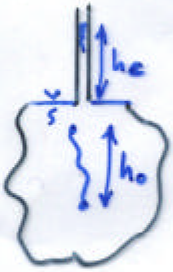
3.8 Behaviour of DNAPLS

3.8.1 Vadose zone migration

- Similar characteristics to LNAPL but ↑ density → more penetrative (water table)
- Preferentially chooses <u>large</u> pores and continuous pore throat channels
- Displaces air and reaches capillary zone.
- Displaces water @ capillary zone.

3.8.2 Vertical movement in saturated zone

Static fluid: Hobson's Formula – defines required critical height for penetration, h_o



$h_o \neq h_c$

$$\boxed{h_o = \frac{+2\sigma\cos\theta\,(1/r_t - 1/r_p)}{g(\rho_w - \rho_o)}}$$

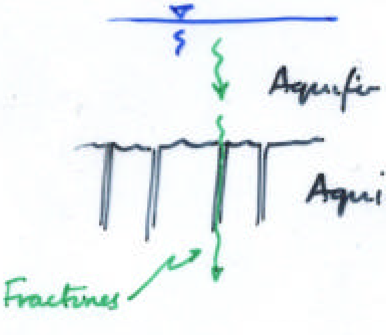
r_p = pore radius
r_t = throat radius

$h_c = \frac{P_b}{\gamma_o}$

Rhombohedral packing, $r_p = .212d$, $r_t = .077d$ } d = grain diameter

Same as $h = \frac{h_c}{(1 - \rho_w/\rho_{nw})}$ if $h_c = \frac{2\sigma\cos\theta}{r^*\gamma_{nw}}$

as h_c includes $(\theta, \sigma, r^*, \gamma_{nw})$



Capillary tube: $h_c = \frac{4\sigma}{d\gamma_w}\cos\theta$

Fracture: $h_c = \frac{2\sigma\cos\theta}{b\gamma_w}$

Monitoring wells:

- Place at aquifer base to collect flow from mobile DNAPL –
  Will separate in well into individual components.
  - water at saturation (potentially).

- DNAPL level is intermediate within zone of mobile water and DNAPL
- Deep wells record false DNAPL depth.

Vertical distribution of DNAPL

Accumulation depends on grain size (actually pore size) distribution –> since controlls capillary pressure distribution.

Small pores/fractures: Low K ⟶ thin pure DNAPL layer
thick DNAPL + water

Large pores / fractures: High K ⟶ thick pure DNAPL layer
thin DNAPL + water.

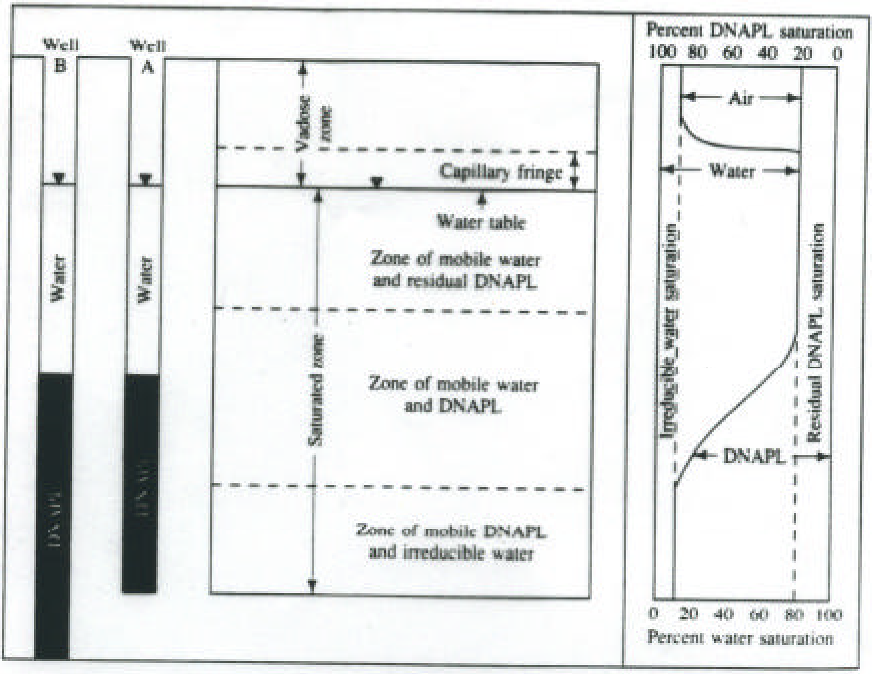
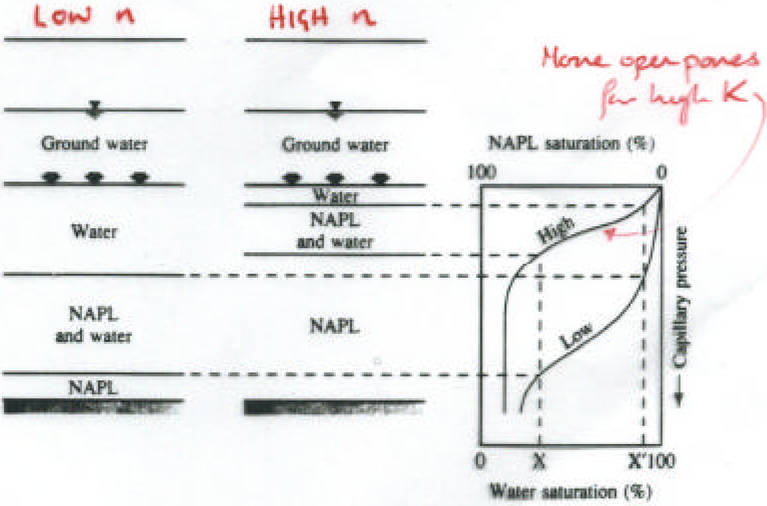


FIGURE 5.23 Zones of a DNAPL and the relationship of mobile DNAPL and nonmobile DNAPL to the DNAPL saturation; relationship of mobile DNAPL thickness to thickness of DNAPL is measured in a monitoring well.



LOW n

HIGH n

More open pores for high K

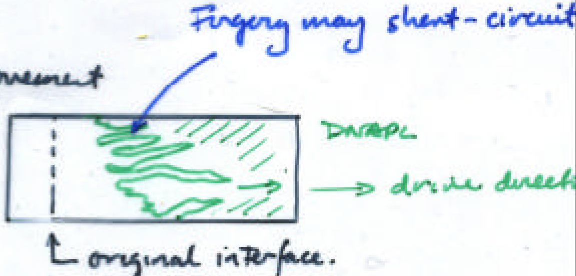
FIGURE 5.24 Effect of high and low permeability (and porosity) on the distribution of mobile DNAPL at the bottom of an aquifer; the arrows indicate level of original injection of the DNAPL. Source: J. F. Villaume, *Ground Water Monitoring Review* 5, no. 2 (1985):60–74. Copyright © 1985 Water Well Journal Publishing Co.

3.8.3. Horizontal Movement in Saturated Zone

- Difficult to estimate potential for movement
  - Water drive will produce fingering

    Classical fingering

    1) Due to instability
    2) Accentuated by heterogeneity
       - heterogeneity has overriding effect in most shallow aquifers.



Gradient required to move DNAPL (horizontally)

$$\nabla p = \frac{2\sigma}{L_0 \cancel{(1/r_t - 1/r_p)}\, r^*}$$

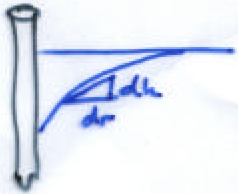
L_0 = length of continuo

DNAPL phase

r_t = throat ; r_p = pore radii

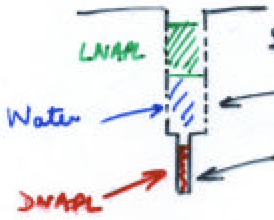
eg. to determine radius of influence of capture well :

$$\frac{dp}{dr} = \frac{1}{r_w} \frac{dh}{dr}$$



Difficulty in estimating L_0.

3.9 MONITORING LNAPL & DNAPL



Screen for LNAPL

Screen perforations large to allow penetration

Sump for DNAPL - sample with bailer

DNAPL - Bottom loading bailer

LNAPL - Top loading bailer scooping from upper surface

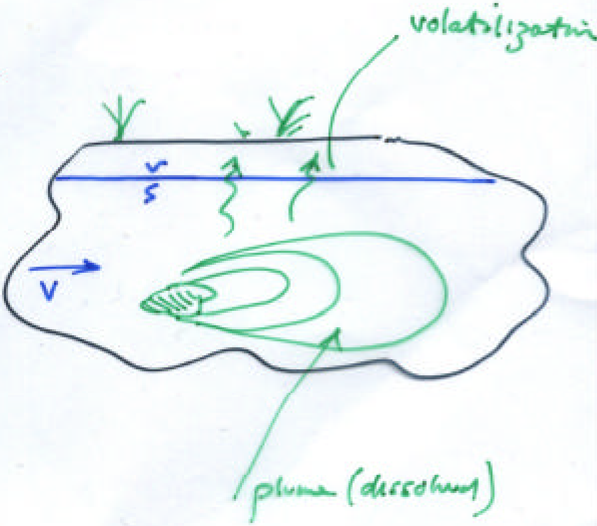
- Allow fluids to separate in sample → decant.
- Partial emulsion induced by sampling process.

Fractured bedrock sampling most difficult -

☐ Pooled DNAPL locations

☐ Infer source

☐ Drilling may remobilize "free" product by dilating fractures:



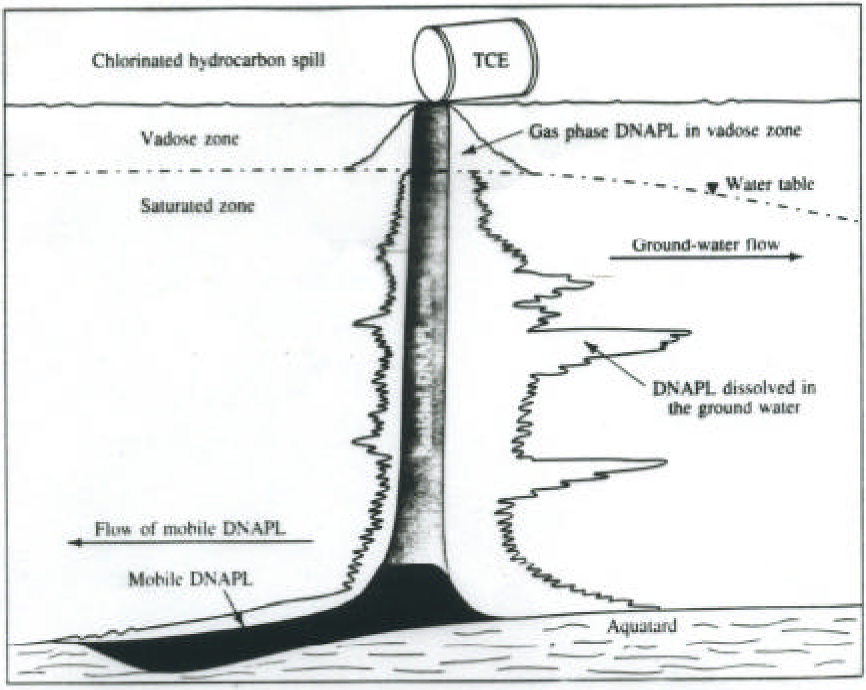


FIGURE 5.25 Distribution of a dense nonaqueous phase liquid in the vadose and saturated zone.

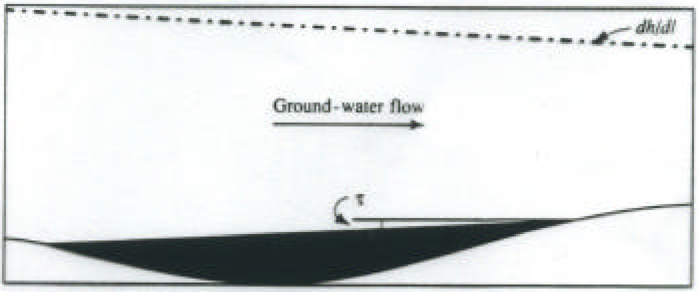


FIGURE 5.26 Sloping interface between a static layer of DNAPL and flowing ground water.

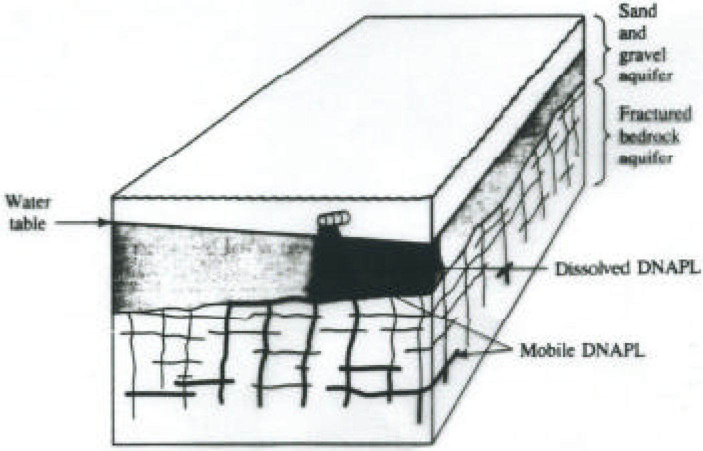


FIGURE 5.27 Movement of a DNAPL into a fractured bedrock aquifer that underlies a sand and gravel aquifer.

[2:7] Unsaturated Flow

Recap

Concept of Matric Potential

Empirical P_c-S_w and k_r-S_w relationships

- Brooks-Corey
- van Genuchten

4. UNSATURATED FLOW

- Contaminants traverse vadose zone
  - Pesticides (deliberate application)
  - Immiscible
  - Dissolved

- Clay mineralogy

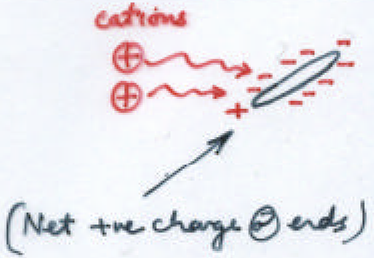
  Reactive clays in many soils (clay $< 2\mu m$)

  Weathering products – Aluminium, Silica, Oxygen

  Kaolinite (china clay) $5-20\ m^2/g$

  Montmorillonite – high surface area $700\ m^2/g$.

- Why important –



① Electrical double layer captures colloid

(unbalanced -ve surface)

attracts +ve cations

∴ good buffers or attenuators

② Electrostatic double layer affects hydrolog

Swelling clays swell and seal pathways.

Water salinity ↑ → swelling → ↓ conductivity

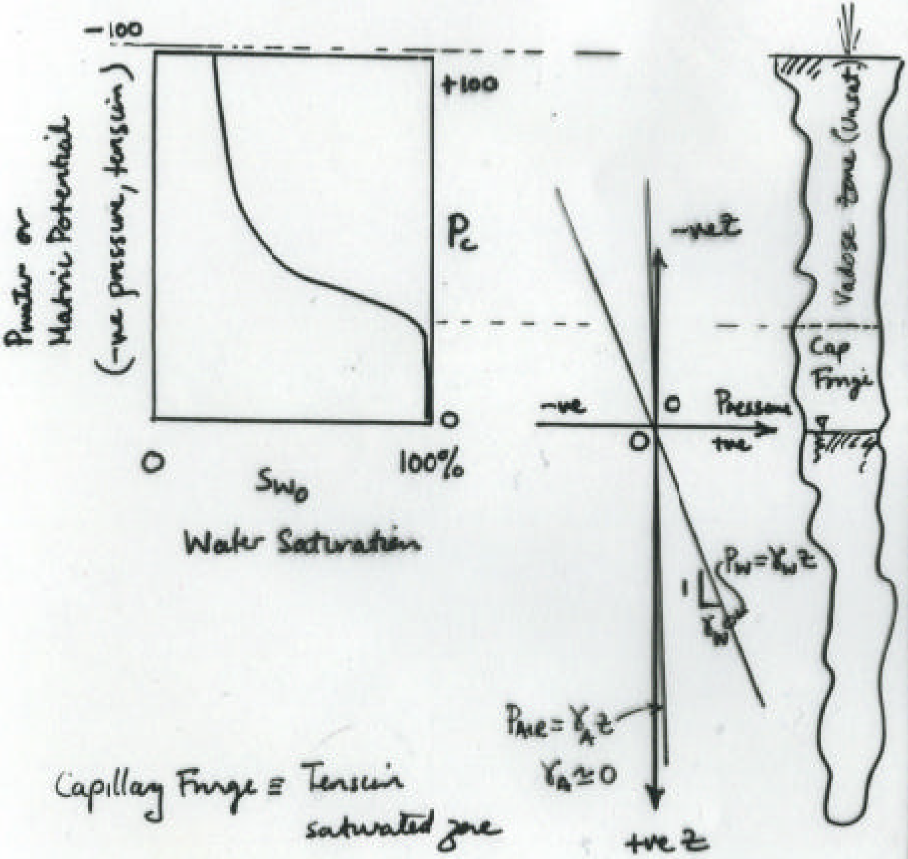
Process reverses if flushed by fresh water.

STATIC SYSTEMS

$P_c = P_{nw} - P_w$

Vadose zone

$P_c = P_{air} - P_{water}$



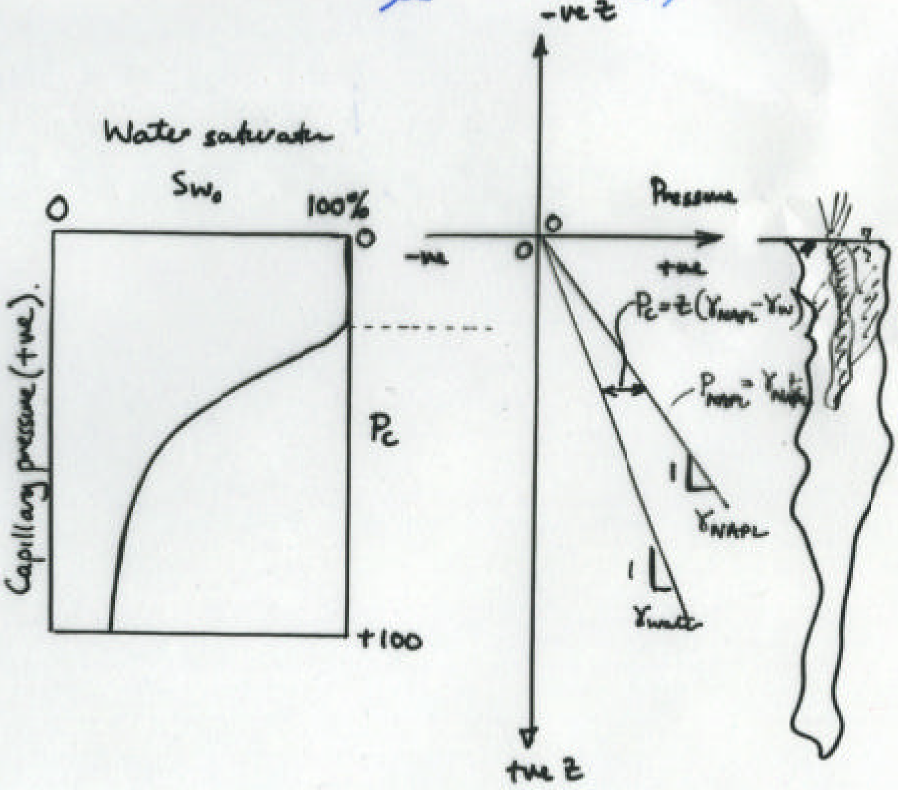
Capillary Fringe ≡ Tension saturated zone

NAPL in Groundwater

$P_c = P_{NAPL} - P_{WATER}$

$$v_d = q = -K(\theta)\frac{dh}{dx} = -k_r K(\theta)\frac{dh}{dx}$$

$$= k_r \frac{k}{\mu}\left(\frac{\partial P}{\partial x} + \rho g \frac{\partial z}{\partial x}\right)$$



4.1 FLOW OF WATER IN THE UNSATURATED ZONE

- Neglect osmotic pressures
  (flow due to concentration gradients)
- Neglect electrochemical processes

$$h = \underset{\frac{P}{\gamma_w}}{\psi(\theta)} + z + \overset{0}{\cancel{\frac{v^2}{2g}}}$$

h = total head

z = elevation head

$\psi(\theta)$ = matric potential
i.e. wetting fluid pressure

θ = moisture content.

$$\psi(\theta) = \frac{P(\theta)}{\gamma_w}$$

Matric pressure, $P(\theta)$ is a unique function of moisture content, θ.

Two popular relations (empirical) for $P(\theta)$-vs-θ
or $P(S_w)$-vs-S_w

1. Brooks and Corey (1966).
2. van Genuchten (1980).

4.1.1. Brooks & Corey (1966)

May define for p_c-vs-Θ or p_c-vs-S_w.

$$\Theta = \Theta_{w_0} + (\Theta_s - \Theta_{w_0})\left(\frac{P}{P_b}\right)^{-\lambda}$$

Θ_{w_0} = irreducible water conte
Θ_s = saturated water conten
P_b = bubbling pressure
P = capillary pressure

$$\frac{\Theta}{\Theta_s} = \frac{\Theta_{w_0}}{\Theta_s} + \left(\frac{\Theta_s}{\Theta_s} - \frac{\Theta_{w_0}}{\Theta_s}\right)\left(\frac{P}{P_b}\right)^{-\lambda} \Rightarrow S = S_{w_0} + (1 - S_{w_0})\left(\frac{P}{P_b}\right)$$

$$\underbrace{\frac{(S - S_{w_0})}{(1 - S_{w_0})}}_{S_e} = \left(\frac{P}{P_b}\right)^{-\lambda}$$

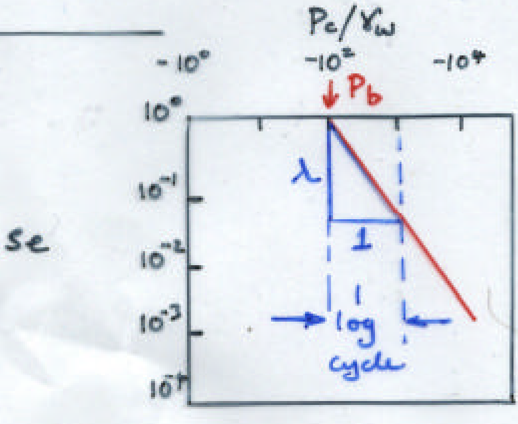
This is an empirical relation: $S_e = (P/P_b)^{-\lambda}$

$$\log S_e = -\lambda \log(P/P_b)$$

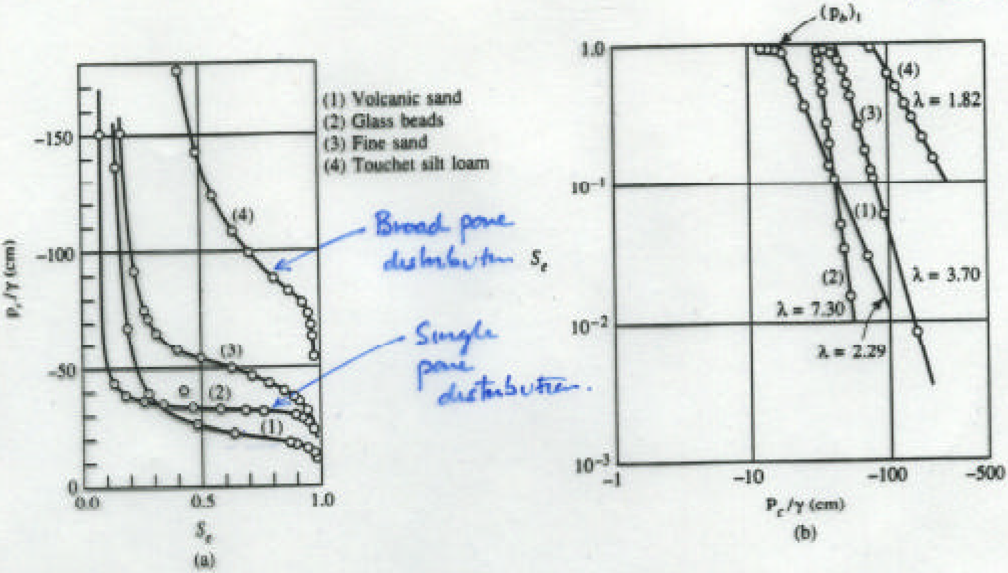
$$\log S_e = -\lambda [\log P - \log P_b]$$

Limiting conditions:

For $P \equiv P_b$ then $\log S_e = 0$; $S_e = 1$



$\lambda\downarrow$ as broader pore throat distribut



Broad pore distribution S_e

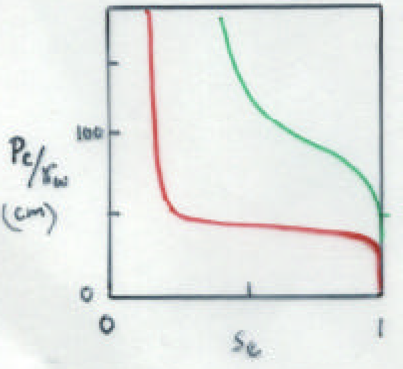
Single pore distribution.

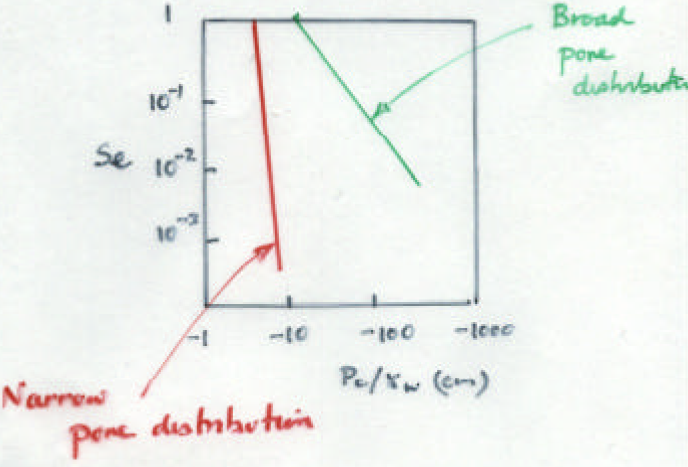
FIGURE 4.5 Capillary pressure head as a function of effective saturation for porous materials with various pore sizes. (a) Plotted on arithmetic paper and (b) plotted on log-log paper. Source: R. H. Brooks and A. T. Corey, *Proceedings, American Society of Civil Engineers, Irrigation and Drainage Division* 92, no. IR2 (1966):61–87.

BEHAVIOR DESCRIBED BY TWO PARAMETERS:

1) P_b - BUBBLING PRESSURE

2) λ - SLOPE OF GRAPH OVER 1 LOG CYCLE





Broad pore distribution

Narrow pore distribution

4.1.2 van GENUCHTEN (1980) Empirical.

M. van Genuchten, Soil Science Society of America, Journal 44 (1980) 892–898.

Moisture Content

$$\theta = \theta_r + \frac{(\theta_s - \theta_r)}{\left[1 + \left(\alpha \frac{P}{\gamma_w}\right)^n\right]^m}$$

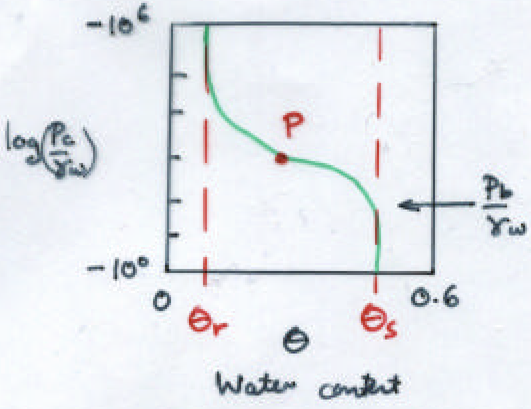
$$\theta_e = \frac{1}{\left[1 + \left(\alpha \frac{P}{\gamma_w}\right)^n\right]^m}$$

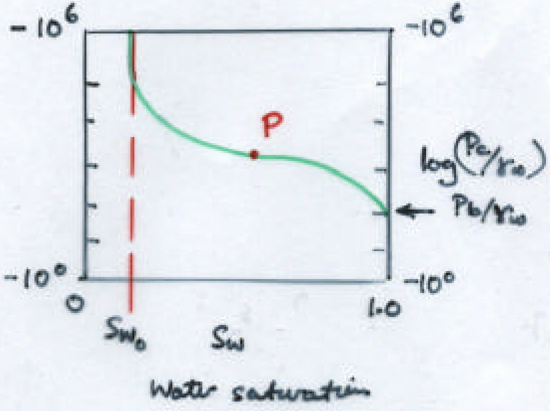
Saturation

$$S = S_{w_0} + \frac{(1 - S_{w_0})}{\left[1 + \left(\alpha \frac{P}{\gamma_w}\right)^n\right]^m}$$

$$Se = \frac{1}{\left[1 + \left(\alpha \frac{P}{\gamma_w}\right)^n\right]^m}$$

Parameters: m, n, α

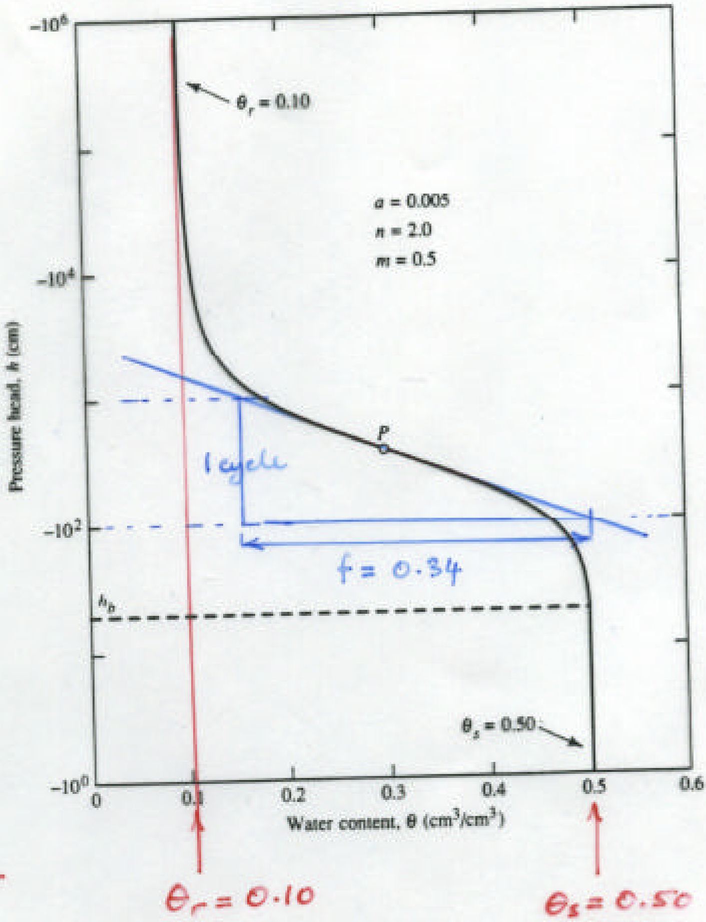




not porosity $\longrightarrow n = 1/(1-m)$

$$\alpha = \frac{\gamma_w}{P_b}\left(2^{1/m} - 1\right)^{(1-m)} \qquad \alpha \simeq \frac{1}{h_b} \simeq \frac{\gamma_w}{P_b}$$

DETERMINING PARAMETERS



MEAN MOISTURE CONTENT

$$\theta_p = \frac{1}{2}(\theta_s + \theta_r)$$

$$= \frac{1}{2}(0.5 + 0.1) = 0.3$$

SLOPE AT θ_p

$$f = 0.34$$

DIMENSIONLESS SLOPE

$$f_p = \frac{f}{\theta_s - \theta_r}$$

$$f_p = \frac{0.34}{0.5 - 0.1} = 0.85$$

$$m = \begin{cases} 1 - \exp(-0.8 f_p) & 0 \leq f_p \leq 1 \\ 1 - \dfrac{0.5755}{f_p} + \dfrac{0.1}{f_p^2} + \dfrac{0.025}{f_p^3} & f_p > 1 \end{cases} \qquad m = 0.5$$

$$n = \frac{1}{1-m} = \frac{1}{1-.5} = 2$$

$$\alpha = \frac{\gamma_w}{P_b}\left(2^{1/m} - 1\right)^{1-m} = \frac{\gamma_w}{P_b}(1.73) \qquad \alpha \simeq \frac{1}{P_b/\gamma_w}$$

4.2 FLOW OF WATER IN THE UNSATURATED ZONE

4.2.1 Hydraulic Conductivity

k = intrinsic permeability

k_r = relative permeability

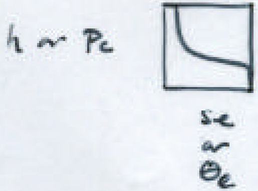
$$K(\theta) = k_r(\theta)\,\frac{k}{\mu_w}\,\rho_w g$$

van Genuchten (1980) Empirically relate k_r to θ

$$K(\theta) = K_{sat}\,Se^{1/2}\left[1-\left(1-Se^{1/m}\right)^m\right]^2 \qquad Se = \frac{(\theta-\theta_r)}{(\theta_s-\theta_r)}$$

$$K(h) = K_{sat}\,\frac{\left\{1-(\alpha h)^{n-1}\left[1+(\alpha h)^n\right]^{-m}\right\}^2}{\left[1+(\alpha h)^n\right]^{m/2}}$$

Note: $h = \frac{P}{\gamma_w}$ and P related to Se or θ



Useful in complex numerical models for unsaturated flow.

VAN GENUCHTEN CURVES (1980)

Ideally, the relative conductivity, moisture content, and water capacity curves are determined directly by performing a series of tests on the soils involved in the study. However, in many cases they can be approximated using a set of measured or approximated constants and a set of empirical relationships. For example, one option for generating the curves is to use the van Genuchten functions (van Genuchten, 1980). The van Genuchten relationships are:

$$\boxed{K_r = \theta_e^{0.5}\left[1-\left(1-\theta_e^{1/\gamma}\right)^{\gamma}\right]^2}$$

and

$$S_e = \theta_e = \left[1+(\alpha h)^{\beta}\right]^{-\gamma} \quad \text{for } h<0$$

$$\theta_e = 1 \quad \text{for } h \geq 0$$

where:

$$\theta_w = \theta_r + \theta_e(\theta_s - \theta_r)$$

$$\gamma = 1-\frac{1}{\beta}$$

and

θ_w = moisture content (dimensionless)

$S_e = \theta_e$ = effective moisture content (dimensionless)

θ_s = saturation moisture content (dimensionless)

θ_r = residual moisture content (dimensionless)

β, γ = soil-specific exponents (dimensionless)

α = soil-specific coefficient

COMPARISON WITH "FETTER" TERMINOLOGY

$$S_e = \theta_e = \frac{(\theta_w - \theta_r)}{(\theta_s - \theta_r)}$$

$$\gamma = m$$

$$\beta = n$$

Free parameters

$$\left.\begin{array}{l}\alpha \text{ represents } 1/(P_b/\gamma_w)\\ \beta \text{ represents slope of } P_c\text{-vs-}S_e\end{array}\right\} S_e = \theta_e$$

Table 5.1 lists a set of saturated and residual moisture contents and the van Genuchten α and β terms for a variety of common soil types. When applying the α term, care should be taken to convert it to the proper units.

Table 5.1
Representative Soil Parameters

Soil Type	Saturated Moisture Content, θ_s	Residual Moisture Content, θ_r	α [cm^{-1}]	β (n)
Clay**	0.38	0.068	0.008	1.09
Clay Loam	0.41	0.095	0.019	1.31
Loam	0.43	0.078	0.036	1.56
Loam Sand	0.41	0.057	0.124	2.28
Silt	0.46	0.034	0.106	1.37
Silt Loam	0.45	0.067	0.020	1.41
Silty Clay	0.36	0.070	0.005	1.09
Silty Clay Loam	0.43	0.089	0.010	1.23
Sand	0.43	0.045	0.145	2.68
Sandy Clay	0.38	0.100	0.027	1.23
Sandy Clay Loam	0.39	0.100	0.059	1.48
Sandy Loam	0.41	0.065	0.075	1.89

** Agricultural soil, less than 60% clay
Source: Carsel and Parrish (1988)

3

Contaminant Hydrology

[3:1] Contaminant Transport - Mechanisms

Recap

Transport Mechanisms

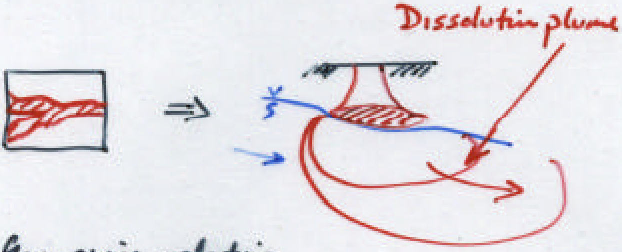
- Diffusion/Dispersion
- Advection

Dispersion

- Mechanical dispersion
- Hydrodynamic dispersion

5. MASS TRANSPORT IN SATURATED MEDIA

Context:



1. Immiscible flow gives relative location and saturation.

If truly immiscible → no problem.

But → • Slightly soluble
• Hazardous @ less than solubility

Mass transport accommodates:

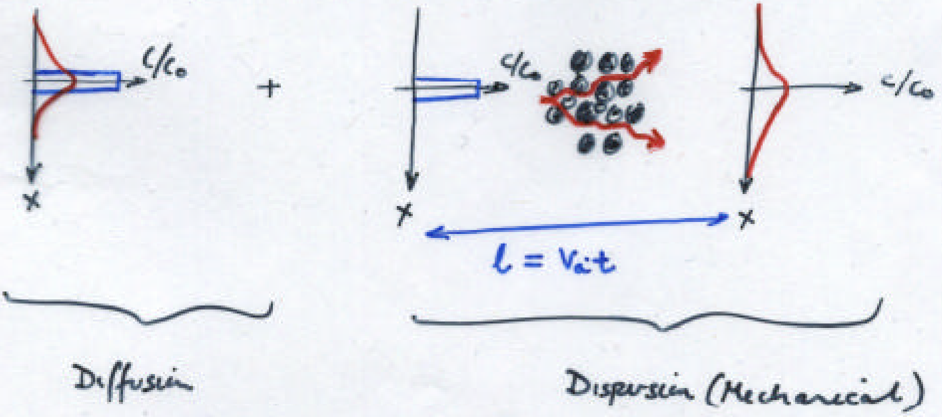
a) Species carried as a dissolved aqueous plume

b) Same density as water (ppm or ppb)

sometimes density important — salt concentration

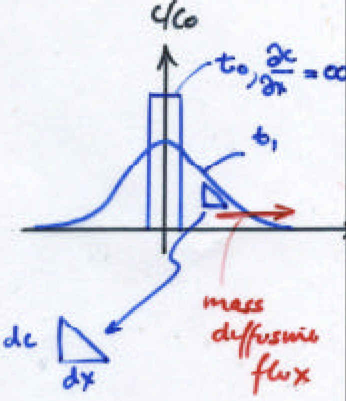
Transport Mechanisms

1. Advection; $v_a = l/t$ $\quad l = v_a t$
2. Diffusion + Mechanical dispersion = Hydrodynamic dispersion



5.1 DIFFUSION

- Driven by concentration gradient
- Process of mollecular diffusion (Brownian motion)
- Characteristic for entropy (disorder) to increase
- Stagnant fluid



Fick's first law: $F = -D_d \frac{dc}{dx}$

F = mass of solute per unit area per unit time (M/L^2T)

D_d = diffusion coefficient (L^2/T)

$\left(D_d \approx 10^{-9}\ m^2/s \text{ (range)} \right)$

$\frac{dc}{dx}$ = concentration gradient $((M/L^3)/L)$

Time dependent concentration

=1 since not porous medium

$$n \frac{\partial c}{\partial t} = -\left(\frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z} \right)$$

Substituting Fick's first law:

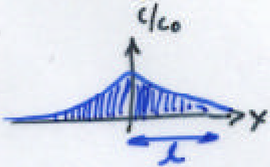
$$\frac{\partial c}{\partial t} = D_d \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right)$$

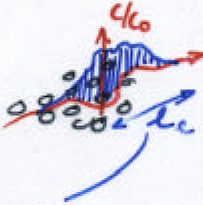
One dimensional equation

$$\frac{\partial c}{\partial t} = D_d \frac{\partial^2 c}{\partial x^2}$$

D_d is the "free" diffusion coefficient (i.e. in a beaker)

In porous medium the "effective" diffusion coefficient is used $D_d \rightarrow D^*$ due to the tortuous flow path



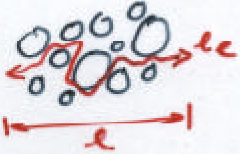


Effective length due to tortuous flow path

$$D^* = \omega D_d$$

ω is related to tortuosity, $T = l_e/l$

$T \geq 1$



Laboratory studies $0.01 < \omega \leq 0.5$

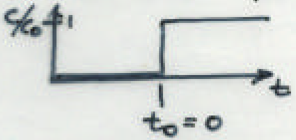
but lab studies not very useful.

SOLUTION OF DIFFUSION EQUATION

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

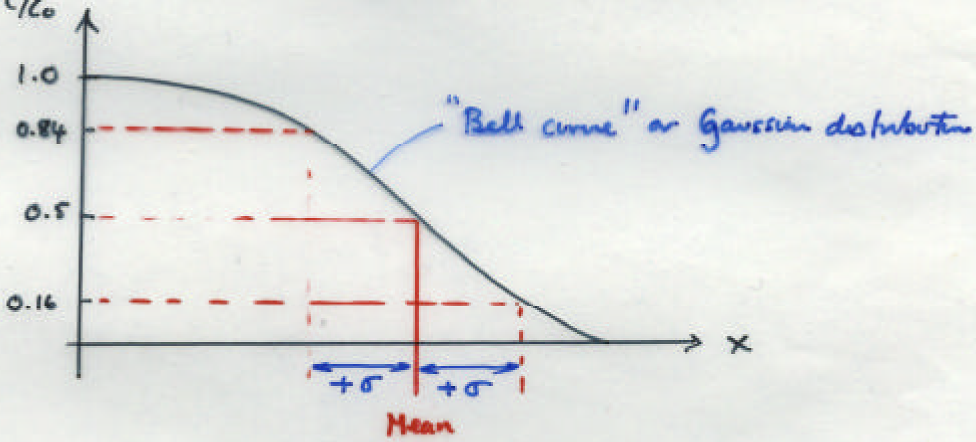
$c = 0$ $\quad 0 > t$ $\quad$ initial condition (no solute)

$c = C_0$ $\quad x = 0 \quad t \geq 0$ $\quad$ step input



Solution:
$$\frac{c}{C_0}(x,t) = \mathrm{erfc}\left(\frac{x}{2\sqrt{D^* t}}\right) = \frac{2}{\sqrt{\pi}} \int_x^{\infty} e^{-u^2}\, du$$

$$\mathrm{erfc}(x) = 1 - \mathrm{erf}(x)$$



5.2 ADVECTION (Convection – movement by "bulk" motion of the fluid (water))

$$V_x^a = -\frac{K_x}{n}\frac{dh}{dx} \quad (1)$$

V_a = average linear advective velocity

n = "effective" porosity

no-dead-end pores.

Advective flux; F_x.

$$F_x = V_x^a n \, c \quad (2)$$

volume of water flowing at concentration, c.

Conservation equation:

$$n\frac{\partial c}{\partial t} = -\left(\frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z}\right) \quad (3)$$

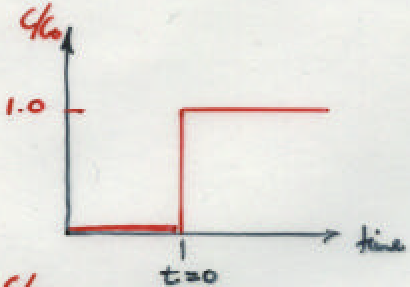
Substitute V_x^a from (2) and similar for V_y^a; V_z^a into (3)

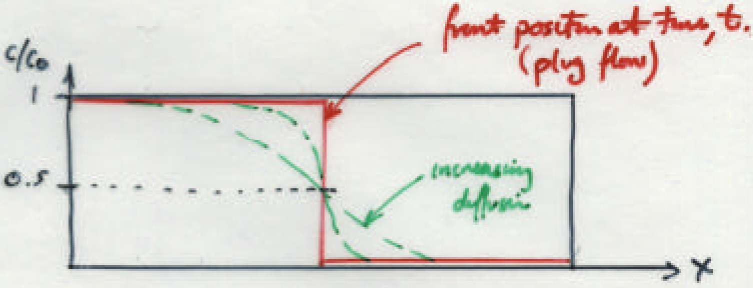
$$n\frac{\partial c}{\partial t} = -\left(\underbrace{V_x^a n}_{V_x^a n = V_d}\frac{\partial c}{\partial x} + V_y^a n\frac{\partial c}{\partial y} + V_z^a n\frac{\partial c}{\partial z}\right) \quad (4)$$

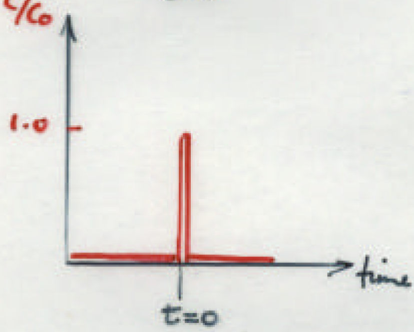
Remove, n in (4)

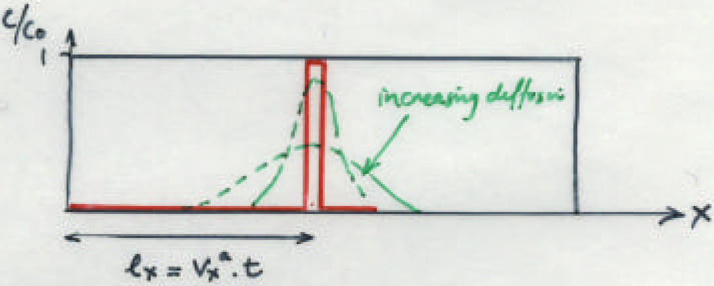
$$\boxed{\frac{\partial c}{\partial t} = -\left(V_x^a\frac{\partial c}{\partial x} + V_y^a\frac{\partial c}{\partial y} + V_z^a\frac{\partial c}{\partial z}\right)} \quad ⑤$$

What does this mean, physically?







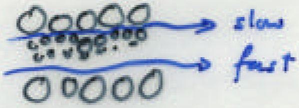


Boundary conditions

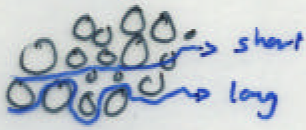
5.3 MECHANICAL DISPERSION

CAUSES

1. Pore size

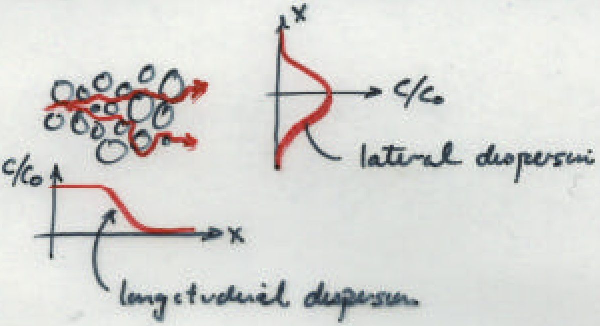


2. Path length



3. Taylor dispersion

Average behavior ⟶ dispersion coefficients, α



Coefficient of longitudinal dispersion = α_L (L

Coefficient of transverse (lateral) dispersion = α_T (L

Units of length, L.

Pre-multiplied by advective velocity to give a dispersion coefficient as $D = \alpha\, v_i$

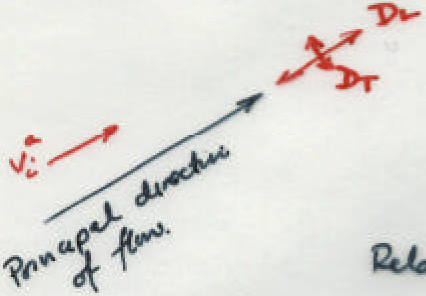
$$L\; L/T \doteq L^2/T$$

$$D_L = \alpha_L v_i$$

$$D_T = \alpha_T v_i$$

5.4 HYDRODYNAMIC DISPERSION

Hydrodynamic dispersion = Diffusion + Mechanical dispersion $(L^2/T$



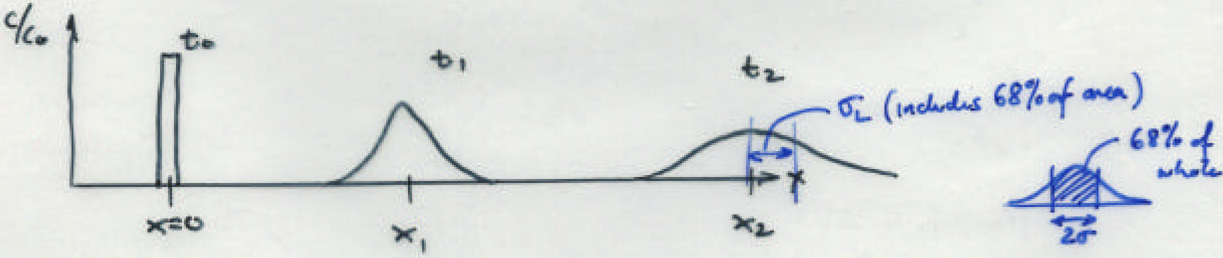
$$\boxed{\begin{aligned} D_L &= \alpha_L v_i^a + D^* \\ D_T &= \alpha_T v_i^a + D^* \end{aligned}}$$

Relative dominance of diffusion depends on:

1) Clays, $v \rightarrow 0$ ∴ diffusion dominant
(also retardation)

2) Sands, gravels, fractured rock. $v \rightarrow$ high
∴ mechanical dispersion dominan

Measure in situ for best results.



$$D_L = \frac{\sigma_L^2}{2t} \quad ; \quad D_T = \frac{\sigma_T^2}{2t}$$

σ = standard deviation

σ^2 = variance

$D_L = \alpha_L V + D_d^*$

$D_T = \alpha_T V + D_d^*$

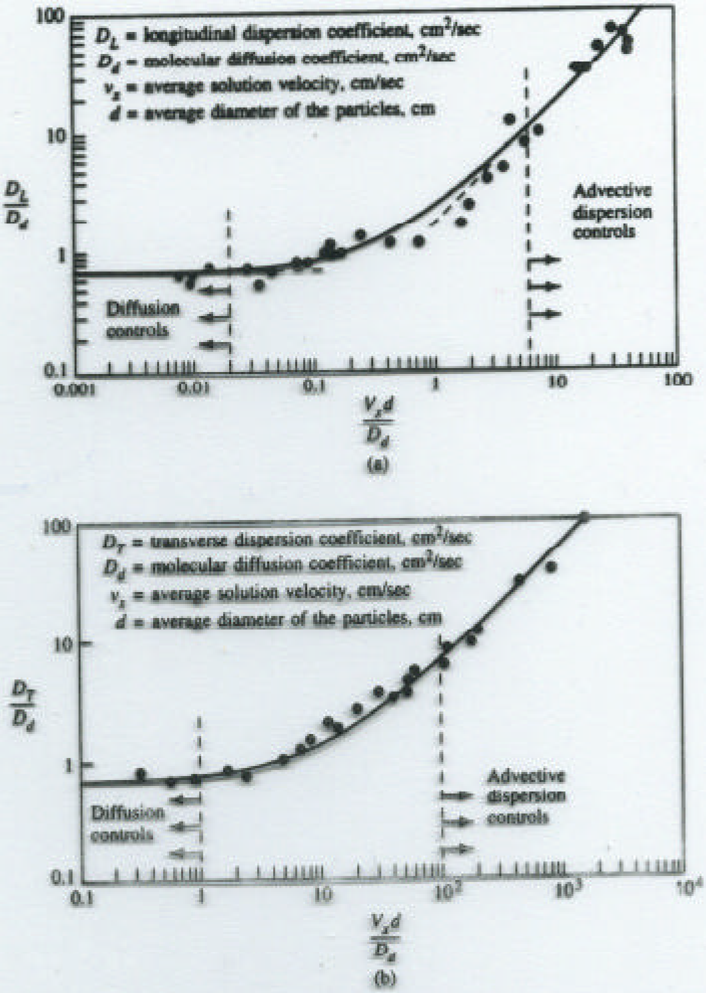


FIGURE 2.7 Graph of dimensionless dispersion coefficients versus Peclet number, $P = v_x d/D_d$. (a) D_L/D_d versus P and (b) D_T/D_d versus P. Source: T. K. Perkins and O. C. Johnson, *Society of Petroleum Engineers Journal*, 3 (1963):70–84. Copyright 1963, Society of Petroleum Engineers.

$P_E = \frac{V^* L}{D_L}$

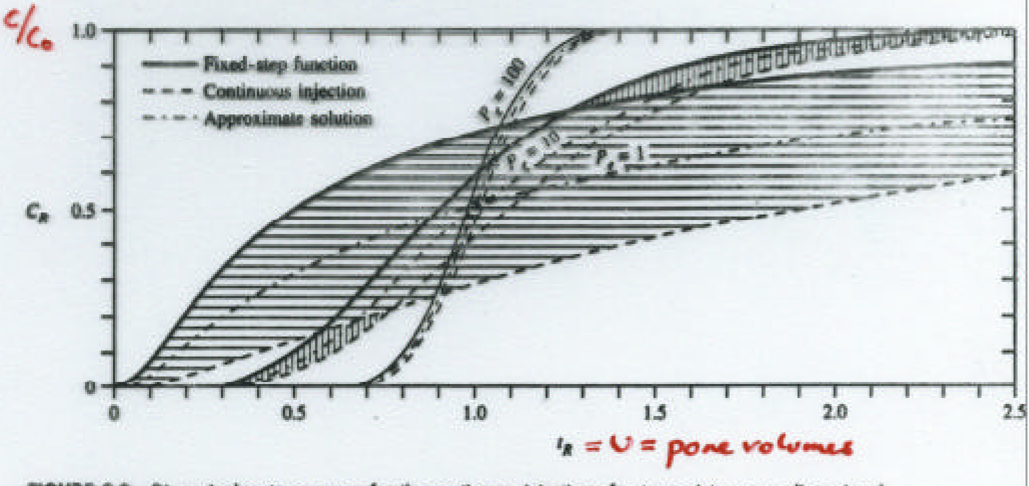


FIGURE 2.9 Dimensionless-type curves for the continuous injection of a tracer into a one-dimensional flow field. Source: J. P. Sauty, *Water Resources Research* 16, no. 1 (1980):145–58. Copyright by the American Geophysical Union.

[3:2] Contaminant Transport - Quantification

Recap

Advection-Dispersion Equation

- 1-D Flows
- 3-D Flows

5.5 ADVECTION-DISPERSION EQUATION

Summing the diffusive and advective components:

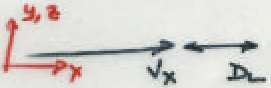
$$n\frac{\partial c}{\partial t} = n\left\{\frac{\partial}{\partial x}D_x\frac{\partial c}{\partial x} + \frac{\partial}{\partial y}D_y\frac{\partial c}{\partial y} + \frac{\partial}{\partial z}D_z\frac{\partial c}{\partial z}\right\}$$

$$-\left\{\frac{\partial}{\partial x}(v_x^d c) + \frac{\partial}{\partial y}(v_y^d c) + \frac{\partial}{\partial z}(v_z^d c)\right\}$$

Reduces to:

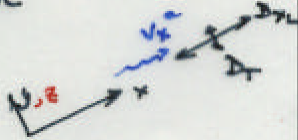
1-D case:

$$D_L\frac{\partial^2 c}{\partial x^2} - \overset{v_x^a}{\boxed{\frac{v_x^d}{n}}}\frac{\partial c}{\partial x} = \frac{\partial c}{\partial t}$$



2-D case:

$$D_L\frac{\partial^2 c}{\partial x^2} + D_T\frac{\partial^2 c}{\partial y^2} - \overset{v_x^a}{\boxed{\frac{v_x^d}{n}}}\frac{\partial c}{\partial x} = \frac{\partial c}{\partial t}$$



Usual assumptions:

- Homogeneous medium
- Constant value of D_L, D_T

} analytical solutions

- Heterogeneous
- Velocity dependent D_L, D_T

} numerical solutions.

5.6 ANALYTICAL SOLUTIONS.

Why? - Determine off-site migration
- Approximate geometries

What parameters are important?

1. Diffusion } hydrodynamic dispersion
2. Mechanical dispersion } $D_L = \alpha_L v^a + D^*$
3. Groundwater velocity field, v^a

Solutions:

Fetter sections 2.8 pp 56-64.

Analytical Solutions

1. Simplify geometry 1-D etc
2. Simplify heterogeneity (assume an equivalent magnitude of dispersion).
3. Simple solutions (but accurate).

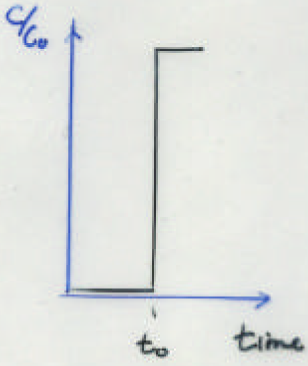
Numerical Solutions

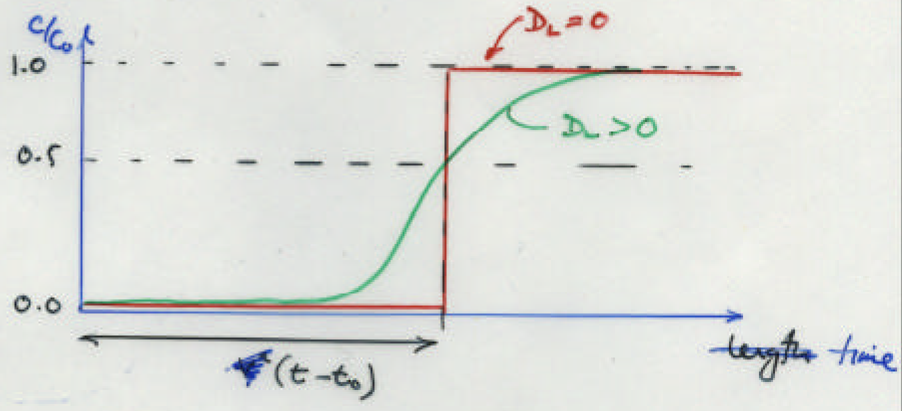
1. Enable complex 'real' geometries
2. Complex heterogeneity incorporated
3. Computer solutions – may include "numerical" dispersion.

Philosophical Trade:

- Data accuracy / reliability
- Sensitivity studies.

LIMITS OF APPLICABILITY OF APPROXIMATIONS





This view of the RTD curve is true only for large Peclet Nos (Pe)

$$Pe \geq 10$$

$$Pe = \frac{V^a L}{D_L} \longleftarrow D_L = \cancelto{0}{D^*} + \alpha_L V^a$$

$$\alpha_L \simeq \frac{1}{10} L$$

$$\therefore\ D_L \cong \frac{L V^a}{10}$$

Resubstituting then

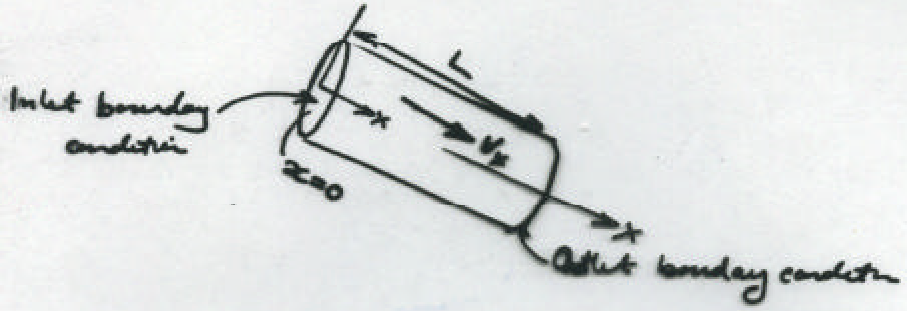
$$Pe = \frac{V^a L}{L V^a} \cdot 10 = 10$$

∴ ok to use approximations.

ANALYTICAL SOLUTIONS (1-D)

or Temperature, T.

Equation :
$$D\frac{\partial^2 c}{\partial x^2} - v_x\frac{\partial c}{\partial x} = \frac{\partial c}{\partial t}$$



Boundary Condition Types:

First type: Fixed concentration: $C = C_0$

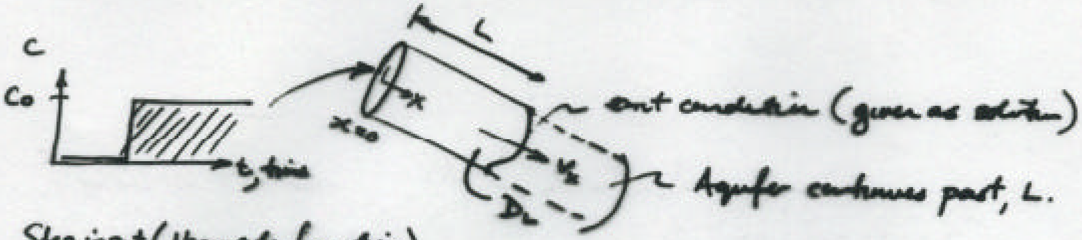
Second type: Fixed gradient $\left.\frac{\partial c}{\partial x}\right|_{x=?}$ = constant

includes zero flux $\partial c/\partial x = 0$
(accumulating mass).

Third type: Variable flux $-D\frac{\partial c}{\partial x} + v_x c = v_x c(t)$

i.e. input flux of constant
concentration as VC_0 = prescribed m

ONE-DIMENSIONAL STEP CHANGE IN CONCENTRATION (Ogata & Banks, 1961)



Step input (Heaviside function)

Initial conditions: $c(x,0) = 0 \qquad x \geqslant 0$

Boundary conditions: $c(0,t) = C_0 \qquad t \geqslant 0^+$

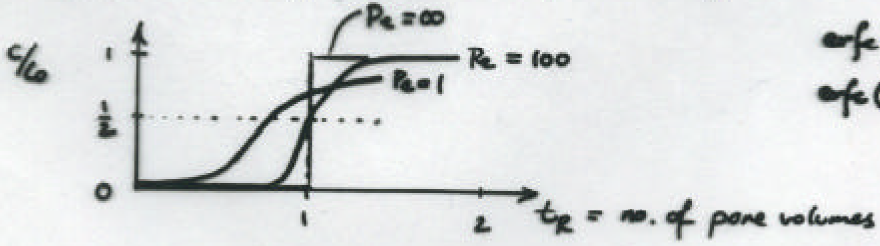
$c(\infty,t) = 0 \qquad t \geqslant 0^+$

$$c = \tfrac{1}{2}C_0\left[\operatorname{erfc}\left(\frac{L-V_x t}{2\sqrt{D_L t}}\right) + \exp\left(\frac{V_x L}{D_L}\right)\operatorname{erfc}\left(\frac{L+V_x t}{2\sqrt{D_L t}}\right)\right]$$

Non-dimensionalize: $P_e = \dfrac{V_x L}{D_L}$; $t_R = \dfrac{V_x t}{L} \equiv$ 'pore' volumes. as $V_x =$

$$\frac{C}{C_0} = \frac{1}{2}\left[\operatorname{erfc}\left[\left(\frac{P_e}{4t_R}\right)^{1/2}(1-t_R)\right] + \exp(P_e)\operatorname{erfc}\left[\left(\frac{P_e}{4t_R}\right)^{1/2}(1+t_R)\right]\right]$$

Observe change in C/C_0 at location, L, downstream (with time).

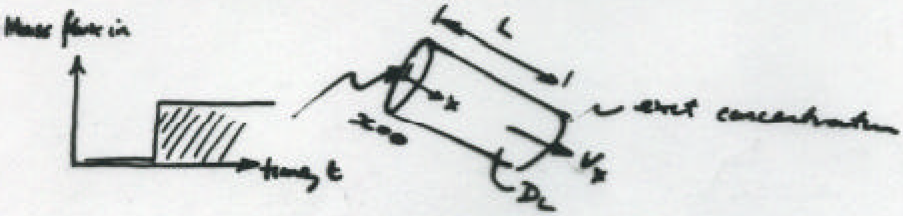


$\operatorname{erfc}(0) = 1$

$\operatorname{erfc}(\infty) = 0$

ONE - DIMENSIONAL CONTINUOUS INJECTION AT CONSTANT CONCENTRATION, C_0.

(Sauty, 1980)



Initial conditions: $C(x,0) = 0 \qquad -\infty < x < +\infty$

Boundary conditions: $\int_{-\infty}^{+\infty} n_e C(x,t)\,dx = C_0 n_e V_x t \qquad t > 0$

Dispersion occurs both downstream and upstream

$C(\infty,t) = 0 \qquad t \geq 0$

$$C = \tfrac{1}{2} C_0 \left[\operatorname{erfc}\left(\frac{L - V_x t}{2\sqrt{D_L t}}\right) - \exp\left(\frac{V_x L}{D_L}\right) \operatorname{erfc}\left(\frac{L + V_x t}{2\sqrt{D_L t}}\right)\right]$$

Non-dimensional:

Same as step injection but -ve.

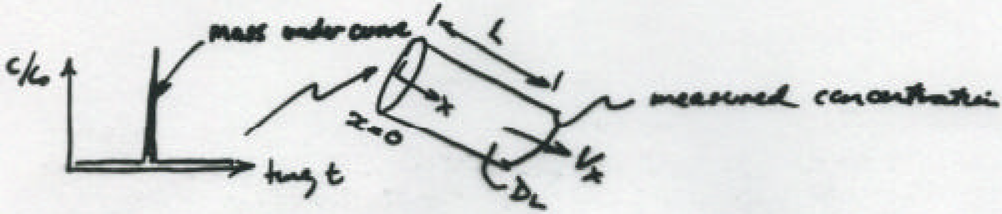
$$\frac{C}{C_0} = \frac{1}{2}\left[\operatorname{erfc}\left\{\left(\frac{P_e}{4t_R}\right)^{1/2}(1-t_R)\right\} - \exp(P_e)\operatorname{erfc}\left\{\left(\frac{P_e}{4t_R}\right)^{1/2}(1+t_R)\right\}\right]$$

For $P_e \to \infty \qquad \dfrac{C}{C_0} \simeq \dfrac{1}{2}\operatorname{erfc}\left\{\left(\dfrac{P_e}{4t_R}\right)^{1/2}(1-t_R)\right\}$

Solution identical for both $\left\{ \begin{array}{l} C_0 = \text{constant} \\ VC_0 = \text{constant} \end{array} \right.$

i.e. @ $P_e \to \infty$ Dispersive effects → 0.

ONE – DIMENSIONAL – SLUG INJECTION (Sauty, 1980)



Mass slug injected: At some later time, a maximum concentration, C_{max}, results at time, t_{max}.

$$C_R = \frac{E}{(t_R)^{1/2}} \exp\left\{-\frac{P_e}{4t_R}(1-t_R)^2\right\}$$

$$E = (t_{R_{max}})^{1/2} \cdot \exp\left\{\frac{P_e}{4t_{R_{max}}}(1-t_{R_{max}})^2\right\}$$

$t_{R_{max}}$ = time of peak concentration

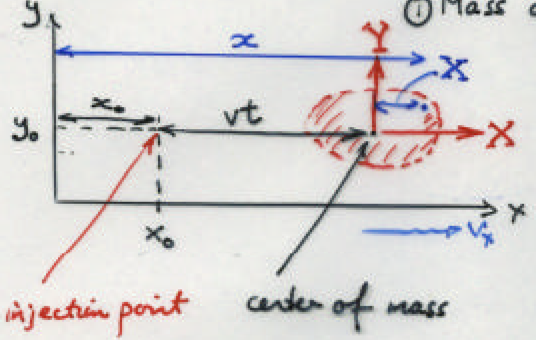
$= (1 + P_e^{-2})^{1/2} - P_e^{-1}$

$C_R = C/C_{max}$

5.6.6 3-D Flow field – Slug Injection

(C₀ × volume)

$$C(x,y,z,t) = \frac{M}{8(\pi t)^{3/2}\sqrt{D_x D_y D_z}} \exp\left\{ -\frac{(x-(x_0+Vt))^2}{4D_x t} - \frac{(y-y_0)^2}{4D_y t} - \frac{(z-z_0)^2}{4D_z t} \right.$$



① Mass of injection at location x_0, y_0, z_0

② Moves downstream @ velocity V

③ At time, t, center of mass at $x = x_$

Note coordinates: $x_0 + vt + X = x$

or $X = x - (x_0 +$

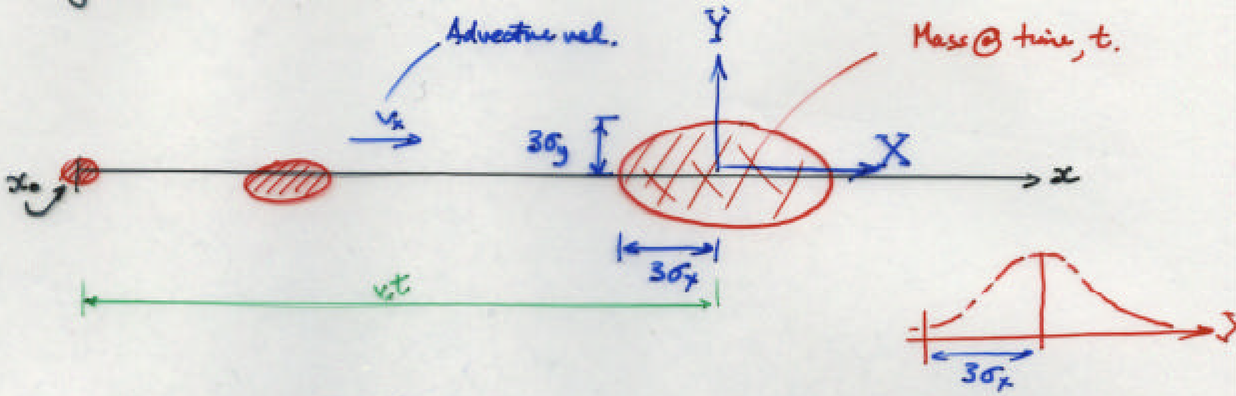
∴ resubstitute into (1)

$$c = \frac{M}{8(\pi t)^{3/2}\sqrt{D_x D_y D_z}} \exp\left\{ -\frac{X^2}{4D_x t} - \frac{Y^2}{4D_y t} - \frac{Z^2}{4D_z t} \right\}$$

Max concentration; set $X = Y = Z = 0$

$$C_{max} = \frac{M}{8(\pi t)^{3/2}\sqrt{D_x D_y D_z}}$$

Note downgradient form:



Zone consisting of 99.7% of Mass

contained in the 3-D ellipsoid of

dimensions:

$$3\sigma_x = 3\sqrt{2D_x t} = 3(2D_x t)^{1/2} \text{ etc.}$$

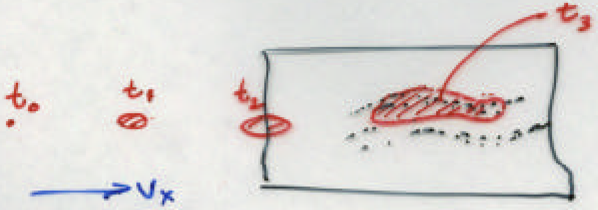
$$3\sigma_y = 3\sqrt{2D_y t}$$

$$3\sigma_z = 3\sqrt{2D_z t}$$

∴ ① Measure ellipsoid in field

and ② evaluate D_x etc.

Preferable method since includes <u>large</u> scale heterogeneity



[3:3] Contaminant Transport - Measurement

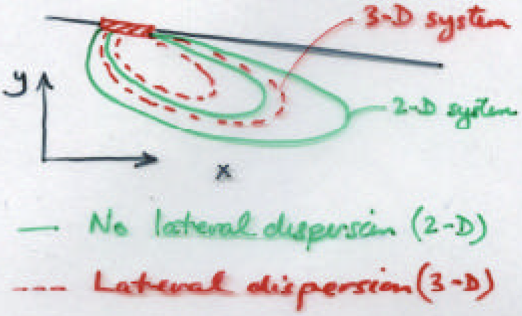
Recap

Evaluating dispersivity

- Laboratory approaches
- Well testing
- Natural gradient experiments

5.7 EVALUATING DISPERSIVITY

Note: transverse dispersion will affect the resultig form of the plume due to lateral attenuation

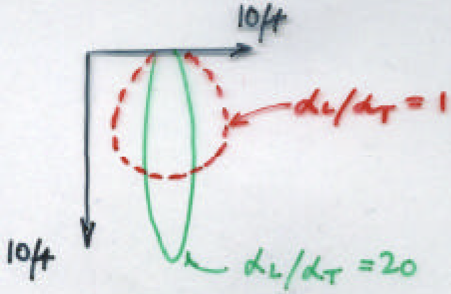


This is important if:

3-D systems are represented as 2-D

2-D systems are represented as 1-D

Have to incorporate these effects when they are important.



- Large ratio gives greater linear propagation length
- Small ratio gives lateral attenuat

Methods:

- Laboratory
- Field
  - Induced gradient
  - Natural gradient - { Contaminated sites. Tests will remobilize contaminants.

GEOMETRY

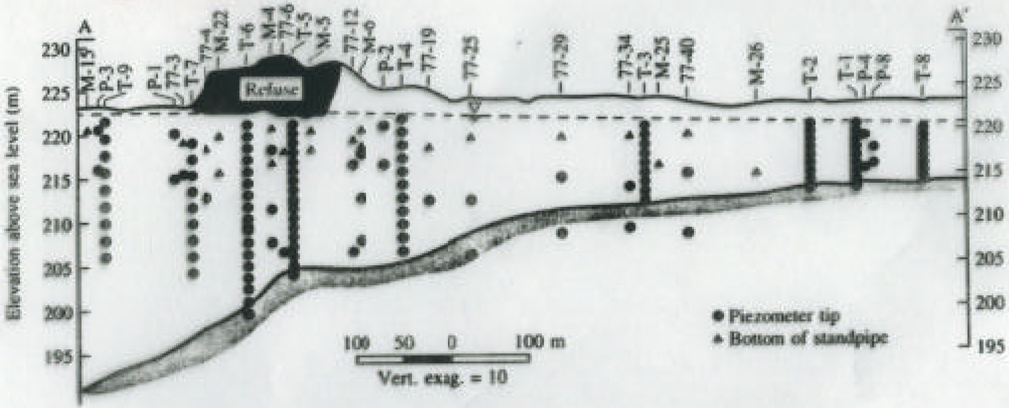


FIGURE 2.33 Cross section of aquifer at the Borden landfill showing the location of multilevel monitoring devices. *Source:* E. O. Frind and G. E. Hokkanen, *Water Resources Research* 23, no. 5 (1987):918–30. Copyright by the American Geophysical Union.

CHLORIDE PLUME

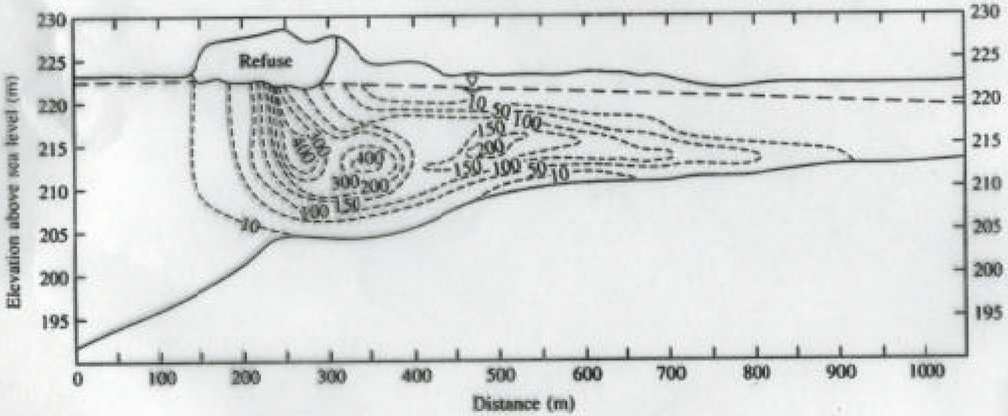
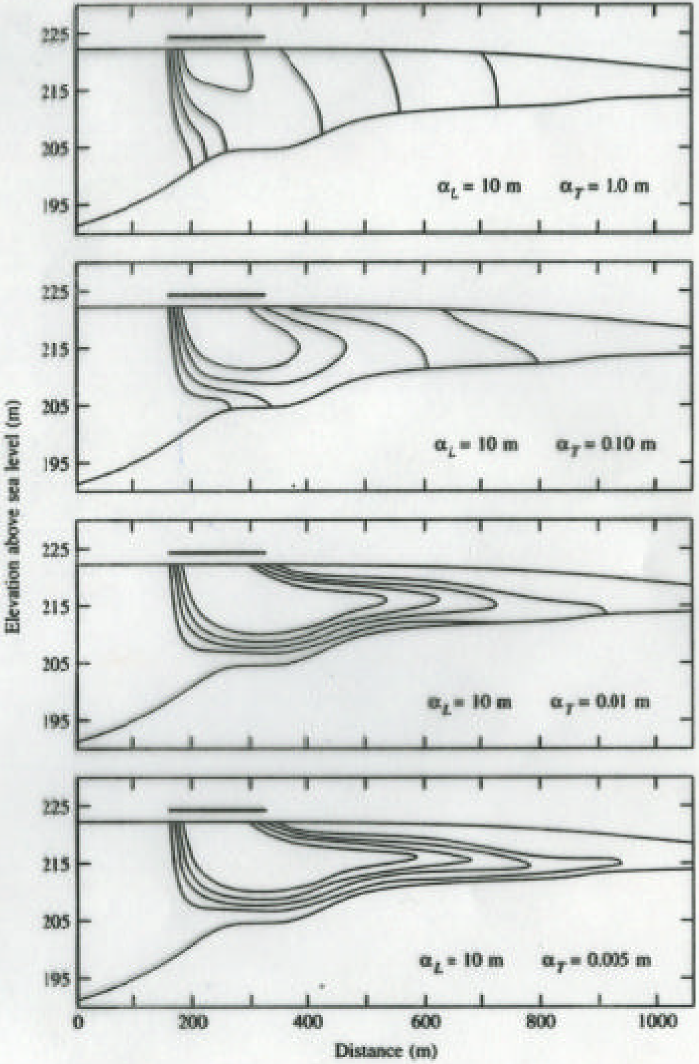


FIGURE 2.34 Chloride plume along the Borden landfill cross section in 1979. Values are in milligrams per liter. *Source:* E. O. Frind and G. E. Hokkanen, *Water Resources Research* 23, no. 5 (1987):918–30. Copyright by the American Geophysical Union.

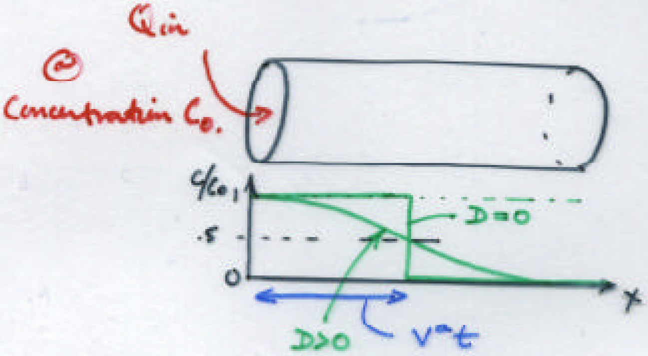
CONSTANT α_L ; VARIABLE α_T

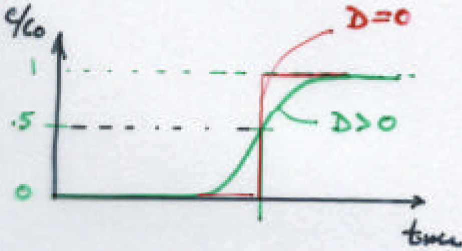


Reducing α_T enables longer propagation since less lateral loss ⊥ to profile

5.7.1 Laboratory Tests:

- Not very useful since scale dependent!
- General method
  - Inject solute of known concentration and measure outlet concentration w/ time.
  - Fit to curve.



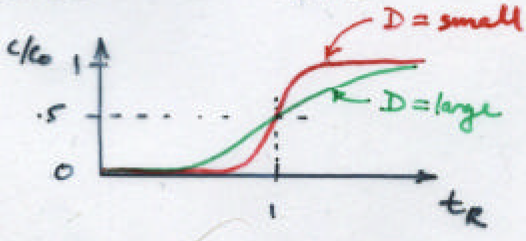


Define flow rate relative to number of pore volumes -

- when ×1 pore volume flushed through, the flow of the contaminant should also break through at $c = \frac{1}{2} c_0$

Define No of pore volumes of sample, as U

$$u = \frac{\text{total discharge}}{\text{pore volume}} = \frac{\overset{\text{advective vel}}{v_x^a} A n t}{A L n} = \frac{v_x^a t}{L} = t_R$$

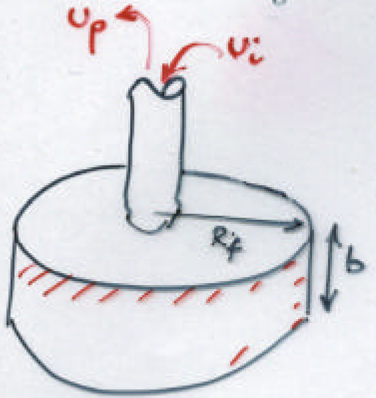


$$\frac{C}{C_0} \cong \frac{1}{2} \operatorname{erfc}\left[\frac{1-U}{2(U D_L / v_x L)^{1/2}}\right]$$

$$\operatorname{erfc}(0) = 1$$

5.7.2 Single Well Tracer Test

- Higher than natural gradient
- Incorporates scale effects
- Needs only single wellbore — Injection then recovery of fluid
- Neglects diffusion — incorporates dispersion



U_p = cumulative volume recovered at initial concentration, C_0.

U_i = total volume injected

R_f = average frontal position of injected water at end of injection

n = porosity

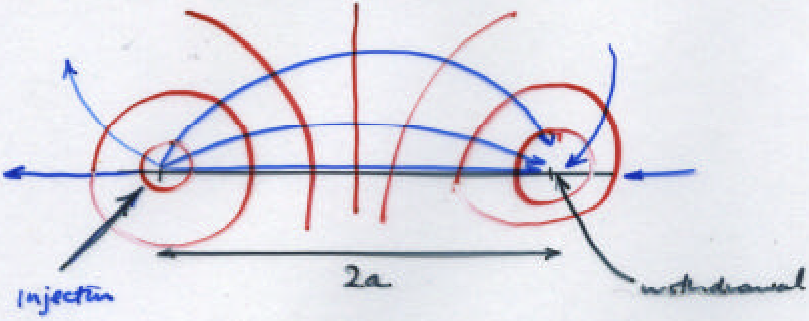
b = aquifer thickness or wellbore zone.

$$\left.\begin{aligned} \text{Volume in} &= Qt \\ \text{Volume occupied} &= \pi R_f^2 b n \end{aligned}\right\} \quad Qt = \pi R_f^2 b n$$

$$R_f^2 = \frac{Qt}{\pi b n}$$

$$\frac{c}{c_0} = \frac{1}{2}\,\mathrm{erfc}\left\{\frac{(U_p - U_i) - 1}{\left\{\frac{16}{3}(\alpha_L/R_f)\left[2 - (1 - U_p/U_i)\right]^{1/2}\left[1 - (U_p/U_i)\right]\right\}^{1/2}}\right\}$$

5.7.3 Twin Well Tracer Test



1. Inject tracer
2. Record outlet at withdrawal well.

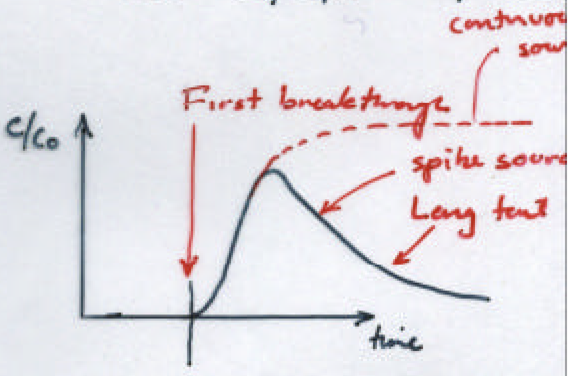
Transit time for plug flow: along a given streamline

$$t_\theta = \frac{4\pi a^2 b}{q \sin^2\theta}\left(1 - \frac{\theta}{\tan\theta}\right)$$

q = injection rate
θ = streamtube "angle"
b = aquifer thickness
a = half separation of wells

$$L = \frac{2a\theta}{\sin\theta}$$

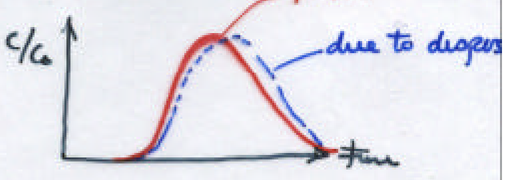
Fit measured curve to theoretical curve



$$t_\theta = \frac{4\pi a^2 b}{q \sin^2\theta}\left(1 - \frac{\theta}{\tan\theta}\right)\bigg|_{\theta=0}$$

Problems:

- Test induces dispersion due to nature of test, alone.
  ∴ obscures actual dispersion due to the porous medium.
- Natural gradient tests preferred
- Avoids this "geometric" dispersion due to severe flow-field



NATURAL GRADIENT

Evaluation of advective vel, $V_x = l/t$

t(d)	l(m)	V(m/d)
85	9.5	0.11
462	38	0.08
647	61	0.09

$\bar{V} \simeq 0.09$ m/d

Evaluation of Dispersivity, D_x

$3\sigma_x = 3\sqrt{2D_x t}$ $D_x = (3\sigma_x)^2/18t$

Half length ($3\sigma_x$)	Time (t)	Dispersivity D_x
5m	85	.016 m²/d
14m	462	.023
15m	647	.019

$\bar{D}_x = .019$

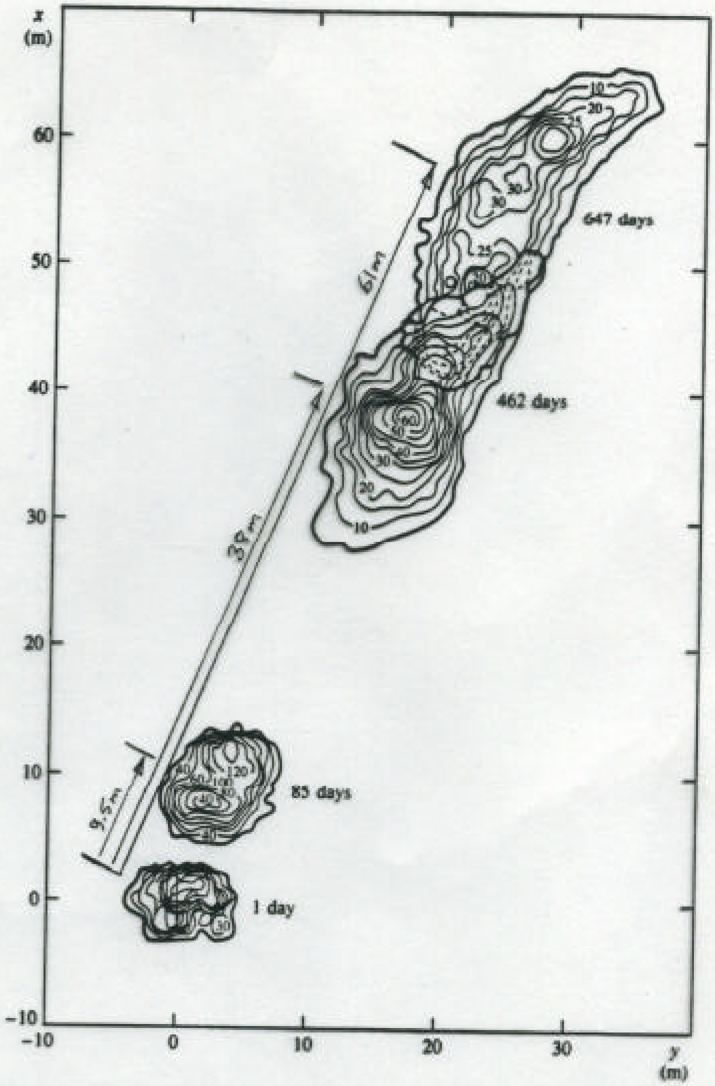


FIGURE 2.13 Vertically averaged chloride concentration at 1 day, 85 days, 462 days, and 647 days after the injection of a slug into a shallow aquifer. *Source:* D. M. Mackay et al. *Water Resources Research* 22, no. 13 (1986):2017–29. Copyright by the American Geophysical Union.

Transverse Dispersivity, D_y

Half length ($3\sigma_y$)	Time (t)	Dispersivity D_y
4.5m	85	.013 m²/d
6.0	462	.004
6.5	647	.004

$\bar{D}_y \simeq .007$ m²/d

Compare with estimate: $\alpha_L = \frac{1}{10}x$

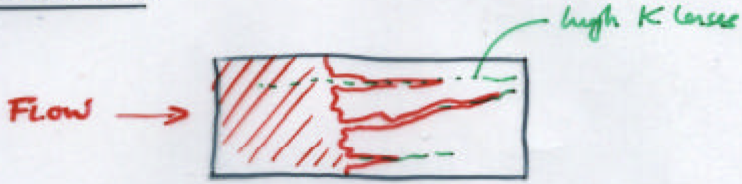
x = scale of measurement $\simeq$ 61m

$D_L = \cancel{D^*}^{\to 0} + \alpha_L V_x = (6.1\,m)(0.09\,m/d)$

$D_L = 0.55$ m²/d

not very close to 0.019 m²/d.

5.7.4 SCALE EFFECTS OF DISPERSION



Macrodispersion – variability in conductivity field → variability in velocity field.

– Gives enhanced dispersion – at all scales.

Hence scale effect:

Larger scale → larger variation in conductivity distribution
→ increasing dispersivity

Some controversy over upper limit (of scale)
scale of 10,000 m ?
new sources of heterogeneity – regional geology.

Stochastic methods may be applied
- treat heterogeneity as the defining parameter
- define heterogeneity → define dispersion characteristics

Approx magnitudes:

$$\alpha_L = \frac{1}{10} x$$

$$\alpha_T = \frac{1}{10}\alpha_L \text{ to } \frac{1}{3}\alpha_L$$

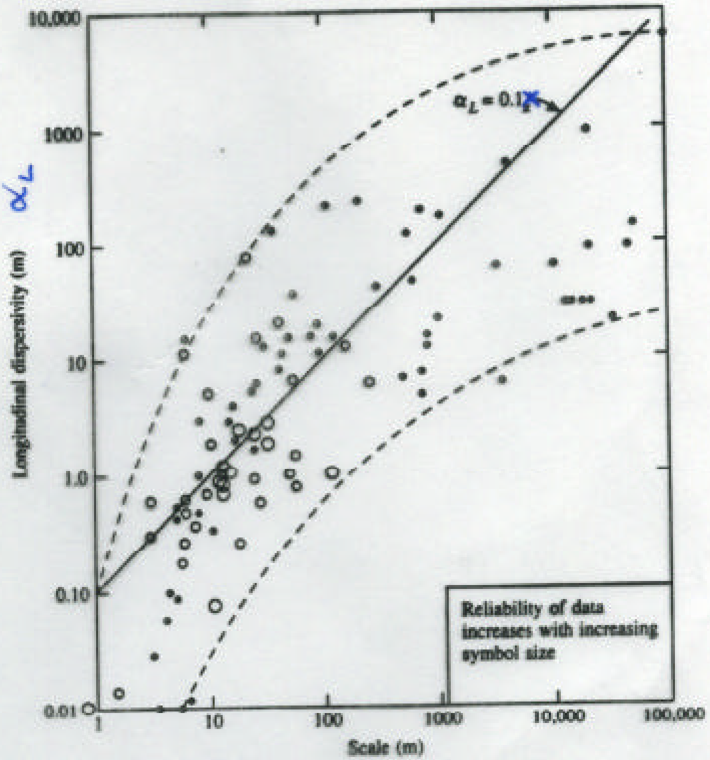


FIGURE 2.18 Field-measured values of longitudinal dispersivity as a function of the scale of measurement. The largest circles represent the most reliable data. Source: L. W. Gelhar, *Water Resources Research* 22, no. 9 (1986):1355–1455. Copyright by the American Geophysical Union.

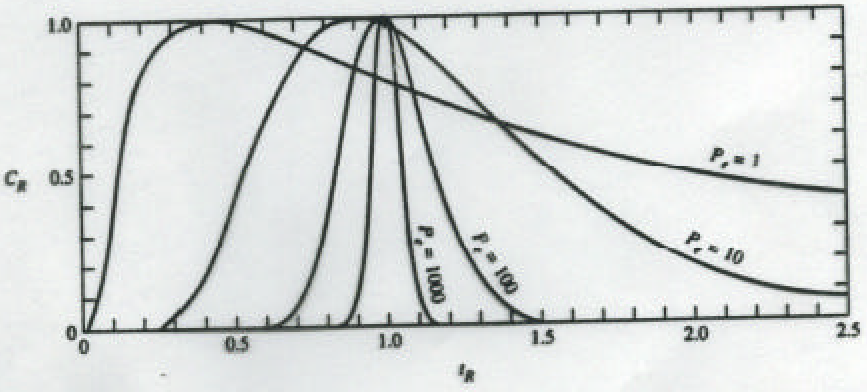


FIGURE 2.10 Dimensionless-type curve for the injection of a slug of a tracer into a one-dimensional flow field. Source: J. P. Sauty, *Water Resources Research* 16, no. 1 (1980):145–58. Copyright by the American Geophysical Union.

4

Retardation & Attenuation

[4:1] Retardation & Attenuation

- Recap
- Retardation and attenuation
  - Sorption and isotherms
  - Measurements
  - Sorption-like behavior – fractured rock
- Predictions of sorption

6. RETARDATION & ATTENUATION

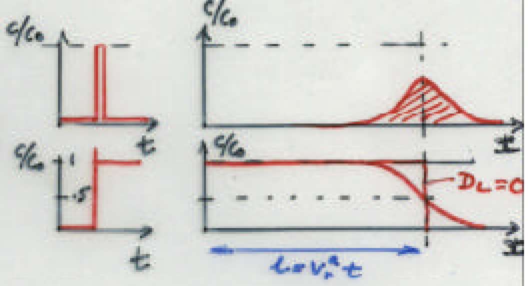
Reversible — Non-reversible

Advection }
Dispersion } mechanisms of propagation of a "conservative" solute.

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v^a \frac{\partial c}{\partial x}$$

Consequences: 1. Center of mass moves at velocity, v^a.

2. $c/c_0 = \frac{1}{2}$ moves @ v^a.



Potential for retardation:

Changes in concentration due to "reactions": — Within aqueous phase
— With solid grains
— With gas in unsaturated zone.

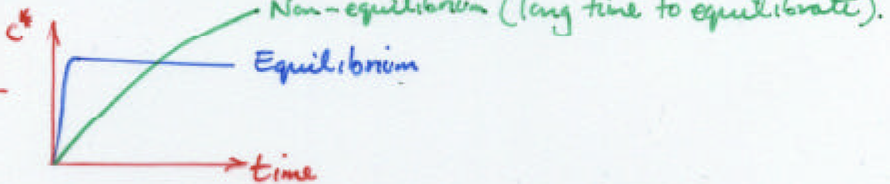
Reactions group as:

Sorption (Removal).
1. Adsorption - desorption
eg. Organic solvents sorbing onto organic matter

Reactions (transformation)
2. Acid-base reactions. eg. AMD on limestone/carbonate
3. Solution-precipitation reactions. eg. Silica dissolution/feldspar in HD
4. Oxidation-reduction reactions. eg. Oxidation of Fe in AMD
5. Ion-pairing and complexation reactions
6. Microbial cell synthesis reactions: eg. Biodegradation of gasoline and solvents. → methan

\+ Radioactive decay

CLASSIFICATION OF CHEMICAL REACTIONS



Reversible:
eg. Re-dissolution of precipitates →

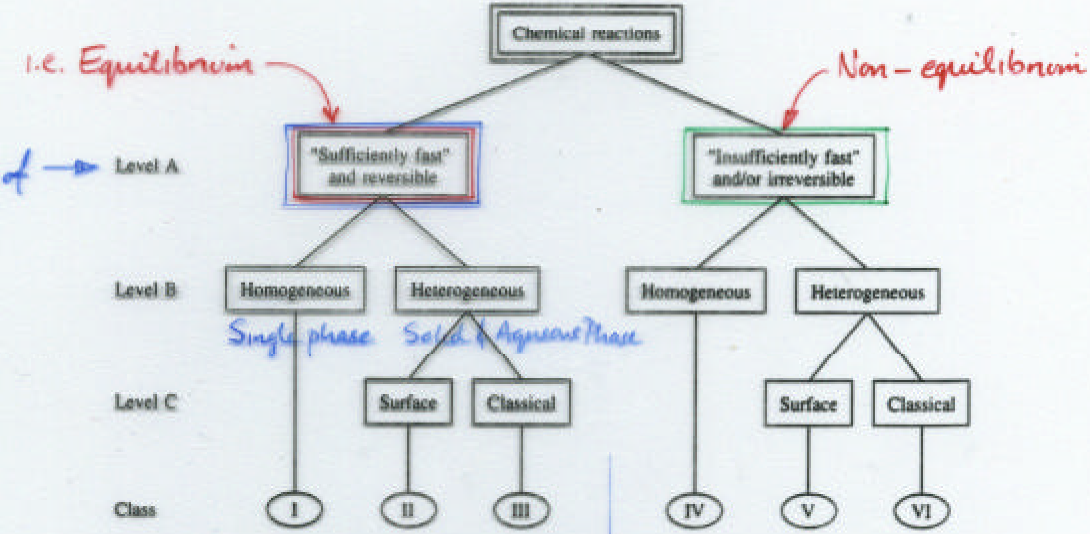


FIGURE 3.1 Classification of chemical reactions useful in solute transport analyses. Source: J. Rubin, *Water Resources Research* 19, no. 5 (1983):1231–52. Published by the American Geophysical Union.

SORPTION PROCESSES

NON-EQUILIBRIUM REACTIONS

All these reactions accommodated by simple retardation type models.

Use

$$\frac{\partial c}{\partial t} = \frac{D_m}{R}\frac{\partial^2 c}{\partial x^2} - \frac{V}{R}\frac{\partial c}{\partial x}$$

6.1 SORPTION PROCESSES

Adsorption: Solute clings to surface – chemical capture on clay particles

Absorption: Solute diffuses into interior of a particle.

→ Both result in "partitioning" of solute to solid phase i.e. removed.

Test: Mix solid with solute at known concentration
– measure amount removed per unit volume of solid
→ Equilibrium sorption isotherm.

also: Kinetic sorption isotherm (reaction slow but *not* reaching equilibrium).

Isotherms provide a convenient way of accommodating sorption in the "advection – dispersion" equation representing retardation effects.

Rewrite "advection – dispersion" equation for reactive (non conservative) system to accommodate retardation.

(solute is removed)

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v_x^a \frac{\partial c}{\partial x} - \frac{\rho_d}{\theta} \frac{\partial c^*}{\partial t} + \left(\frac{\partial c}{\partial t}\right)_r \qquad (1)$$

(Dispersion) (Advection) (Sorption) (Reaction)

"equilibrium"

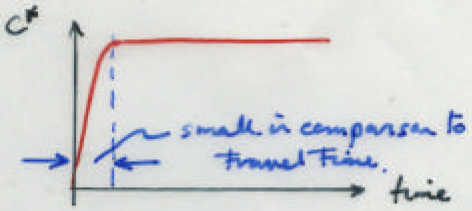
ρ_d = bulk density of aquifer

θ = volumetric moisture content (n if saturated)

c^* = amount of solute sorbed per unit weight of solid (aquife

r = subscript for biological or chemical reaction

Assume that reactions in groundwater are fast compared to flow rates. Then amount of solid sorbed is related to solute concentration, directly.

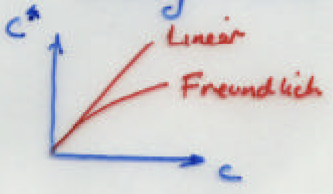


then $c^* = f(c)$

Therefore $\frac{\partial c^*}{\partial t} = \left(\frac{\partial c^*}{\partial c}\right) \frac{\partial c}{\partial t}$

Resubstitute into (1) and defines c (concentration in solute) as only variable

$\therefore$ Determine $\frac{\partial c^*}{\partial c} \Rightarrow$



Defined as distribution coefficient, $K_d = \frac{\partial c^*}{\partial c}$

6.2 EQUILIBRIUM SURFACE REACTIONS

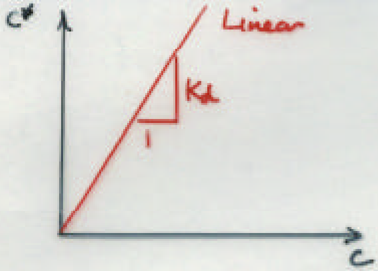
Linear Isotherm

$$\boxed{C^* = K_d C}$$

C^* (mg/kg) solute sorbed onto surface

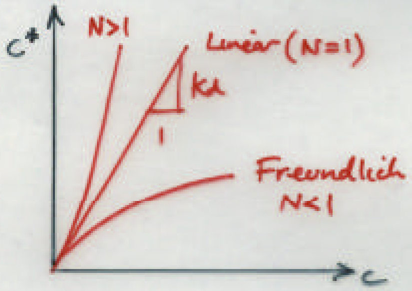
c (mg/L) concentration of solute in equilibrium with solid

K_d (L/kg) distribution coefficient.

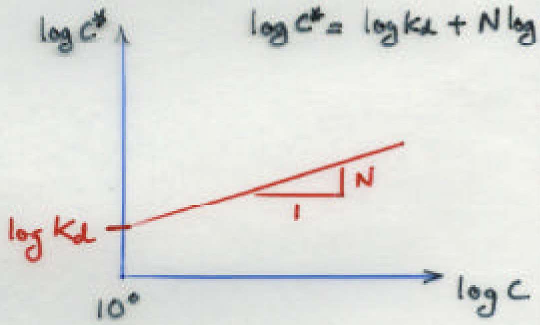


Freundlich Isotherm

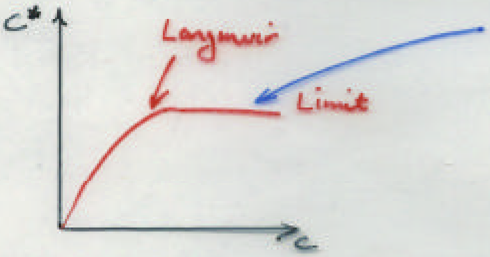
$$\boxed{C^* = K_d C^N}$$



$\log C^* = \log K_d + N \log$



Langmuir Isotherm



Represents a finite no. of sorption sites

$$\frac{c}{C^*} = \frac{1}{\alpha\beta} + \frac{c}{\beta} = \frac{\alpha\beta c}{1+\alpha c}$$

α = absorption coefficient related to binding energy

β = max amount of solute that may be absorbed to solid (mg/kg)

Why interested in Isotherms

Recall:

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v_x^a \frac{\partial c}{\partial x} - \frac{\rho_d}{\theta}\frac{\partial c^*}{\partial t} + \cancelto{0}{\left(\frac{\partial c}{\partial t}\right)_r}$$

$$\frac{\partial c^*}{\partial t} = \frac{\partial c^*}{\partial c}\left(\frac{\partial c}{\partial t}\right) = K_d \frac{\partial}{\partial c}$$

Move retardation term to L.H.S.

$$\frac{\partial c}{\partial t} + \frac{\rho_d}{\theta}\overset{K_d}{\left(\frac{\partial c^*}{\partial c}\right)}\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v_x^a \frac{\partial c}{\partial x}$$

$$\underbrace{\left[1 + \frac{\rho_d}{\theta} K_d\right]}_{\text{Retardation coefficient, } R}\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v_x^a \frac{\partial c}{\partial x}$$

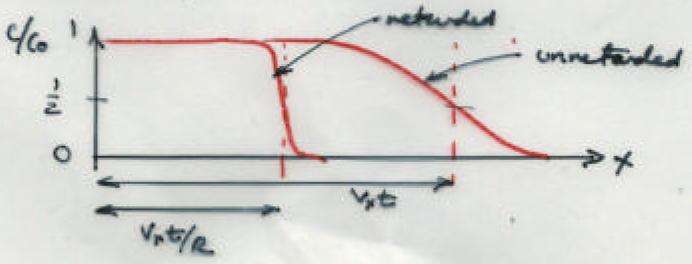
$$\frac{\partial c}{\partial t} = \frac{D_L}{R}\frac{\partial^2 c}{\partial x^2} - \frac{v_x^a}{R}\frac{\partial c}{\partial x}$$

Effective (retarded) parameters.

Effect:

1. Retards velocity as $V_{effective} = v_x^a/R$
2. Reduces effective dispersion as D_L/R

} Apply these to all previous expressions.



DISTRIBUTION COEFFICIENTS

Form	Relation	$K_d = \partial c^* / \partial c$	
Linear	$c^* = K_d c$	$\frac{\partial c^*}{\partial c} = K_d$	$R = \left[1 + \frac{\rho_d}{\theta} K_d\right]$
Freundlich	$c^* = K_d c^N$	$\frac{\partial c^*}{\partial c} = N K_d c^{N-1}$	$R = \left[1 + \frac{\rho_d}{\theta} N K_d c^{N-1}\right]$
Langmuir	$c^* = \frac{\alpha \beta c}{1 + \alpha c}$	$\frac{\partial c^*}{\partial c} = \frac{\alpha \beta}{(1 + \alpha c)^2}$	$R = 1 + \frac{\rho_d}{\theta} \frac{\alpha \beta}{(1 + \alpha c)^2}$

Typical magnitudes of R

K_d in the range 0 to 10^3 ml/g

$\rho_d = 2500 \text{ kg/m}^3 \longrightarrow 2.5 \text{ g/ml}$

$\theta = 0.2$ to 0.4

$R \doteq \left(1 + \frac{2.5}{.25} K_d\right)$ $\qquad$ $R \doteq (1 + 10 K_d) \Rightarrow 1$ to 10^4

Range.

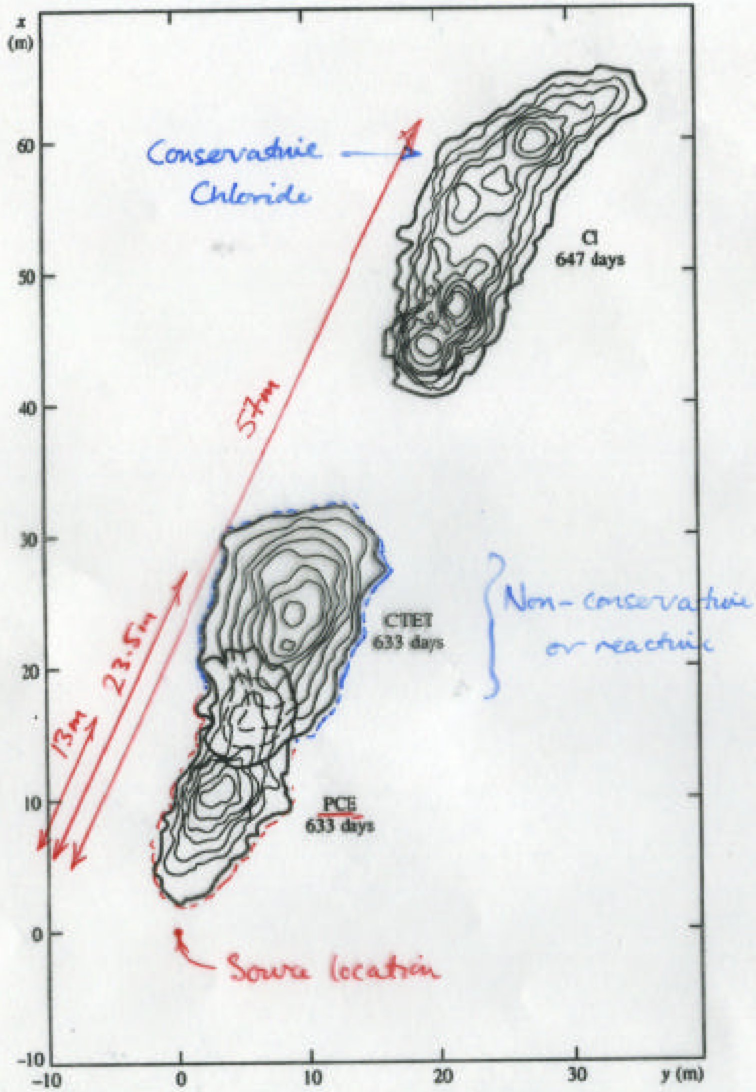


FIGURE 3.16 Plumes of chloride, carbon tetrachloride, and tetrachloroethylene at the end of the experimental period. The plumes are based on depth-averaged values. Source: P. V. Roberts, M. N. Goltz, and D. M. Mackay, *Water Resources Research* 22, no. 13 (1986):2047–59. Copyright by the American Geophysical Union.

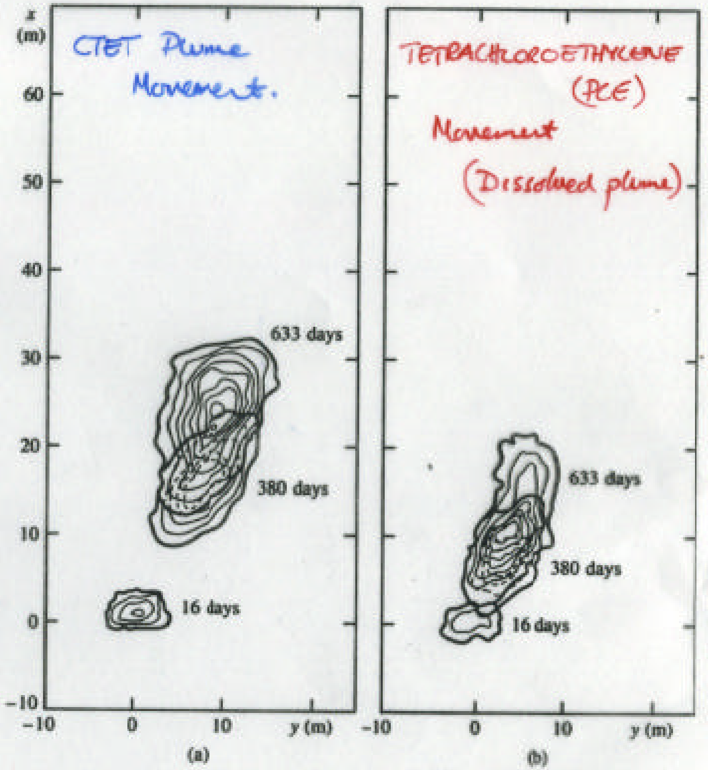


FIGURE 3.17 (a) Growth of carbon tetrachloride plume with time; (b) growth of tetrachloroethylene plume with time. Source: P. V. Roberts, M. N. Goltz, and D. M. Mackay, *Water Resources Research* 22, no. 13 (1986):2047–59. Copyright by the American Geophysical Union.

Why are different compounds differentially mobile ??

Assuming Cl is unretarded: $R = \frac{v^a_{cl}}{v^a} = \frac{l_{cl}}{t}\frac{t}{l}$

CTET => $R = 2.42$

PCE => $R = 4.38$

$$2000\ \text{Kg/m}^3 = 2000\,\frac{\text{Kg}}{\text{m}^3}\,\frac{1\,\text{m}^3}{1000\,\text{L}} = 2\,\frac{\text{Kg}}{\text{L}} = 2\,\frac{\text{g}}{\text{mL}}$$

$1\,\text{m}^3 = 1000\,\text{L}$

$$\frac{\theta}{\rho_d} = \frac{.3}{2}\,\frac{\text{L}}{\text{kg}} = .15$$

Rearranging

$$R = \left[1 + \frac{\rho_d}{\theta} K_d\right]$$

$$(R-1)\frac{\theta}{\rho_d} = K_d$$

Solute	$(R-1)$	$(R-1)\frac{\theta}{\rho_d} = K_d$ (L/kg or mL/g)	
CTET	1.42	.213	
PCE	3.38	.507	(tetrachloroethylene)
		K_d	

(Note can also check dispersion)

Note: organic content very low ~ 0.02%

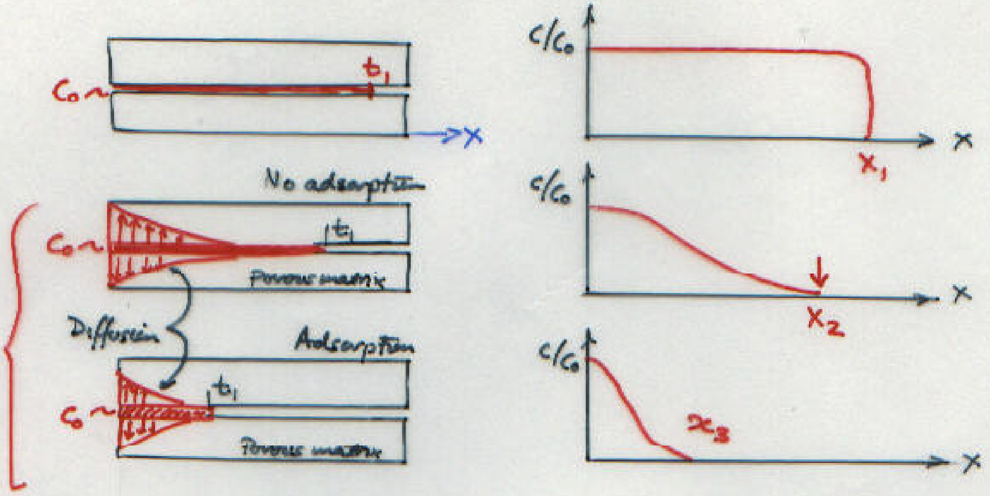
∴ adsorption limited

Estimates

	Solute	Solubility	log Kow (octanol-water partition)
	CTET	805 mg/l @ 30°C	2.7
(Tetrachloroethylene)	PCE	1503 mg/l @ 25°C	2.6

6.3 FRACTURED ROCK

- Retardation in fractured rock may be considered as a non-equilibrium reac
- Conditioned by fracture surface area.



Flow into porous matrix out from fracture

Diffusive process – is reversible
– is not in equilibrium with the groundwater flow

Approximate representation as a linear isotherm

$$K_d = \frac{\text{mass of solute on solid phase per unit "area" of solid phase}}{\text{concentration of solute in solution}}$$

i.e. K_d per unit surface area, not volume $\quad \frac{\bar{V}}{V_c} = 1 + A K_d = R$

$$A = \text{surface area / void volume of fracture} = \frac{2A}{Ab} = \frac{2}{b}$$

Planar fracture $\quad \frac{\bar{V}}{V_c} = \underbrace{1 + \frac{2}{b} K_d}_{R}$ $\quad$ Small fractures have greater retardation capacity.

[4:2] Retardation & Attenuation

Recap

Predictors of sorption

- Octanol-water partition coeff, K_{ow}
- Solubility, S

Multi-component mixtures – Raoult's Law

Mass removal rates

Mass in place

6.4 SORPTION OF HYDROPHOBIC (ORGANIC) COMPOUNDS

1. Low solubility in water   eg. CTET   Solubility 805 mg/l → 805 pp
   Drinking H_2O limit 5ppb.

2. Adsorbed onto • solid surfaces (since hydrophobic)
   • organic matter (important site)
   exclusively sorbed onto organic if $f_{oc} \geq 0.1\%$

$$f_{oc} = \frac{\text{organic carbon w}}{\text{bulk wt.}}$$

Two limits for behavior:

If $f_{oc} \geq 0.1\%$ then

$$K_{oc} = \frac{K_d}{f_{oc}}$$

K_{oc} = organic carbon partition coefficient.

If only know wt of organic matter, $K_{oc} = 1.724\, K_{om}$
since organic carbon less wt than organic matter

If $f_{oc} \leq 0.1\%$ then mineral surfaces are an important (relatively) site for the hydrophobic compounds.

$\therefore$ $K_d = K_{oc} f_{oc}$ does not apply.

If $f_{oc} \geq 0.1\%$ then

Koc may be estimated from two methods:

1. Kow – octanol-water partition coefficient defines solubility of octanol in water
2. Solubility data specific to the solvent compound.

For example: ($f_{oc} > 0.1\%$)

$$K_d = K_{oc} f_{oc}$$

$$\boxed{\text{eg.}\quad K_{oc} = 0.63\, K_{ow}}$$

Table 3.2, 3.3, 3.4

$$\boxed{\text{eg.}\quad \log K_{oc} = 3.64 - 0.55 \log S}$$

Solubility in mg/L

see table 3.5, 3.6

TABLE 3.5 Empirical equations by which K_{oc} can be estimated from S.

Equation Number	Equation	Reference
(T13)	$\log K_{oc} = 0.44 - 0.54 \log S$ S in mole fraction, $r^2 = 0.94$	Karickhoff, Brown, and Scott 1979
(T14)	$\log K_{oc} = 3.64 - 0.55 \log S$ S in mg/L	Kenaga 1980
(T15)	$\log K_{oc} = 4.273 - 0.686 \log S$ S in mg/L	Means et al. 1980
(T16)	$\log K_{oc} = 3.95 - 0.62 \log S$ S in mg/L	Hassett et al. 1983
(T17)	$\log K_{om} = 0.001 - 0.729 \log S$ S in moles/L, $r^2 = 0.996$	Chiou, Porter, and Schmedding 1983

$\log K_{oc} = 3.64 - 0.55 \log S$

$S_{\text{ETHYL BENZENE}} = 140 \text{ mg/L}$

$\log S = 2.15$

$\log K_{oc} = 3.64 - 0.55(2.15) = 2.46$

$\therefore K_{oc} = 288 \text{ L/kg or } (\text{mL/g})$

TABLE 3.6 K_{oc} values estimated from the aqueous solubility.

Compound:	Dichloroethane	Benzene	Trichloroethene	Ethyl Benzene	Tetrachloroethene	Napthalene	2,2′-Dichlorobiphenyl	Pyrene
Molecular weight:	98.96	78.12	131.38	165.82	106.18	128.18	223.10	202.26
				Solubility (mg/L)				
	5500	1780	1100	140	150	31	1.86	0.032
Log S:	3.74	3.25	3.04	2.15	2.18	1.49	0.269	−1.50
				Solubility (moles/L)				
	5.56×10^{-2}	2.28×10^{-2}	8.37×10^{-3}	8.44×10^{-4}	1.41×10^{-3}	2.42×10^{-4}	8.32×10^{-6}	1.58×10^{-7}
Log S:	−1.25	−1.64	−2.08	−3.07	−2.85	−3.62	−5.08	−6.80
				Solubility (Mole Fractions)				
	1.00×10^{-3}	4.10×10^{-4}	1.51×10^{-4}	1.52×10^{-5}	2.54×10^{-5}	4.35×10^{-6}	1.49×10^{-7}	2.84×10^{-9}
Log S:	−3.00	−3.39	−3.82	−4.82	−4.60	−5.36	−6.83	−8.55
Equation Number*				Estimated log K_{oc}				
(T13)	2.06	2.27	2.50	3.04	2.87	3.33	4.13	5.06
(T14)	1.58	1.85	1.97	2.46	2.44	2.82	3.79	4.47
(T15)	1.67	2.01	2.15	2.76	2.74	3.21	4.46	5.27
(T16)	1.63	1.94	2.07	2.62	2.60	3.03	4.12	4.88
(T17)	1.15	1.43	1.75	2.47	2.31	2.88	3.93	5.19
Range	1.15–2.06	1.43–2.27	1.75–1.50	1.80–3.04	2.31–2.87	2.82–3.33	3.79–4.46	4.47–5.27
Mean	1.62	1.90	2.09	2.67	2.59	3.05	4.09	4.97
St. dev.	0.32	0.31	0.27	0.24	0.22	0.22	0.25	0.32
Coef. var	0.08	0.07	0.06	0.05	0.04	0.04	0.05	0.08

* The equation numbers in his table refer to Table 3.1.

Equation Number	Equation	Chemicals Used	Reference
(T1)	$\log K_{om} = 0.52 \log K_{ow} + 0.62$	72 substituted benzene pesticides	Briggs, 1981
(T2)	$\log K_{oc} = 1.00 \log K_{ow} - 0.21$	10 polyaromatic hydrocarbons	Karickhoff, Brown, and Scott 1979
(T3)	$K_{oc} = 0.63 K_{ow}$	Miscellaneous organics	Karickhoff, Brown, and Scott 1979
(T4)	$\log K_{oc} = 0.544 \log K_{ow} + 1.377$	45 organics, mostly pesticides	Kenaga and Goring 1980
(T5)	$\log K_{oc} = 1.029 \log K_{ow} - 0.18$ $r^2 = 0.91;\ n = 13$	13 pesticides	Rao and Davidson 1980
(T6)	$\log K_{oc} = 0.94 \log K_{ow} + 0.22$	s-triazines and dinitroanalines	Rao and Davidson 1980
(T7)	$\log K_{oc} = 0.989 \log K_{ow} - 0.346$ $r^2 = 0.991;\ n = 5$	5 polyaromatic hydrocarbons	Karickhoff 1981
(T8)	$\log K_{oc} = 0.937 \log K_{ow} - 0.006$	Aromatics, polyaromatics, triazines	Lyman 1982
(T9)	$\ln K_{oc} = \ln K_{ow} - 0.7301$	DDT, tetrachlorobiphenyl, lindane, 2,4-D, and dichloropropane	McCall, Swann, and Laskowski 1983
(T10)	$\log K_{om} = 0.904 \log K_{ow} - 0.779$ $r^2 = 0.989;\ n = 12$	Benzene, chlorinated benzenes, PCBs	Chiou, Porter, and Schmedding 1983
(T11)	$\log K_{oc} = 0.72 \log K_{ow} + 0.49$ $r^2 = 0.95;\ n = 13$	Methylated and chlorinated benzenes	Schwarzenbach and Westall 1981
(T12)	$\log K_{oc} = 1.00 \log K_{ow} - 0.317$ $r^2 = 0.98;\ n = 22$	22 polynuclear aromatics	Hassett et al. 1980

log Koc

TABLE 3.4 Experimentally derived (K_{oc}) values.

Compound	log(K_{oc})	Reference
Benzene	1.50	Chiou, Porter, and Schmedding 1983
	1.92	Karickhoff, Brown, and Scott 1979
	1.98	Rogers, McFarlane, and Cross 1980
Ethylbenzene	2.22	Chiou, Porter, and Schmedding 1983
2,2'-Dichlorobphenyl	3.92	Chiou, Porter, and Schmedding 1983
Tetrachloroethene	2.32	Chiou, Peters, and Freed 1979
Napthalene	3.11	Karickhoff, Brown, and Scott 1979
Pyrene	4.92	Karickhoff, Brown, and Scott 1979
	4.80	Means et al. 1980

EXPERIMENTAL VALUES

COMPARE?

TABLE 3.3 Estimated values of K_{oc} based on published K_{ow} values.

	Dichloroethane	Benzene	Trichloroethene	Ethyl Benzene	Tetrachloroethene	Napthalene	2,2'-Diclorobiphenyl	Pyrene
Log K_{ow}	1.79	2.13	2.29	3.14	3.40	3.37	4.80	5.32
Equation Number*	Estimated log K_{oc}							
(T1)	1.79	1.96	2.05	2.49	2.62	2.61	3.35	3.62
(T2)	1.58	1.92	2.10	2.93	3.19	3.16	4.59	5.11
(T3)	1.13	~~1.34~~ 1.92	1.44	1.98	2.14	2.16	3.07	3.35
(T4)	2.35	2.54	2.62	3.09	3.23	3.21	3.99	4.27
(T5)	1.66	2.01	2.18	3.05	3.32	3.29	4.76	5.29
(T6)	1.90	2.22	2.37	3.17	3.42	3.39	4.73	5.22
(T7)	1.42	1.76	1.92	2.76	3.02	2.99	4.40	4.92
(T8)	1.67	1.99	2.14	2.94	3.18	3.15	4.49	4.98
(T9)	1.06	1.40	1.56	2.41	2.67	2.64	4.07	4.59
(T10)	1.08	1.39	1.53	2.06	2.30	2.51	3.80	4.27
(T11)	1.78	2.02	2.14	2.75	2.94	2.92	3.95	4.32
(T12)	1.47	1.81	1.97	2.82	3.08	3.05	4.48	5.00
Range	1.06–2.35	1.34–2.54	1.44–2.62	1.98–3.17	2.14–3.42	2.16–3.39	3.07–4.76	3.35–5.29
Mean	1.57	1.86	2.00	2.70	2.93	2.92	4.14	4.58
St. dev.	0.38	0.35	0.33	0.39	0.41	0.37	0.54	0.63
Coef. var.	0.24	0.19	0.17	0.14	0.15	0.13	0.13	0.14

* The equation numbers in this table refer to Table 3.2

log Kow = 2.13
10^x it !!
Kow = 135
Koc = 0.63 Kow
= 84.98
log Koc = 1.92

TAKE CARE IN APPLYING $f_{oc} \geq .1\%$ where $f_{oc} < 0.1\%$.

eg. Border results: $f_{oc} = 0.02\%$

$$K_d = K_{oc} f_{oc}$$

For Carbon Tetra Chloride (CTET) Solubility, S = 805 mg/L

Using (T14) $\log K_{oc} = 3.64 - 0.55 \log S$

$= 3.64 - 0.55(2.9) = 2.04$

$K_{oc} = 110$ ~~mg/L~~ mL/g

From calculation $f_{oc} > 0.1\%$ $\boxed{K_d = 110(0.0002) = 0.02 \cancel{mg/L}}$ mL/g

From plume $\boxed{R = 2.42; \quad K_d = 0.213 \cancel{mg/L}}$ mL/g

1. Estimated value is too low — neglects the significant of the mineral surfaces.
2. Reasonable correspondence.

This table sheds some insight into the foc contents of typical sands and gravels

TABLE 4.1 Field Studies that Have Yielded Reliable Estimates Of Organic Contaminant Retardation in Sand/Gravel Aquifers

Site Location and Test Type (reference)[a]	Retardation Factors Determined For Listed Contaminants		Organic Carbon Content Of Solids (reference)
	Contaminant	Factor	
Palo Alto, California			nr[c]
Forced gradient (1)	Chloroform	2.5-3.6	
	Bromoform	6.0	
	1,1,1-Trichloroethane	12.0	
	Chlorobenzene	33.0	
R. Aare, Switzerland			nr
River infiltration (2)	Tetrachloroethene	5.0	
Gloucester, Ontario			0.1-0.25% (4, 5)
Forced gradient (3, 4)	1,4-Dioxane	1.4	
	Tetrahydrofuran	2.2	
	Diethyl ether	3.0	
Plume interpretation (4, 5)	1,4-Dioxane	1.6	
	Tetrahydrofuran	2.2	
	Diethyl ether	3.2	
	1,2 Dichlorobenzene	7.6	
	Benzene	6.8	
	Carbon tetrachloride	23.0	
Borden, Ontario			0.02% (6, 11)
Natural gradient (6, 7)	Bromoform	1.9-2.7	
	Carbon tetrachloride	1.8-2.5	
	Tetrachloroethene	2.7-5.9	
	1,2-Dichlorobenzene	3.9-9.0	
	Hexachloroethane	5.0-7.9	
Moffett Naval Air Station, California			0.11% (8)
Forced gradient (8)	Trichloroethene	6-9	
	1,1,1-Trichloroethane	1.4-2.0	
Otis Air Force Base, Massachusetts			0.01-0.75% (9)
Plume interpretation (9)	Trichloroethene	1.0	
	Tetrachloroethene	1.0	
	Dichlorobenzene	1.0-1.1	
	DTBB[b]	2.4-2.6	
	P-Nonylphenol	1.1-3.3	
Rocky Mountain Arsenal, Colorado			0.005% (12)
Forced gradient (10)	Trichloroethene	1-2	
	1,1,1-Trichloroethane	1-2	

[a] References: (1) Roberts et al., 1982; (2) Schwarzenbach et al., 1983; (3) Whiffin and Bahr, 1985; (4) Patterson et al., 1985; (5) Jackson et al., 1985; (6) Mackay et al., 1986; (7) Roberts et al., 1986; (8) Semprini et al., 1987; (9) Barber et al., 1988; (10) Mackay et al., 1986; (11) Ball et al., 1989; (12) Mackay et al., unpublished results.

1985b

1986a

[b] DTBB is 2,6-di-tert-butyl-p-benzoquinone.

[c] nr: not reported.

Source: Mackay, D. Characterization of the Distribution and Behavior of Organic Contaminants in the Subsurface. In Proceedings of a National Research Council Symposium. National Academy Press (in press 1990)

Rocky Mtn Arsenal ∴ $f_{oc} \approx 0.005\%$

TCE @ 5 mg/l

K_d TCE ≈ 0.2 cm³/g

$\Rightarrow S \cdot K_d C = 10^{-6} \frac{\text{gms TCE}}{\text{gm solid}}$ i.e. f_{oc} from TCE ≈ 10^{-6} i.e. no appreciable contribution of TCE to the organic carbon content.

6.4.1 Multiple Solutes

- Solubility is reduced where multiple hydrophobic components are encountered.
- Concentration is <u>lower</u> than if solute is alone.

$$S_i^e = X_i \, S_i$$

S_i = pure phase solubility, (mg/L) for compound i

X_i = mole fraction of component i in DNAPL

ie Lab analysis of source

* Mole fraction since solubility controlled by available molecules

S_i^e = effective solubility of i

$$\text{Mole fraction} = \frac{\text{Moles of compound } i}{\text{Total moles of soln}}$$

☐ Effective solubility is an <u>upper</u> theoretical bound

☐ Does not account for co-solvency and other non-ideal behavior

<u>Smithville</u>

Compound	"Free phase" %by wt	Formula Wt (g)	Moles per 100g of cocktail	X_i Mole fract	Pure phase Solubility (mg/L)	S_i^e(
TCE	2%	131.4	$\frac{2}{131} = 0.0152$	$\frac{.0152}{.677} = 2.2\%$	1060	23
TCB	10	181.45	.055	8.12%	19	1.5
PCB	50	220 (average)	.227	33.5%	.2	.0
Mineraloils	38	100 (guess)	.38	56.1%		
			.677			

moles per 100g

i.e. $.677 \times 10^{23}$ molecules

1 mg/L = 1 ppm.

Mole of substance = formula wt in g.

Moles of solute per liter of solution = MOLARITY = $\frac{\text{Density}}{\text{Formula wt}}$

Water = $\frac{1000\text{ g/L}}{(16+2)}$ = 55.

Worksheet 7-1: Calculation of Effective Solubility (from Newell and Ross, 1992; after Shiu et al., 1988; and Feenstra et al., 1991)

For a single-component DNAPL, the pure-phase solubility of the organic constituent can be used to estimate the theoretical upper-level concentration of organics in aquifers or for performing dissolution calculations. For DNAPLs comprised of a mixture of chemicals, however, the effective solubility concept should be employed:

$$S^e_i = X_i S_i$$

where

S^e_i = the effective solubility (the theoretical upper-level dissolved-phase concentration of a constituent in groundwater in equilibrium with a mixed DNAPL; in mg/l)

X_i = the mole fraction of component i in the DNAPL mixture (obtained from a lab analysis of a DNAPL sample or estimated from waste characterization data)

S_i = the pure-phase solubility of compound i in mg/l (usually obtained from literature sources)

For example, if a laboratory analysis indicates that the mole fraction of trichloroethylene (TCE) in DNAPL is 0.10, then the effective solubility would be 110 mg/l. This is derived by multiplying the pure phase solubility of TCE by the TCE mole fraction:

$$1100 \text{ mg/l} * 0.10 = 110 \text{ mg/l}$$

Effective solubilities can be calculated for all components in a DNAPL mixture. Nearly insoluble organics in the mixture (such as long-chained alkanes) will reduce the mole fraction and effective solubility of more soluble organics, but will contribute little dissolved-phase organics to groundwater.

Please note that this relationship is approximate and does not account for non-ideal behavior of mixtures, such as co-solvency, etc.

6.4.2 EVALUATE THE POTENTIAL THAT "FREE" PRODUCT NAPL IS PRESENT @ SI

Worksheet 7-2: Method for Assessing Residual NAPL Based on Organic Chemical Concentrations in Soil Samples (from Newell and Ross, 1992; after Feenstra et al., 1991)

To estimate if NAPLs are present, a partitioning calculation based on chemical and physical analyses of soil samples from the saturated zone (from cores, excavation, etc.) can be applied. This method tests the assumption that all the organics in the subsurface are either dissolved in groundwater or adsorbed to soil (assuming dissolved-phase sorption, not the presence of NAPL). By using the concentration of organics on the soil and the partitioning calculation, a theoretical pore-water concentration of organits in groundwater is determined. If the theoretical pore-water concentration is greater than the estimated solubility of the organic constituent of interest, then NAPL may be present at the site. A worksheet for performing this calculation is presented below; see Feenstra et al. (1991) for the complete methodology.

Step 1: Calculate $\overset{S_e}{S^e_i}$, the effective solubility of organic constituent of interest. See Worksheet 7-1.

Step 2: Determine $\overset{K_{oc}}{K_{oc}}$, the organic carbon-water partition coefficient from one of the following:

- Appendix A and associated references or
- Empirical relationships based on K_{ow}, the octanol-water partition coefficient, which also is found in Appendix A. For example, K_{oc} can be estimated from K_{ow} using the following expression developed for polyaromatic hydrocarbons:

$$\operatorname{Log} \overset{K_{oc}}{K_{oc}} = 1.0 * \operatorname{Log} \overset{K_{ow}}{K_{ow}} - 0.21$$

Step 3: Determine f_{oc}, the fraction of organic carbon on the soil, from a laboratory analysis of clean soils from the site. Values for f_{oc} typically range from 0.03 to 0.00017 mg/mg. Convert values reported in percent to mg/mg.

Step 4: Determine or estimate ρb, the dry bulk density of the soil, from a soils analysis. Typical values range from 1.8 to 2.1 g/ml(kg/l). Determine or estimate θw, the water-filled porosity.

Step 5: Determine Kd, the partition (or distribution) coefficient between the pore water (ground water) and the soil solids:

$$Kd = \overset{K_{oc}}{K_{oc}} * \overset{f_{oc}}{f_{oc}}$$

Step 6: Using Ct, the measured concentration of the organic compound in saturated soil in mg/kg, calculate the theoretical pore water concentration assuming no DNAPL (i.e., Cw in mg/l):

$$Cw = \frac{(Ct * \rho b)}{(Kd * \rho b + \theta w)}$$

C_t = total concentration in saturated soil

Cw = concentration in water only. ← Equilibrium concentrati

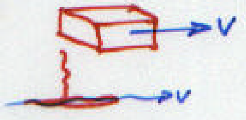
Step 7: Compare Cw and S^e_i (from Step 1):

Cw > S^e_i suggests possible presence of DNAPL ← Remaining source of DNAPL. (in the sample)

Cw < S^e_i suggests possible absence of DNAPL

* May measure Cw directly by pore-water extraction

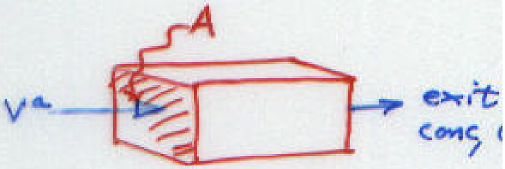
6.4.3 TIME REQUIRED FOR DISSOLUTION – two forms { Distributed / Pool



a) Distributed throughout volume

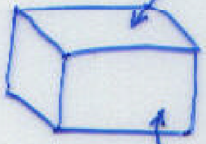
- Slow dissolution rate
- Decreases with time due to reduction in contact area.

$$t = \frac{\text{Mass of NAPL}}{\text{Mass rate of removal}} = \frac{m}{V_i n_e C_w A}$$



V^a = advective velocity
n_e = effective porosity
A = c/s area of flow
m = NAPL mass
C_w = dissolved exit concentration

eg.



1m³ sandy soil

$K = 10^{-3}$ cm/s
$i = 0.01$
$n_e = 0.3$

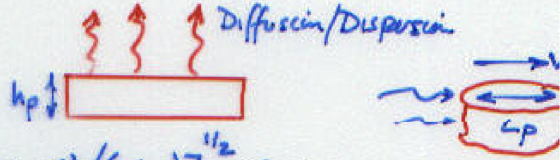
$$V^a = \frac{Ki}{n} = \frac{10^{-3}\,10^{-2}}{.3}$$
$$= 3 \times 10^{-5}\ \text{cm/s}$$
$$= 3\ \text{cm/d} = .03$$

Residual @ 30L/m³ of PCE $\rho = 1.63$ g/cm³
Solubility = 200 mg/L
Assume solubility @ 10% → 20 mg/L

t = 744 years

Magnitudes consistent with persistent DNAPL contamination problems in 40s, 50s, 60s.

b) <u>Residual Pool Sources</u>



M_a = Surface area averaged mass transfer rate ($M/L^2/T$)

$$M_a = \left[(4 D_v V^a)/(\pi L_p)\right]^{1/2} C_{sat}\, n_e$$

D_v = coef of vertical dispersion
$= D^* + V^a \alpha_T \quad (L^2/T)$
V^a = average advection g/w velocity
L_p = pool length
n_e = effective porosity
C_{SAT} = saturation concentration (solubility)
(may be 10% of this due to mass transfer rate effects)

Assuming pool area remains constant:

$$t_d = \overbrace{P_h \quad n\, \rho_{nw}}^{\text{Mass of NAPL per unit area}} S_n \,/\, M_a$$

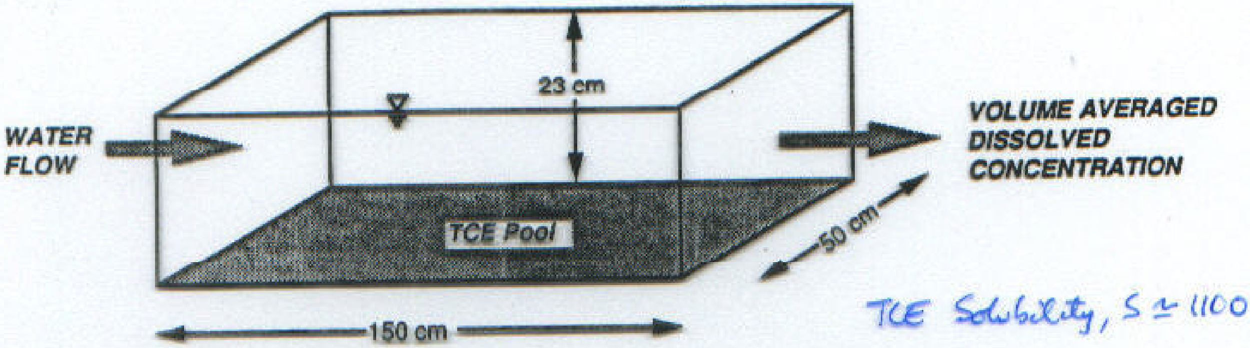
Mass rate of
remov

t_d = dissolution time
P_h = pool height
S_n = NAPL saturation
ρ_w = Density of NAPL

eg TCE in sand

Schwille experiment.

SCHWILLE POOL DISSOLUTION EXPERIMENT



TCE Solubility, S ≃ 1100mg

From Schwille (1988)

RESULTS OF POOL DISSOLUTION EXPERIMENT:

Linear Velocity (m/day)	Concentration (mg/L)	Relative Concentration
1.1	90	8.2 %
2.3	67	6.1 %
2.3	87	7.9 %
4.5	73	6.6 %
6.8	77	7.0 %

Much lower than absolute solubility

CONCLUSION FROM POOL DISSOLUTION EXPERIMENT:

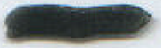
* Dissolved concentrations can be considerably less than saturation concentrations

→ Contact time of groundwater with solvent

→ Area of contact (Related to pool size).

6.4.4 EQUIVALENT DNAPL MASS – Present in Dissolved Plume.

Table 5.3. Equivalent DNAPL mass associated with some relatively well-documented organic contaminant plumes in sand-gravel aquifers (modified from Mackay and Cherry, 1989).

SITE LOCATION AND PLUME MAP	PRESUMED SOURCES	PREDOMINANT DNAPL CONTAMINANTS	PLUME VOLUME (LITERS)	ESTIMATED CHEMICAL MASS DISSOLVED IN PLUME (AS EQUIVALENT DNAPL VOLUME IN LITERS OR 55-GAL DRUMS)
 Ocean City, NJ	chemical plant	Trichloroethene 1,1,1-Trichloroethane Tetrachloroethene	5,700,000,000	15,000 (72 drums)
 Mountain View, California	electronics plant	Trichloroethene 1,1,1-Trichloroethane	6,000,000,000	9800 (47 drums)
 Cape Cod, Ma.	sewage infiltration beds	Trichloroethene Tetrachloroethene	40,000,000,000	1500 (7 drums)
 Gloucester, Ont.	special waste landfill	1,4-Dioxane Freon 113	102,000,000	190 (0.9 drum)
 San Jose, Cal.	electronics plant	1,1,1-Trichloroethane Freon 113 1,1-Dichloroethene	5,000,000,000	130 (0.6 drum)
 Denver, Colorado	trainyard, airport	1,1,1-Trichloroethane Trichloroethene Dibromochloropropane	4,500,000,000	80 (0.4 drum)

Evaluate total NAPL (dissolved) in plume → Evaluate source NAPL (volume).

Plume = Dissolved mass + Sorbed mass

$$M_T = C\,n\,V_T + C^{*}\rho_b V_T$$

$$C^{*} = K_d\,C \left(\frac{M}{M}\right)$$

$$\boxed{M_T = C\,n\,V_T\,R} \leftarrow R = \left[1 + \frac{\rho_b}{n} K_d\right]$$

6.5 RADIOACTIVE DECAY

Recall:

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - v^a \frac{\partial c}{\partial x} - \underbrace{\frac{\rho_d}{\theta}}_{\text{Retardation}} \frac{\partial c^*}{\partial t} + \underbrace{\left(\frac{\partial c}{\partial t}\right)_{rxn}}_{\text{Reaction}}$$

- ☐ Radioactive chain decay
- ☐ Abiotic hydrolysis (natural degradation of hydrocarbons

$$\left(\frac{\partial c}{\partial t}\right)_{decay} = \frac{-\ln(2)}{\lambda} c$$

λ = half life (in same units as time)

The previous figure introduced the concept of half-life to define the abiotic rxn rate. You will recall that this derives from the first-order rate laws, which is often assumed to apply to abiotic rxns:

$$-\frac{d(RX)}{dt} = k_T [RX]$$

where half life, $t_{1/2} = 0.693/k_T$

Vogel et al (1987) give the following table of half-lives:

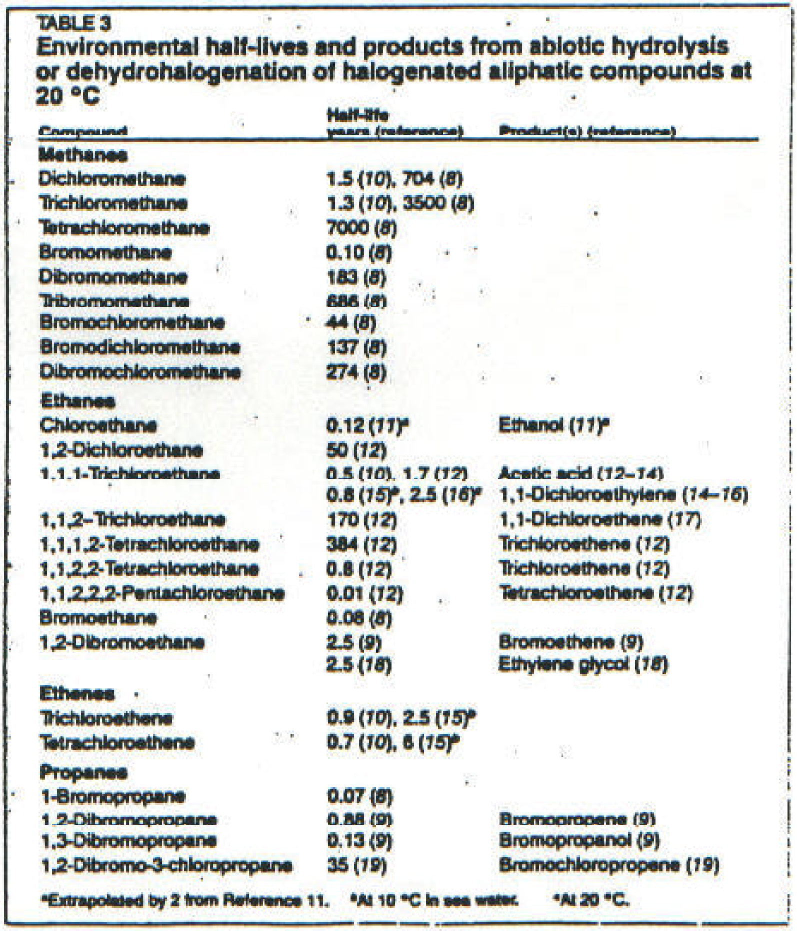


TABLE 3
Environmental half-lives and products from abiotic hydrolysis or dehydrohalogenation of halogenated aliphatic compounds at 20 °C

Compound	Half-life years (reference)	Product(s) (reference)
Methanes		
Dichloromethane	1.5 (*10*), 704 (*8*)	
Trichloromethane	1.3 (*10*), 3500 (*8*)	
Tetrachloromethane	7000 (*8*)	
Bromomethane	0.10 (*8*)	
Dibromomethane	183 (*8*)	
Tribromomethane	686 (*8*)	
Bromochloromethane	44 (*8*)	
Bromodichloromethane	137 (*8*)	
Dibromochloromethane	274 (*8*)	
Ethanes		
Chloroethane	0.12 (*11*)[a]	Ethanol (*11*)[a]
1,2-Dichloroethane	50 (*12*)	
1,1,1-Trichloroethane	0.5 (*10*), 1.7 (*12*) 0.8 (*15*)[b], 2.5 (*16*)[c]	Acetic acid (*12–14*) 1,1-Dichloroethylene (*14–16*)
1,1,2-Trichloroethane	170 (*12*)	1,1-Dichloroethene (*17*)
1,1,1,2-Tetrachloroethane	384 (*12*)	Trichloroethene (*12*)
1,1,2,2-Tetrachloroethane	0.8 (*12*)	Trichloroethene (*12*)
1,1,2,2,2-Pentachloroethane	0.01 (*12*)	Tetrachloroethene (*12*)
Bromoethane	0.08 (*8*)	
1,2-Dibromoethane	2.5 (*9*) 2.5 (*18*)	Bromoethene (*9*) Ethylene glycol (*18*)
Ethenes		
Trichloroethene	0.9 (*10*), 2.5 (*15*)[b]	
Tetrachloroethene	0.7 (*10*), 6 (*15*)[b]	
Propanes		
1-Bromopropane	0.07 (*8*)	
1,2-Dibromopropane	0.88 (*9*)	Bromopropene (*9*)
1,3-Dibromopropane	0.13 (*9*)	Bromopropanol (*9*)
1,2-Dibromo-3-chloropropane	35 (*19*)	Bromochloropropene (*19*)

[a] Extrapolated by 2 from Reference 11. [b] At 10 °C in sea water. [c] At 20 °C.

~ DATA IS AVAILABLE
BUT may not be reliable

PSUEDO FIRST [illegible]
(at least seems to be)

6.6 BIODEGRADATION

In addition to abiotic processes → Biodegradation of hydrocarbons

Biofilm + Oxygen → Aerobic biodegradation

→ Growth of microbial population

AEROBIC

Need oxygen source – dissolved in water

– pumped in for remediation

Monod – function governs rates:

3 rate laws (coupled) (H) Hydrocarbon concentration

(O) Oxygen availability in fluid

(M) Biofilm mass

→ 3 conservation equations and 3 unknowns

Solve for (H).

ANAEROBIC

Microbes use other metabolic source eg. nitrate available from fertilizer

$$\left.\begin{array}{l}\text{1 rate law required only}\\ \text{1 conservation equation}\end{array}\right\}\ \text{solve for hydrocarbon concentration.}$$

BIODEGRADATION – More complex than simple reaction since requires

AEROBIC

3 Growth/Decay laws – Inter-related

$$\frac{dH}{dt} = -M_t k_h \left(\frac{H}{K_h + H}\right)\left(\frac{O}{K_o + O}\right) \tag{3.59}$$

Hydrocarbon

$$\frac{dO}{dt} = -M_t k_h G \left(\frac{H}{K_h + O}\right)\left(\frac{O}{K_o + O}\right) \tag{3.60}$$

Oxygen

$$\frac{dM_t}{dt} = M_t k_h Y \left(\frac{H}{K_h + H}\right)\left(\frac{O}{K_o + O}\right) + k_c Y C_{oc} - b M_t \tag{3.61}$$

Microbial population

where

H = hydrocarbon concentration in pore fluid (ML^{-3})
O = oxygen concentration in pore fluid (ML^{-3})
M_t = total aerobic microbial concentration (ML^{-3})
k_h = maximum hydrocarbon utilization rate per unit mass of aerobic microorganisms (T^{-1})
Y = microbial yield coefficient (g cells/g hydrocarbon)
K_h = hydrocarbon half-saturation constant (ML^{-3})
K_o = oxygen half-saturation constant (ML^{-3})
k_c = first-order decay rate of natural organic carbon
C_{oc} = natural organic carbon concentration (ML^{-3})
b = microbial decay rate (T^{-1})
G = ratio of oxygen to hydrocarbon consumed

The microorganisms will grow on both naturally occurring organic carbon as well as hydrocarbon contaminants. The microorganisms tend not to move in the aquifer because they generally adhere to aquifer materials (Harvey, Smith, and George 1984). Even if the microbes are free to move, the natural tendency of the aquifer matrix will be to filter them out. There will be some tendency for microbes to transfer from the solid surface to solution. As a first approximation this can be considered to be a linear function of the total mass of microorganisms.

We can combine Equations 3.59, 3.60, and 3.61 individually with Equation 3.1 to obtain solute transport equations for hydrocarbon, oxygen and microorganisms. The hydrocarbon is assumed to sorb onto the solid surfaces following a linear sorption

3 Conservation equations – inter-related

isotherm. The resulting equations are (Borden and Bedient 1986)

$$\frac{\partial H}{\partial t} = \frac{1}{r_h}\left(D_L \frac{\partial^2 H}{\partial x^2} - v_x \frac{\partial H}{\partial x}\right) - \frac{k_h M_s}{r_h}\left(\frac{H}{K_h + H}\right)\left(\frac{O}{K_o + O}\right) \tag{3.62}$$

$$\frac{\partial O}{\partial t} = D_L \frac{\partial^2 O}{\partial x^2} - v_x \frac{\partial O}{\partial x} - k_h M_s F\left(\frac{H}{K_h + H}\right)\left(\frac{O}{K_o + O}\right) \tag{3.63}$$

$$\frac{\partial M_s}{\partial t} = \frac{1}{r_m}\left(D_L \frac{\partial^2 M_s}{\partial x^2} - v_x \frac{\partial M_s}{\partial x}\right) + k_h M_s Y\left(\frac{H}{K_h + H}\right)\left(\frac{O}{K_o + O}\right) + \frac{K_c Y C_{oc}}{r_m} - b M_s \tag{3.64}$$

where

M_s = concentration of aerobic microbes in solution
r_h = retardation factor for hydrocarbon
r_m = microbial retardation factor
v_x = average linear ground-water velocity

ANAEROBIC

Some microorganisms can degrade hydrocarbons in the absence of oxygen. These microbes use another electron acceptor, such as nitrate (Major, Mayfield, and Barker 1988). Anaerobic decomposition of hydrocarbons can be described by another variation of the Monod function, which describes two-step catalytic chemical reactions (Bouwer and McCarty 1984). This function is

1 Rate law

$$\frac{dH}{dt} = -k_{ua} M_a \left(\frac{H}{K_a + H}\right) \tag{3.65}$$

where

M_a = total mass of anaerobic microbes
k_{ua} = maximum hydrocarbon utilization rate per unit mass of anaerobic microbes
K_a = half maximum rate concentration of the hydrocarbon for anaerobic decay

The solute transport and decay equation for anaerobic biodegradation in the aqueous phase is

Conservation eqn.

$$\frac{\partial H}{\partial t} = \frac{1}{r_h}\left(D_L \frac{\partial^2 H}{\partial x^2} - v_x \frac{\partial b}{\partial x}\right) - \frac{k_{ua} M_a}{r_h}\left(\frac{H}{K_a + H}\right) \tag{3.66}$$

If the concentration of the hydrocarbon, H, is much less than K_a, the half-maximum rate concentration, then Equation 3.65 can be simplified to a linear form by neglecting H in the denominator (Bouwer and McCarty 1984). This results in a first-order decay term:

$$\frac{dH}{dt} = -\left(\frac{k_{ua} M_a}{K_a}\right) H \tag{3.67}$$

Under these conditions the solute-transport equation with anaerobic biodegradation becomes

$$\frac{\partial H}{\partial t} = \frac{1}{r_h}\left(D_L \frac{\partial^2 H}{\partial x^2} - v_x \frac{\partial b}{\partial x}\right) - \underbrace{\left(\frac{k_{ua} M_a}{r_h K_a}\right)}_{\text{Reaction term to equation}} H \tag{3.68}$$

LINEARIZED ANAEROBIC

Hydrocarbon conc << Ka
then linearizes as

$$\frac{dh}{dt} = -h_{ua} M_a \left(\frac{H}{K_a + H}\right) \Rightarrow \frac{-h_{ua} M_a H}{K_a}$$

6.7 COLLOID TRANSPORT

☐ Particles with diameter < 1 μm
  - Organic macromolecules
  - Metal complex-es
  - Radioactive complex-es (eg Plutonium)

☐ Colloids may sorb other solutes and mobilize

☐ Solutes with high retardation may sorb onto colloids and be mobile with very low retardation

eg Plutonium – low R for colloids
high R for soil

Main issues

1. Retardation/attenuation mechanisms do not operate
   a) No sorption and reduced concentration
   b) No slowing down due to V/R

2. Presence in monitoring wells may be due to accidental introduction of colloids – from equipment
   – precipitation of iron when O_2 added.

3. Some evidence to suggest some attenuation mechanisms
   a) Multiphase interfaces trap due to surface tension
      air/water   water/sediment etc.
   b) Non-neutral charges → electrical attraction & capture
      especially clays
   c) Mechanical straining in fine grained media.

4. Lack of attenuation make colloids attractive as Tracers (conservative) and unretarded.

5

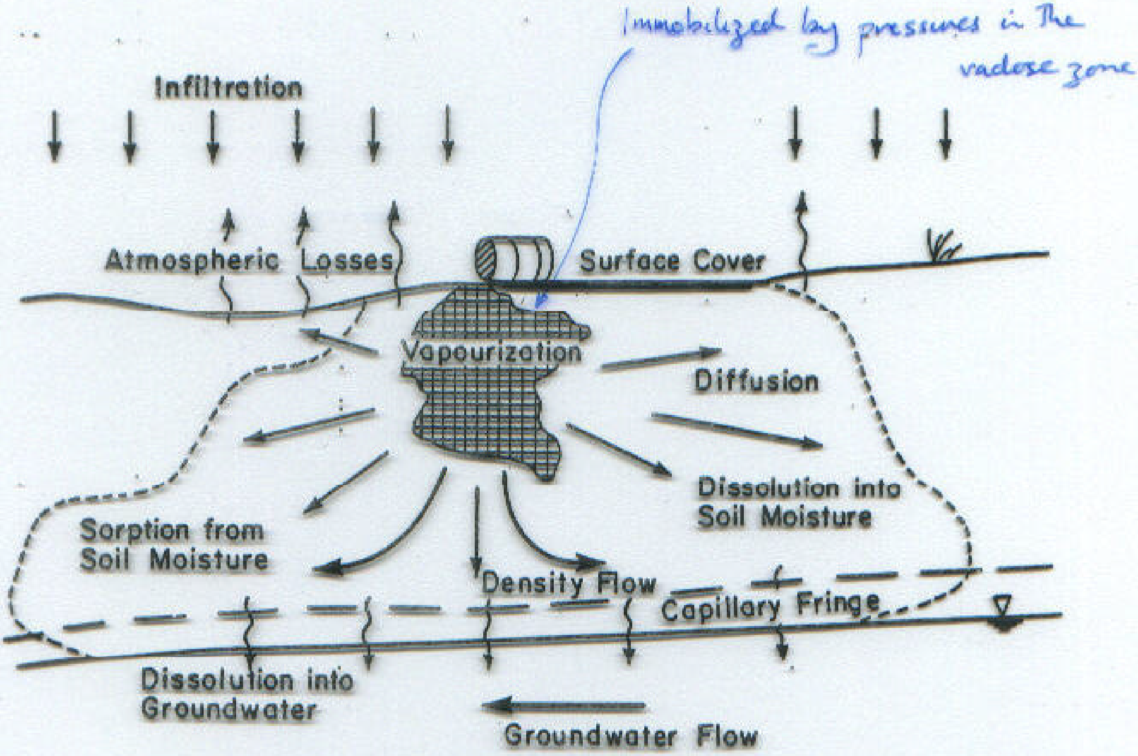
Vapor Mobility

[5:1] Vapor Mobility

- Transport Mechanisms
  - Diffusion
    - Partitioning
    - Retardation
  - Aqueous advection

7 PHYSICAL BEHAVIOR OF CONTAMINANT VAPORS IN THE UNSATURATED ZONE

Conceptual Model



Basic transport processes and fate of contaminants

VOLATILIZATION – Escape to atmosphere of VOCs

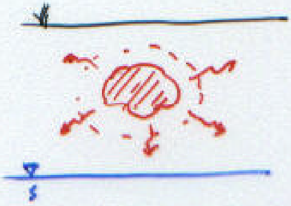
– Transport depends on partitioning

PARTITIONING

a) Between VOC dissolved in water and air   Henry's La

b) Between free phase NAPL(VOC) and air   Raoult's Law

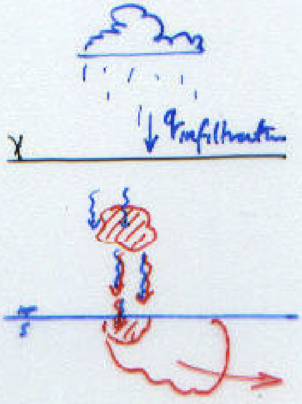
7.1 TRANSPORT MECHANISMS



DIFFUSION

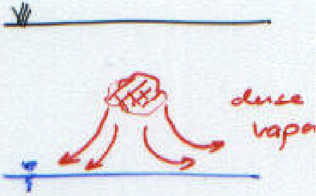
i.e. No infiltration of g/w (small)

No Gas-phase advection



WATERBORNE ADVECTION

Carried by infiltration



GAS-PHASE ADVECTI

{ Density driven
Temperature drive

increasing complexity (reality)

Each of these transport modes may be used to define anticipated (approximate) behavior.

VOLATILIZATION

Henry's Law

- Assumes local equilibrium between concentration in the air and concentration in other fluids. (i.e. water carrying dissolved NAPL)

$P = H'C_w$

H' = Henry's Law Constant (atm. m^3/mole)

C_w = Concentration in water

$C_{w_{max}}$ = solubility

P = Partial pressure of NAPL in gas phase (atm)

Tendency to volatilize ↑ with ↑ H' - See table Appendix A.

Raoult's Law

- Equilibrium between pure NAPL solution and air.

$P_i = X_i P_i^\circ$

P_i = vapor pressure of chemical i over the NAPL solution

X_i = mole fraction of compound i in NAPL solution

P_i° = vapor pressure of pure compound i

i.e. To determine "effective" vapor pressure of a "cocktail" of NAPL.

7.1.1 Diffusive Transport

Fick's first law

$$q_D = \Theta_g D_g^* \frac{\partial c_g}{\partial x}$$

q_D = diffusive mass flux

c_g = Concentration of VOC in gas phase

Θ_g = Volumetric gas content

D_g^* = "Effective" diffusion coefficient of gas.

Fick's second law   Mass continuity/Conservation of mass equation.

$$R \frac{\partial c_g}{\partial t} = D_g^* \frac{\partial^2 c_g}{\partial x^2}$$

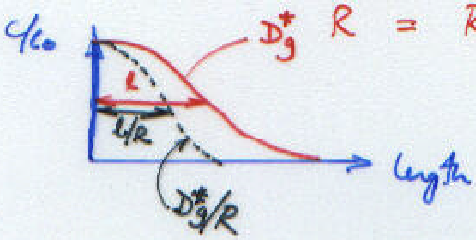
R = Retardation factor
- accounts for sorption between phases

This ignores:

1. Advection of vapors due to pumping (vacuum stripping)
2. Advection due to density/temperature effects
3. Infiltration due to rain/etc.

Controlling Parameters

D_g^* - Diffusive transport



R = Retardation of the diffusive transport.

At same time, t_1

□ Note the physical meaning of these parameters.

"Effective" Diffusion Coefficient, D_g^*

$$D_g^* = \tau D_g$$

τ = tortuosity

D_g = "Free" diffusion coeffic
(L^2/T)

Tortuosity

1. Experimental Measurement

$$\tau = \left(\frac{L}{L_e}\right)^2$$

2. Empirical estimates

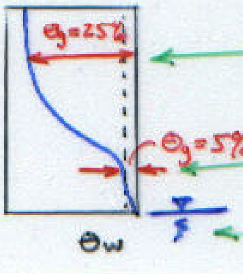
e.g. $\tau = \dfrac{\theta_g^{7/3}}{\theta_t^2}$ (Millington and Quirk, 1961)

θ_t — Total porosity (i.e. Saturate

Estimates of D_g^*

TCE @ 20°C $D_g = 8.1 \times 10^{-6}\ m^2/s$ (typical for chlori
solvent).

Assume θ_t = 35%



Residual water zone: $\theta_g = 25\%$ $\tau = 0.32$ H

$D_g^* = 2.6 \times 10^{-6}\ m^2/s$

Transition zone: $\theta_g = 5\%$ $\tau = 0.0075$

$D_g^* = 6.1 \times 10^{-8}\ m^2/s$

D^* in water (saturated) $D^* = 2 \times 10^{-9}\ m^2/s$

PARTITIONING BEHAVIOR

Retardation results from two mechanisms $\begin{cases} \text{Gas} \rightarrow \text{Water partitioning ①} \\ \text{Water} \rightarrow \text{Solid partitioning. ②} \end{cases}$

---

① Gaseous/Aqueous Partitioning

Described by Henry's Law.

$$H = \frac{C_g}{C_w}$$

C_w = water concentration (in same units as C_g)

H = "Dimensionless" Henry law coeff.

Alternate (usual) form of Henry's Law

$$H' = \frac{C_g'}{C_w'} = \frac{P_v}{S}$$

i.e. $P = H'C_w$

P_v = vapor pressure

S = saturation of "solvent" in water, Max value = Solubili

H' units of atm. m^3/mol

---

② Aqueous/Solid Partitioning

- Identical to saturated zone.

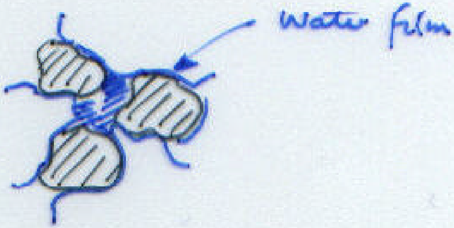
i.e.

$$K_D = K_{oc} \cdot f_{oc}$$

RETARDATION FACTOR

Assume equilibrium partitioning between phases $\left\{ \begin{array}{l} \text{water} \\ \text{solid} \end{array} \right.$

$$R = 1 + \underbrace{\frac{\theta_w}{\theta_g} \cdot \frac{1}{H}}_{\text{Partitioning to Water}} + \underbrace{\frac{\rho_b}{\theta_g} \cdot \frac{k_D}{H}}_{\text{Partitioning to solid via water}}$$



Note: H adjusts the proportion present in the water as a function of concentration in the gas phase ie. $H = \frac{C_g}{C_w}$

This is the non-dimensional Henry's constant.

RETARDATION FACTOR MAGNITUDES

Magnitudes are dependent on the two retardation mechanisms $\begin{cases} \text{gas} \rightarrow \text{water} \\ \text{gas} \rightarrow \text{solid (via water)} \end{cases}$

TCE @ 20°C $\quad H = 0.3$

$K_{oc} = 126$ ml/g.

Assume: $\theta_w = 10\%$ and $\rho_b = 1.65$ g/cm^3

$\theta_g = 25\%$

Contrast low and high organic content soils.

$f_{oc} = 0.01\%$ $\quad f_{oc} = 1\%$

f_{oc}	$\frac{\theta_w}{\theta_g} \cdot \frac{1}{H}$	$\frac{\rho_b}{\theta_g} \cdot \frac{K_d}{H}$	R
0.01%	1.33	.27	2.61
1%	1.33	27.7	30.1

⇒ As expected, higher f_{oc} has proportionately greater sorption of vapor

- Note vapor sorbed to f_{oc} is sorbed via water

i.e. gas → water → solid

DIFFERENTIAL RETARDATION – o Gas movement

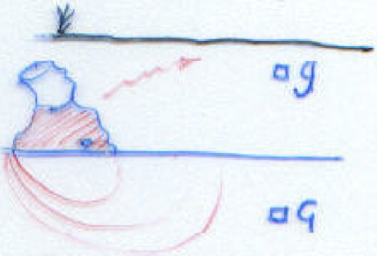
o Aqueous dissolution and movement

Aqueous. Effective velocity, $= \frac{V}{R_a}$

$$R_a = \left[1 + \frac{\rho_b}{\theta_{w_{sat.}}} K_d\right]$$

Gaseous. Retardation, $R_g = \left[1 + \frac{\theta_w}{\theta_g} \cdot \frac{1}{H} + \frac{\rho_b}{\theta_g} \cdot \frac{K_d}{H}\right]$

Implication of these two different retardation coeffs is that the order of arrival @ a "vadose" monitoring location and a "groundwater" monitoring location may be different.



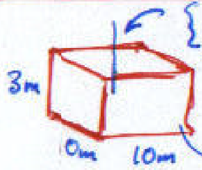
Dimensionless Henry's coeff.

Table 5-2. Parameters and values used to calculate the relative order of transport velocity for TCA, TCA, and MC and Chapter 5.3.15 (reprinted from ACS, 1992)

Koc Kd Ra H Rg Ⓖ ⓖ

Chemical	K_{oc} (ml/g)	K_d (ml/g)	R	K_H	R_g	Relative Order of Movement in Groundwater	Relative Order of Movement in Vapor
1,1,1-Trichloroethane (TCA)	152	2.58	16.9	0.599	55.8	3	2
Trichloroethene (TCE)	126	2.14	14.2	0.379	73.3	2	3
Methylene Chloride (MC)	8.8	0.15	1.93	0.084	34.9	1	1

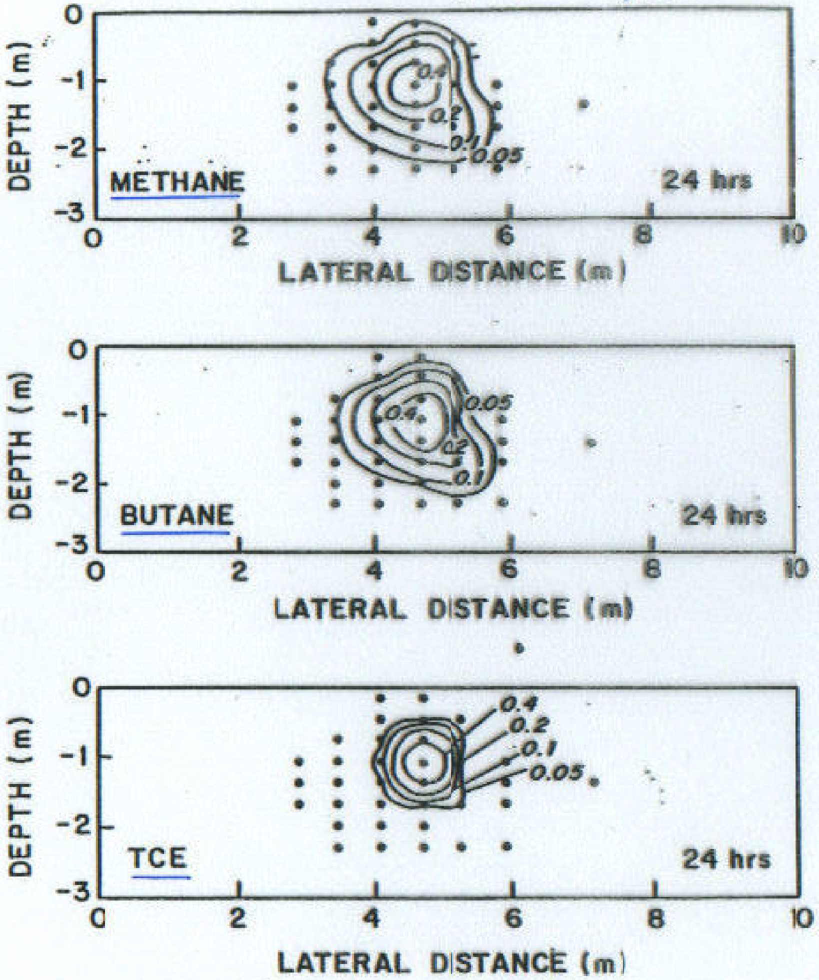
VAPOR EXPERIMENT (OGI)



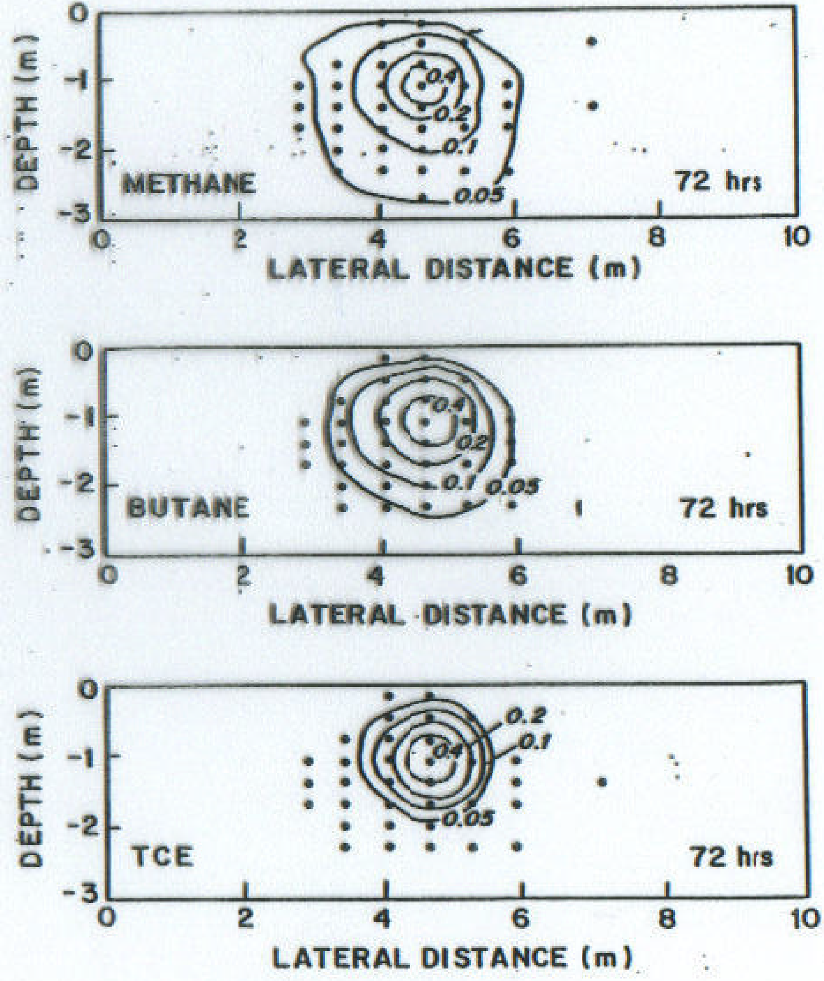
{Methane Butane Trichloroethylene (TCE)} + Nitrogen carrier gas

Monitoring @ 60cm x 25cm centers.

Residual m/c. & Low foc



[RELATIVE CONCENTRATIONS]



[RELATIVE CONCENTRATIONS]

FOR EXPERIMENTAL RESULTS

Henry's Law Coeffs.

Methane	~ 8
Butane	~ 12
TCE	$\sim .4$

$$\therefore \quad H_{meth} \simeq H_{but} > H_{TCE}$$

$\therefore$ since $$R = 1 + \frac{\theta_w}{\theta_g}\frac{1}{H} + \frac{\rho_b}{\theta_g}\frac{K_d}{H}$$

$$R_{meth} ; R_{but} < R_{TCE}$$

and TCE vapors migrate more slowly.

HENRY'S LAW COMPARISONS

Two forms:

$$H = \frac{C_g}{C_w}$$

$$H' = \frac{P_v}{C_w}$$

C_w in (mol/m³)

Ideal gas law: $P_v = \rho \frac{\bar{R}}{M} T$

$\bar{R}$ = universal gas const

= 8.20575×10^{-5} [(atm. m³)/(mol °K)

T = °K = °C + 273.16°K

M = mass of 1 mole

i.e. Atomic wt. (mass/mole)

Substituting:

$$H' = \frac{P_v}{C_w} = \frac{\rho \bar{R} T}{M C_w}$$

$$H' = \left(\frac{\rho}{M C_w}\right)(\bar{R}T) = H(\bar{R}T)$$

Correspondingly: $H = \frac{H'}{(\bar{R}T)}$

Check form of H:

$$H = \frac{\rho}{M C_w} \quad \text{and} \quad \frac{\rho}{M} = C_g$$

since $\frac{\text{grams}}{m^3} \cdot \frac{1}{\text{Molec. Wt}} = \frac{\text{moles}}{m^3}$

i.e. $\frac{\rho}{M} = C_g$!! ∴ ok.

Example for TCE @ 20°C = 293°K

H' or (K_H) = 9.1×10^{-3} atm. m³/mol

$$H = \frac{9.1 \times 10^{-3}}{(8.2 \times 10^{-5})\,293} \left[\frac{\text{atm. m}^3}{\text{mol}} \; \frac{\text{mol}\ ^\circ K}{\text{atm. m}^3} \; \frac{1}{^\circ K} \right]$$

$H \hat{=} 0.38$

Table 4-6. Vapor concentration and total gas density data for selected DNAPLs at 25°C (from Falta et al., 1989).

Chemical	Molecular Weight, M g/mole	Vapor Pressure kPa (@25°C)	Saturated Vapor Concentration (kg/m³)	Total Gas Density kg/m³
Trichloroethene	131.4	9.9	0.52	1.58
Chloroform	119.4	25.6	1.23	2.11
Tetrachloroethene	165.8	2.5	0.17	1.31
1,1,1-Trichloroethane	133.4	16.5	0.89	1.87
Methylene Chloride	84.9	58.4	2.00	2.50
1,2-Dichloroethene	96.9	43.5	1.70	2.37
1,2-Dichloroethane	99.0	10.9	0.44	1.48
Chlorobenzene	112.6	1.6	0.07	1.23
1,1-Dichloroethane	99.0	30.1	1.20	2.03
Tetrachloromethane	153.8	15.1	0.94	1.93
Air at 1 atm, 25°C	28.6	(101.3)		1.17

; 25°c

Check Results

TCE: $C_{g_{max}} = .52 \text{ kg/m}^3 = 520 \text{ mg/l}$

$C_{w_{max}}$ @ 20°C = 1100 mg/l

$$H = \frac{520}{1100} \simeq 0.47$$

This compares with .38 previously since vapor data at 25°c. ∴ different temperature.

CONCENTRATIONS

Vapor Concentrations : C_g

Variety of units :
- molar basis → mol/m³
- weight basis → mg/l
- volume basis → ppmv or %
- pressure basis → atm., Pa or mm Hg.

All are related through ideal gas law $P = \rho \frac{\bar{R}}{M} T$

Aqueous Concentrations: C_w

Related to C_g by Henry's Law. $H = \frac{C_g}{C_w}$

Max C_w will be solubility.

Note that vapor concentration depends on mixture in liquid contaminant

Equilibrium concentration : $C_g = X_i \frac{P_v}{RT} = X_i \frac{P_v}{T} \frac{M_i}{R}$

Gas const

Universal gas const

$$\boxed{R = \frac{\bar{R}}{M}}$$

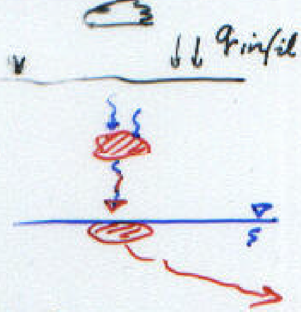
C_g has units of mol/m³

X_i = mole fraction of compound i in liquid

Non-equilibrium:

$$\left.\begin{array}{l}\text{- slow vaporization kinetics}\\ \text{- dispersed or isolated residual DNAPL}\end{array}\right\} \text{same as water!!}$$

7.1.2 ADVECTION DUE TO INFILTRATION



① Assume steady vertical plug flow displacement

$$v_w^a = \frac{q_{inf}}{\theta_w}$$

q_{inf} = Infiltration amount

v_w^a = Advective velocity of water

θ_w = Volumetric moisture content

Resulting infiltration – advective flux

$$q_M = \underbrace{\theta_w v_w^a}_{\text{Darcy flux (velocity)} (q_w)} C_w$$

q_w = Darcy volumetr flux.

q_M = mass flux.

Note C_w max is solubility (aqueous).

Conservation of mass => Gaseous and Aqueous Transport

(Aqueous is carried by infiltration)

i.e. Net reduction of source volume by:

- Gaseous diffusion 
- Aqueous movement. 

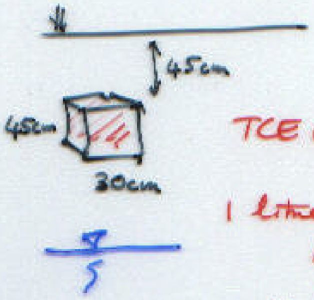
$$R \frac{\partial c_g}{\partial t} = D_g^* \frac{\partial^2 c_g}{\partial x^2} - \underbrace{\frac{\theta_w}{\theta_g} \cdot \frac{1}{H}}_{\text{Partitioning of vapor into water – same as in R.}} v_w^a \frac{\partial c_g}{\partial x}$$

Neglects:

- Aqueous dispersion
- ~~Ad~~ Gaseous advection.

Estimates of aqueous transport

eg. Border TCE experiment

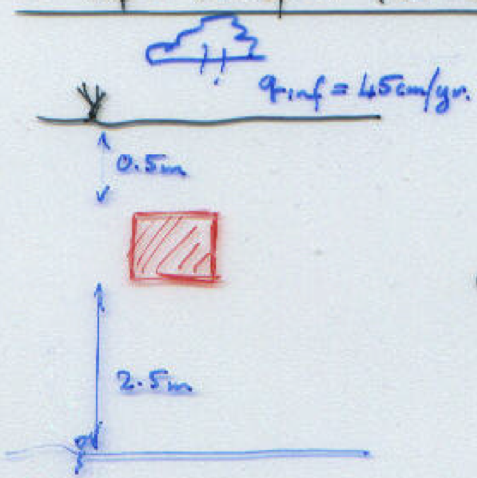


TCE @ residual sat.

1 litre of TCE over 45 x 30 cm area

~ 16 l/m³

No vapor transport (assume)



$\theta_w = 10\%$

Solubility, $S \equiv C_w = 1100$ mg/l

Questions?:

① How long to reach water table:

$$V_w^a = \frac{q_{inf}}{\theta_w} = \frac{.45 \text{ m/yr}}{.1} = 4.5 \text{ m/yr}$$

∴ 2.5 m travel ≃ ½ year.

(This ignores retardation).

② What loading from aqueous phase (i.e. q_w)

$$q_M = \theta_w V_w^a C_w = \underline{(0.1)(4.5)}(1100 \text{ mg/L})$$

Note 1 m/yr ≡ 1(m³/yr) per m²

$$q_M = 0.45 \text{ m/yr } (1100 \text{ mg/L})$$

$.45 \text{ m}^3 = 450 l$ ∴ $q_M = 450 l \times 1100 \text{ mg/l}$

$\cong .5 \times 10^6 \text{ mg}$

$\simeq \underline{\underline{.5}}$ Kg/yr. per m²

Relatively small loading — removed from source.

LOADINGS MAY BE CHECKED USING MORE SOPHISTICATED MODEL

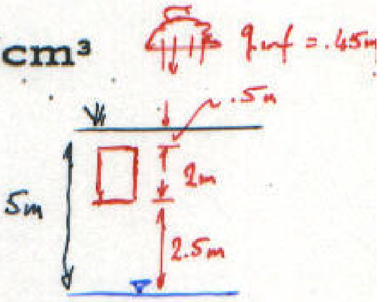
Transport Examples

porous medium:

very low sorption onto organic

θ_w = 10% f_{oc} = 0.01%

θ_g = 25% ρ_b = 1.65 g/cm³



q_{inf} = 45 cm/yr

depth to watertable 5 m

TCE @ 20°C:

D_g = 8.1 x 10^{-6} m²/sec Gaseous diffusion coef.

H = 0.30

K_{oc} = 126 ml/g

P_v = 60 mm Hg (C_g = 7.9%)

S = 1100 mg/l

source:

height 2.0 m

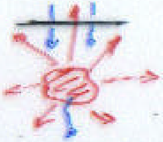
radius 1.0 m

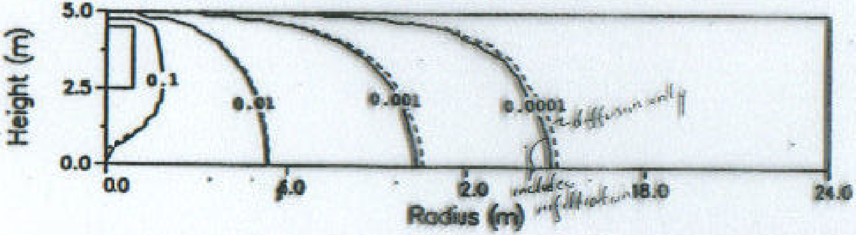
depth to top 0.5 m

Gaseous and Aqueous Transport

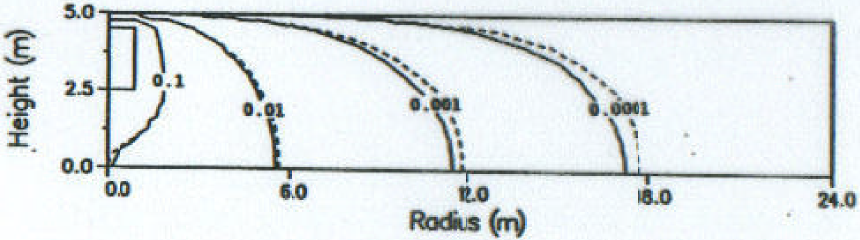
Example

- uncovered ground surface
  - Passive remediation (good)
  - Infiltration to groundwater (bad)





5.75 kg to groundwater after 6 months

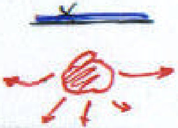


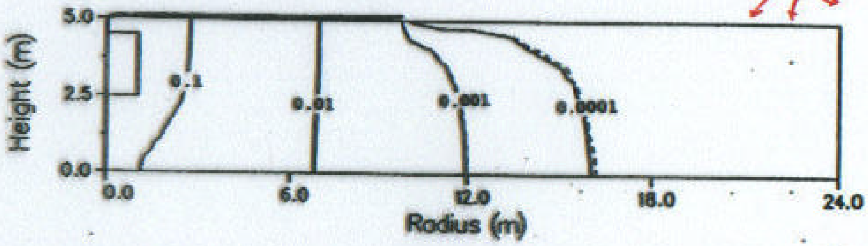
15.8 kg to groundwater after 1 year

Gaseous and Aqueous Transport

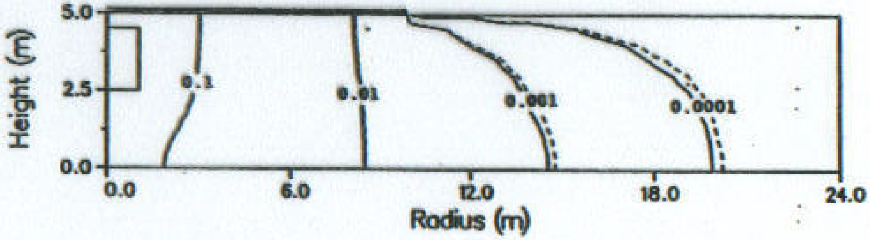
Example

- covered ground surface ∴ No infiltration
  - Decreased passive remediation (bad?)
  - Decreased infiltration (good).





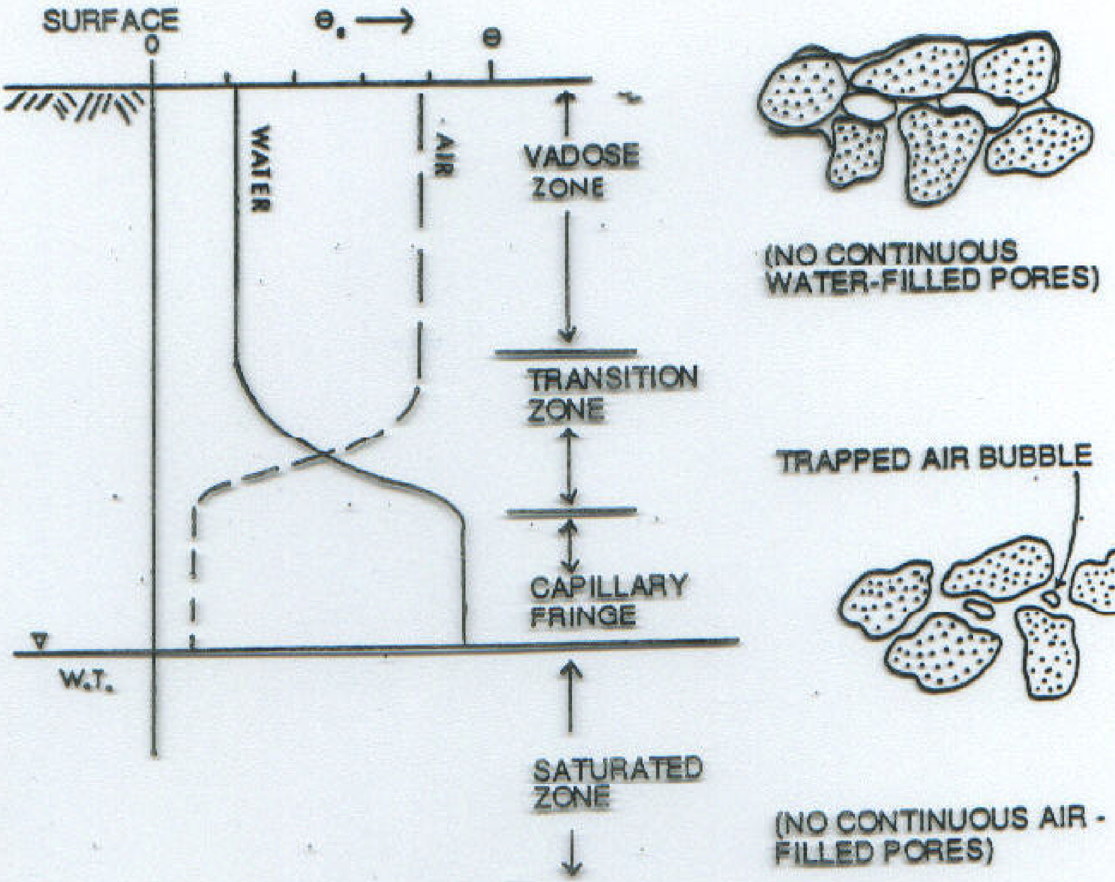
0.35 kg to groundwater after 6 months



2.95 kg to groundwater after 1 year

N. INFILTRATION

Watertable (Capillary Fringe) Boundary



- very slow vapour transport in transition zone

- top of fringe impermeable to vapours

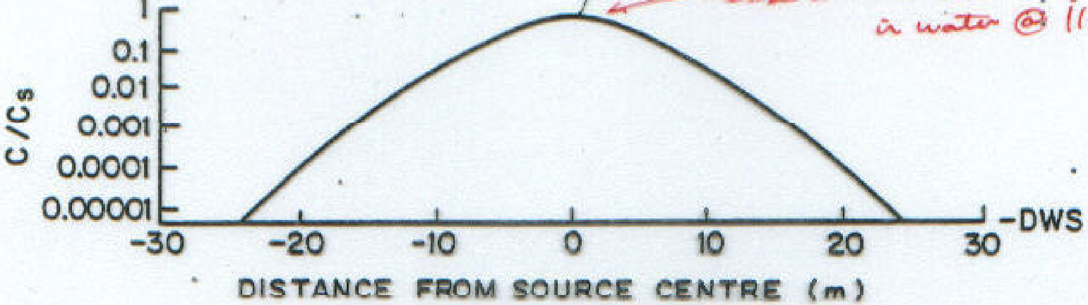
  but, contaminants partition to water

Watertable Fluctuation

- contaminated soil moisture placed in saturated zone

- consider diffusive transport example

watertable concentration profile
(covered; after 6 months)



Nearly sat. [illegible]

Close to max solubility in water @ 1100 mg/L.

- a 50 cm rise in watertable elevation

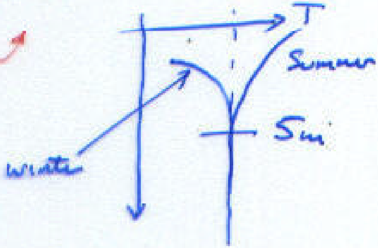
→ **3.3 kg TCE placed in groundwater**

This is an order of magnitude increase in water table loading – from 0.35 kg.

7.1.3 Gas-phase Advection

Gas-phase Advection

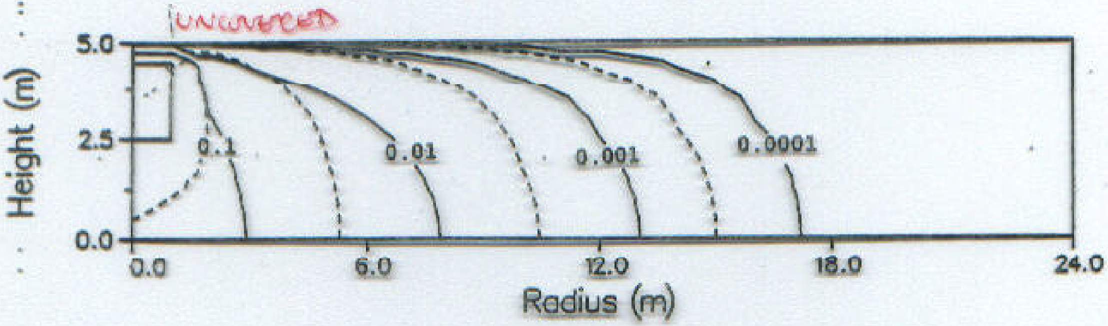
- driving forces include:
  - pressure gradients due to:
    - barometric pressure variation
    - water movement (Vadose zone)
    - vapourization at source
    - microbial activity
  - density gradients due to:
    - composition – Different proportions of compounds in gas mixture
    - temperature (convection cell)



Gas-phase Advection

Example

- advection due to compositional density
- medium-grained sand ($k^* = 10^{-11}\ m^2$)



- 13.8 kg to groundwater after 6 months

Compared to 5.7Kg after 6 months for uncovered.

6

Mathematical Models

[6:1] Mathematical Models

Overview

Example - Atlantic City

Finite differences

- Flow
- Advective transport

FLOW & TRANSPORT EQUATIONS

Multi dimensional flow and Transport equations all drop to a common form:

Flow: $S_s \dfrac{\partial h}{\partial t} = K \dfrac{\partial^2 h}{\partial x^2}$

Transport $R \dfrac{\partial c}{\partial t} = D \dfrac{\partial^2 c}{\partial x^2} - v_x \dfrac{\partial c}{\partial x}$

$$\left.\begin{array}{l} S_s \dfrac{\partial h}{\partial t} = K \dfrac{\partial^2 h}{\partial x^2} \\ R \dfrac{\partial c}{\partial t} = D \dfrac{\partial^2 c}{\partial x^2} - v_x \dfrac{\partial c}{\partial x} \end{array}\right\} R \frac{\partial \psi}{\partial t} = D \frac{\partial^2 \psi}{\partial x^2} - V \frac{\partial \psi}{\partial x}$$

System	Dependent variable, ψ	R $\frac{\partial \psi}{\partial t}$	D $\partial^2\psi/\partial x^2$	V $\partial\psi/\partial x$
Flow	h	S_s	K	0
Aqueous transport	C_w	$\left(1 + \frac{\rho_d}{\theta} K_d\right)$	$D_w^* + \alpha_L \lvert V \rvert$	advective V_w^a
Gas diffusion	C_g	$1 + \frac{\theta_w}{\theta_g}\frac{1}{H} + \frac{\rho_b}{\theta_g}\frac{K_d}{H}$	D_g^*	0
gas diffusion + aqueous transport	C_g	"	"	$\frac{\theta_w}{\theta_g} \cdot \frac{1}{H} V_w^a$

Correspondingly – any model that solves the "master" equation will represent all of these systems.

General Equation form:

$$R\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} + D\frac{\partial^2 c}{\partial y^2} - v_x\frac{\partial c}{\partial x} - v_y\frac{\partial c}{\partial y}$$

Transforms to:

$$\underbrace{R\int_V \underline{b}^T\underline{b}\,dV}_{\underline{S}}\,\dot{\underline{c}} + \underbrace{\int_V \underline{a}^T\underline{D}\,\underline{a}\,dV}_{\underline{K}_1}\,\underline{c} + \underbrace{\int_V \underline{b}^T\underline{v}\,\underline{a}\,dV}_{\underline{K}_2}\,\underline{c} = \underline{q}$$

Where: $\underline{b}$ = a matrix of shape functions $\qquad b = [b_1, b_2 \,..\, b_n]$

$\underline{a} = \begin{Bmatrix} \partial/\partial x \\ \partial/\partial y \end{Bmatrix}\underline{b}$ derivative of shape functions

$\underline{D}$ = Dispersion tensor or hydraulic conductivity

$\underline{c}$ = Concentration at nodal points

$\dot{\underline{c}} = \frac{\partial}{\partial t}\underline{c}$

$\underline{v}$ = vector of advective velocities, $\underline{v} = [v_x, v_y]$

q = Fluxes at prescribed boundaries (mass fluxes).

FINAL FORM

$$\underline{S}\,\dot{\underline{c}} + [\underline{K}_1 + \underline{K}_2]\,\underline{c} = q$$

Steady: $[K_1 + K_2]\,\underline{c} = \underline{q}$ Solve for $\underline{c}$ as linear system of equations.

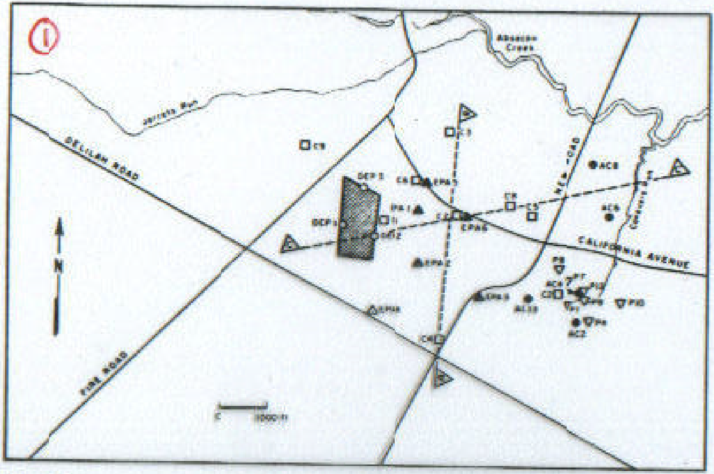


Figure 5.1.
Vicinity of Price Landfill (shaded region) with wells screened in upper zone of the Cohansey indicated (after Gray and Hoffman, 1983).

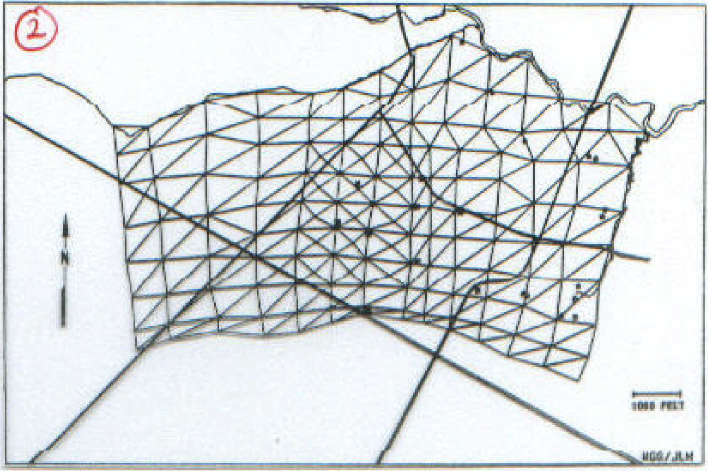


Figure 5.7.
Triangular finite element grid used in numerical simulation study (after Gray and Hoffman, 1983).

③

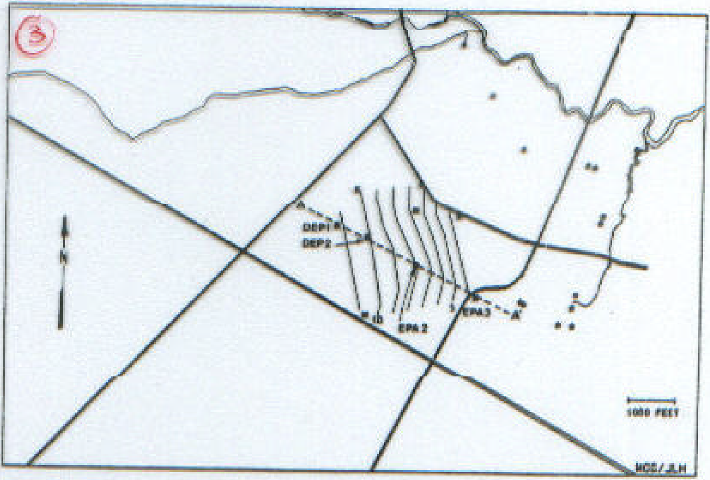
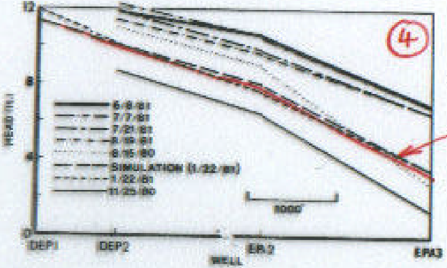


Figure 5.5.
Linearly interpolated water table contours for January 22, 1981 (elevations in feet above MSL) (after Gray and Hoffman, 1983).



④

Simulation fitted to data —
∴ K distribution.

Figure 5.6.
Measured and simulated head gradient along section *AA'* of Figure 5.5 (after Gray and Hoffman, 1983).

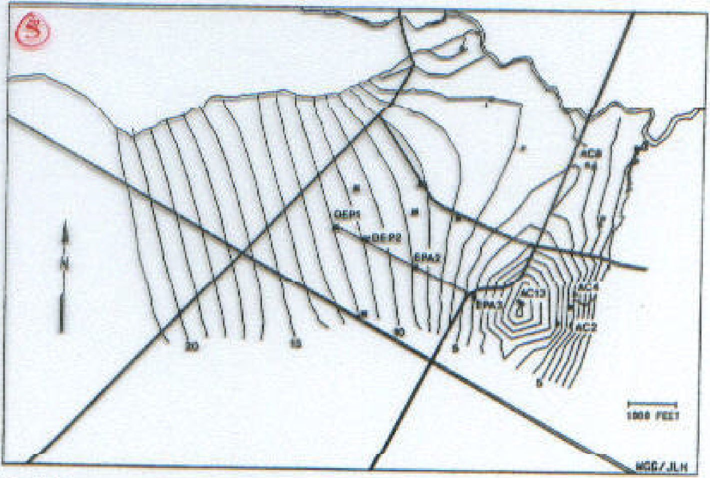


Figure 5.9.
Simulation of water table in the Upper Cohansey using average pumping rates of last ten years (after Gray and Hoffman, 1983).

Concentrations after pumping – No remedial measures

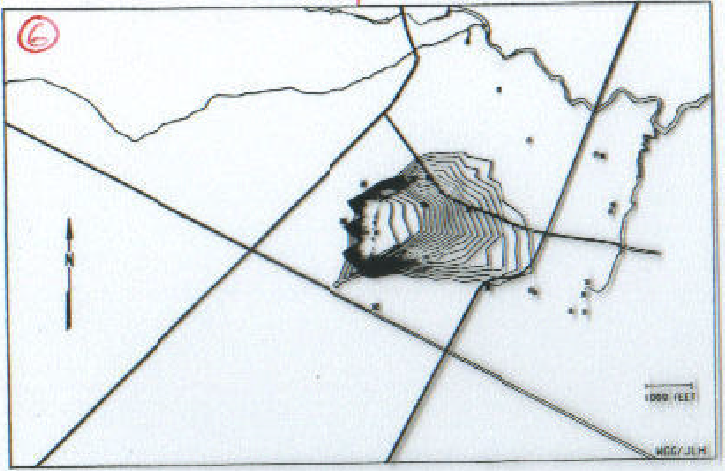


Figure 5.11.
Contaminant distribution after ten years using the head distribution of Figure 5.9 (after Gray and Hoffman, 1983).

Revised water table contours – interceptor wells

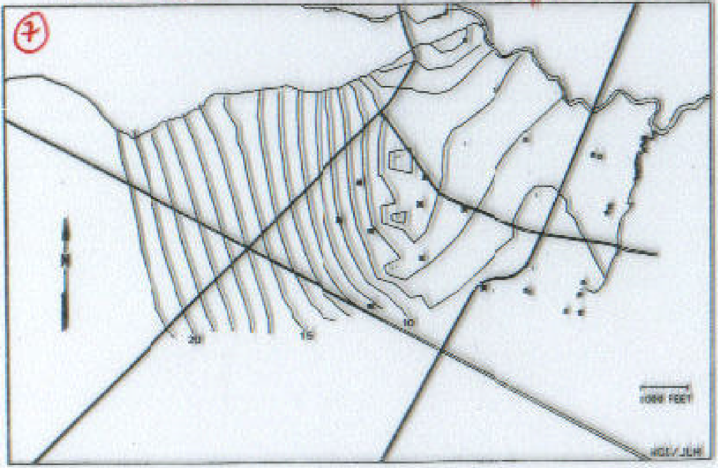


Figure 5.14.
Water-table contours for RS2 pumping 10 mgm from each well at "P" and injecting 2 mgm into each well at "I" (after Gray and Hoffman, 1983).

Concentration after 10 yr

⑧

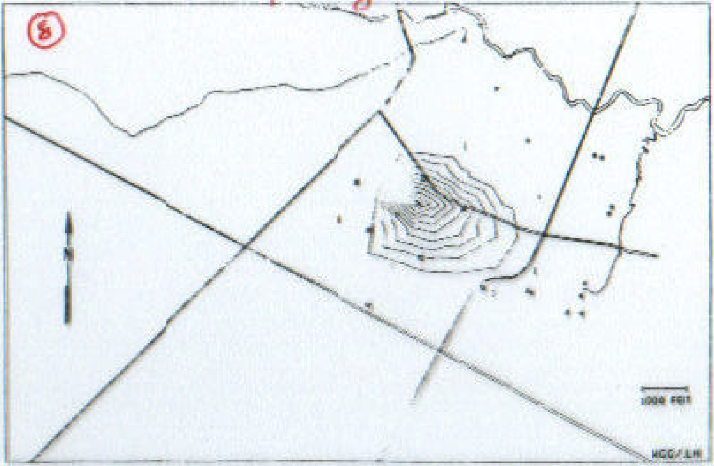


Figure 5.06.
Concentration distribution for R52 after ten years (after Gray and Hoffman, 1983)

Concentrations after 25 yr.

④

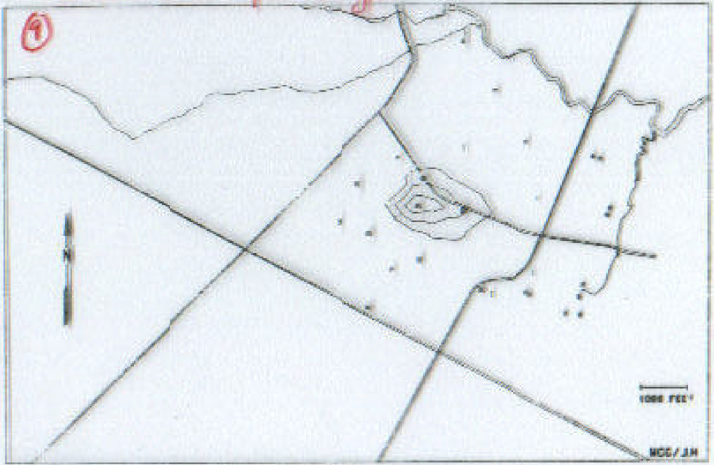
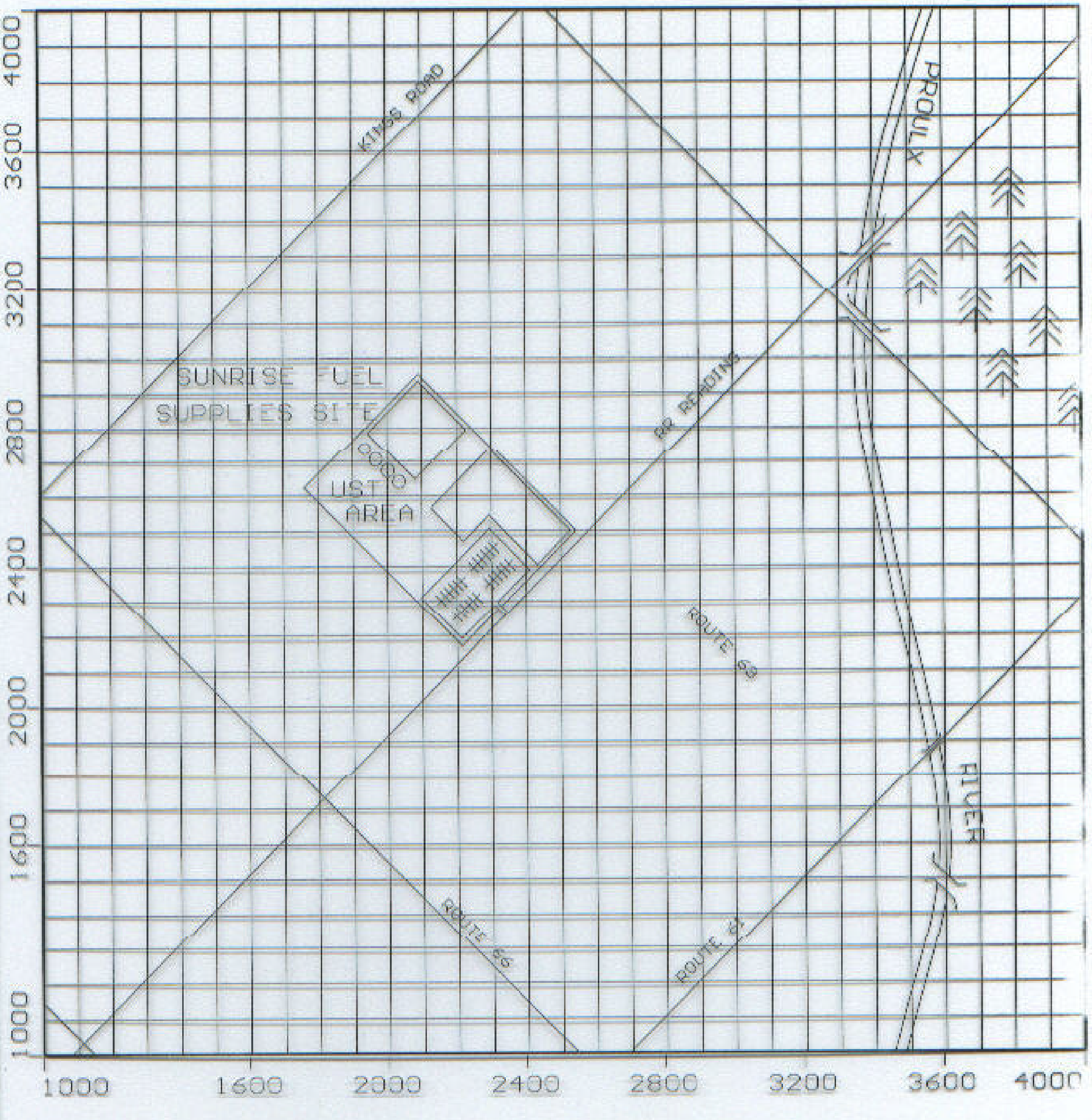


Figure 5.37.
Concentration distribution for RS2 after 25 years (after Gray and Hoffman, 1983)

[6:2] Mathematical Models

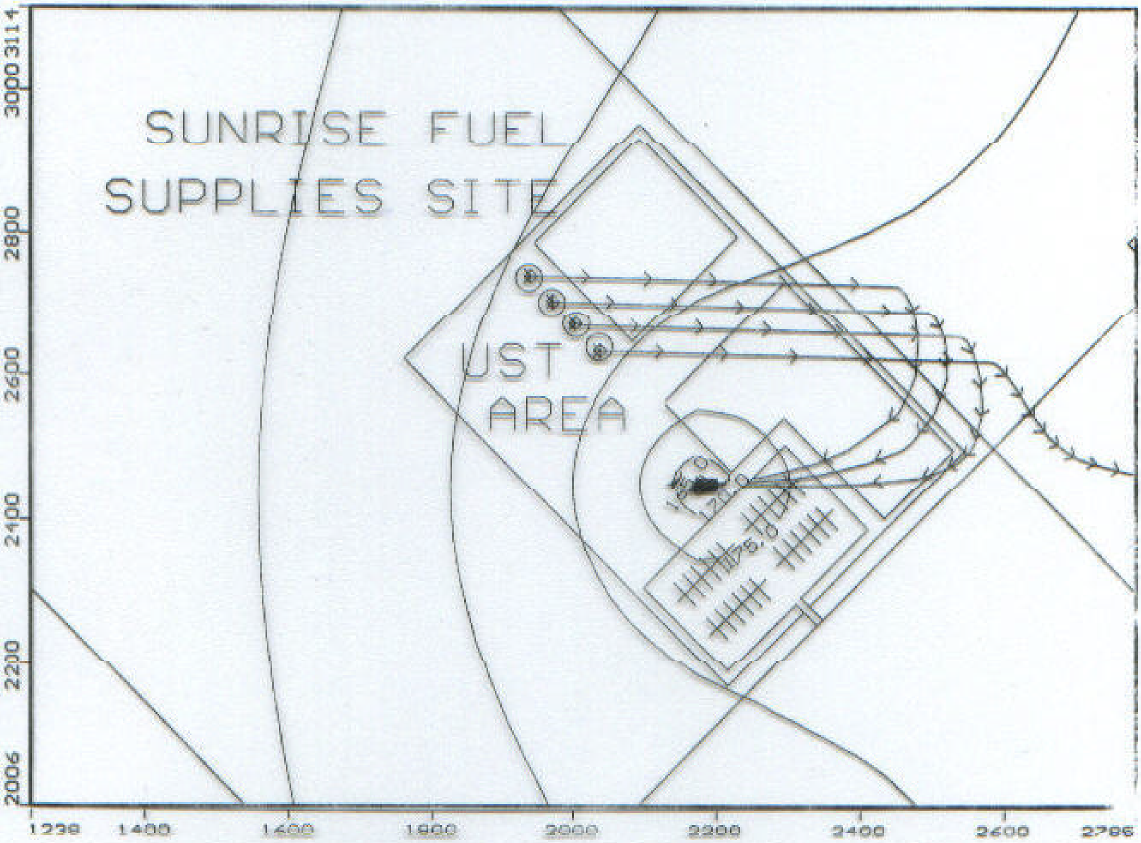
Software

- Flow - Visual Modflow
- Advective transp. – Modpath
- Advection-Dispersion - MT3D



Visual MODFLOW Student Version
30 Mar 99

Visual MODFLOW v.2.61, (C) 1995-1997
Waterloo Hydrogeologic, Inc.
NC: 30 NR: 30 NL: 1
Current Layer: 1



26 Mar 99

Visual MODFLOW v.2.61, (C) 1995-1997
Waterloo Hydrogeologic, Inc.
NC: 36 NR: 39 NL: 1
Current Layer: 1

7

Aquifer and Aquiclude Characterization

[7:1] Direct Investigation (Drilling and Instrumentation)

Drilling

Soil – Augering/Cable drilling/Tricone

Rock – Tricone/Diamond drilling

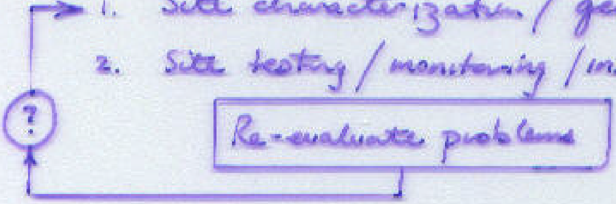
GROUNDWATER RESOURCE EVALUATION / CHARACTERIZATION

Require knowledge of geology and hydrogeology:

1. Evaluate quantities available for use: Domestic/industrial
2. Establish baseline characteristics (pre-mining).
3. Estimate potential for problems –
    - large inflows
    - water pressures & instability

Two phases

1. Site characterization / geological investigation
2. Site testing / monitoring / instrumentation

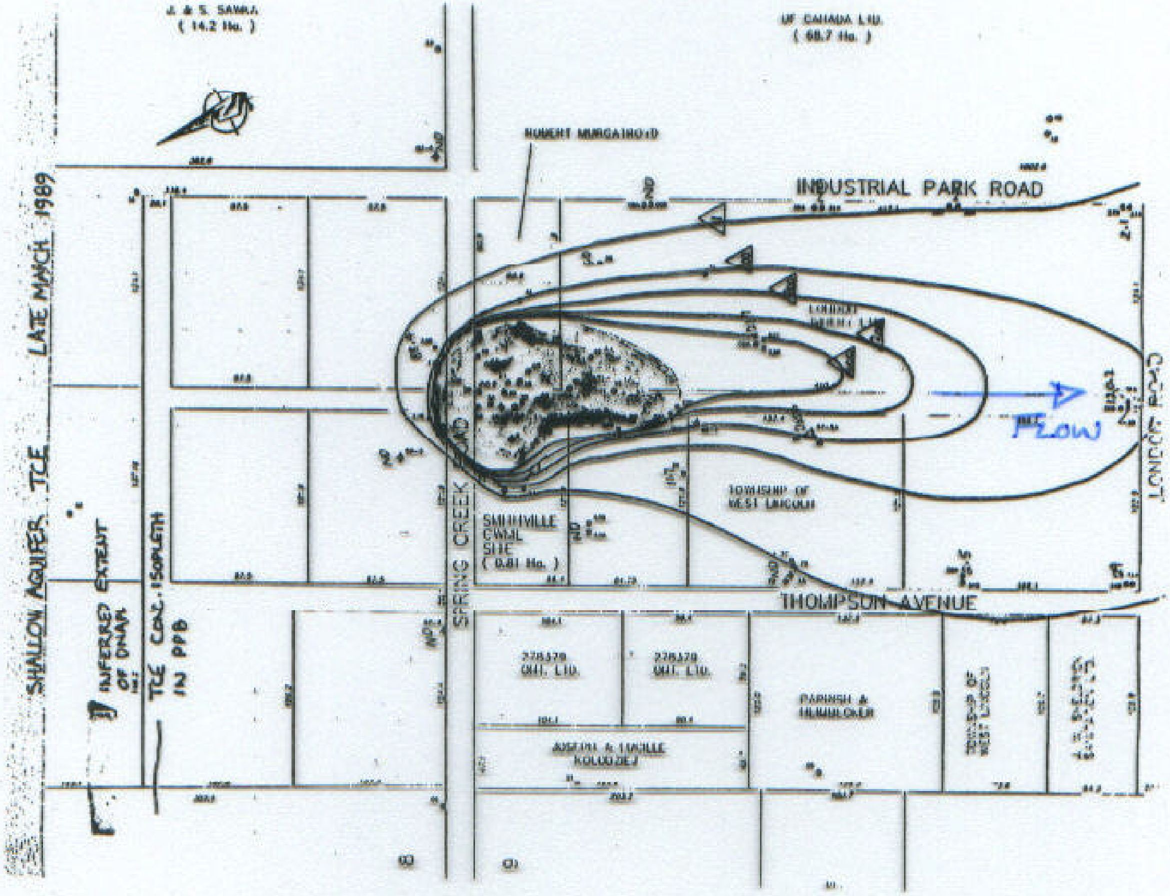


Site characterization

1. Existing materials search
2. Additional site data acquisition.

SITE EVALUATION

- Pre-purchase recon./evaluation (assumption of liability).
- Establishing baseline conditions.
- Projecting hydrologic behavior under proposed use.



TCE contours under transport.

Pre-contaminated site

Evaluate extent of contamination
Propose remediation program

} 1. plume extent
2. aquifer characteristics

INVESTIGATION PROCEDURE

Desk Study

- Previous reports – adjacent and current properties
  - confidentiality
  - public record reports (DER/EPA/Regulato
  - geological guides/maps. (USGS/PA Geol. S)

- Aerial photographs –
  - geology/surficial geology
  - seep locations/wetlands

  Stereo photos – 3-D and geology
  - Orthophotos (mosaics) c̄ contouring
  - Low angle lights/obliques
  - Invisible wavelength (infra red).

Field Mapping

- Verify results from air mapping
- Sampling for analysis and material characterization
  - confirm/determine materials

INVESTIGATION PROCEDURES (Continued).

Methods of detailed investigation

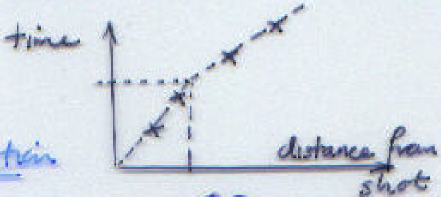
- ▫ <u>Indirect</u> (non-intrusive/non-destructive)
- ▫ <u>Direct</u> (intrusive . . . .).

Require to determine 'geology' or 'hydrogeology'.

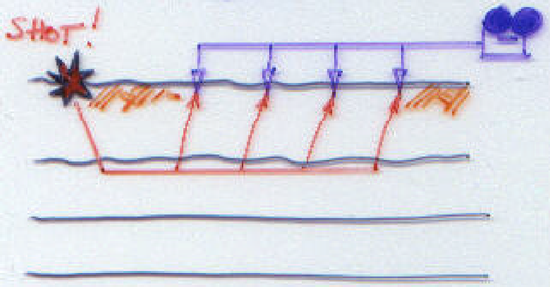
INDIRECT

Geophysical methods to 'see' inside porous media. Detect geological boundaries <u>but</u> also define changing saturation boundaries.

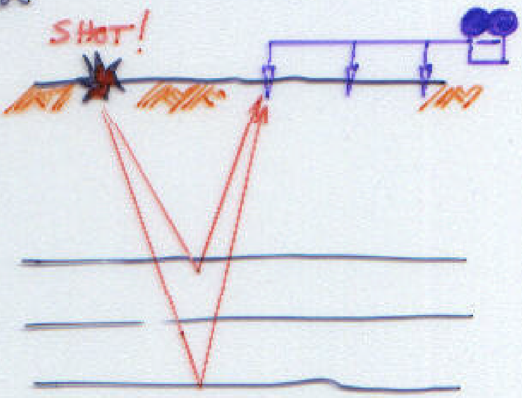
SEISMIC METHODS



Seismic <u>refraction</u>



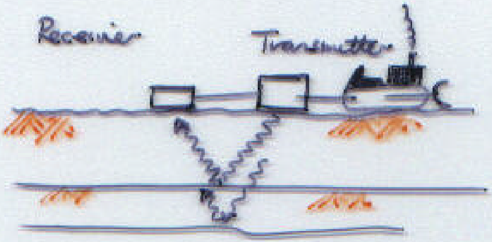
Seismic <u>reflection</u>



1. Problems in defining layers/strata in complex geology
2. Recognizes 'seismic' differences in materials and not necassarily 'hydrologic' defferences
3. Influenced by water levels (influences seismic vel)
4. Correlation with boreholes.

INVESTIGATION PROCEDURES (Continued)

GPR (Ground Penetrating Radar)



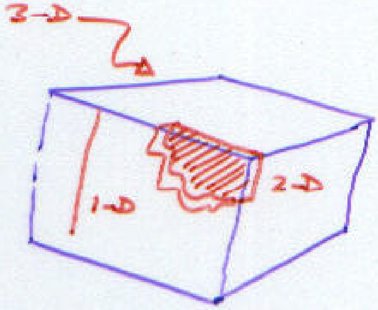
- ☐ E-M radiation @ 10-100 MHz
- ☐ Controlled by dielectric constant
- ☐ Measure arrival times/transmission strength

Picks-up interfaces of dielectric constants.
Very sensitive to saturation and saturant

Plume evolution studies using geophysical methods.

INVESTIGATION PROCEDURES (Continued).

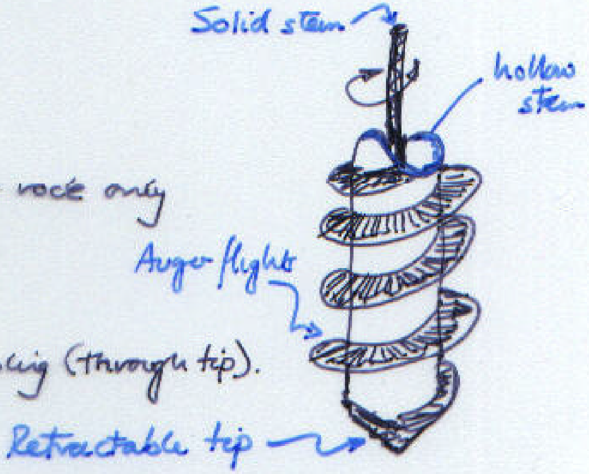
DIRECT METHODS



- 1-D Drilling and adits
  2-D Trenching with backhoe
  3-D Geophysical

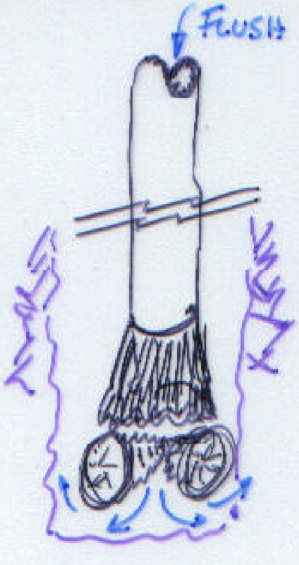
Drilling Methods

Auger boring



- Soils and v. soft rock only
- No casing needed
- Fast
- Undisturbed sampling (through tip).

Air or Water Flush Boring

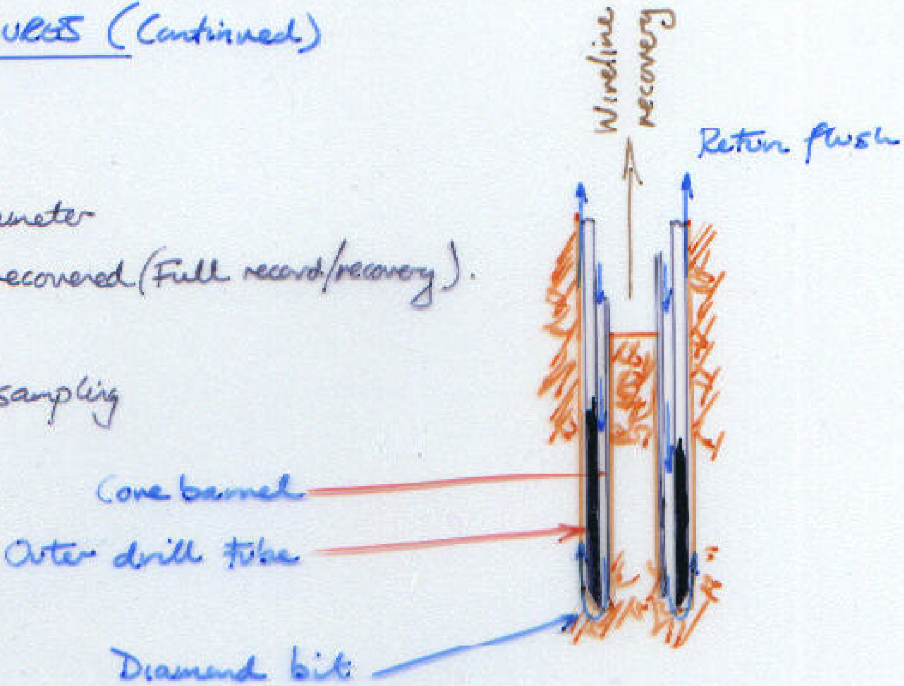


- Tricone bit
- Air / water flush – fluid losses → formation
- Casing or mud supported hole
- Soil and rock boring
- Soil testing and sampling – retract line
- No sample recovered.

INVESTIGATION PROCEDURES (Continued)

Diamond Drilling

- □ Small diameter
- □ Samples recovered (Full record/recovery).
- □ Slow
- □ Wireline sampling



RESULTING HOLES USED TO MAX EXTENT — INSTRUMENTATION

$10/ft. diamond drill (1993).

Table 1. Advantages and Disadvantages of Auger, Rotary, and Cable Tool Drilling

Type	Advantages	Disadvantages
Auger	• Minimal damage to aquifer • No drilling fluids required • Auger flights act as temporary casing, stabilizing hole for well construction • Good technique for unconsolidated deposits • Continuous core can be collected by wire-line method	• Cannot be used in consolidated deposits • Limited to wells less than 150 ft in depth • May have to abandon holes if boulders are encountered
Rotary	• Quick and efficient method • Excellent for large and small diameter holes • No depth limitations • Can be used in consolidated and unconsolidated deposits • Continuous core can be collected by wire-line method	• Requires drilling fluids, which alter water chemistry • Results in a mud cake on the borehole wall, requiring additional well development, and potentially causing changes in chemistry • Loss of circulation can develop in fractured and high-permeability material • May have to abandon holes if boulders are encountered
Cable Tool	• No limitation on well depth • Limited amount of drilling fluid required • Can be used in both consolidated and unconsolidated deposits • Can be used in areas where lost circulation is a problem • Good lithologic control • Effective technique in boulder environments	• Limited rigs and experienced personnel available • Slow and inefficient • Dificult to collect core

Source: EPA (1989).

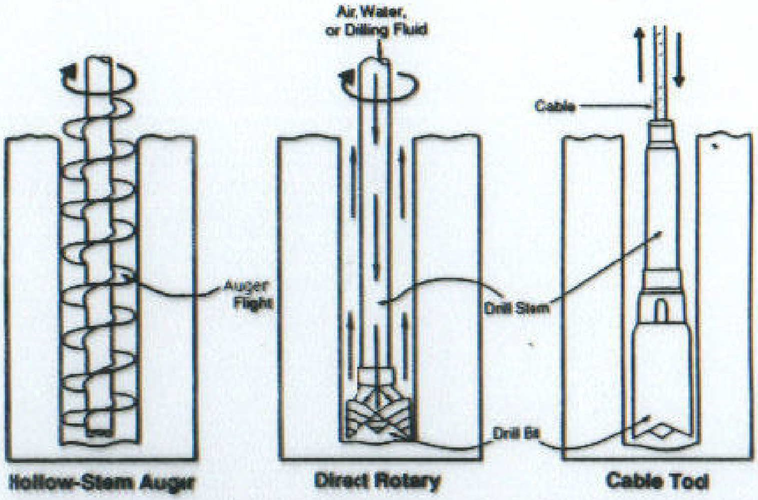


Figure 2. Illustration and advantages and disadvantages of auger, rotary, and cable tool drilling. *Source:* EPA (1989).

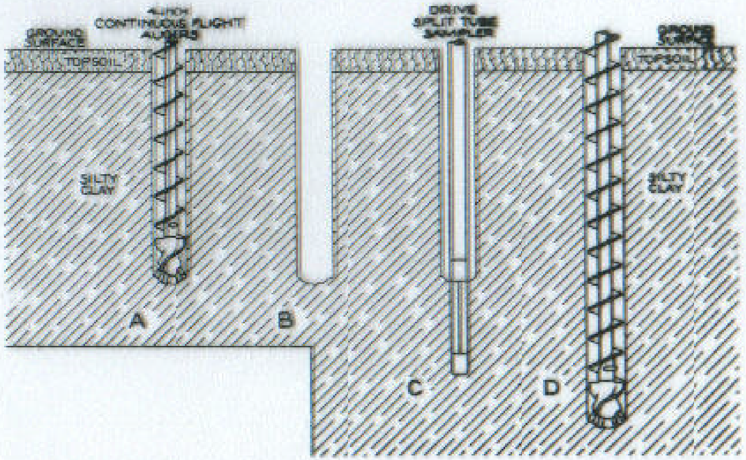


Figure 3. Continuous flight auger drilling. A. Advance auger to sampling inerval; B. Remove flight augers; C. Advance split-spoon sampler; D. Advance auger to next sample interval. *Source:* University of Missouri, Rolla (1981).

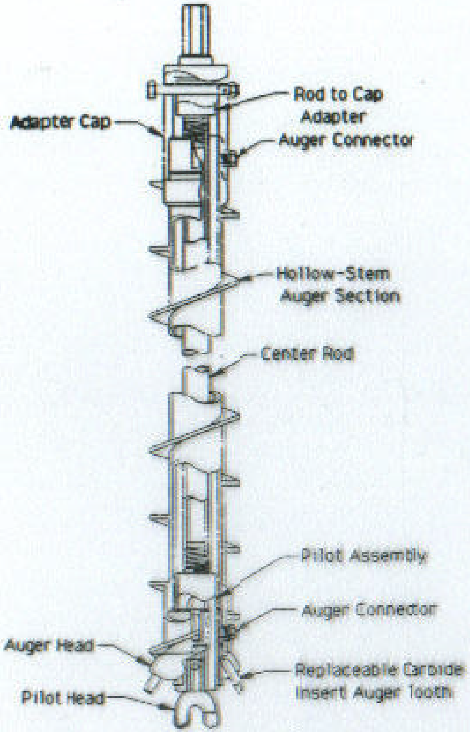


Figure 5. Components of a consolidated mining equipment hollow-stem auger. *Source:* University of Missouri, Rolla (1981).

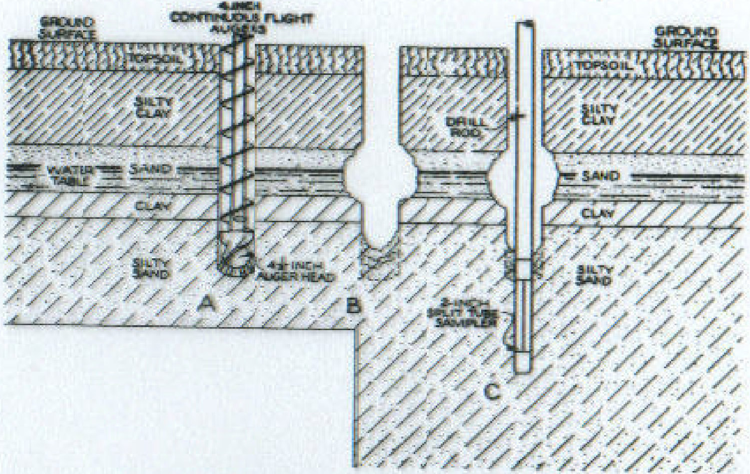


Figure 4. Continuous flight auger drilling though caving material. A. Auger to sample interval; B. Saturated sand stratum flows causing borehole to "bell"; C. Sampler must advance through sand "flow" slough to sample in-placesilty sand. *Source:* University of Missouri, Rolla (1981).

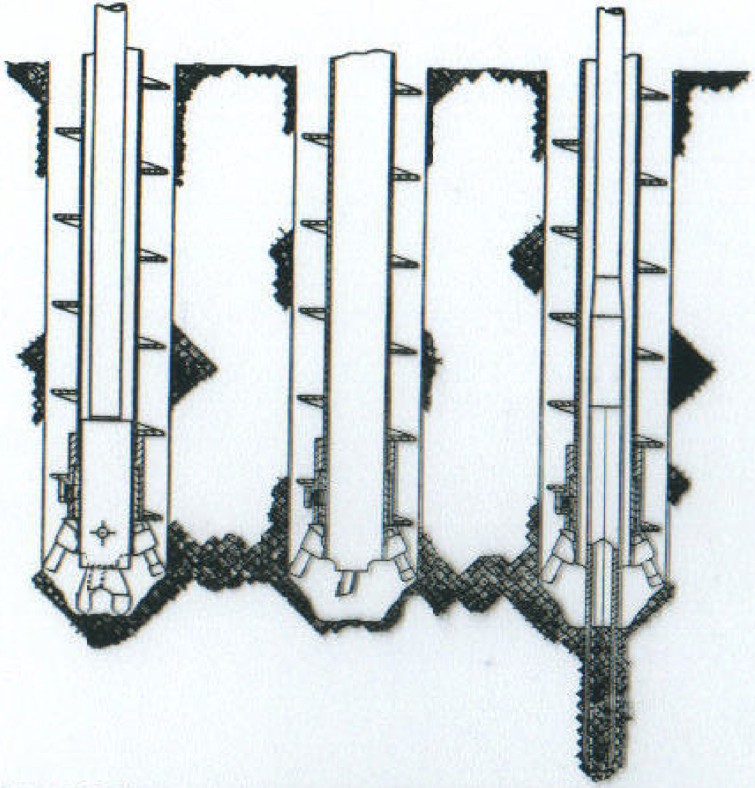


Figure 6. Driving a soil sampler through the hollow-stem auger. *Source:* University of Missouri, Rolla (1981).

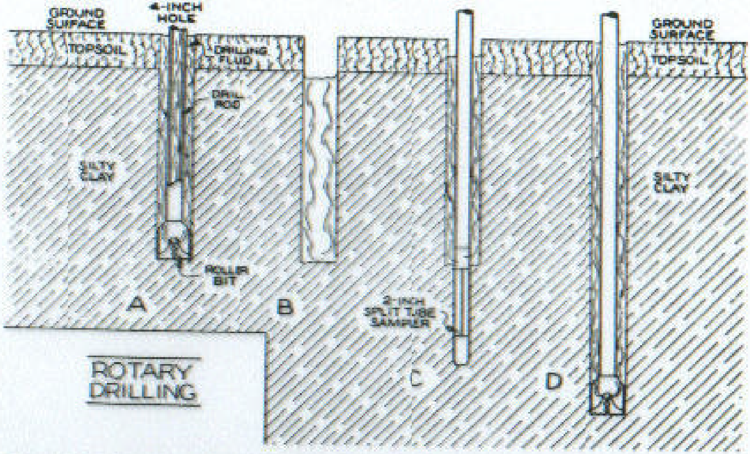


Figure 7. Rotary drilling. A. Mud rotary driling advance to sampler interval; B. Drilling mud holds borehole walls up; C. Split-spoon sampler advanced; D. New drill rod attached and borehole advanced. *Source:* University of Missouri, Rolla (1981).

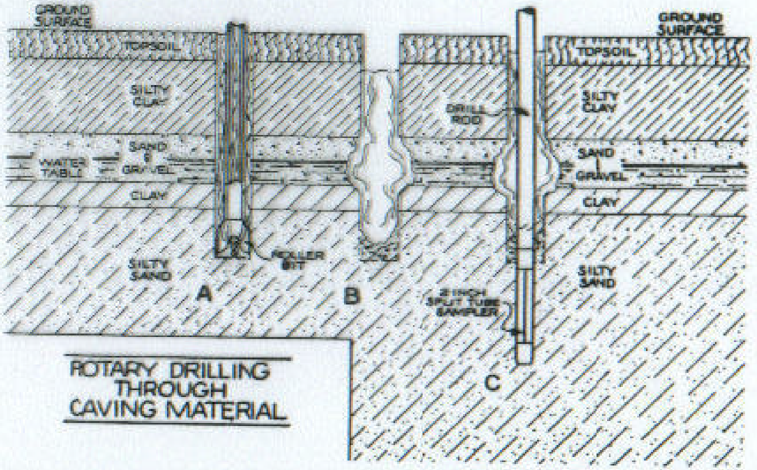
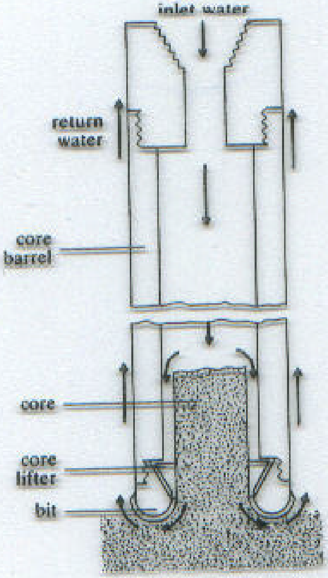


Figure 8. Rotary drilling through caving material. A. Rotary drilling advances borehole to below water table; B. Drilling mud holes borehole walls open to minimize "flow" and caving; C. Split spoon advanced at desired sample depth. *Source:* Unversity of Missouri, Rolla (1981).


inlet water
return water
core barrel
core
core lifter
bit

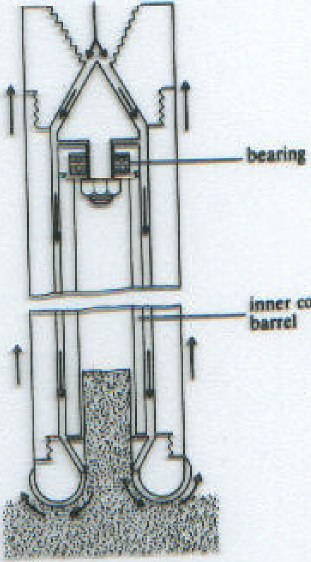

bearing
inner core barrel

Table 9-3. Drilling methods, applications, and limitations (modified from Aller et al., 1989; GRI, 1987; Rehm et al., 1985; USEPA, 1987).

METHOD	APPLICATIONS/ADVANTAGES	LIMITATIONS
HAND AUGERS – A hand auger is advanced by turning it into the soil until the bucket or screw is filled. The auger is then removed from the hole. The sample is dislodged from the auger, and drilling continues. Motorized units are also available.	• Shallow soil investigations (0 to 15 ft) • Soil samples collected from the auger cutting edge • Water-bearing zone identification • Contamination presence examination; sample analysis • Shallow, small diameter well installation • Experienced user can identify stratigraphic interfaces by penetration resistance differences as well as sample inspection • Highly mobile, and can be used in confined spaces • Various types (i.e., bucket, screw, etc.) and sizes (typically 1 to 9 inches in diameter) • Inexpensive to purchase	• Limited to very shallow depths (typically < 15 ft) • Unable to penetrate extremely dense or rocky or gravelly soil • Borehole stability may be difficult to maintain, particularly beneath the water table • Potential for vertical cross-contamination • Labor intensive
SOLID-FLIGHT AUGERS – A cutter head (≥ 2-inch diameter) is attached to multiple auger flights. As the augers are rotated by a rotary drive head and forced down by either a hydraulic pulldown or a feed device, cuttings are rotated up to ground surface by moving along the continuous flighting.	• Shallow soils investigations (< 100 ft) • Soil samples are collected from the auger flights or using split-spoon or thin-walled samplers if the hole will not cave upon retrieval of the augers • Vadose zone monitoring wells • Monitor wells in saturated, stable soils • Identification of depth to bedrock • Fast and mobile; can be used with small rigs • Holes up to 3-ft diameter • No fluids required • Simple to decontaminate	• Low-quality soil samples unless split-spoon or thin-wall samples are taken • Soil sample data limited to areas and depths where stable soils are predominant • Unable to install monitor wells in most unconsolidated aquifers because of borehole caving upon auger removal • Difficult penetration in loose boulders, cobbles, and other material that might lock up auger • Monitor well diameter limited by auger diameter • Cannot penetrate consolidated materials • Potential for vertical cross-contamination
HOLLOW-STEM AUGERS – Hollow-stem augering is done in a similar manner to solid-flight augering. Small-diameter drill rods and samplers can be lowered through the hollow augers for sampling. If necessary, sediment within the hollow stem can be cleaned out prior to inserting a sampler. Wells can be completed below the water table using the augers as temporary casing.	• All types of soil investigations to <100 ft below ground • Permits high-quality soil sampling with split-spoon or thin-wall samplers • Water-quality sampling • Monitor well installation in all unconsolidated formation • Can serve as a temporary casing for coring rock • Can be used in stable formations to set surface casing • Can be used with small rigs in confined spaces • Does not require drilling fluids	• Difficulty in preserving sample integrity in heaving (running sand) formations • If water or drilling mud is used to control heaving will invade the formation • Potential for cross-contamination of aquifers where annular space not positively controlled by water or drilling mud or surface casing • Limited auger diameter limits casing size (typical augers are: 6¼-in OD with 3¼-in ID, and 12-in OD with 6-in ID) • Smearing of clays may seal off interval to be monitored

Table 9-3. Drilling methods, applications, and limitations (modified from Aller et al., 1989; GRI, 1987; Rehm et al., 1985; USEPA, 1987).

METHOD	APPLICATIONS/ADVANTAGES	LIMITATIONS
DIRECT MUD ROTARY – Drilling fluid is pumped down the drill rods and through a bit attached to the bottom of the rods. The fluid circulates up the annular space bringing cuttings to the surface. At the surface, drilling fluid and cuttings are discharged into a baffled sedimentation tank, pond, or pit. The tank effluent overflows into a suction pit where drilling fluid is recirculated back through the drill rods. The drill stem is rotated at the surface by top head or rotary table drives and down pressure is provided by pull-down devices or drill collars.	• Rapid drilling of clay, silt, and reasonably compacted sand and gravel to great depth (>700 ft) • Allows split-spoon and thin-wall sampling in unconsolidated materials • Allows drilling and core-sampling in consolidated rock • Abundant and flexible range of tool sizes and depth capabilities • Sophisticated drilling and mud programs available • Geophysical borehole logs	• Difficult to remove drilling mud and wall cake from outer perimeter of filter pack during development • Bentonite or other drilling fluid additives may influence quality of ground-water samples • Potential for vertical cross-contamination • Circulated cutting samples are of poor quality; difficult to determine sample depth • Split-spoon and thin-wall samplers are expensive and of questionable cost effectiveness at depths > 150 ft • Wireline coring techniques for sampling both unconsolidated and consolidated formations often not available locally • Drilling fluid invasion of permeable zones may compromise integrity of subsequent monitor well samples • Difficult to decontaminate pumps
AIR ROTARY – Air rotary drilling is similar to mud rotary drilling except that air is the circulation medium. Compressed air injected through the drill rods circulates cuttings and groundwater up the annulus to the surface. Typically, rotary drill bits are used in sedimentary rocks and down-hole hammer bits are used in harder igneous and metamorphic rocks. Monitor wells can be completed as open hole intervals beneath telescoped casings.	• Rapid drilling of semi-consolidated and consolidated rock to great depth (>700 ft) • Good quality/reliable formation samples (particularly if small quantities of drilling fluid are used) because casing prevents mixture of cuttings from bottom of hole with collapsed material from above • Allows for core-sampling of rock • Equipment generally available • Allows easy and quick identification of lithologic changes • Allows identification of most water-bearing zones • Allows estimation of yields in strong water-producing zones with short "down time"	• Surface casing frequently required to protect top of hole from caving • Drilling restricted to semi-consolidated and consolidated formations • Samples reliable, but occur as small chips that may be difficult to interpret • Drying effect of air may mask lower yield water producing zones • Air stream requires contaminant filtration • Air may modify chemical or biological conditions; recovery time is uncertain • Potential for vertical cross-contamination • Potential exists for hydrocarbon contamination from air compressor or down-hole hammer bit oils
AIR ROTARY WITH CASING DRIVER – This method uses a casing driver to allow air rotary drilling through unstable unconsolidated materials. Typically, the drill bit is extended 6 to 12 inches ahead of the casing, the casing is driven down, and then the drill bit is used to clean material from within the casing.	• Rapid drilling of unconsolidated sands, silts, and clays • Drilling in alluvial material (including boulder formations) • Casing supports borehole, thereby maintaining borehole integrity and reducing potential for vertical cross-contamination • Eliminates circulation problems common with direct mud rotary method • Good formation samples because casing (outer wall) prevents mixture of caving materials with cuttings from bottom of hole • Minimal formation damage as casing pulled back (smearing of silts and clays can be anticipated)	• Thin, low pressure water-bearing zones easily overlooked if drilling not stopped at appropriate places to observe whether or not water levels are recovering • Samples pulverized as in all rotary drilling • Air may modify chemical or biological conditions; recovery time is uncertain

Table 9-3. Drilling methods, applications, and limitations (modified from Aller et al., 1989; GRI, 1987; Rehm et al., 1985; USEPA, 1987).

METHOD	APPLICATIONS/ADVANTAGES	LIMITATIONS
DUAL-WALL REVERSE ROTARY – Circulating fluid (air or water) is injected through the annulus between the outer casing and drill pipe, flows into the drill pipe through the bit, and carries cuttings to the surface through the drill pipe. Similar to rotary drilling with the casing driver, the outer pipe stabilizes the borehole and reduces cross-contamination of fluids and cuttings. Various bits can be used with this method.	• Very rapid drilling through both unconsolidated and consolidated formations • Allows continuous sampling in all types of formations • Very good representative samples can be obtained with reduced risk of contamination of sample and/or water-bearing zone • Allows for rock coring • In stable formations, wells with diameters as large as 6 inches can be installed in open hole completions	• Limited borehole size that limits diameter of monitor wells • In unstable formations, well diameters are limited to approximately 4 inches • Equipment available more common in the southwest U.S. than elsewhere • Air may modify chemical or biological conditions; recovery time is uncertain • Unable to install filter pack unless completed open hole
CABLE TOOL DRILLING – A drill bit is attached to the bottom of a weighted drill stem that is attached to a cable. The cable and drill stem are suspended from the drill rig mast. The bit is alternatively raised and lowered into the formation. Cuttings are periodically removed using a bailer. Casing must be added as drilling proceeds through unstable formations.	• Drilling in all types of geologic formations • Almost any depth and diameter range • Ease of monitor well installation • Ease and practicality of well development • Excellent samples of coarse-grained media can be obtained • Potential for vertical cross-contamination is reduced because casing is advanced with boring • Simple equipment and operation	• Drilling is slow, and frequently not cost-effective as a result • Heaving of unconsolidated materials must be controlled • Equipment availability more common in central, north central, and northeast sections of the U.S.
ROCK CORING – A carbide or diamond-tipped bit is attached to the bottom of a hollow core barrel. As the bit cuts deeper, the rock sample moves up into the core tube. With a double-wall core barrel, drilling fluid circulates between the two walls and does not contact the core, allowing better recovery. Clean water is usually the drilling fluid. Standard core tubes are attached to the bottom of a drill rod and the entire string of rods must be removed after each core run. With wireline coring, an inner core barrel is withdrawn through the drill string using an overshot device that is lowered on a wireline into the drill string.	• Provides high-quality, undisturbed core samples of stiff to hard clays and rock • Holes can be drilled at any angle • Can detect location and nature of rock fractures • Can use core holes to run a complete suite of geophysical logs • Variety of core sizes available • Core holes can be utilized for hydraulic tests and monitor well completion • Can be adapted to a variety of drill rig types and operations	• Relatively expensive and slow rate of penetration • Can lose a large quantity of drilling water into permeable formations • Potential for vertical cross-contamination

Table 9-3. Drilling methods, applications, and limitations (modified from Aller et al., 1989; GRI, 1987; Rehm et al., 1985; USEPA, 1987).

METHOD	APPLICATIONS/ADVANTAGES	LIMITATIONS
CONE PENETROMETER -- Hydraulic rams are used to push a narrow rod (e.g., 1.5-inch diameter) with a conical point into the ground at a steady rate. Electronic sensors attached to the test probe measure tip penetration resistance, probe side resistance, inclination and pore pressure. Sensors have also been developed to measure subsurface electrical conductivity, radioactivity, and optical properties (fluorescence and reflectance). Cone penetrometer tests (CPT) are generally performed using a special rig and a computerized data collection, analysis, and display system. To facilitate interpretation of CPT data from numerous tests, CPT data from at least one test per site should be compared to a log of continuously sampled soil at an adjacent location. Reference: Robertson and Campanella (1986), Lurk et al. (1990), Smolley and Kappmeyer (1991), Christy and Spradlin (1992), Edge and Cordry (1989), and, Chiang et al. (1992).	• Efficient tool for stratigraphic logging of soft soils • Measurement of some soil/fluid properties (e.g., tip penetration resistance, probe side friction, pore pressure, electrical conductivity, radioactivity, fluorescence), with proper instrumentation, can be obtained continuously rather than at intervals; thus improving the detectability of thin layers (i.e., subtle DNAPL capillary barriers) and contaminants • There are virtually no cuttings brought to the ground surface, thus eliminating the need to handle cuttings • Process presents a reduced potential for vertical cross-contamination if the openings are sealed with grout from the bottom up upon rod removal • Porous probe samplers can be used to collect groundwater samples with minimal loss of volatile compounds • Soil gas sampling can be conducted • Fluid sampling from discrete intervals can be conducted using special tools (e.g., the Hydropunch™ manufactured by Q.E.D. Environmental Systems of Ann Arbor, Michigan)	• Unable to penetrate dense geologic conditions (i.e., hard clays, boulders, etc.) • Limited depth capability (depends on • Soil samples cannot be collected for examination or chemical analyses, unless special equipment is utilized • Only very limited quantities of groundwater can be sampled • Limited well construction capability • Limited availability

Table 1. Well-Drilling Selection Guide

Drilling Method	Drilling Fluid	Casing Advance	Type of Material Drilled	Nominal Drilling Depth, in ft 1_/	Nominal Range of Borehole Sizes, in in.	Samples Obtainable 2_/	Coring Possible	Reference Section
Power Auger (Hollow Stem)	None, Water, Mud	Yes	Soil, Weathered rock	<150	5 - 22	S, F	Yes	6.2
Power Auger (Solid Stem)	Water, Mud	No	Soil, Weathered Rock	<150	2-10	s	Yes	6.3
Power Bucket Auger	None, Water (below water table	No	Soil, Weathered rock	<150	18 -48	S	Yes	6.4
Hand Auger	None	No	Soil	<70 (Above Water Table Only)	2 - 6	S	Yes	6.5
Direct Fluid Rotary	Water, Mud	Yes	Soil, Rock	>1000	2 - 36	S, R	Yes	7.3
Direct Air Rotary	Air, Water, Foam	Yes	Soil, Rock	>1500	2 - 36	S, R, F	Yes	7.4
DTH Hammer	Air, Water, Foam	Yes	Rock, Boulders	<2000	4 - 16	R	Yes	7.5.1
Wireline	Air, Water, Foam	Yes	Soil, Rock	>1000	3-6	S, R, F	Yes	7.6
Reverse Fluid Rotary	Water, Mud	Yes	Soil, Rock	<2000	12 - 36	S, R, F	Yes	7.8
Reverse Air Rotary	Air, Water, Foam	Yes	Soil, Rock	>1000	12 - 36	S, R, F	Yes	7.7
Cable Tool	Water	Yes	Soil, Rock	<5000	6-8	S, R, F (F- Below Water Table)	Yes	8
Casing-Advancer	Air, Water, Mud	Yes	Soil, Rock, Boulders	<2000	2 -16	S, R, F	Yes	9
Direct-Push Technology	None	Yes	Soil	<100	1.5 - 3	F	Yes	10
Sonic (Vibratory)	None, Water, Mud, Air	Yes	Soil, Rock, Boulders	<500	4 -12	S, R, F	Yes	11
Jet Percussion	Water	No	Soil	<50	2 - 4	S	No	12
Jetting	Water	Yes	Soil	<50	4	S	No	12

1/ Actual achievable drilled depths will vary depending on the ambient geohydrologic conditions existing at the site and size of drilling equipment used. For example, large, high-torque rigs can drill to greater depths than their smaller counterparts under favorable site conditions. Boreholes drilled using air/air foam can reach greater depths more efficiently using two-stage positive-displacement compressors having the capability of developing working pressures of 250 to 350 psi and 500 to 750 cfm (particularly when submergence requires higher pressures). The smaller rotary-type compressors are only capable of producing a maximum working pressure of 125 psi. and produce 500 to 1200 cfm. Likewise, the rig mast must be constructed to safely carry the anticipated working loads expected. To allow for contigencies, it is recommended that the rated capacity of the mast be at least twice the anticipated weight load or normal pulling load. 2/ Soil = S (Cuttings), Rock = R (Cuttings), Fluid = F (Some samples might require accessory sampling devices to obtain.)

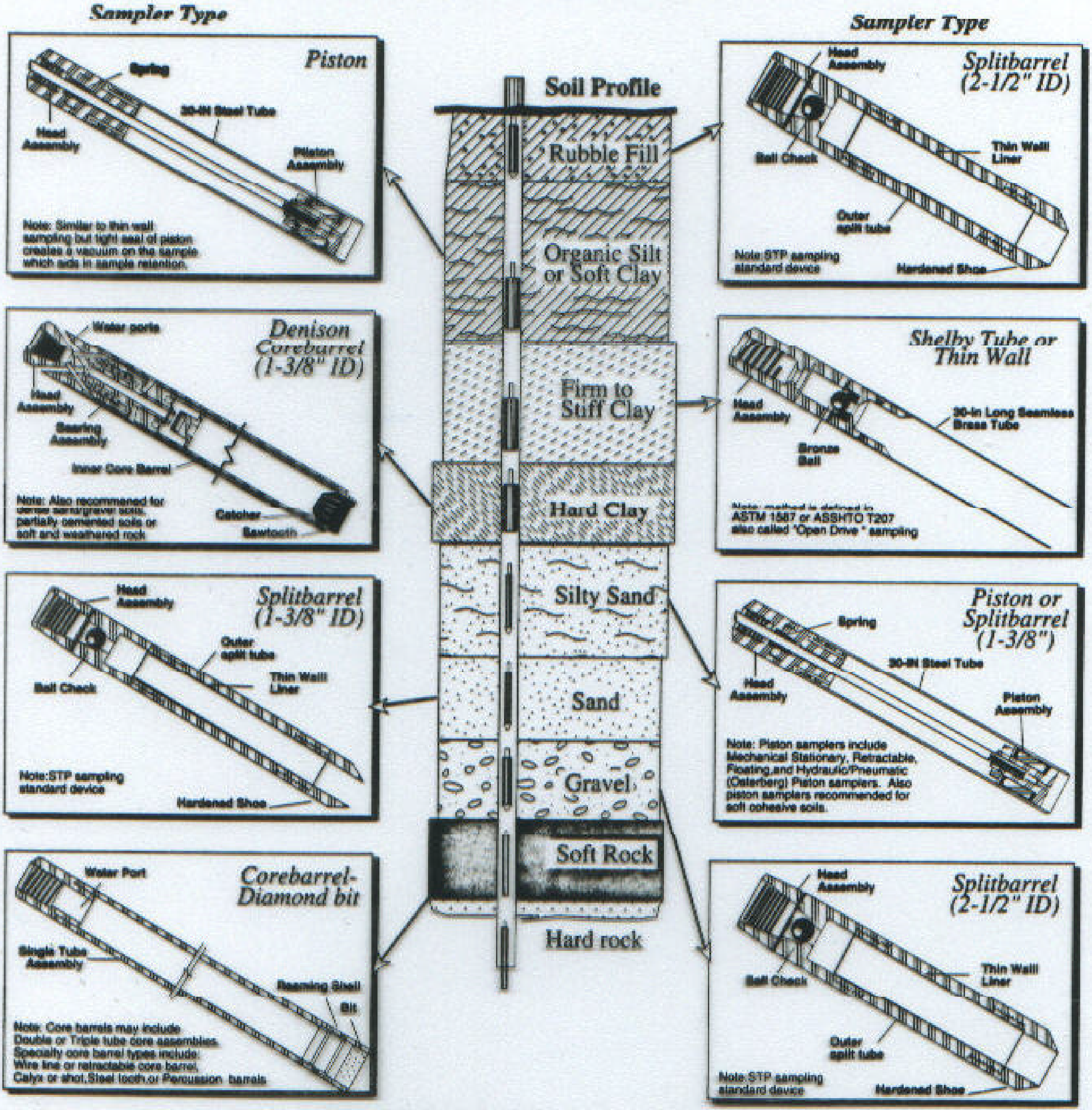
[7:2] Direct Investigation (Drilling and Instrumentation)

Sampling – Soil and Rock

Instrumentation – piezometers/packers

Continuous profiling (soil)

COMMON SAMPLING TOOLS FOR SOIL AND ROCK



Note: Similar to thin wall sampling but tight seal of piston creates a vacuum on the sample which aids in sample retention.

Note: Also recommaned for dense sand/gravel soils, partially cemented soils or soft and weathered rock

Note:STP sampling standard device

Note: Core barrels may include Double or Triple tube core assemblies. Specialty core barrel types include: Wire line or retractable core barrel, Calyx or shot,Steel tooth,or Percussion barrels

Note:STP sampling standard device

Note: method is defined in ASTM 1587 or ASSHTO T207 also called "Open Drive " sampling

Note: Piston samplers include Mechanical Stationary, Retractable, Floating,and Hydraulic/Pneumatic (Osterberg) Piston samplers. Also piston samplers recommended for soft cohesive soils.

Note:STP sampling standard device

FIELD INSPECTION SHOULD DOCUMENT:

1. Driving Energy
2. Sampler Type
3. Sampling Conditions
4. Sampling Sequence
5. Sample Identification
6. Sample Preservation
7. Soil Conditions at Sampling Depth
8. Ground water Measurements
9. Depth of Boring
10. Sample Recovery/percentage

Modified form Hunt(1984)

Figure 4-18a Soil Sampling Methods

Table 9-5. Soil sampler descriptions, advantages, and limitations (modified from Acker, 1974; Rehm et al., 1985; Aller et al., 1989).

METHOD DESCRIPTION	ADVANTAGES	LIMITATIONS
SPLIT-SPOON (SPLIT-BARREL) SAMPLERS The Standard Penetration Test procedure for driving a split-spoon sampler to obtain a representative soil sample and a measure of soil penetration resistance is described by ASTM Test Method D1586-84. The split-spoon sampler is 18 to 30 inches long with a 1½-inch ID and made of steel. It is attached to the end of drill rods, lowered (typically through a hollow-stem auger) to the bottom of the borehole which must be clean, and then hammered into the undisturbed soil by dropping a 140-lb weight a distance of 30 inches onto an anvil that transmits the impact to the drill rods. The number of blows required to drive the sampler each 6-inch interval is counted to determine penetration resistance. Continuous or noncontinuous samples can be taken, and various other split-barrel diameter sizes are available. These samplers can also be pushed into the ground rather than hammered.	• High quality samples can be evaluated for mineralogical, stratigraphic, physical, and chemical properties • Steel, brass or plastic liners can be used with split-spoon samplers so that samples can be sealed to minimize changes in sample chemical and physical conditions prior to delivery to a laboratory • Relatively inexpensive • Widely available	• Hammering creates a stress that can consolidate and alter the sample • Sample transfer from the split spoon can result in disaggregation of cohesionless soil • Sample handling exposes soil to atmosphere and may result in loss of volatile chemicals • Cannot penetrate rock, cobbles, and some gravels • Poor recovery of some loose or flowing cohesionless samples (although sample retainers can be used to minimize this problem)
THIN-WALL (SHELBY) OPEN-TUBE SAMPLERS Open-tube thin-wall samplers consist of a connector head and a 30 or 36 inch long thin-wall steel, aluminum, brass, or stainless steel tube which is sharpened at the cutting edge. The wall thickness should be less than 2½% of the tube outer diameter, which is commonly 2 or 3 inches. The sampler is attached via its connector head to the end of drill rods, lowered (typically through a hollow-stem auger) to the bottom of the borehole which must be clean, and then pushed down into the undisturbed soil using the hydraulic or mechanical pulldown of the drill rig. This procedure is described by ASTM Method D1587-83. The Central Mining Company (CME) recently developed a 5-ft long continuous thin-wall sampling system. The tube is kept in place by a latching mechanism that allows the sample to be retracted by wireline when full and replaced with an empty tube.	• Provides undisturbed samples in stiff, cohesive soils and representative samples in soft to medium cohesive soils • High quality samples can be evaluated for mineralogical, stratigraphic, physical, and chemical properties • Sample can be preserved and stored within the sample tube by sealing its ends, thereby minimizing sample disturbance prior to lab analysis • Widely available • Relatively inexpensive	• The sampler should be at least six times the diameter of the longest particle size to minimize disturbance of the sample • Large gravel or cobbles can disturb the finer grained soil within which they are embedded and/or can damage the sampler walls • Due to thin wall and limited structural strength, the sampler cannot be easily pushed into dense or consolidated materials • Generally not effective for cohesionless soils
THIN-WALL PISTON CORE SAMPLERS These samplers consist of a thin-wall tube, with an internal piston, and mechanisms to control movement between the piston and tube. Thin-wall piston samplers are typically set up and pushed into the ground in the same manner as thin-wall open-tube samplers. The internal pistons generate a vacuum on the sample as the sampler is withdrawn from the hole. Starr and Ingleton (1992) recently developed a drive point piston sampler to collect high quality core samples of sands, silts, and clays without drilling fluids or a drilling rig to a depth of approximately 30 ft.	• Provides undisturbed samples in cohesive soils, silts, and sands above or below the water table • Vacuum enables recovery of cohesionless soils • High quality samples can be evaluated for mineralogical, stratigraphic, physical, and chemical properties • Sample can be preserved and stored within the sample tube by sealing its ends, thereby minimizing sample disturbance prior to lab analysis	• As with open-tube sampler, large particles may disturb sample or damage sampler walls and the sampler cannot be easily pushed into dense or consolidated materials • If used with a clam shell fitted auger head, only 1 sample can be obtained per borehole because the clam shell will not close after being opened; continuous sampling not possible • Some piston samplers require use of drilling fluid for hydrostatic control • Not as widely available as split-spoon or open-tube samplers • Relatively expensive
CORE BARREL SAMPLERS (see ROCK CORING description in Table 9-3)	See ROCK CORING advantages in Table 9-3	See ROCK CORING limitations in Table 9-3

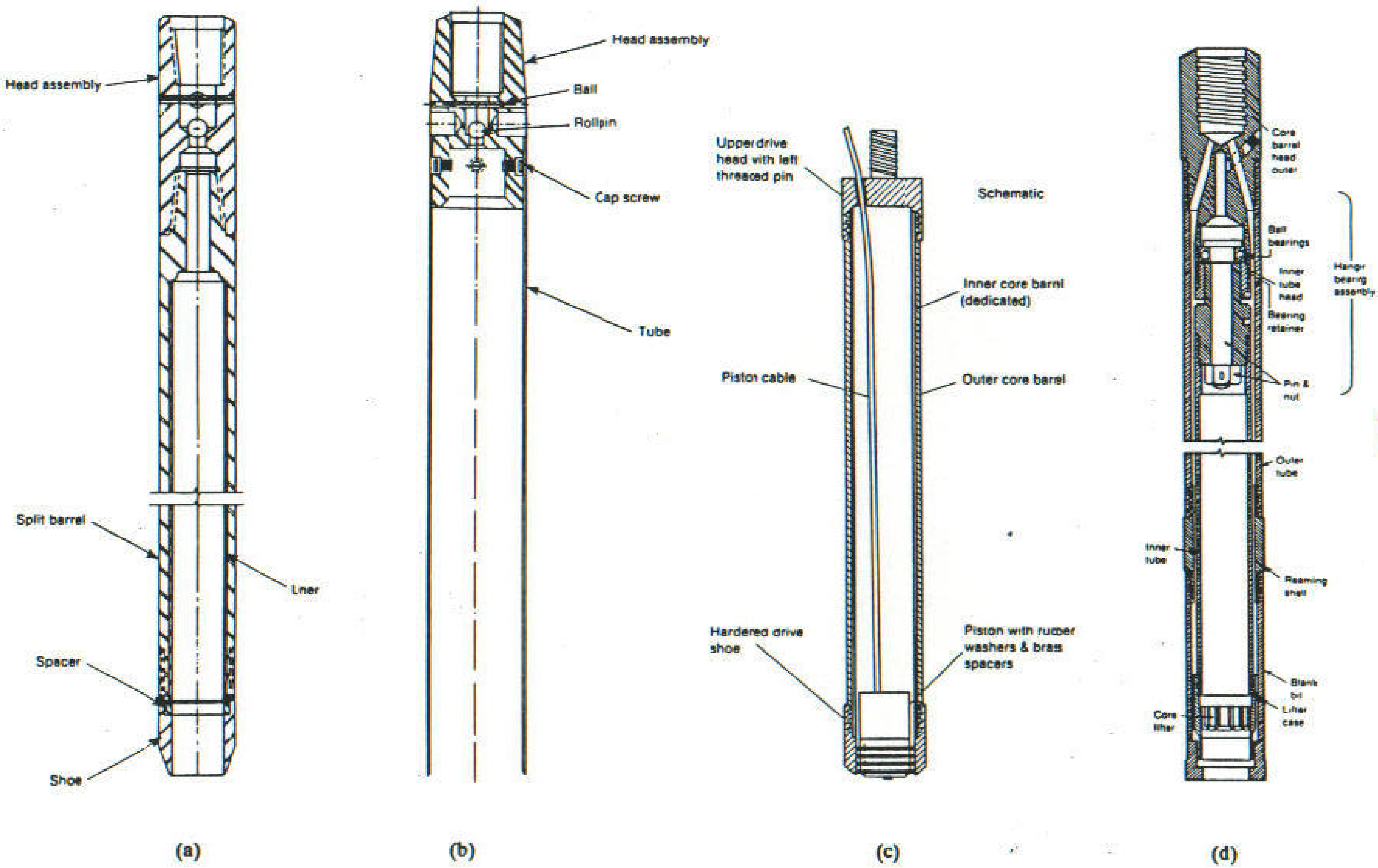


Figure 9-3. Schematic diagrams of a (a) split-spoon sampler, (b) thin-wall open-tube sampler, and (c) thin-wall piston sampler used to obtain undisturbed soil samples; and of a (d) double-tube core barrel used to obtain rock core (modified from Aller et al., 1989).

Table 9-6. Comparison of trichloroethene (TCE) concentrations determined after storing soil samples in jars containing air versus methanol; showing apparent volatilization loss of TCE from soil placed in jars containing air (from WCGR, 1991).

SPLIT-SPOON SAMPLE PLACED IN WIDE-MOUTH JAR CONTAINING AIR AND THEN SUB-SAMPLED, EXTRACTED, AND ANALYZED		SPLIT-SPOON SAMPLE PLACED IN WIDE-MOUTH JAR CONTAINING METHANOL TO PRESERVE VOLATILES AND SUBSEQUENT ANALYSIS OF THE SOLVENT	
Sample Depth (ft BGS)	TCE Concentration (mg/Kg)	Sample Depth (ft BGS)	TCE Concentration (mg/Kg)
5.0 - 7.0	2.2	7.0	3,100
20.0-20.5	9.2	20.0	420
30.0-30.5	<0.022	30.0	210

RECORD OF BOREHOLE 34B

SHEET 1 OF 2

LOCATION SEE.FIGURE

INCLINATION AZIMUTH

BORING DATE JUNE 6/88
MONITORING WELL INSTALLED JUNE 9/88
SAMPLER / PENETRATION TEST HAMMER WEIGHT N/A

DATUM GEODETIC

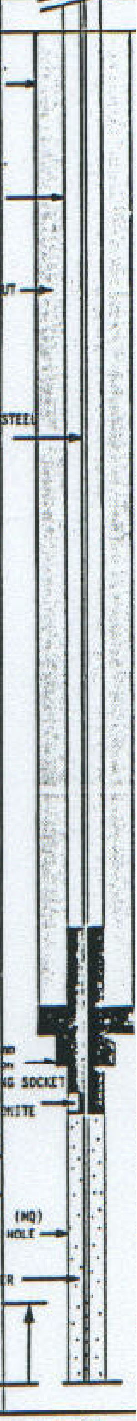
DROP N/A

PRELIMINARY

DEPTH METRES	DRILLING RECORD	DESCRIPTION	ELEV. DEPTH	SAMPLES NUMBER	TYPE	BLOWS/0.3m	DISCONTINUITY DATA TYPE AND SURFACE DESCRIPTION	ADDITIONAL TESTING WATER LEVELS AND NOTES
		GROUND SURFACE	182.49					
0	POWER AUGER - 150mm DIAM. HOLLOW STEM 100mm NOM. DIAM. GROUTED STEEL CASING	Brown becoming grey with depth, FISSURED SILTY CLAY, trace to some sand, trace of gravel (GLACIOLACUSTRINE TILL) Fissures generally near vertical and occ. infilled with silt	0.00					250 mm DIA. AUGER HOLE 100 mm NOM. DIA. STEEL CASING CEMENT GROUT 42 mm ST. STEEL RISER PIPE
6	150mm DIA. TRICONE — CASING SOCKET		185.59					
7		brown SILTY SAND, some gravel, trace of clay (TILL)	6.90					
		BEDROCK SURFACE	185.28					
	AIR FLUSH ROTARY CORE DRILLING HQ ROCK CORE - 96mm DIA. HOLE	ERAMOSA FORMATION (7.21 - 12.47 m) Fresh to moderately weathered, medium brown to brownish grey, medium grained, medium bedded DOLOSTONE with occ. stylolites and black bituminous bedding partings.	7.21	RC 1	HQ RC	–	SL. WEATHERED WEATH VERTICAL JOINT DECOMPD. ROCK. MOD. WEATH BITUMINOUS BEDDING PARTING (BIT B.P.) MOD. WEATH BIT. B.P. GALENA MIN.	150 mm TRICON CASING SOCKET BENTONITE SEAL
			184.72 7.77					
8		7.77 to 8.24 - moderately weathered, porous, vuggy dolostone with traces of tabulate coral and galena mineralization, occ. dolomite crystals and sacc. dolomite in vugs	184.25 8.24	RC 2	"	–	FT. WEATH B.P. WEATH BIT. B.P. MOD. WEATH BIT. B.P. FT. WEATH B.P. FT. WEATH BIT B.P.	96 mm DIA (HQ) HOLE SAND FILTER
9			183.01 9.48 9.60					
10		CONTINUED ON SHEET 2.	182.49 10.00					

RANGE OF WATER LEVEL IN WELL NO. 34B JULY 4, 1988 TO AUG. 23, 1988

INSTRUMENTATION
T.O.C. ELEV. 19.3.



DEPTH SCALE (ALONG HOLE)
1:50 METRIC

Golder Associates

ROCK LOGGED M.D DRAWN SF
DATE AUG 17, 1988 CHECKED

Table 9-2. Information to be considered for inclusion in a drill or test pit log (modified from USEPA, 1987; Aller et al., 1989).

General:

- Project name/number
- Hole name/number
- Date started and finished
- Hole location; map and elevation
- Weather conditions
- Rig type, bit size/auger size
- Classification system used (e.g., Unified Soil Classification)
- Geologist's name
- Driller's name
- Sheet number

Information Columns:

- Depth
- Sample location/number
- Low counts and advance rate
- Percent sample recovery
- Narrative description
- Depth to saturation
- Well construction details
- Other remarks

Narrative Geologic Description:

- Soil/rock type
- Soil/rock texture and structure
- Color (Munsell) and stain
- Petrology and mineralogy
- Friability
- Moisture content (dry, moist, wet)
- Degree of weathering
- Presence of carbonate
- Fractures, joints (orientation, size, and spacing)
- Bedding nature and spacing
- Soil gradation or plasticity
- Discontinuities descriptions
- Water-bearing zones
- Formation strike and dip
- Fossils
- Depositional structures
- Organic content
- Solution cavities
- Rock core total breakage and breaks/ft
- Particle roundness or angularity
- Estimate of density of granular soil or consistency of cohesive soil (usually based on standard penetration test)
- Slickensides
- Roots, rootholes
- Residual or relict structure
- Buried horizons
- Disturbed earth, waste materials
- Rock Quality Designation (RQD)

Sampling Information:

- Types of sampler(s) used
- Diameter and length of sampler(s)
- Number of each sample
- Start and finish depth of each sample
- Percent sample recovery
- Split-spoon sampling
  - size and weight of drive hammer
  - number of blows required to penetrate each 6-inch interval
  - free fall distance used to drive sampler
- Thin-walled sampling
  - ease or difficulty pushing sampler
  - psi required to push sampler
- Rock coring
  - core barrel drill bit design
  - penetration rate
  - fluid gain or loss

Drilling Observations:

- Loss of circulation
- Advance rates
- Rig chatter
- Water-levels
- Changes in drilling method/equipment
- Drilling difficulties
- Amount of water yield/loss during drilling at different depths
- Caving/hole stability
- Amount of air used; air pressure
- Running sands
- Amounts and types of drilling fluids used

Well Construction Details:

- Well Design:
  - casing length, schedule, and diameter
  - joint type
  - screen length, schedule, and diameter
  - screen slot size
  - percent open area in screen
  - filter pack depth interval
  - elevations of top of casing, bottom and top of protective casing, ground surface, bottom of borehole, bottom and top of well screen, annular seal and grout intervals, etc.
  - well location coordinates and map
  - other backfill materials and intervals
- Materials:
  - casing and screen
  - filter pack (i.e., grain size analysis)
  - seal and physical form
  - slurry or grout mix
- Installation:
  - drilling method
  - drilling fluids
  - source of water
  - timing
  - method of sealant/grout emplacement
  - volumes of all materials used
- Development:
  - time and date
  - water level elevation before after development
  - development method
  - time spent developing well
  - volume of fluid removed
  - volume of fluid added
  - clarity of water and sediment before and after development
  - amount of sediment at well bottom
  - pH, specific conductance, and temperature readings

Other Remarks:

- Chemical odors
- Sample fluorescence
- NAPL sheens or presence
- HNU or OVA readings
- Sample shipping reference
- Equipment failures
- Deviations from drilling protocols
- Photograph cross-reference
- Air-monitoring data
- Hydrophobic dye test results
- Equipment decontamination procedures

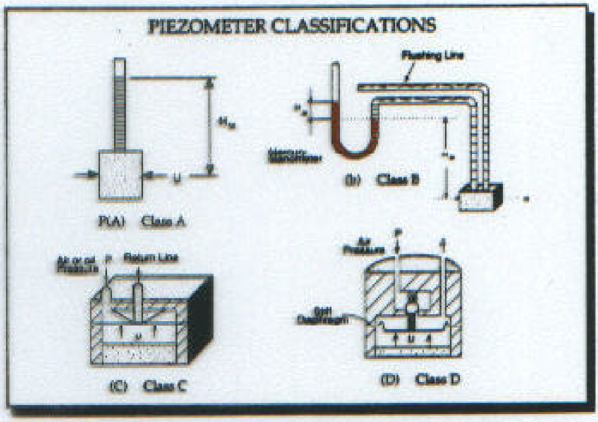


Figure 4-39 Piezometer Classifications

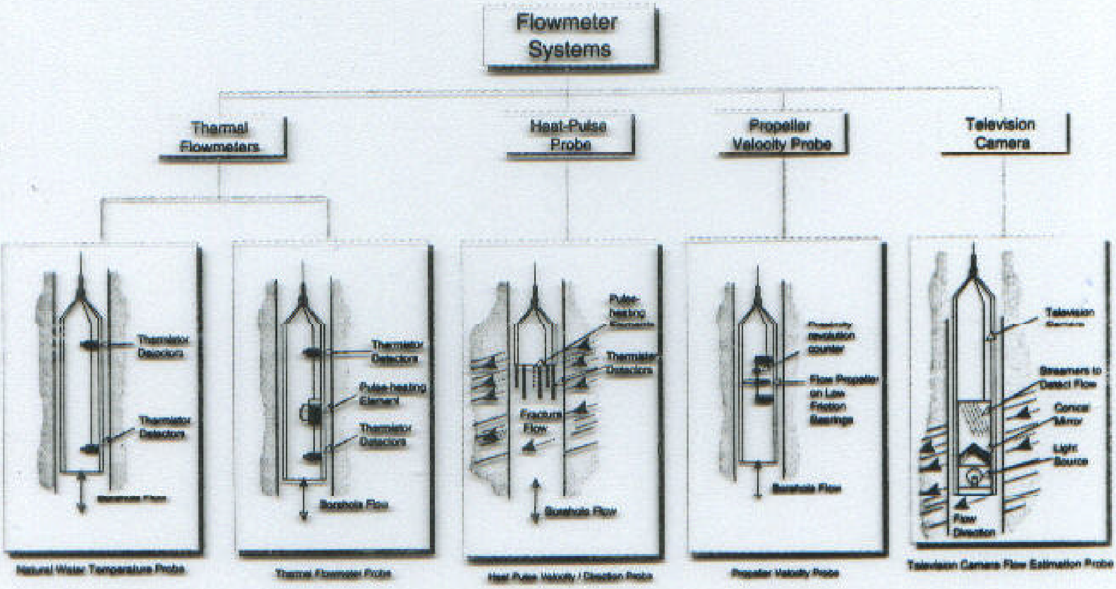


Figure 4-47 Flowmeter Systems

Piezometer Evaluations

Gauge Pressure	Piezometer Type	Pressure Range	Response Time	De-airing Capabiliy	Remote Reading Capability	Long-Term Reliability	Other		Recommendations
							Advantages	Disadvantages	
Positive	Open-hydraulic (Casagrande)	Atmospheric to top of standpipe	Slow	Self de-airing	Not normally, but possible with bubbler system	Very good	Cheap, simple to read & maintain; insitu permeability measurement possible.	Vandal damage often irreparable.	First choice for measurement within positive pressure range unless rapid response or remote readingd required; response peaks can be detected by use of Halcrow buckets system.
	Closed-Hydraulic (Low air entry pressure)	Any positive pressure	Moderate	Can be de-aired	Yes	Depends on pressure measuring system 1) Mercury manometer-very good 2) Bourdon gauge - poor in humid atmosphere 3) Pressure Transducer-moderate but easily replaced.	Fairly cheap; insitu permeability measurement possible; can be made vandal proof if required.	Gauge house usually required; regular de-airing necessary; uncovered tubing liable to rodent damage if left exposed.	Usefull when remote reading, and for artesian pressure.
	Closed-Hydraulic (High air entry pressure)	-1 atmosphere to any positive pressure	Moderate	Can be de-aired	Yes	As above	Fairly cheap; insitu permeability measurements in low permeability soil are possible	As above; very regular de-airing required when measuring sucions.	Useful for measuring small suctions
	Pneumatic	Any positive pressure	Rapid	Cannot be de-aired; only partially self de-airing	Yes some head loss over long distances	Moderate to poor, but very little long term experence available	Fairly cheap; no gauge house required	No method of checking if porewater or pore air pressure is measured	Only suitable when tip almost always below ground water level and no large suction occur.
	Electric vibrating wire type	Any positive pressure	Rapid	As above	Yes but special cable required	Signal quality degenerates with time; instrument life about ten years, but reliability of instrument that cannot be checked is always a question.	-	As above; expensive zero reading liable to drift and cannot be checked.	Not generally recommended
	Electric resistance type	Any positive pressure	Rapid	As above	Yes, but with care because of transmission losses	Poor	-	As above	Not recommended
Negative (suction)	Tensiometer	-1 Atmosphere to positive pressure	Moderate to rapid	Can be de-aired	Yes	Good	Cheap, simple to read and maintin.	Vandal damage often irreparable; regular de-airing required.	First choice for measuring pore suction.
	Psychrometer	Below -1 atmosphere	Variable	Not relevant	Short distances only	Instrument life one to two years; little long term experence available.	-	Not accurate between 0 and -1 atmospheres.	Research stage.

Table 4-11 Piezometer Selection Matrix

Table 9-2. Comparison of measured LNAPL thicknesses using water-detection paste, a clear bottom-loading bailer, and an interface probe (from Sanders, 1984).

Measurement Method	3 Inches Gasoline		1 Inch Gasoline		3 Inches Kerosene		1 Inch Kerosene	
	Ave. (Inches)	Standard Deviation	Ave. (Inches)	Standard Deviation	Ave. (Inches)	Standard Deviation	Ave. (Inches)	Standard Deviation
Water Detection paste on a stick*	3.60	0.21	1.38	0.13	3.36	0.27	1.12	0.75
Clear bottom-loading bailer**	2.58	0.16	0.82	0.13	2.46	0.18	0.80	0.12
Interface probe***	3.18	0.11	1.14	0.11	3.12	0.08	1.10	0.12

Notes: Ave. means average. Five tests were conducted with each method and fluid thickness.

*Gauging stick – 8-ft Bagby Stick Co.; McCabe, Inc. water-detection paste.

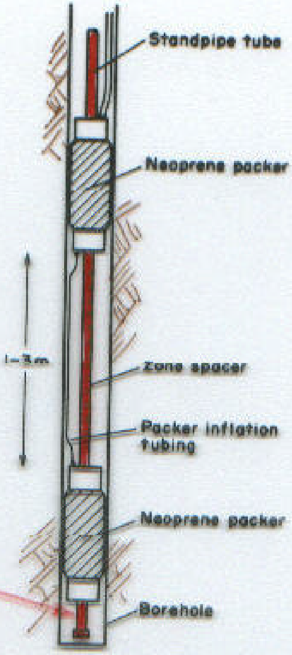
**Surface sampler – 1⅝-inch OD, 12-inches long, bottom-loading bailer.

***ORS interface probe (manufacture date circa 1984).

Table 9-10. **Summary of Test Results (Note: A = NAPL presence apparent based on visual examination; B = NAPL presence suspected based on visual examination; and C = no visual evidence of NAPL presence).**

Method	Sample categories are based upon estimated NAPL saturations as a percent. The volume of NAPL mixed with 172 g of soil and sufficient mL of water to constitute a total fluid content of 35 mL is also given.							Notes and Conclusions
	Blank Samples (No NAPL)	Dissolved Samples (No NAPL)	1% (0.35 mL)	2.86% (1 mL)	5.71% (2 mL)	11.43% (4 mL)	22.86% (8 mL)	
OVA Headspace Analysis using an FID	1.4 - 4.8 ppm (see notes)	1.4-30 ppm	120- >1000 ppm	50- >1000 ppm	60- >1000 ppm	100- >1000 ppm	65- >1000 ppm	1. An effective screening method which may be used, in some cases, to infer NAPL presence. 2. Organic vapor concentration depends on contaminant volatility: measured concentrations were much higher in chlorobenzene and PCE samples than kerosene samples. 3. Two blank samples had OVA concentrations of <10 and <20 ppm due to residual vapors from prior samples.
Unaided Visual Exam	0 A 0 B 11 C	0 A 0 B 11 C	0 A 0 B 11 C	0 A 1 B 11 C	0 A 3 B 8 C	0 A 6 B 5 C	0 A 7 B 4 C	1. Unable to identify presence of colorless NAPL. 2. NAPL presence was suspected in some samples with higher NAPL saturation based on fluid sudsiness.
UV Fluorescence Exam	1 A 1 B 9 C	0 A 2 B 9 C	4 A 1 B 6 C	9 A 1 B 2 C	9 A 1 B 1 C	11 A 0 B 0 C	11 A 0 B 0 C	1. Very effective simple test for fluorescent NAPLs. 2. One false positive in 22 blank or dissolved samples. 3. Only 3 false negatives in 45 samples with estimated NAPL saturations between 1% and 23%. 4. Sensitivity depends on fluorescent intensity of NAPL: at low NAPL saturations, kerosene and chlorobenzene were easier to detect than tetrachloroethene. 5. Greater visual contrast evident between milky white fluorescence and darker soils. 6. Adding more water to the contaminated soil sample improved the detectability of NAPL in some cases by bringing more fluorescent fluid to the polybag wall.
Soil-Water Shake Test Exam	0 A 1 B 10 C	0 A 2 B 9 C	0 A 4 B 7 C	2 A 6 B 4 C	0 A 9 B 2 C	2 A 8 B 1 C	3 A 7 B 1 C	1. Difficult to positively identify clear, colorless NAPL. 2. At relatively high saturations (between 1% and 23%), NAPL presence was usually suspected based on fluid characteristics at the fluid-air interface. 3. As a result, colorless LNAPL (kerosene) was easier to detect than colorless DNAPL (chlorobenzene and tetrachloroethene) using the shake test.
Centrifugation Exam	0 A 1 B 10 C	0 A 1 B 10 C	0 A 4 B 7 C	2 A 5 B 5 C	4 A 3 B 4 C	6 A 1 B 4 C	3 A 4 B 4 C	1. Fairly effective for identification of LNAPL (kerosene), but not DNAPLs, based on fluid characteristics at the fluid-air interface. 2. Seventeen false negatives in 45 samples with estimated NAPL saturations between 1% and 23%; only 15 positive NAPL identifications in these 45 samples.
Hydrophobic Dye Shake Test Exam	0 A 0 B 11 C	0 A 0 B 11 C	4 A 2 B 5 C	8 A 1 B 3 C	10 A 0 B 1 C	11 A 0 B 0 C	11 A 0 B 0 C	1. Very effective simple test. 2. No false positives in 22 blank or dissolved samples. 3. Identified NAPL presence in 40 of 45 samples with estimated NAPL saturations >1%. False negatives recorded in only 4 of these 45 samples. 4. Dye coloration obvious even in black topsoil samples. 5. NAPL density relative to water was correctly determined in 21 samples and misjudged in 1 sample. 6. Can be used to estimate quantity of NAPL in sample.
Centrifugation of Hydrophobic Dye Shake Test Sample	0 A 1 B 10 C	0 A 0 B 11 C	5 A 1 B 5 C	9 A 2 B 1 C	11 A 0 B 0 C	11 A 0 B 0 C	11 A 0 B 0 C	1. Slight enhancement of hydrophobic dye shake test. 2. No false positives in 22 blank or dissolved samples. 3. Identified NAPL presence in 42 of 45 samples with estimated NAPL saturations >1%. False negative recorded in only 1 of these 45 samples. 4. NAPL density relative to water was correctly determined in 43 samples and misjudged in 3 samples. 5. Can be used to estimate quantity of NAPL in sample.

STRADDLE PACKER



Out-of-zone pressures

Figure 11 Packer system showing a straddle packer

PIEZOMETER INSTALLATION

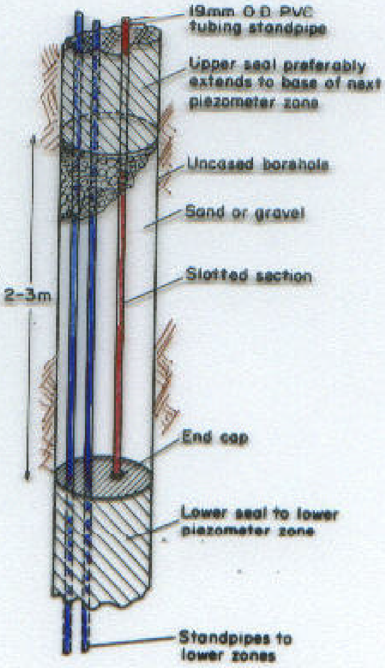


Figure 12 Standpipe piezometer installation

Table 1. Comparison of Well Casing and Screen Materials (1986)

Type	Advantages	Disadvantages
PVC (Polyvinylchloride)	• Lightweight • Excellent chemical resistance to weak alkalies, alcohols aliphatic hydrocarbons, and oils • Good chemical resistance to strong mineral acids, concentrated oxidizing acids, and strong alkalies • Readily available • Low priced compared to stainless steel and Teflon	• Weaker, less rigid, and more temperature-sensitive than metallic materials • May adsorb some constituents from groundwater • May react with and leach some constituents from groundwater • Poor chemical resistance to ketones, esters, and aromatic hydrocarbons
Polypropylene	• Lightweight • Excellent chemical resistance to mineral acids • Good-to-excellent chemical resistance to alkalies, alcohols, ketones, and esters • Good chemical resistance to oils • Fair chemical resistance to concentrated oxidizing acids, alphatic hydrocarbons, and aromatic hydrocarbons • Low priced compared to stainless steel and Teflon	• Weaker, less rigid, and more temperature-sensitive than metallic materials • May react with and leach some constituents into groundwater • Poor machinability—it cannot be slotted because it melts rather than cuts
Teflon	• Lightweight • High impact strength • Outstanding resistance to chemical attack insoluble in all organics except a few exotic fluorinated solvents	• Tensile strength and wear resistance low compared to other engineering plastics • Expensive relative to other plastics and stainless steel

Table 1. Continued

Type	Advantages	Disadvantages
Kynar	• Greater strength and water resistance than Teflon • Resistant to most chemicals and solvents • Lower priced than Teflon	• Not readily available • Poor chemical resistance to ketones, acetone
Mild steel	• Strong, rigid; temperature-sensitivity not a problem • Readily available • Low priced relative to stainless steel and Teflon	• Heavier than plastics • May react with and leach some constituents into groundwater • Not as chemically resistant as stainless steel
Stainless steel	• High strength at a great range of temperatures • Excellent resistance to corrosion and oxidation • Readily available • Moderate price for casing	• Heavier than plastics • May corrode and leach some chromium in highly acidic waters • May act as a catalyst in some organic reactions • Screens are higher priced than plastic screens

Source: Driscoll (1986).

Table 2. Comparison of Well Grouting Materials

Type	Advantages	Disadvantages
Bentonite	• Readily available • Inexpensive	• May produce chemical interference with water quality analysis • May not provide a complete seal because —There is a limit (14% to the amount of solids that can be pumped in a slurry. Thus, there are few solids in the seal; should wait for liquid to bleed off so solids will settle —During installation, bentonite pellets may hydrate before reaching proper depth, thereby sticking to formation or casing and causing bridging —Cannot determine how effectively material has been placed —Cannot assure complete bond to casing
Cement	• Readily available • Inexpensive • Can use sand and/or gravel filter • Possible to determine how well the cement has been placed by temperature logs or acoustic bond logs	• May cause chemical interferences with water quality analysis • Requires mixer, pump, and trémie line; generally more cleanup than with bentonite • Shrinks when it sets; complete bond to formation and casing not assured

Source: Driscoll (1986).

Table 9-4. Borehole and well annulus grout types and considerations (modified from Aller et al., 1989; Edil et al., 1992).

BENTONITE AND BENTONITE-CEMENT GROUTS: Bentonite is a hydrous aluminum silicate comprised primarily of montmorillonite clay. The volume of hydrated bentonite in water is typically 10 to 15 times greater than that of dry bentonite because water is incorporated within the expanding clay lattice. The low permeability and expansion of bentonite in water are desirable properties for sealing abandoned boreholes and well annular spaces. Bentonite grouts are best prepared using mechanical mixers and should be pumped under pressure in place from the base of the interval to be grouted through a tremie pipe. Bentonite grouts should be mixed in batches so that they can be pumped before becoming too viscous. Bentonite grout should not be placed in the vadose zone because it will dry, shrink, and fracture. Bentonite grout may also shrink and fracture in the presence of hydrophobic NAPLs. Several available bentonite grout types are described below.

Bentonite Slurry Grout is commonly prepared by mixing dry bentonite powder in fresh water at a ratio of 15 lbs of bentonite to 7 gallons of water to make 1 ft^3 of slurry. Thick slurries may gel prematurely and be impossible to emplace. Due to their low solids content, bentonite slurries tend to settle as liquid bleeds off, requiring the emplacement of more slurry.

Quick-Gel® Bentonite Drilling Mud Grout is slurry of sodium bentonite and water that is marketed primarily as a drilling mud. Grouts of varying viscosity and strength can be obtained by mixing different proportions of Quick Gel®, water, and sand. Slurries containing sand appear more stable than pure Quick Gel®. Edil et al. (1992) found that Quick Gel® slurries of different sand content and viscosity form poorer annulus seals than neat cement, cement-bentonite, and Benseal®-bentonite slurry grouts.

Volclay® Bentonite Powder Grout is a commercial bentonite-based clay grout that is formulated for sealing boreholes and well annular spaces. Edil et al. (1992) mixed 2.1 lbs of Volclay® per gallon of water and added 2 lbs of magnesium oxide powder as a setting inhibitor to each 50 lbs of Volclay® slurry. They determined that Volclay® grout has a stiff gel structure which adheres to PVC but not steel well casing; and that it is not as effective a well sealant as neat cement, cement-bentonite, and Benseal®-bentonite slurry grouts.

Benseal® - Bentonite Slurry Grout is a mixture of Benseal®, a granular nondrilling mud grade bentonite developed for use in sealing and grouting well casings, and bentonite powder with water. Edil et al. (1992) mixed 30 lbs of Natural Gel® (a natural, unaltered bentonite powder) with 100 gallons of water, and then used a venturi pump to mix in 125 lbs of Benseal® to the slurry. They found that this grout adheres to steel and PVC casing, has low permeability, good swelling characteristics, and flexibility, and is an excellent sealant.

Bentonite-Cement Grout is a slurry incorporating 5 to 6 gallons of water and 2 to 6 lbs of bentonite powder for each 94 lbs (1 ft^3) of Portland cement. Bentonite improves the workability of the cement slurry, reduces slurry density, and reduces grout shrinkage during setting. Edil et al. (1992) found the addition of 5 lbs of bentonite per 94 lbs of cement forms a rigid well annulus seal with low permeability and high durability; and that the grout adheres to steel casing, but appeared to allow some infiltration along the grout-PVC casing interface.

Bentonite Pellets can be used to seal borehole or well annulus intervals. Wet pellets, however, tend to stick to well casing and borehole walls, and bridge high above their intended placement depth. A tamper can be used to break up bridges, but this technique becomes ineffective at depths greater than approximately 20 ft. Pellets can be frozen using refrigeration or liquid nitrogen to increase their fall distance.

PORTLAND CEMENT: Neat cement is a mixture of Portland cement (ASTM C-150) and water in the proportion of 5 to 6 gallons of clean water per bag (94 lbs or 1 ft^3) of cement. Five types of Portland cement are produced: Type I for general use; Type II for moderate sulfate resistance of moderate heat of hydration; Type III for high early strength; Type IV for low heat of hydration; and Type V for high sulfate resistance. Type I is most widely-used in well construction or hole abandonment. A typical 14 lb/gallon neat cement slurry with a mixed volume of 1½ ft^3 will have a set volume of 1.2 ft^3, reflecting a 17% shrinkage. The setting time ranges from 48 to 72 hrs depending primarily on water content.

Common additives include: (1) 2 to 6% bentonite to reduce shrinkage, improve workability, reduce density, and produce a lower cost per volume of grout; (2) 1 to 3% calcium chloride to accelerate the setting time and thereby create higher early strength, of particular value in cold climates; (3) 3 to 6% gypsum to produce a quick-setting very hard cement that expands upon setting; (4) <1% aluminum powder to produce a quick-setting strong cement that expands upon setting; (5) 10 to 20% flyash to increase sulfate resistance and provide early compressive strength; (6) hydroxylated carboxylic acid to retard setting time and improve workability without compromising set strength; and (7) diatomaceous earth to reduce slurry density, increase water demand and thickening time, and reduce set strength.

Edil et al. (1992) found neat cement grout forms a rigid seal with low permeability and high durability that adheres fairly well to steel and PVC casing. Kurt and Johnson (1982), however, report that neat cement annular seals are subject to channeling between the casing and grout due to temperature changes during curing, swelling and shrinkage during curing, and poor bonding between the ground and casing. Cement shrinkage can produce fractures, thereby degrading the integrity of the grout seal. Cement slurries can infiltrate the well sandpack, particularly if well development occurs prior to when the cement has completely set. Thus, a minimum of 1 to 2 ft of filter pack is usually extended in the annulus above the top of the well screen. The high heat of cement hydration can compromise the integrity of thermoplastic casing. Cement is a highly alkaline substance with a pH that ranges from 10 to 12. This can alter groundwater pH.

Table 9-7. Advantages and disadvantages of some common well casing materials (modified from Driscoll, 1986; GeoTrans, 1989; and Nielsen and Schalla, 1991).

TYPE	ADVANTAGES	DISADVANTAGES
FLUOROPOLYMERS such as polytetrafluoroethyene (PTFE), tetrafluoroethylene (TFE), and fluorinated ethylene propylene (FEP)	• Excellent chemical resistance to organic chemicals and corrosive environments; practically insoluble in all organic liquids except a few fluorinated solvents • Lightweight • High impact strength	• Lower tensile strength and wear resistance compared to other plastics, iron, or steel • Expensive relative to steel and other plastics
THERMOPLASTICS: POLYVINYLCHLORIDE (PVC) AND ACRYLONITRILE BUTADIENE STYRENE (ABS)	• Lightweight • Easy workability (with threaded couplings) • Inexpensive compared to fluoropolymers and steel • Resistant to alcohols, aliphatic hydrocarbons, weak and strong alkalies, oils, strong mineral acids, and oxidizing acids • Completely resistant to galvanic and electrochemical corrosion • High strength-to-weight ratios, and resistant to abrasion	• More reactive than PTFE • Poor chemical resistance to aromatic hydrocarbons, esters, ketones, and organic solvents • Much lower tensile, compressive, and collapse strength than steel or iron • May adsorb or elute trace organics • PVC glues, if used, may contribute organic chemicals to well water
STAINLESS STEEL such as Type 304 and Type 316	• Stronger, more rigid, and less temperature-sensitive than plastic materials • Good chemical resistance to organic chemicals • Resistant to corrosion and oxidation • Readily available	• Expensive • May catalyze some organic chemical reactions • May corrode if exposed to long-term corrosive conditions and leach chromium • Heavy
CARBON STEEL	• Stronger, more rigid, and less temperature-sensitive than plastic materials • Less expensive than stainless steel or teflon	• Expensive • Rusts easily, providing high sorptive and reactive capacity for many metals and organic chemicals • Subject to corrosion (under conditions of low pH, high dissolved oxygen, H^2S presence, > 1000 mg/L total dissolved solids, > 50 mg/L CO_2 or > 500 mg/L Cl^- • Heavy
GALVANIZED STEEL	• Stronger, more rigid, and less temperature-sensitive than plastic materials	• Expensive • Will rust if galvanized coating is scratched • Resistance to corrosion provided by zinc coating may be short-lived • May be source of zinc • Heavy

Table 9-1. Drilling and excavation costs in April, 1987 dollars (from GRI, 1987).

ITEM	HIGH COST	LOW COST	MEAN COST
Drilling Soil Borings (3½")	$39/ft	$18/ft	$28/ft
Rock Coring	$50/ft	$40/ft	$44/ft
Stainless Steel Screen (2", installed)	$375/5 ft	$175/5 ft	$252/5 ft
Stainless Steel Riser Pipe (2", installed)	$37/ft	$11/ft	$21/ft
PVC Screen (2", installed)	$50/5 ft	$35/5 ft	$43/5 ft
PVC Riser Pipe (2", installed)	$8/5 ft	$5/5 ft	$6/5 ft
Protective Casing	$150/each	$90/each	$113/each
Shelby Tube Samples (3")	$125/each	$40/each	$85/each
Water Truck Rental			$400/day
Steam Cleaner Rental	$125/day	$60/day	$85/day
Steam Cleaning Time	$140/hr	$112/hr	$125/hr
Stand By Time	$140/hr	$112/hr	$125/hr
Drilling in Level C Protection (Add)	$125/hr	$35/hr	$87/hr
Mobilization and Demobilization (200 miles)	$1250	$900	$1075
Test Pit Excavation Small Rubber Tired Backhoe and Operator			$70 - $110/hr
Large, Track-Mounted Backhoe (2 yd^3 shovel) and Operator			$100 - $170/hr
Mobilization and Demobilization			$50 - $100/hr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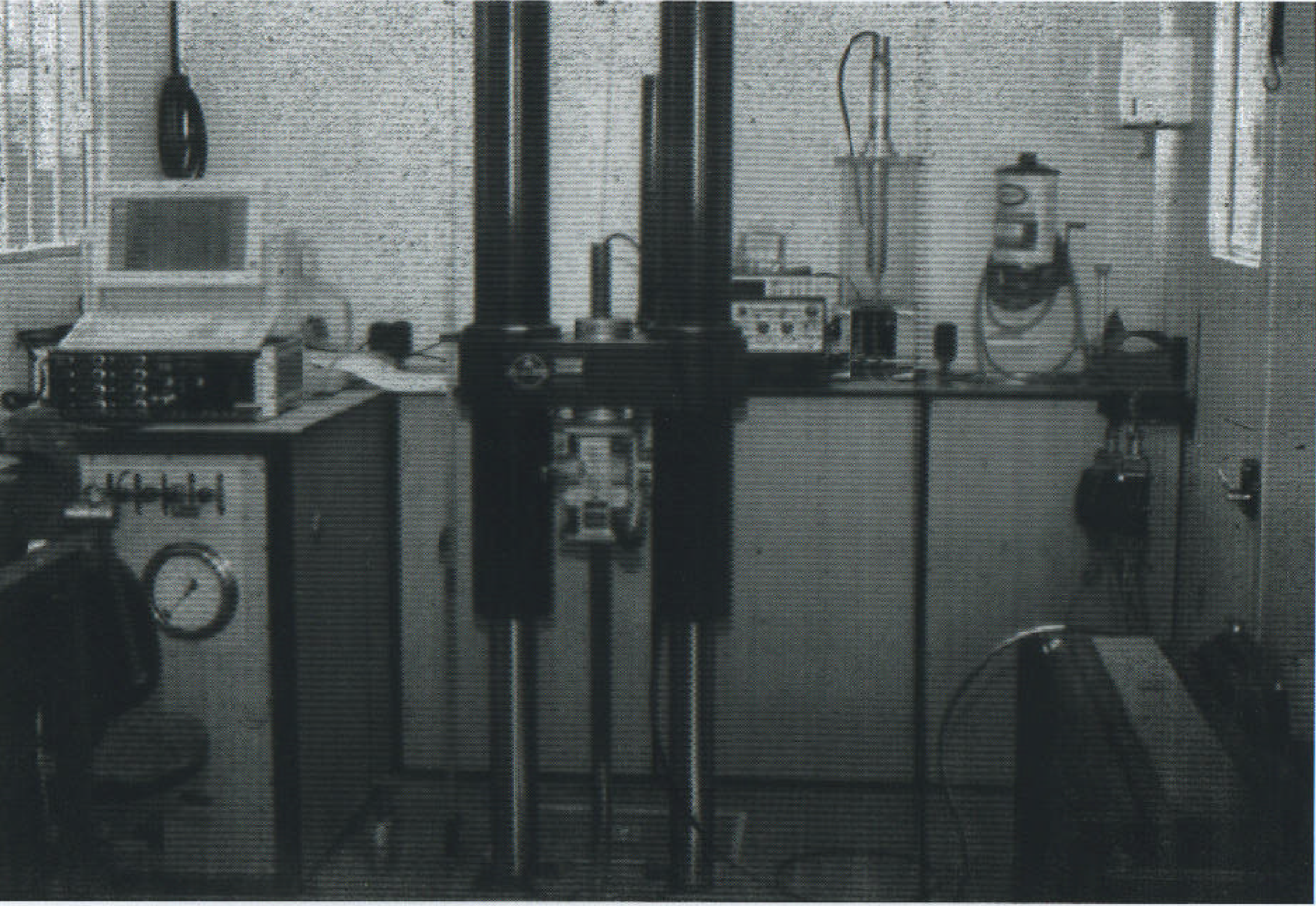


CONE PENETROMETER

Principle

- ☐ Penetrate 60° cone tip into ground 2cm/s 1.78"
- ☐ Measure:
  - Tip resistance
  - Sleeve resistance (Friction ratio)
  - Pore pressures
  - Other signals/indices
- ☐ Interpret:
  - Stratigraphy
  - Mechanical properties
  - Hydraulic properties
  - Contaminants.
- ☐ Application:
  - Soils only
  - Depths to 150'+?
- ☐ Advantages
  - Fast ∴ inexpensive
  - Large coverage
  - Some hydraulic props
- ☐ Disadvantages:
  - No direct samples taken.
    Lithology inferred.

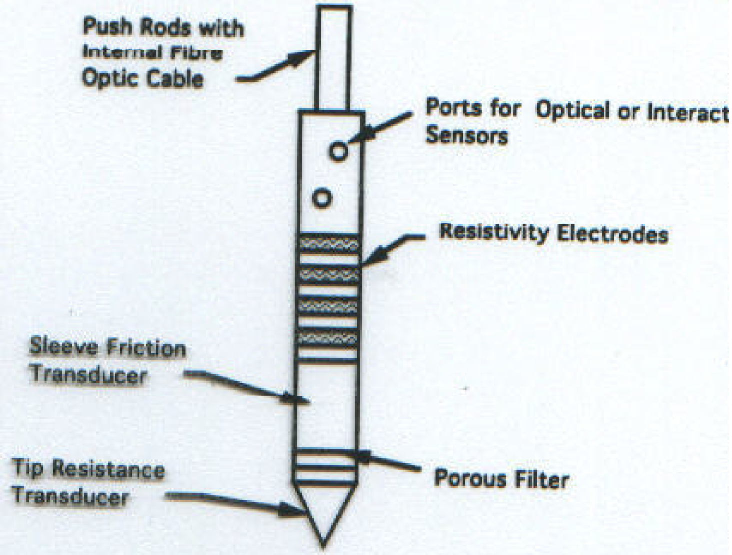


Figure 1. Cone Penetrometer with Geoenvironmental Sensors. Not to scale.

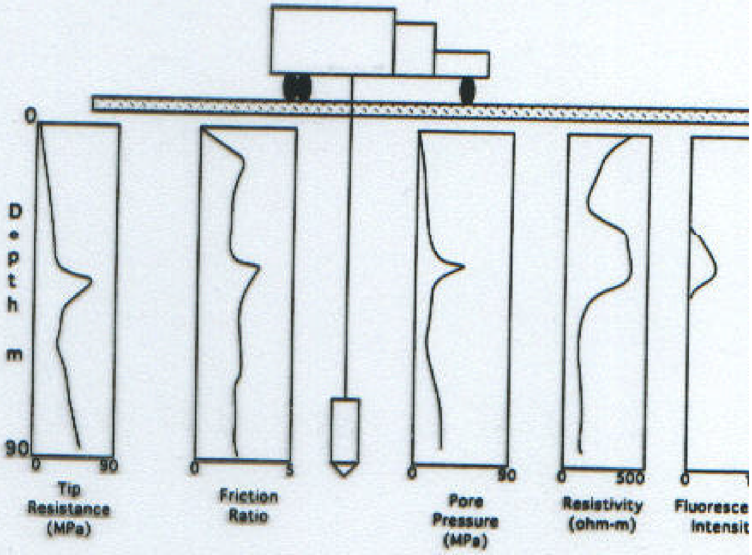
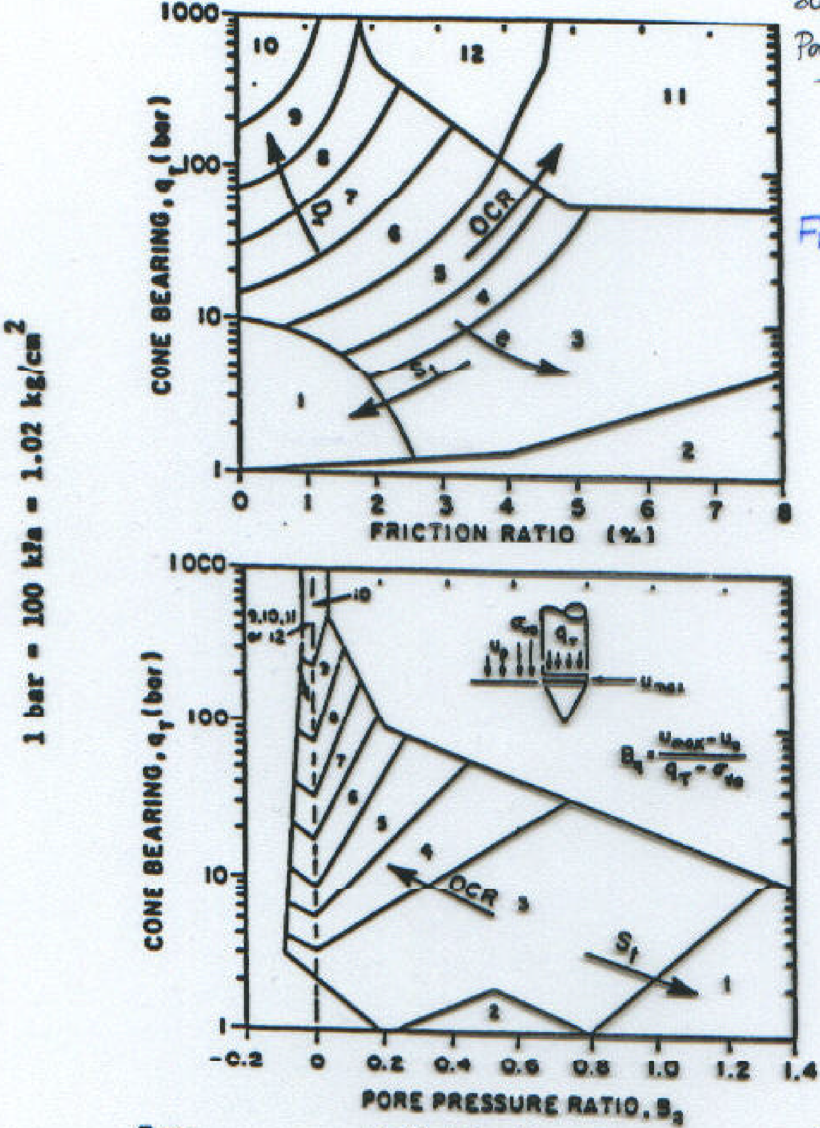


Figure 2. Typical Subsurface Information Resulting from Cone Penetration Test



Zone	Soil Behaviour Type
1	sensitive fine grained
2	organic material
3	clay
4	silty clay to clay
5	clayey silt to silty clay
6	sandy silt to clayey silt
7	silty sand to sandy silt
8	sand to silty sand
9	sand
10	gravelly sand to sand
11	very stiff fine grained*
12	sand to clayey sand*

* overconsolidated or cemented.

Figure 8. Proposed soil behavior type classification system (after Robertson et al, 1986)

Measure:

Tip resistance, q_c

Sleeve friction, F_s

Pore pressure, u

Interpret:

$$F_R = \frac{F_s}{q_T} = \frac{F_s}{q_c - u}$$

$$B_q = \frac{U_{max} - U_0}{q_T - \sigma_{v_0}}$$

Some correlations, K.

$$K = \frac{5}{8}\,\frac{\pi r \rho g}{8(\Delta u)}\ ;\ U_D < 10$$

$$K = \frac{1}{2}\,\frac{\rho g c}{\Delta u}\ ;\ U_D > 10$$

$$U_D = \frac{\pi r}{2c}$$

$$c = \frac{K}{S_s}$$

[7:3] Indirect Investigation (Geophysics)

Geomagnetic methods

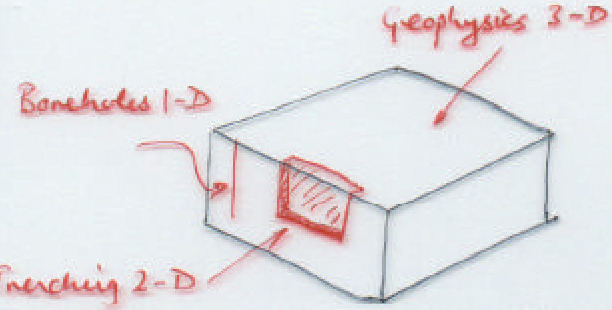
Geoelectric methods DC/AC/EM

Seismic methods

Gravity methods

Well logging

GEOPHYSICAL METHODS OF INVESTIGATION



Investigation Scales

small scale – representativeness of sample
– large scale structures
v. imp for groundwater since large scale structure controls flow/ transport behavior.
– use of pump tests.

large scale – – big picture
– correlation with real behavior through boreholes.

Geophysical Methods:

fast/ large volume/area coverage → inexpensive

1. Geomagnetic methods
2. Geoelectric methods
    - 2.1 Direct Current
    - 2.2 Electromagnetic (Radar)
3. Seismic methods
    - 3.1 Refraction
    - 3.2 Reflection
4. Gravity methods

Miscellaneous: Well logging.

DIAGRAM OF DELIVERABLES FOR A PHASE II
MONITORING WELL DESIGN PROJECT

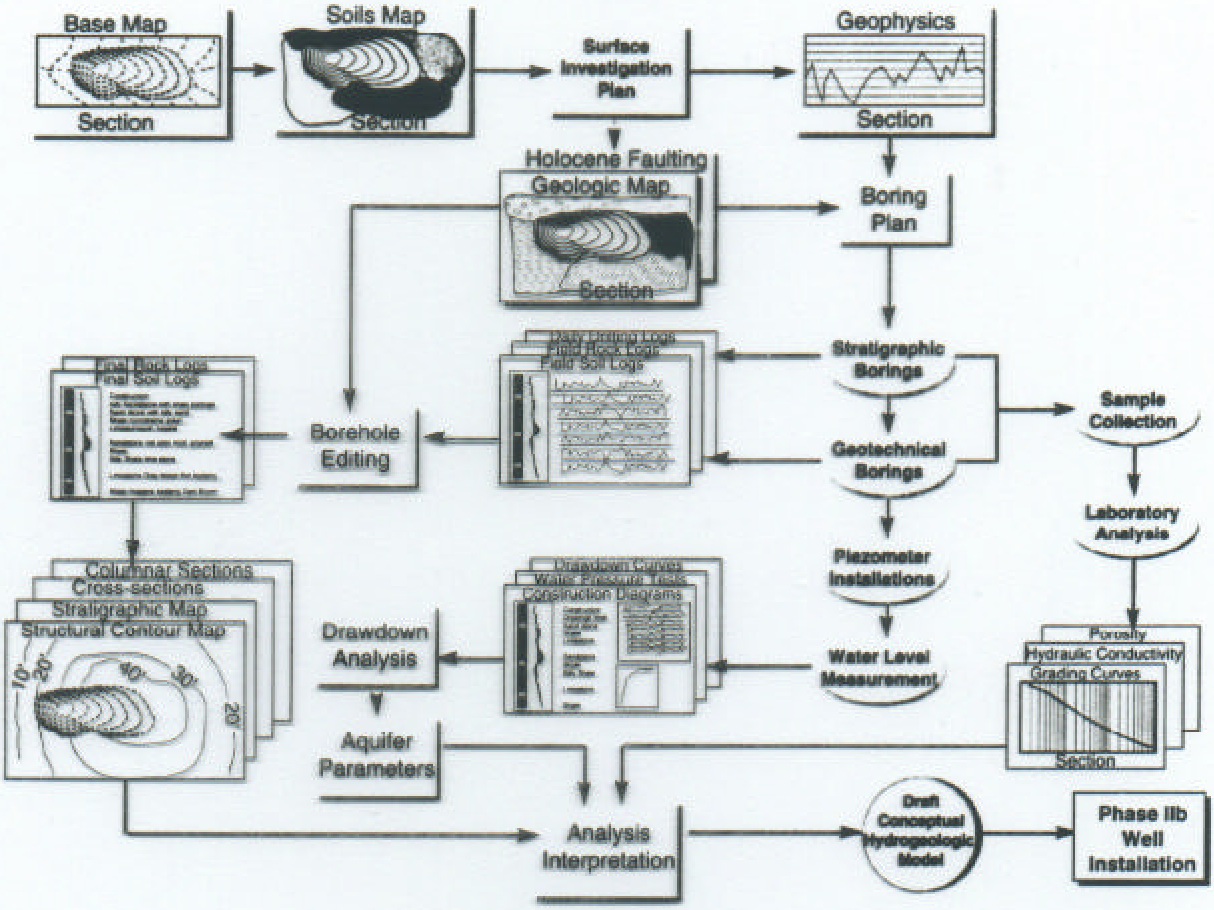
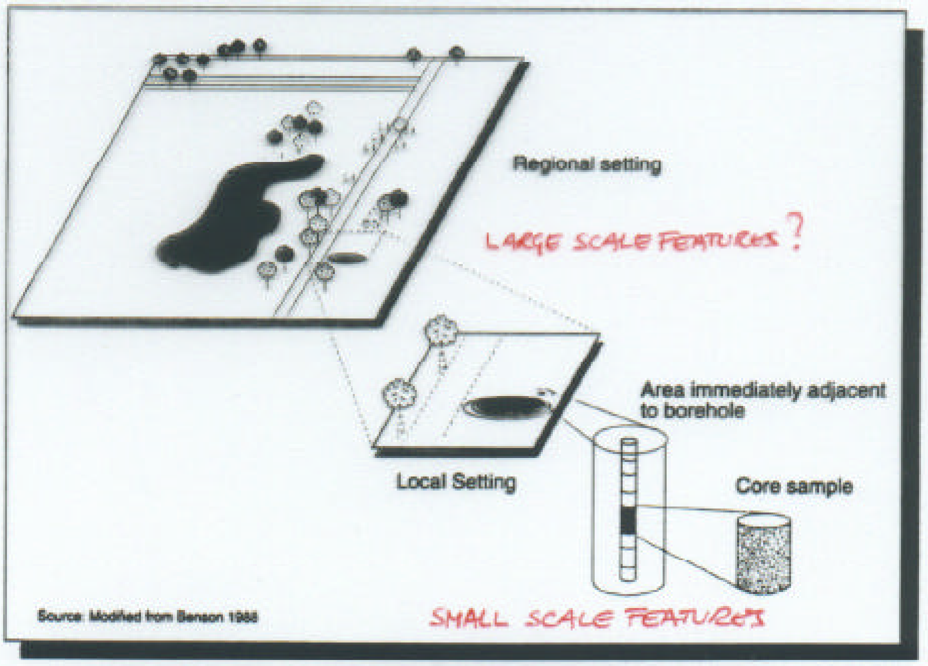


Figure 3-3a Phase II Flow Diagram

CONCEPTS OF SCALE



LARGE SCALE FEATURES?

SMALL SCALE FEATURES

Source: Modified from Benson 1988

Figure 3-12 Regional to Core Sample Scales

1. GEOMAGNETIC METHODS

- Measure change in Earth's mag. field
  ∴ Locates ferrous targets

- Response proportional to
  1. Mass of target, M.
  2. $\frac{1}{r^3}$ separation of target.

- Susceptibility to urban utilities
  ∴ rural areas better

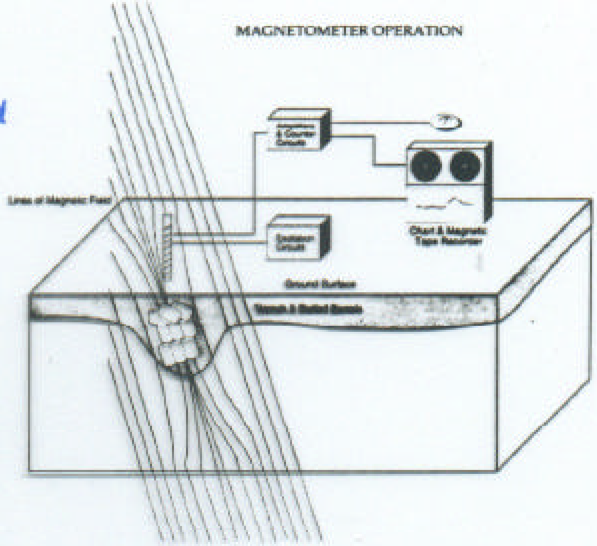


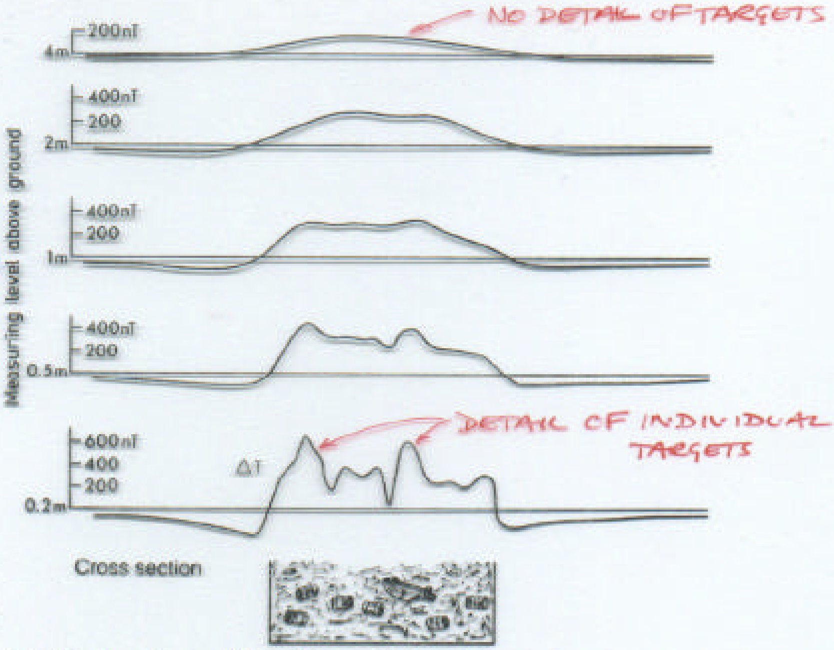
Figure 3-20 Magnetometry

- Measurement in nTeslas
  i.e. 10^{-9} Teslas

- Resolution ↓ with ↑ target depth since $1/r^3$

Max Depths

- 1 drum @ 10 ft.
- Multi-drums @ 30ft.



NO DETAIL OF TARGETS

DETAIL OF INDIVIDUAL TARGETS

Fig. 2.1. Magnetic anomalies at different heights above ground

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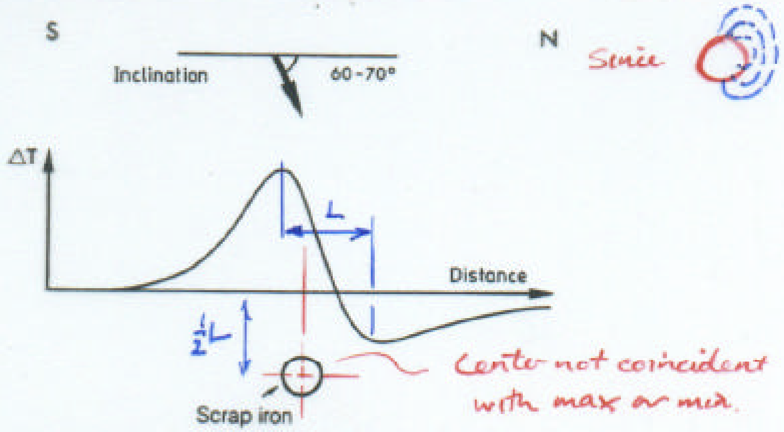
Anomoly influenced by inclination of Earth's mag. field. (60° in U.S.)

Max to South

Depth = $\frac{1}{2}$L.



Since

Center not coincident with max or min.

Fig. 2.2. Magnetic section of the total intensity DT over a globe-shaped concentration of scrap iron at 65° latitude

Two types of magnetometers

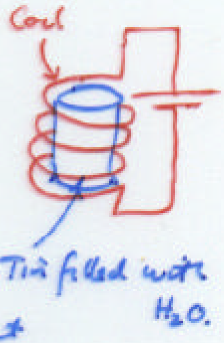
1. Permanent Magnet Magnetometers

{ Magnetic field balance
{ Torsion magnetometer

- Measures ↑ and → magnetic components
- Accuracy 1 nT
- Slow but v. accurate

2. Proton Magnetometers

- Measures total field, T, or variations, ΔT.
- Principle:
  - Apply a strong 1 second duration magnetic field
  - Causes hydrogen protons to spin (changes spin)
  - Shut off magnetic field and measure spin frequency.



- Fast, but records only max field component
- Accuracy $\frac{1}{2}$ nT

2. GEOELECTRIC METHODS

- D.C. METHODS
    - PROFILING
    - SOUNDING
- ELECTROMAGNETIC (GPR)

DC. METHODS

- Uses electrical conductivity/resistivity contrasts.
- Apply D.C. field.
- Measure modified field

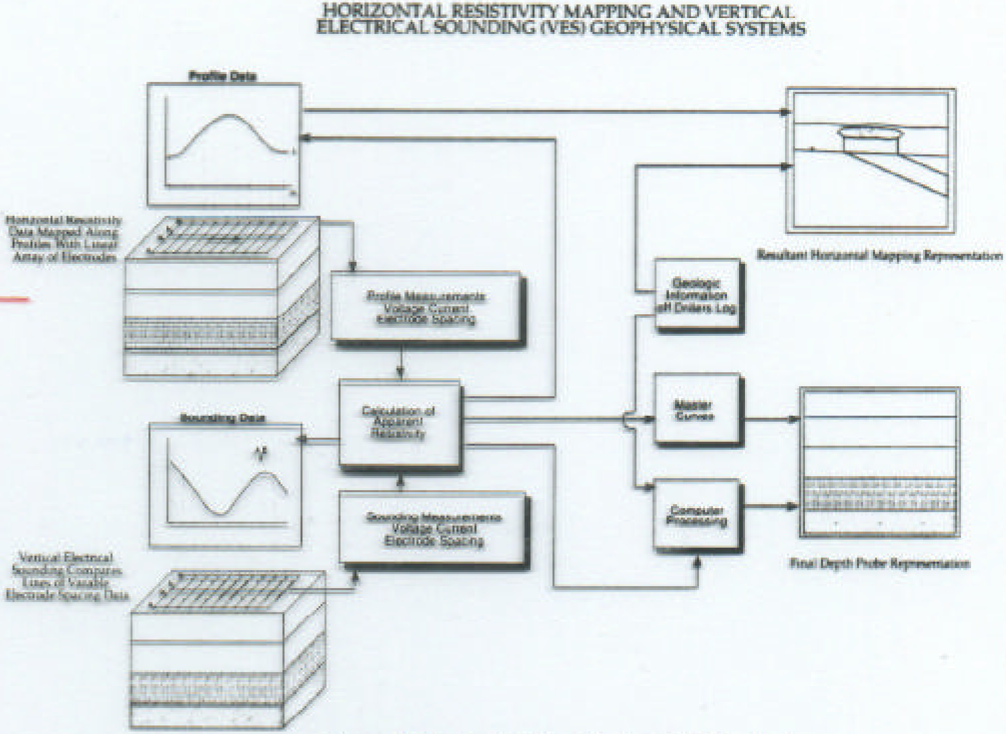
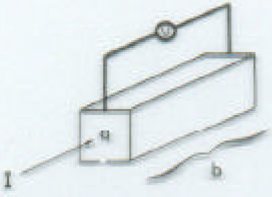


Figure 3-27 Resistivity Geophysical Method

Ohm's Law

$U = I \cdot R$

R = resistance [Ω]



I = Current (A)
U = Potential (V)
q = Cross section of rectangular parallelepiped
b = Length of parallelepiped

Fig. 2.3. Current flow through a limited conductor

$R = \frac{b}{q} \rho$

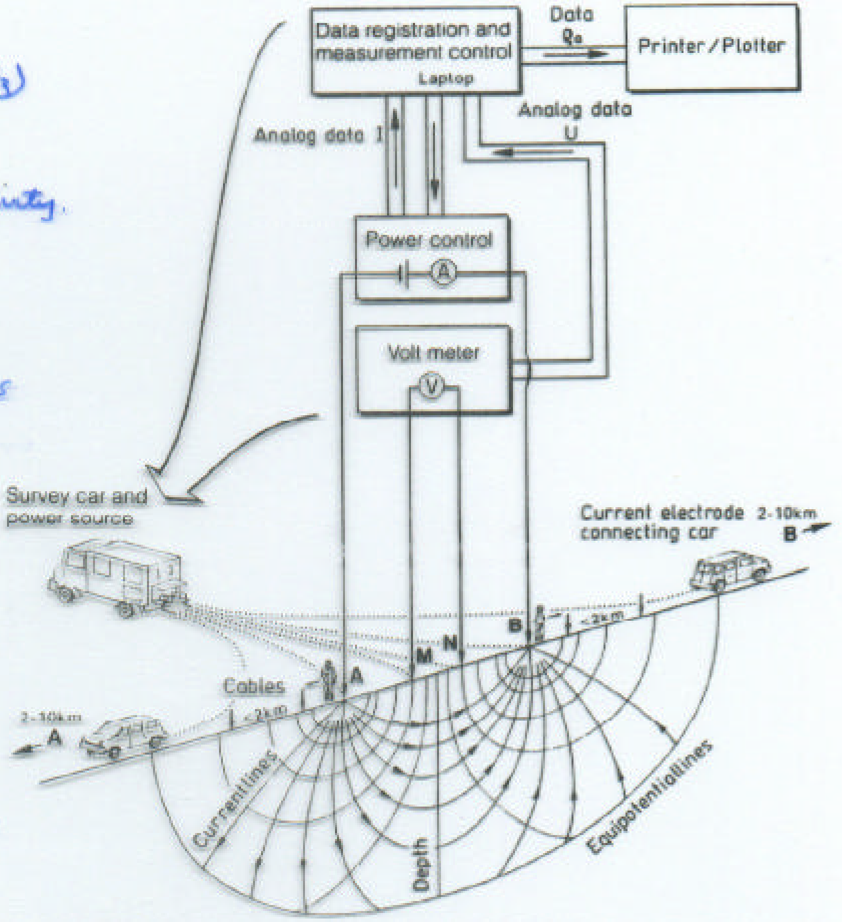
ρ = Specific resistivity [Ωm]

Method

Apply 1. DC

2. AC @ low frequency (< 100Hz)

- Two stakes with high conductivity.
- Causes potential field
- Measure field by increasing spacing of input electrodes to ↑ depth penetration.
- Infer distribution of conducting layers.



I = Current (A)
U = Potential (V)
A, B = Current electrodes
M, N = Potential electrodes: non-polarizable

Fig. 2.4. Principle of measurement and potential field for geoelectric DC surveys

Data Reduction

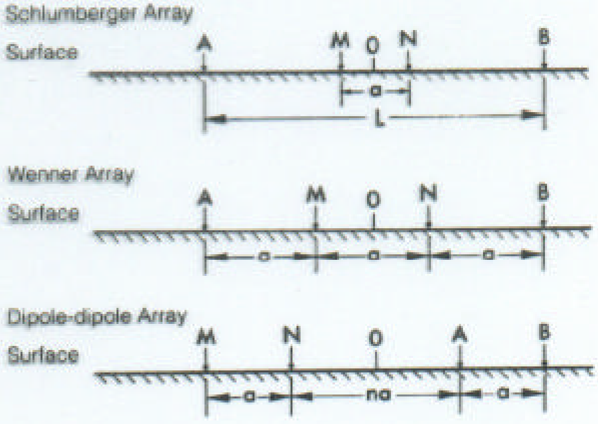
Plot $\frac{U}{I}$ at variable separation.

$\frac{U}{I} \approx R$ but are really specific resistivities, ρ_a, since measured at top of half-space.

Correct to specific resistivities as:

$$\rho_s = K\left(\frac{U}{I}\right)$$

	K
Schlumberger	$\frac{\pi}{a}[(\frac{1}{2}L)^2 - (\frac{1}{2}a)^2]$
Wenner	$2\pi a$
Dipole-dipole	$\pi a \cdot n(n+1)(n+2)a$

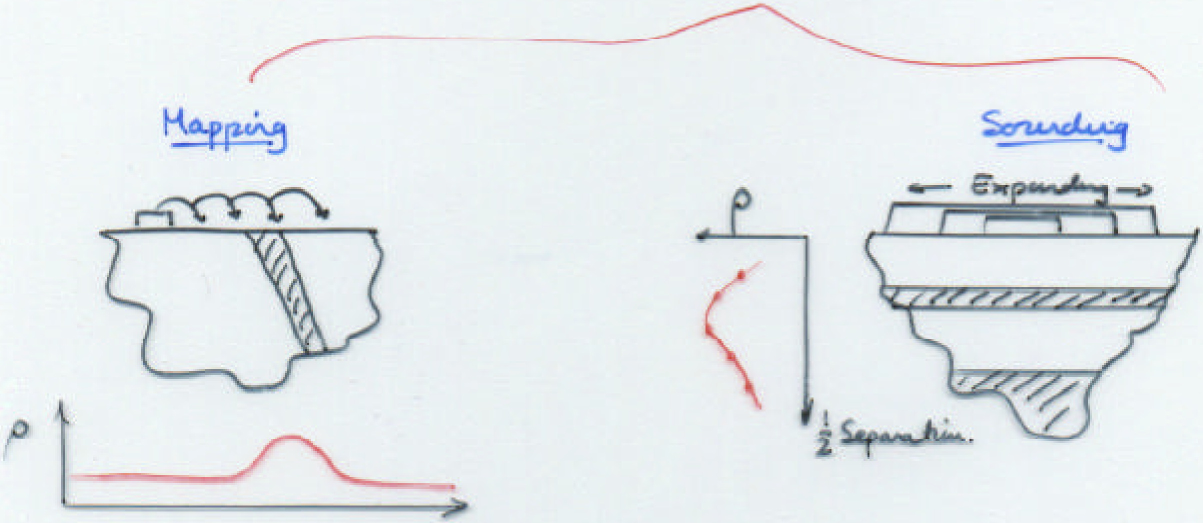


L = AB = Separation current electrodes
a = MN = Separation potential electrodes
O = Point of measurement

Fig. 2.5. Arrays for geoelectric mapping and sounding

Connect the magnitudes to ρ_s:

Method depends on resistivity contrast between layers



Mapping

- Locate rim of disposal sites / or drums / or plumes

- Fixed array separation ∴ locate changes in ρ_s or absolute magnitude of ρ_s
- Separation between electrodes chosen for sampling depth.
  Wenner array commonly used.
- Require contrasts in ρ_s

Garbage	< 20 Ωm	
Gravel/sandstone	1000 Ωm	Contrast ok
Clays	3–30 Ωm	No contrast.

SOUNDING

Determine:

1. Apparent resistivities of strata
2. Thickness and depth of interfaces

Mainly Schlumberger array

1. Increase separation logarithmically
2. Plot $\rho_a = \frac{U}{I}$ with half spacing L/2
3. Match with model type curves, or invert numerically.

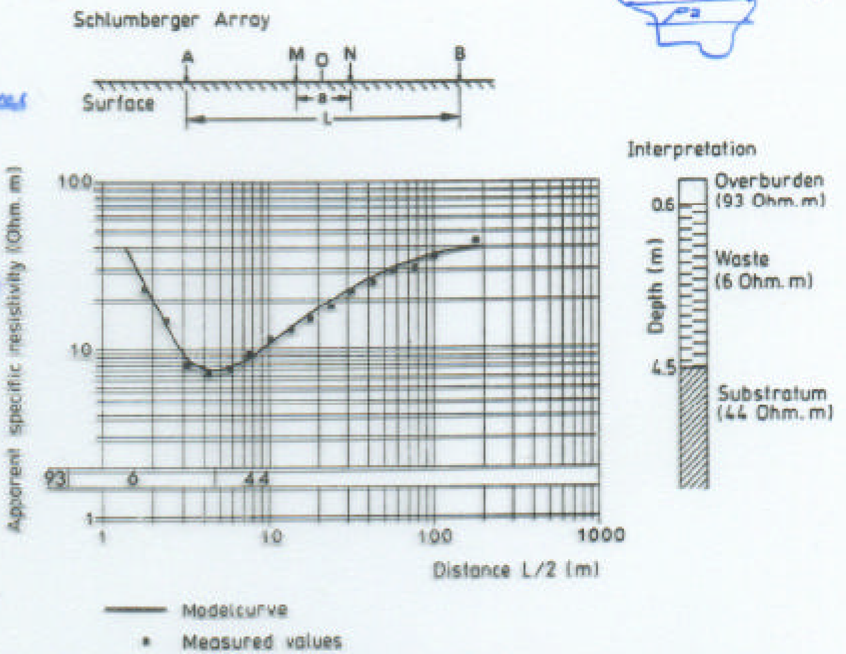


Fig. 2.6. Geoelectric sounding curve (VES) of a Schlumberger array with digital interpretation and computed model curve of the minimum type "H"

Problems

1. Omitted beds

   Thin layers or layers masked by very conductive beds

2. Equivalence

   Non-unique curves since equivalence of behaviour

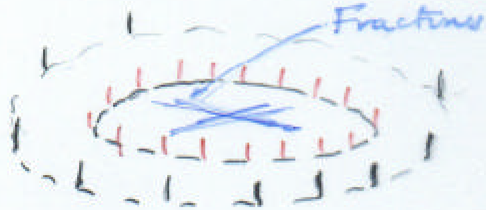
Table 2.1. Specific resistivities

Rock type/Material	Specific resistivity [Ωm]
Rock type	
clay, marl, rich	3 – 30
clay, marl, meagre	10 – 40
clay, sandy, silt	25 – 150
sand, with clay	50 – 300
sand, gravel in ground water	200 – 400
sand, gravel, dry	800 – 5000
rubble, dry	1000 – 3000
limestone, gypsum	500 – 3500
sandstone	300 – 3000
salt beds and salt domes	> 10000
granite	2000 – 10000
gneis	400 – 6000
Deposited refuse	
domestic garbage	12 – 30
debris and dumped soil	200 – 350
industrial mud	40 – 200
scrap metal	1 – 12
pieces of broken glass and porcelain	100 – 550
casting sand	400 – 1600
wastepaper (wet)	70 – 180
contaminated plume of domestic-garbage dump	1 – 10
used oil	150 – 700
tar	300 – 1200
cleaning clothes and materials	30 – 200
used lacquer and paint	200 – 1000
barrels (empty)	5 – 20

Equivalence

- Non-unique solution
- Match with borehole data
- Effect of saturant may influence results.

Fracture detection methods



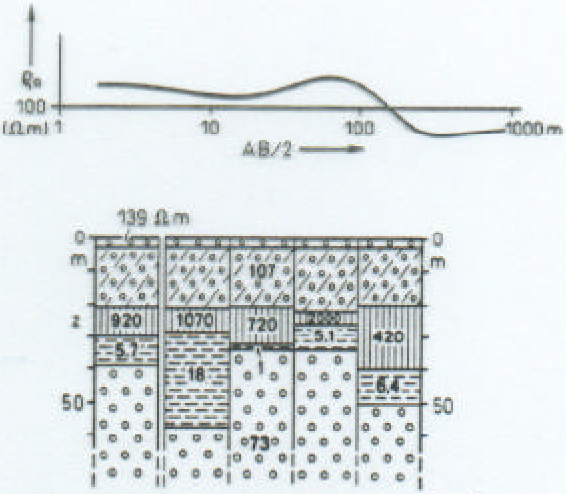


Fig. 2.7. Equivalent digital interpretations of a Schlumberger sounding curve. Left column = mathematically best model. The selection of the most suitable model has to consider neighboring curves and the known geology

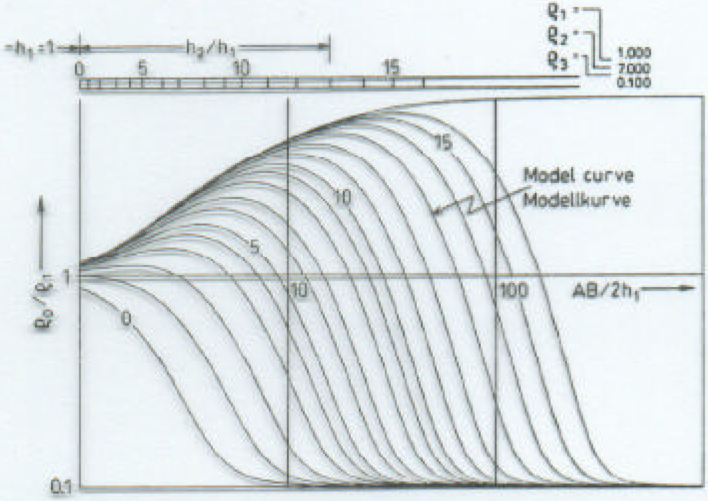
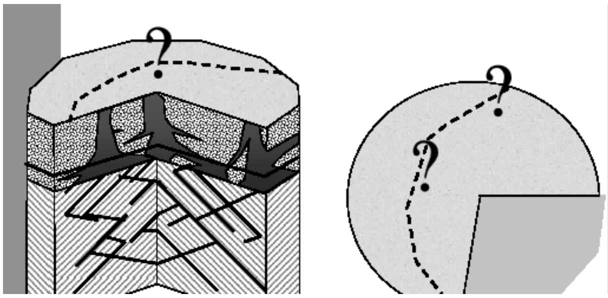


Fig. 2.8. Three-layer master curves in a log-log graph of the INGESO atlas. The resistivities of the three beds are in the ratios 1:7:0.1; first layer : second layer : third layer. The sounding curve, which has been drawn on log-log graph paper in the field, is laid on top of the master curve and moved around until one of the master curves tallies with the field curve. The thickness of the second layer, which has here seven times the pa-value of the first layer (see the resistivity values at the top right) can be found by the number of the curve no.13. On the thickness beam at the top left, which is divided from 0 to 16, the thickness h_2 can be directly determined

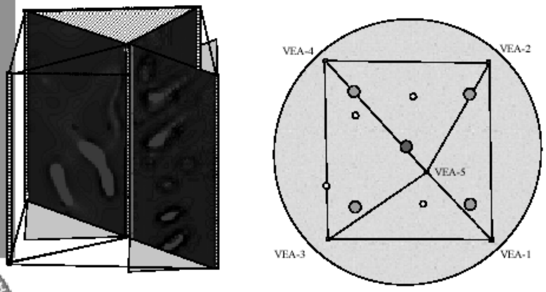
Edwards AFB, CA – Thermal Remediation Monitoring with ERT

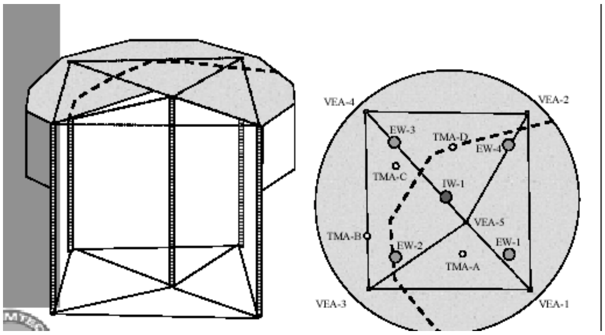
Edwards Air Force Base, Edwards, CA

Contaminants Treated:	TCE
Hydrology:	Groundwater at 30 feet bgs
Geology:	Fractured granite
Starting Contaminant Levels:	DNAPL expected
Cleanup Levels Achieved:	Project Awarded in 2000
Remediation Time Period:	May-June 2002
Client Reference:	Scott Palmer, Earth Tech, San Jose CA, (408)-232-2826
Remediation Design Engineers:	Dr. Gorm Heron, Dr. Steve Carroll, Mr. Hank Sowers

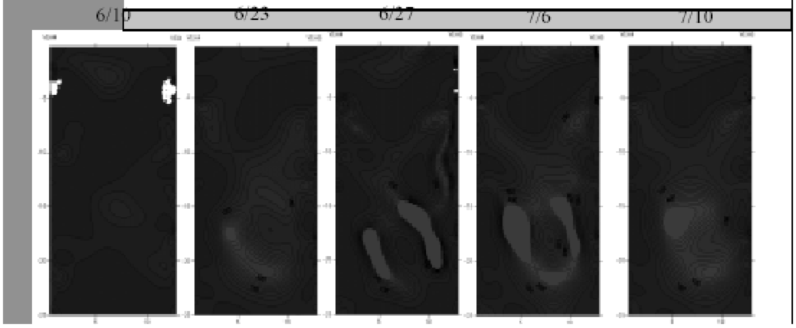


ERT data planes





Example ERT data plane



INDUCED POLARIZATION (INDUCED POTENTIAL)

- Apply DC current as Wenner or Schlumberger.
- Cut current and measure voltage decay with time 1s – 8s
- Reverse current to erase remnant charge

Effective depth penetration, D

$D \sim a(n+1)\frac{1}{2}$

Dipole lengths n = 1 to 6

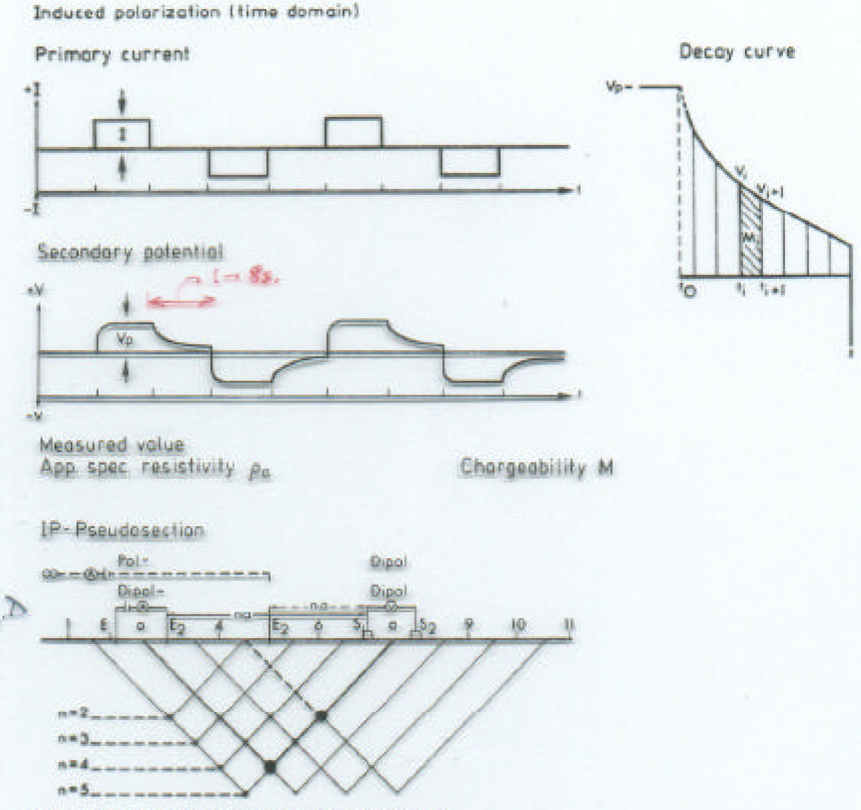


Fig. 2.9. Principle of induced polarization (IP)

SELF POLARIZATION

- Measures natural geo-electric field
- Results from chemical reactions (natural battery) eg Redox.

30mV – 200 mV

- sometimes results from rapid fluid flow <10mV.

2.2 ELECTROMAGNETIC METHODS

NOTE: $v = f\lambda$

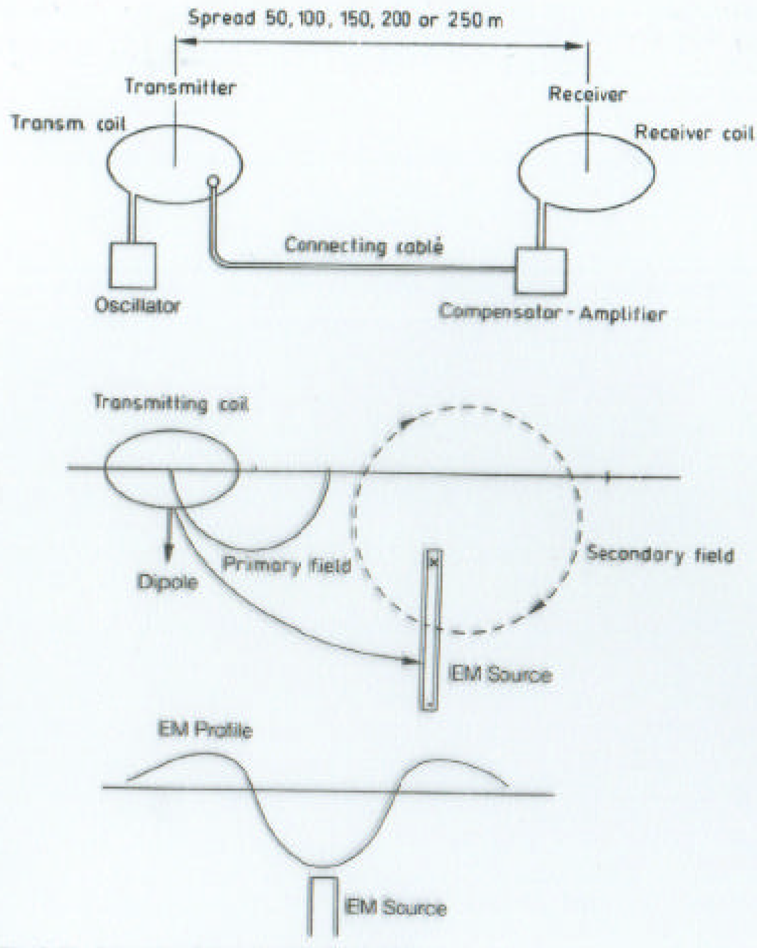
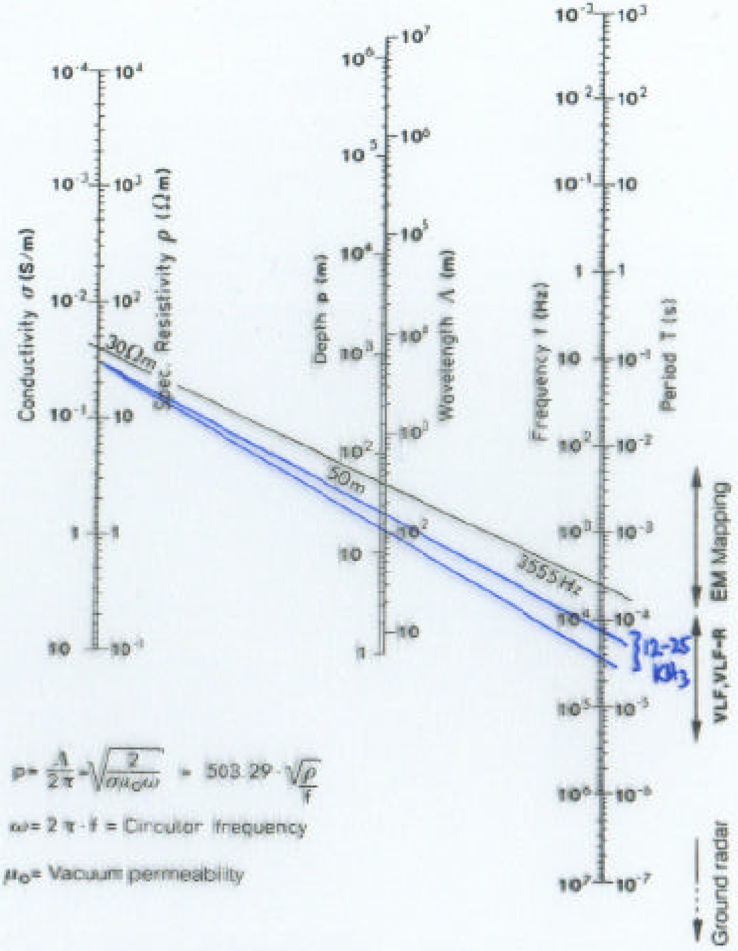


Fig. 2.11. Principle of electromagnetic mapping



$$p = \frac{\Lambda}{2\pi} = \sqrt{\frac{2}{\sigma\mu_0\omega}} = 503.29 \cdot \sqrt{\frac{\rho}{f}}$$

$\omega = 2\pi \cdot f$ = Circular frequency

μ_0 = Vacuum permeability

Fi. 2.12. Nomogram showing the relations of specific resistivity (left column), depth of penetration (middle column) and frequency (right column) of a homogenous plane wave

EM Mapping (Longitudinal profile)

- Primary EM field by primary coil
- Induces secondary EM field in body of different specific resistivity ρ_x
- Resolve interpretive ambiguities using multiple frequencies. (perhaps 12)

EM by Distant Transmitter (VLF)

- Permanent transmitters around globe (12 - 25kHz) (Submarine navigation)
- Measure induced secondary fields & interpret.
- Set frequency ∴ depth of penetration ~ 15m for $\rho_a < 30\ \Omega m$.

TIME-DOMAIN ELECTROMAGNETICS (TDM)

⇒ Similar to IP but decay of EM signal is measured with time.

⇒ Transmitter loop of 5m to 100m diameter but achieve large depth penetration 50 - 1000m.

Applied to determine brine pools and salt water intrusion.

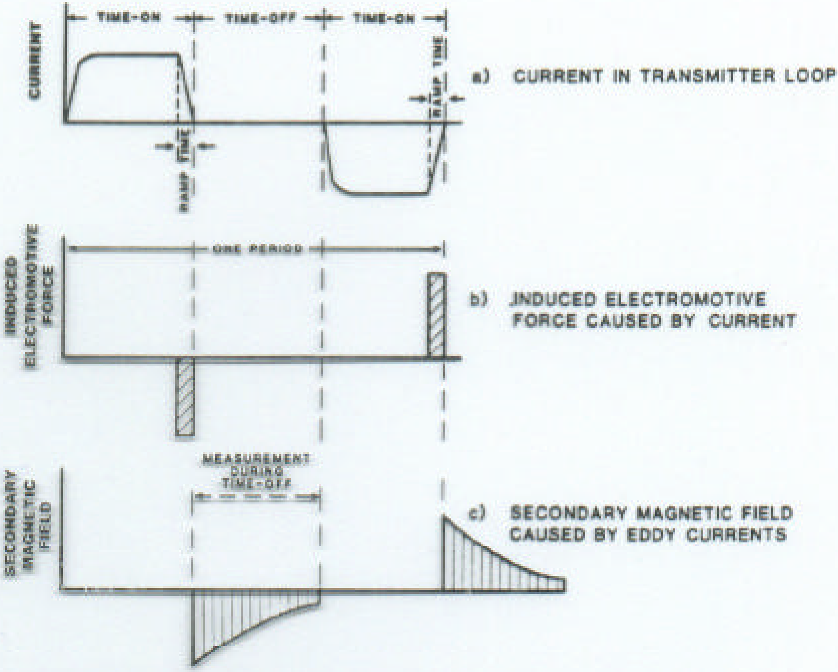
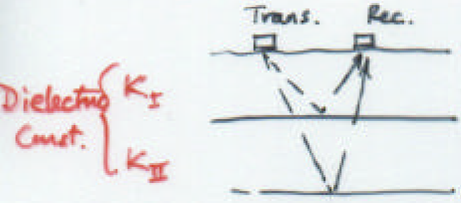
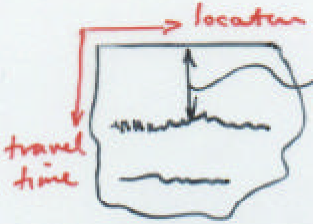


Fig. 2.15. System wave forms employed by the TDEM method

GROUND-PENETRATING RADAR (GPR)





Records travel time that must be scaled to a velocity → depth.

- Shallow depth penetration for EM waves 8 MHz – 4 GHz
  Reflection from interfaces with dielectric constant contrast, K

- Dielectric constant, $K = \frac{\text{Capacitance of material}}{\text{Capacitance of vacuum}} = \varepsilon$ (non-dimensional)

- Depth penetration – Limited in low conductivity (high resistivity)
  Clays 0.2 m
  Salt, ice, dry granite > 300m
  Typically 3–10m.

- High dielectric contrast of water (80) greatly influences response
  – Changing saturation (record infiltration in real time)
  – Type of saturant (LNAPL or DNAPL)

- Depth penetration controlled by frequency
  ↑ frequency → reduce penetration and increase resolution
  (see nomogram)

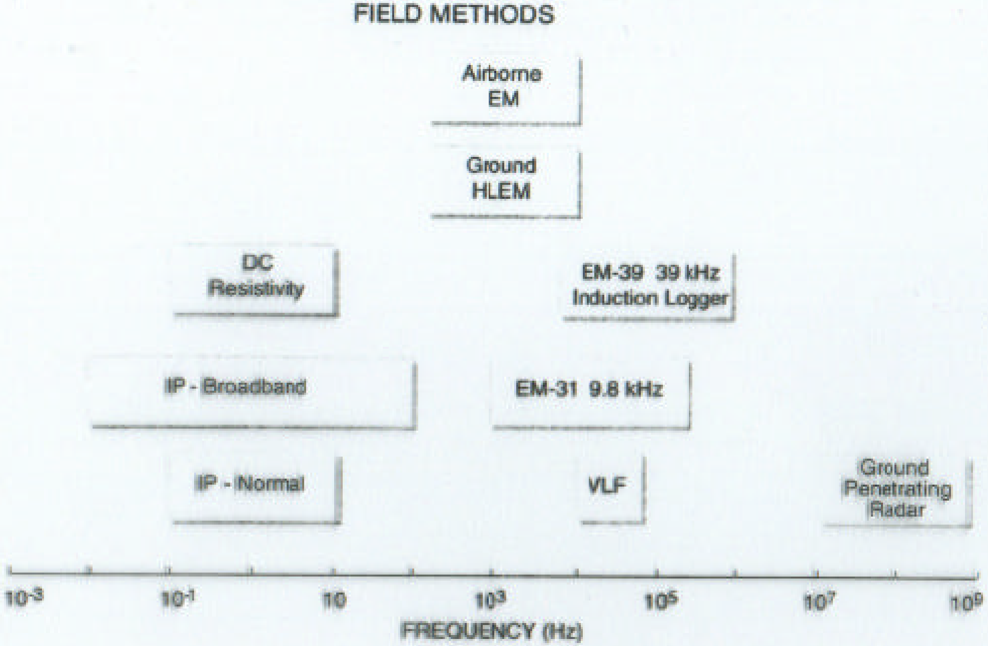
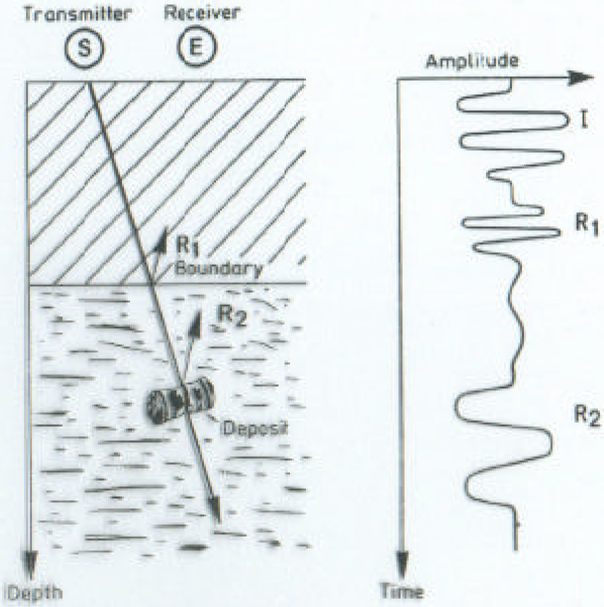


Figure 3-22 Frequencies Used By Electrical Geophysical Methods



I = Transmitted radar-pulse
R_1, R_2 = Reflected pulses

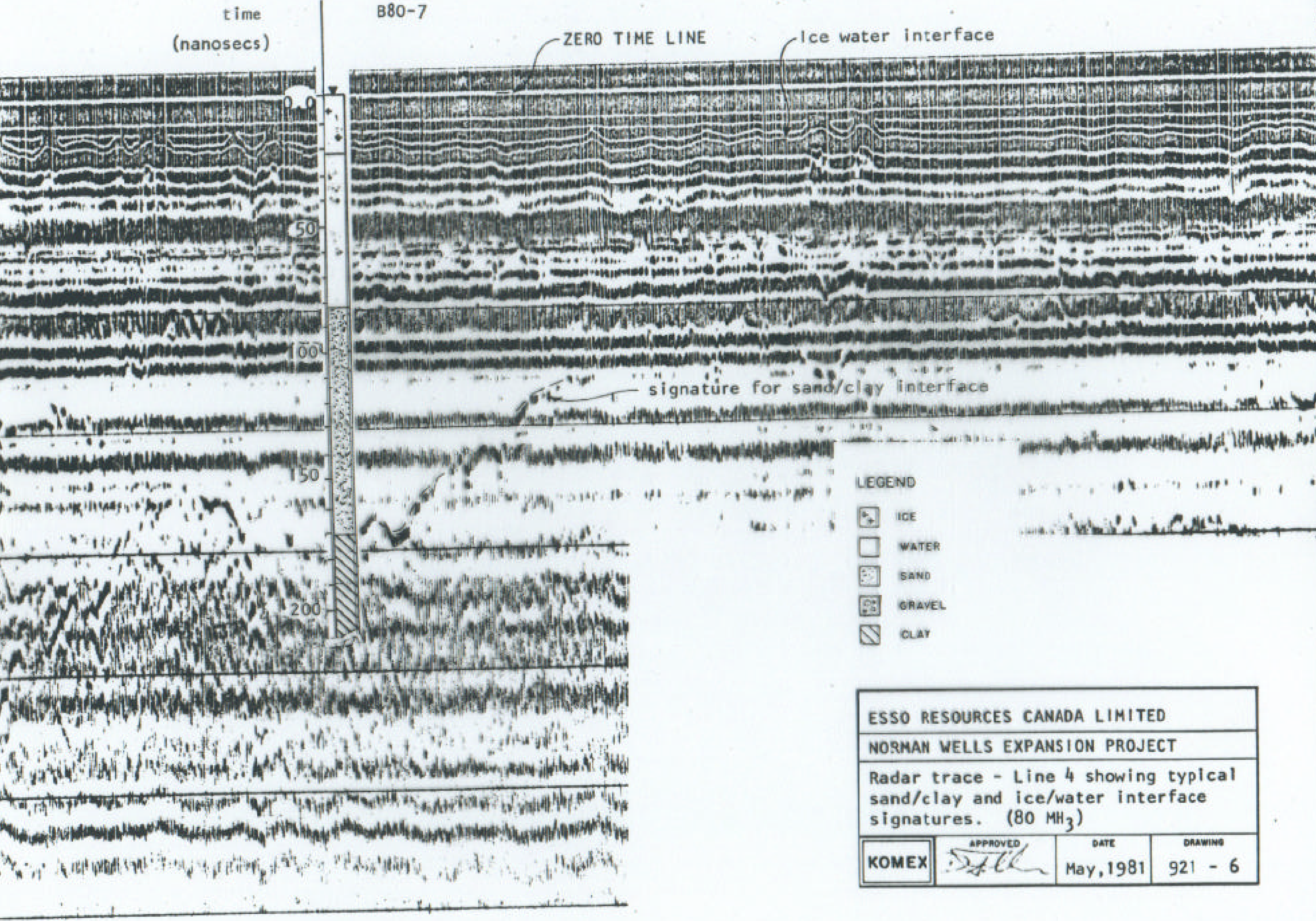
Fig. 2.17. Principle of ground radar measurements

Table 2.3. Dielectric constants (K), electric conductivity (σ), electric velocity and attenuation (a) at a frequency of 100 MHz. Davis and Anan (1989)

Material	K	σ(mS/m)	v (m/ns)	a (dB/m)
Air	1	0	0,3	0
Freshwater	80	0,01	0,33	$2 \cdot 10^{-1}$
Seawater	80	$3.0 \cdot 10^{1}$	0,01	0,1
Dry sand	4	0,01	0,15	0,01
Wet sand, Aquifer	25	$0{,}1^{-1}$	0,06	0,03
Limestone	6	$0{,}5^{2}$	0,12	0,04
Fat clay	5–35	0,05	0,06	1,0–300
Granite	5	0,1–1	0,13	0,01
Rock salt	6	0,1–1	0,13	0,01
Slate	5–15	0,03	0,09	1,0–100

↑ Velocity of EM wave enables calculation of reflector depth

↑ Dielectric const defines the potential for attenuation



ESSO RESOURCES CANADA LIMITED

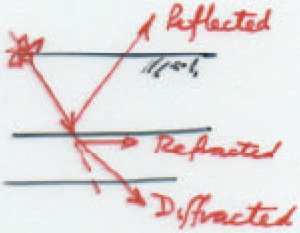
NORMAN WELLS EXPANSION PROJECT

Radar trace - Line 4 showing typical sand/clay and ice/water interface signatures. (80 MH_3)

	APPROVED	DATE	DRAWING
KOMEX		May,1981	921 - 6

3. SEISMIC METHODS

- ☐ Measures elastic properties of rocks ($V_s = ?$)
  evidenced through seismic velocity
- ☐ Locates interfaces between different V_s



At interfaces; seismic waves are { Diffracted / Refracted / Reflected

Procedure

1. Arrange geophones along single line
2. Provide initial shock input. Hammer/Drop hammer/Explosive/Air gun.
3. Record first (primary) and sometimes secondary (shear wave) arrivals

↓

Evaluate { 1. Bed thickness / 2. Seismic velocity

1. Primary compressional wave (P wave)
2. Shear wave (slower) S-wave.

S wave attenuated by fluid saturated materials
eg fluid filled fractures.

Typically:

1. V_s increases with depth (due to $\uparrow E$)
2. Weathered surface zones have $\downarrow V_s$
3. Two methods of interpretation

3.1 Seismic Refraction

3.2 Seismic Reflection.

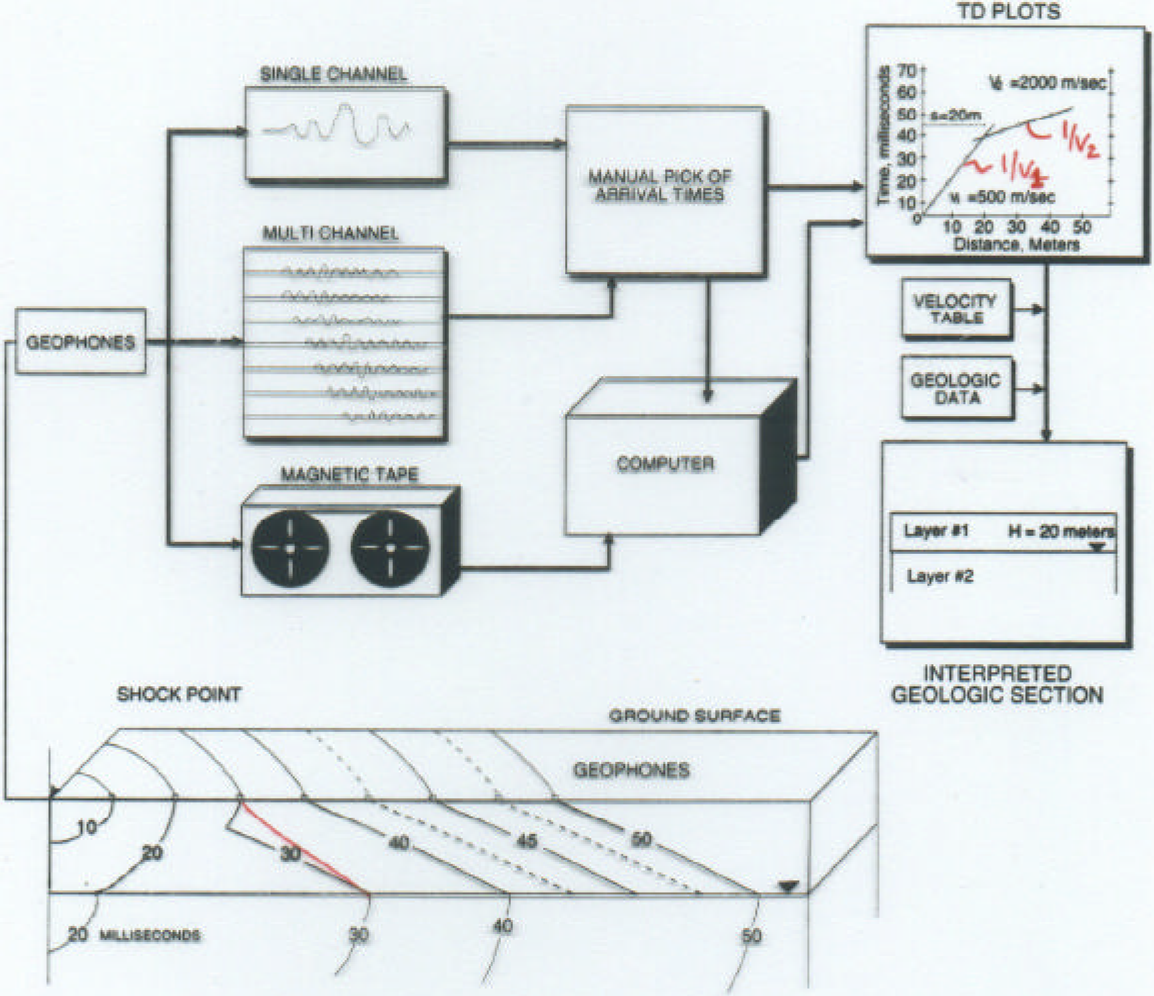
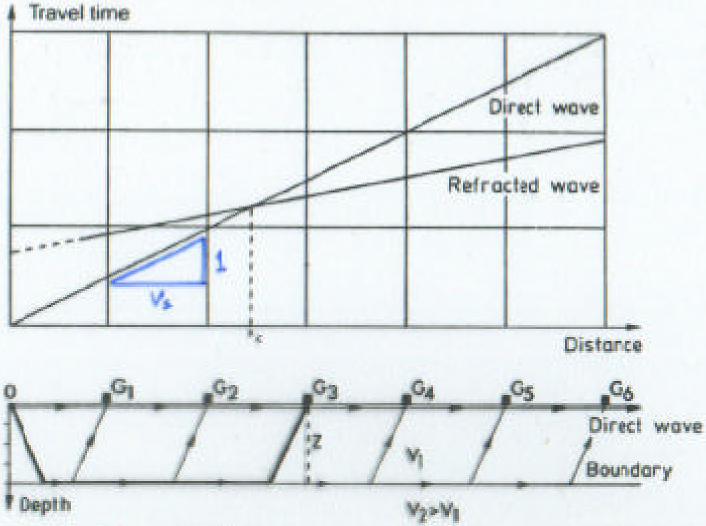


Figure 3-15 Seismic Geophysical Method

3.1 SEISMIC REFRACTION



G_1 - G_6 = Geophones
V_1, V_2 = Seismic velocities
x_c = Critical distance

Fig. 2.18. Principle of seismic refraction

1. Fire shot and plot
   time distance graph of first arrivals.
2. Evaluate unit velocities of units
   from slope of curve
3. Evaluate layer depths from inflection points

String length defines depth penetration

String length / 5 = desired penetration depth

typical depths of <50m

Ambiguities – weathering

water table

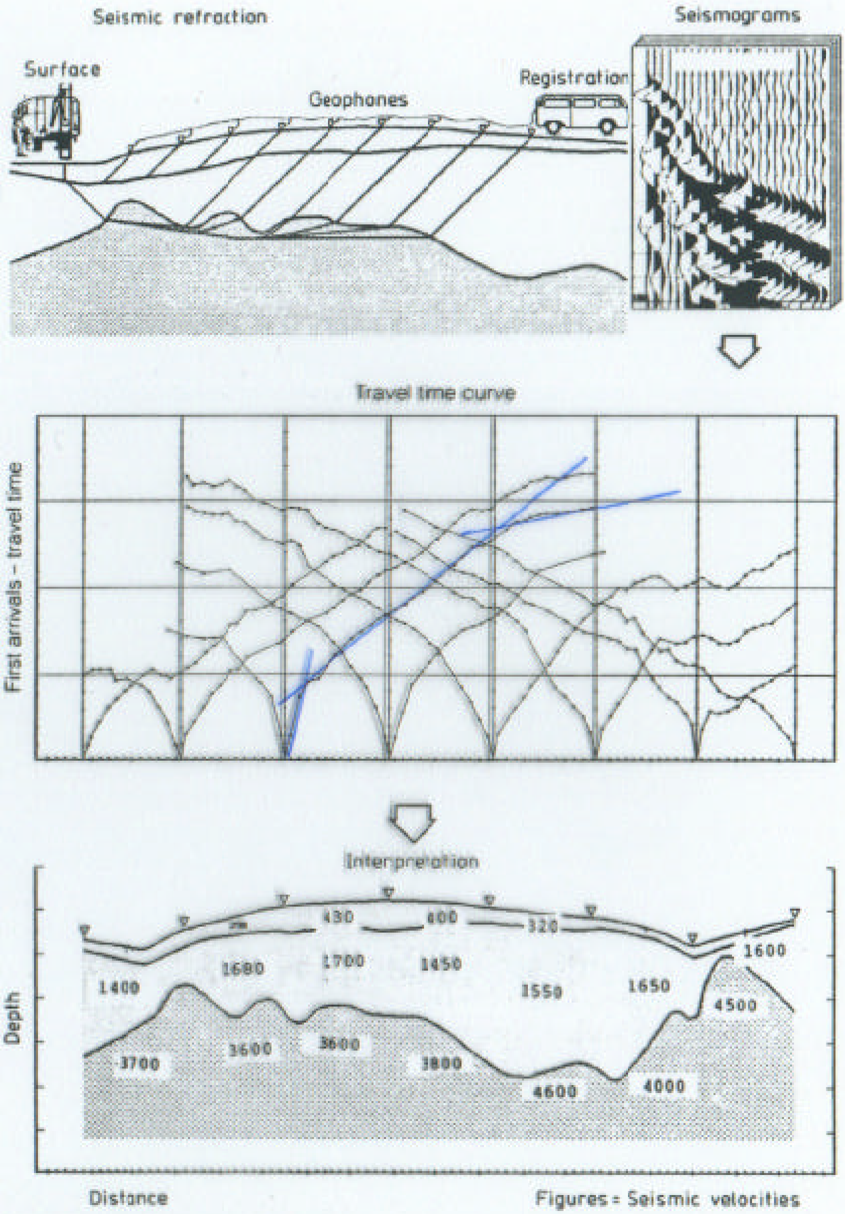


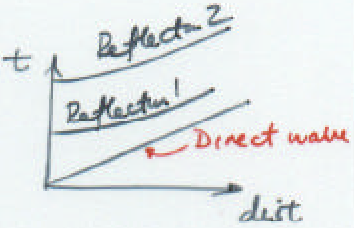
Fig. 2.19. Pattern of seismic refraction

3.2 SEISMIC REFLECTION

Source impulse creates shock front reflected by interfaces.

Reflection occurs @ interfaces with "seismic impedence" changes. Seismic impedence = ρV_s

density



Measure arrival times and plot as time – distance.

Advantages over Refraction

1. Increased depth penetration with small string length

Disadvantages

1. Reflected wave arrives so quickly that surface waves are present and must be filtered out.

To use @ depth < 50m, need:

① Receivers with high sampling rate and high frequency source

② Sophisticated filtering and data analysis methods.

REFLECTION

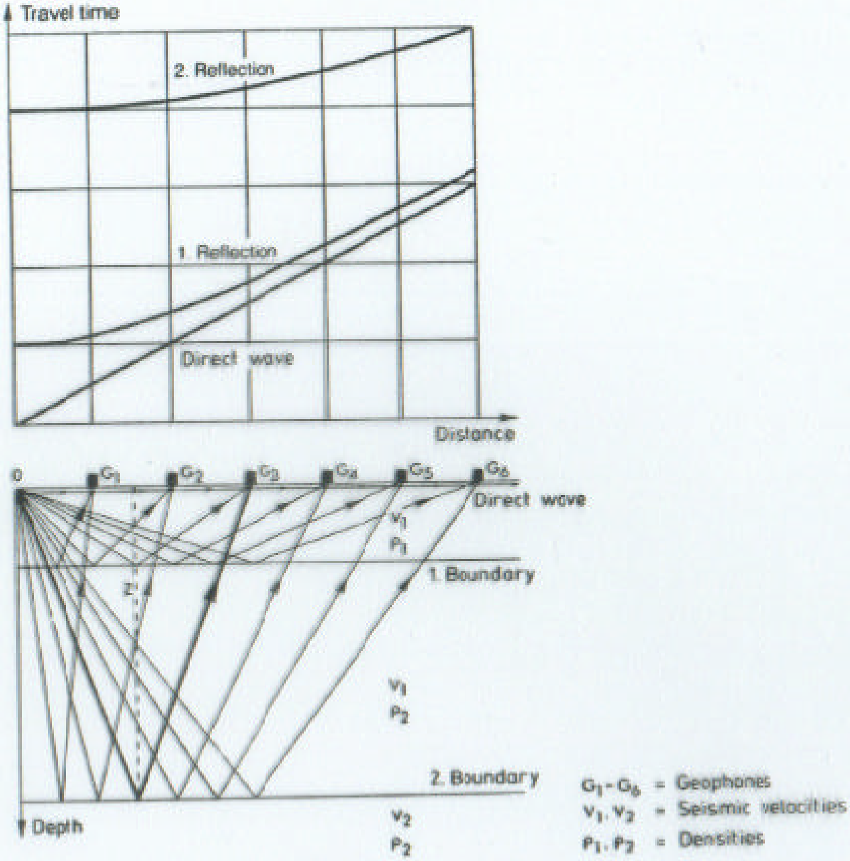


Fig. 2.21. Principle of seismic reflection

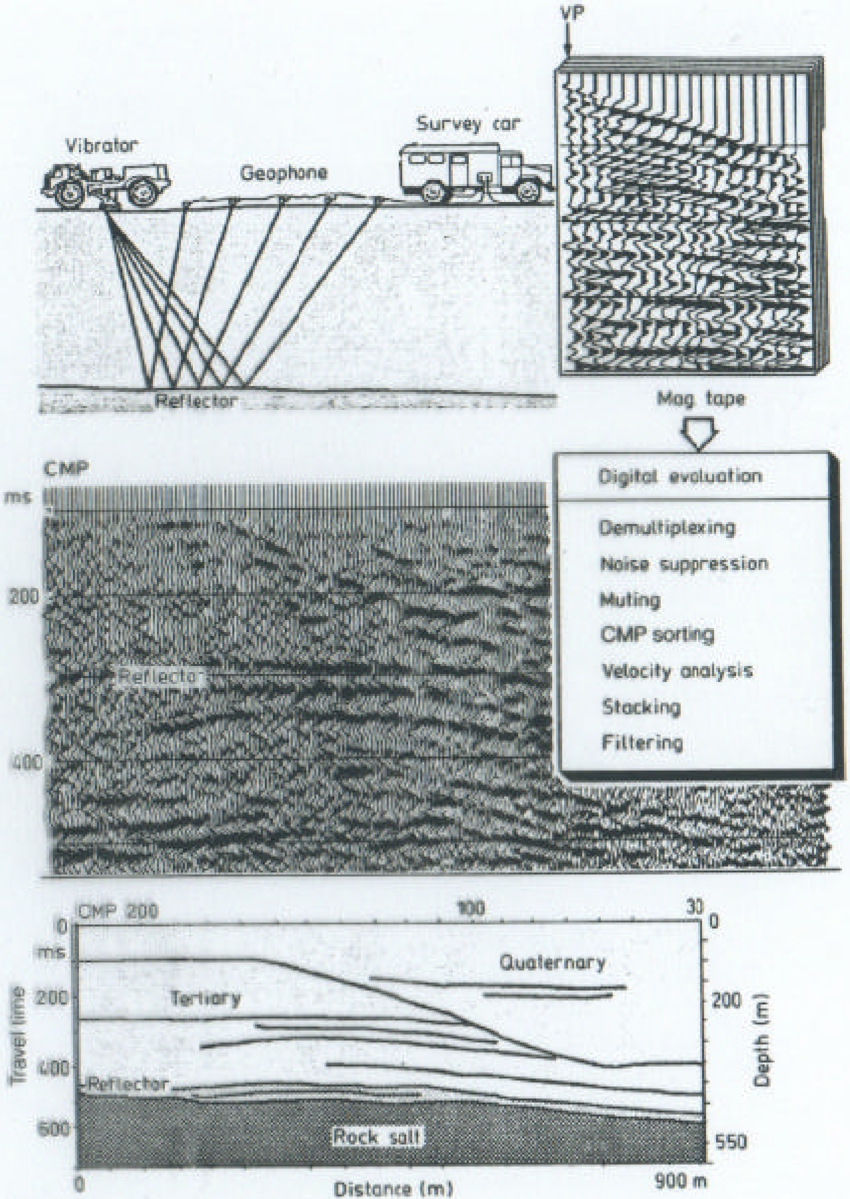


Fig. 2.22. Pattern of seismic reflection

4. GRAVITY METHODS

Detect changes in density according to Newton's Law of gravitational attraction

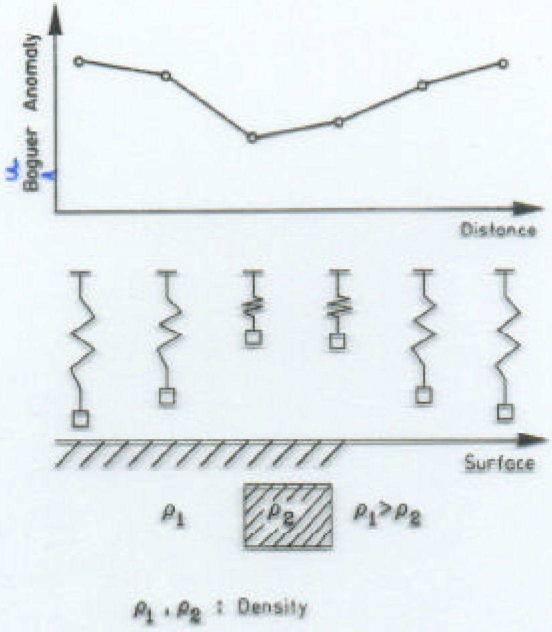
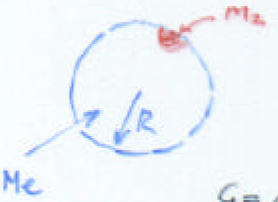


Fig. 2.23. Principle of gravity measurements

$$g = \frac{F}{m_2} = \frac{GM_e}{R^2}$$



G = gravitational constant 6.67×10^{-8} degree $\frac{cm^2}{g^2}$

g = grav. accn.

Gravitometers measure variation in $g = 9.8\, m/s^2$ of $10^{-5}\, m/s^2$

Gravity depends on:

1. Latitude (Non-perfect sphere) 
2. Elevation (R) [Free air correction]
3. Topography (m_2) [Terrain correction]
4. Earth tides [Isostatic correction]
5. Density variations in subsurface [Bouguer correction]

Density is the only important factor in gravity measurements, but effect is much less than all other factors

Limited applicability to Environmental Surveys:

1. Small signal
2. High cost.

5. WELL LOGGING

- Applicable to materials in vicinity of wellbore
- Variety of logging signals available
- Recorded continuously with depth.

Methods

Gamma Ray	- Measures natural gamma radiation - Pick up clay layers to .3m resolution
Density Log	- Artificial source ^{137}Cs @ probe base and gamma detector @ top - Adsorption of gamma radiation by rock is proportional to density (Compton effect)
Neutron Log	- Artificial Neutron source - Measure backscattering to determine moisture content (presence of Hydrogen) → porosity log.
Electric Log	- Apparent resistivity in sidewall rock (Multiple pt. arrays) - May simultaneously measure self potential - Records mixed resistivity ∴ correct for mud/water effects
Salinometer	- Resistivity of borehole fluid.
Temperature	
Sonic velocity	
Caliper	
Flowmeter	
Deviation	

Table 2.4. Logging methods, measured parameters and objects of investigation

Symbol	Parameter	Result	Object
GR	count of natural gamma radiation	natural radioactivity of rocks	petrography clay content
D	counts of compton scattered rays	density of rocks	fracturing, porosity
N	counts of secondary neutron-neutron rays	lithology	stratigraphy porosity
EL, ES	apparent resisitivity	true resistivity	hydraulics, lithology
ML, MLL	apparent resistivity at borehole wall	true resistivity small scale	lithology, hydraulics
IEL	app. conductiviy, focused induction	true conductivity	lithology
FEL, LL	focused electric log	true resistivity of rock	lithology
SP	self-potential (probe-to-surface)	sources of electric potentials	oxidizing bodies
SAL	resistivity of borehole fluid	salinity	total salt content of fluid
TEMP	temperature of borehole fluid	geothermal field	thermal gradient
SONIC SV	travel time of seismic waves	seismic velocity	seismic velocity
CAL	borehole diameter	shape of borehole walls	correction of other logs
FLOW	revolutions of a spinner	velocity of fluid flow	zones of in- and outflow of water
DV	compass and dipmeter	inclination + azimuth of borehole	spatial drill path
OPT	video signals, photography	state of borehole walls	direct view of lithology

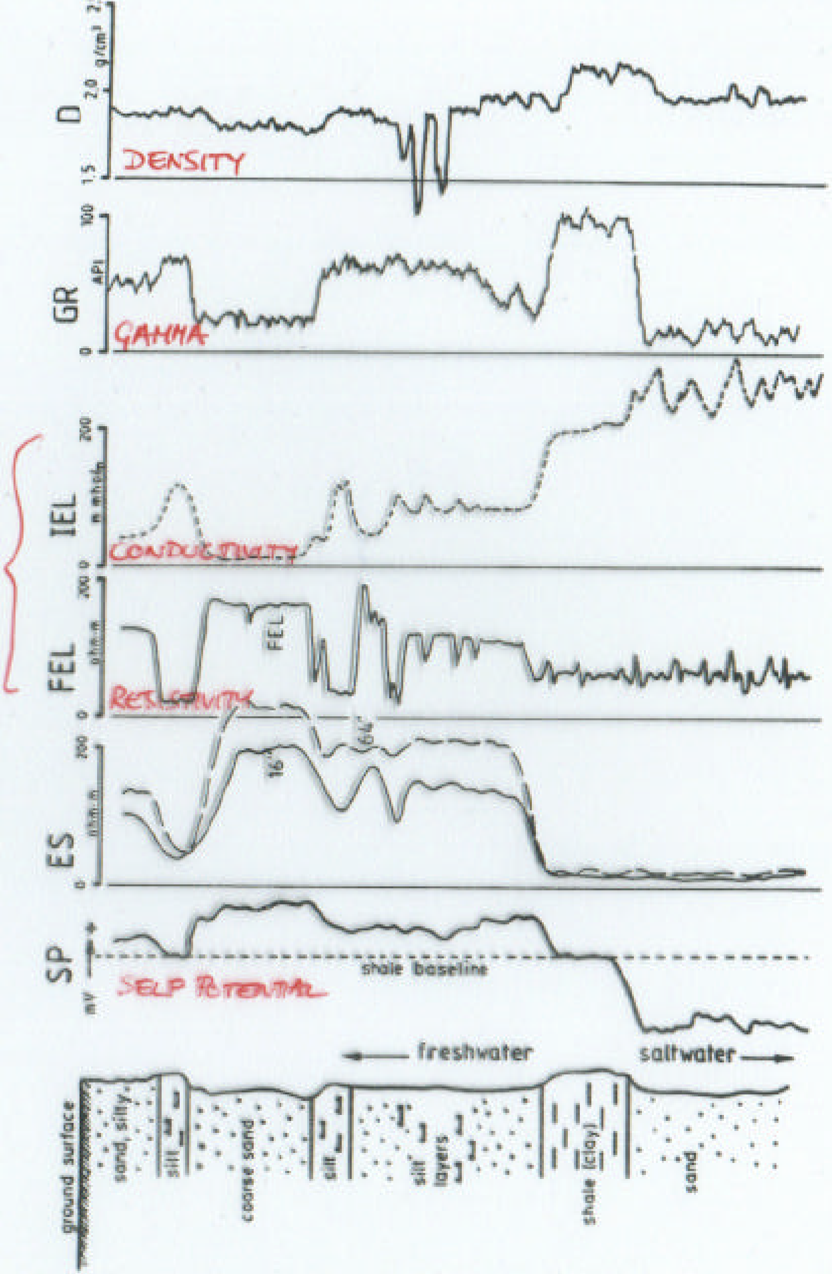


Fig. 2.24. Comparison of different logs with the lithology of cores.
SP = self-potential survey; ES = electrical survey measures resistivity in 16" and 64" point array; FEL = focused electrical log for thin layers; IEL = induction electric log measures electric conductivity; GR = gamma ray measures natural radiation; D = density log by artificial gamma source and detector

Table 2.4. Logging methods, measured parameters and objects of investigation

Symbol	Parameter	Result	Object
GR	count of natural gamma radiation	natural radioactivity of rocks	petrography clay content
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FEL, LL	focused electric log	true resistivity of rock	lithology
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OPT	video signals, photography	state of borehole walls	direct view of lithology

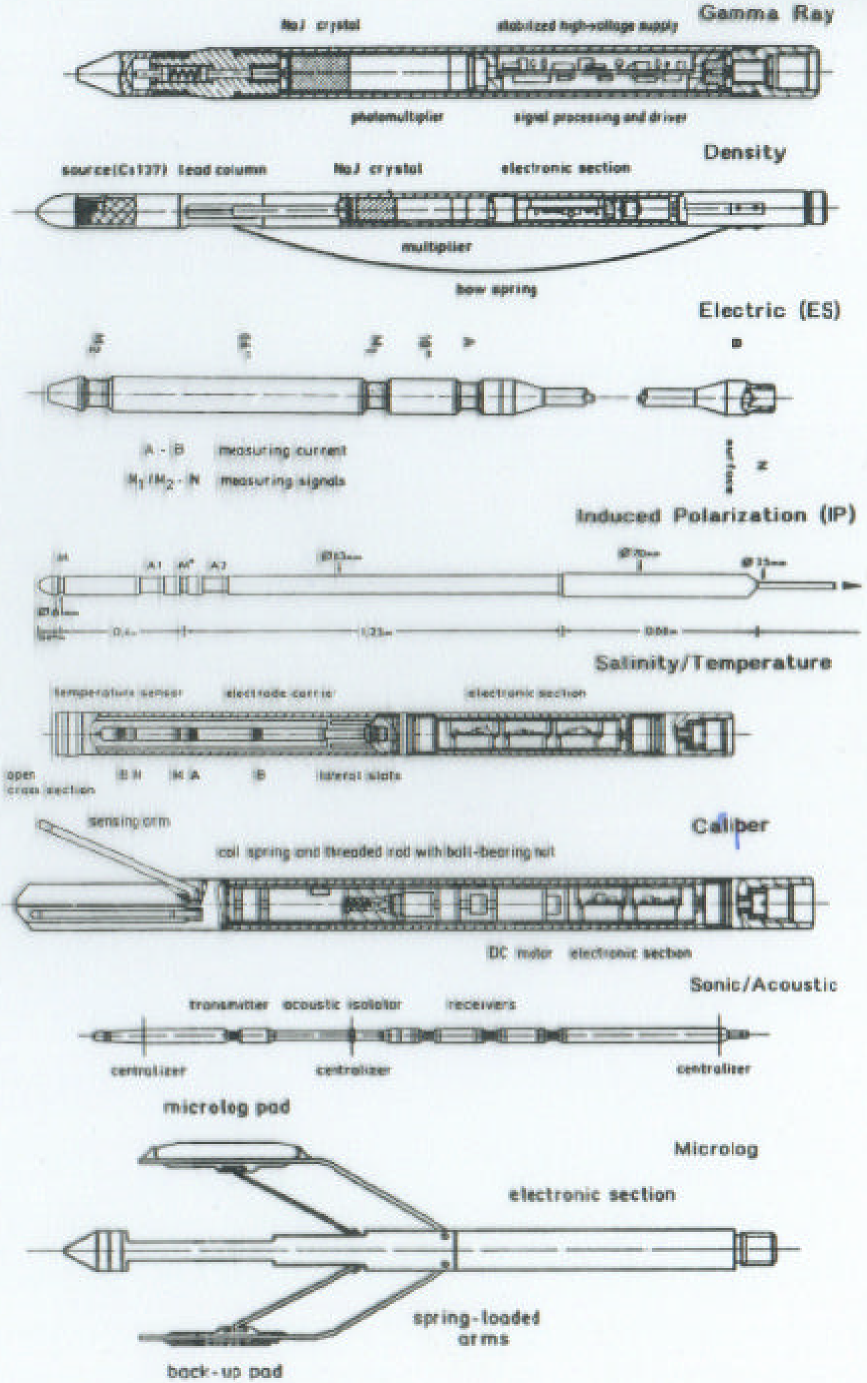


Fig. 2.25. Probes for geophysical well logging

This table is intended as a general guide. The application ratings given are based upon actual experience at a large number of sites. The rating system is based upon the ability of each method to produce results under general field conditions when compared to other methods applied to the same task. One must consider site-specific conditions before recommending an optimum approach.

In some cases a method rated 3 or NA may in fact solve the problem due to unique circumstances. For example, seismic refraction is rated NA for evaluating organic contaminants. However, in some cases where the contaminant flow is controlled by bedrock, the seismic method may provide an effective evaluation by mapping bedrock depth.

Organic Vapor Analysis

Application	GPR	EM	Res.	Seis.	MD	Mag.	OVA
Evaluation of natural geologic and hydrologic conditions							
Depth and thickness of soil and rock layers and vertical variations	1[a]	2	1	1	NA	NA	NA
Mapping lateral variations in soil and rock (fractures, karst features, etc.)	1[a]	1	2	2 (Refr.) 1 (Refl.)	NA	NA	NA
Depth of water table	3	2	1		NA	NA	NA
Evaluation of subsurface contamination and post-closure monitoring							
Inorganics (high TDS and electrically conducive)							
Early warning contaminant detection	3	1	2	NA	NA	NA	NA
Detailed lateral mapping	3	1	2	NA	NA	NA	NA
Vertical extent	3	2	1	NA	NA	NA	NA
Changes of plume with time (flow direction and rate)	3	1	2	NA	NA	NA	NA
Post cleanup/closure monitoring	3	1	2	NA	NA	NA	NA
Organics (typically nonconducive)							
Early warning contaminant detection	3	3	3	NA	NA	NA	1
Detailed lateral mapping	2[a]	2	3	NA	NA	NA	1
Vertical extent	2[a]	3	2	NA	NA	NA	2
Changes of plume with time (flow direction and rate)	3	3	3	NA	NA	NA	1
Post cleanup/closure monitoring	3	3	3	NA	NA	NA	1
Location of buried wastes and delineation of trench boundaries							
Bulk waste trenches—without metal	1	1	2	3	NA	NA	NA[d]
Bulk waste trenches—with metal	1	1	2	3	1[c]	1[b]	NA[d]
Depth of trenches and landfills	2	3	2	2	NA	NA	NA[d]
Detection of 55-gal steel drums	2[a]	2	NA	NA	1[c]	1	NA[d]
Estimates of depth and quantity of 55-gal steel drums	2[a]	3	3	NA	2	1	NA[d]
Location of utilities							
Buried pipes and tanks	1	1[c]	NA	NA	1[c]	1[b]	NA[d]
Potential pathways of contaminant migration via conduits and permeable trench backfill	1	2	NA	NA	2	2	NA[d]
Abandoned wells with metal casing	3	NA	NA	NA	2	1[b]	NA[d]

1 = Primary choice under most field conditions.
2 = Secondary choice under most field conditions.
3 = Limited field application under most field conditions.
NA = Not applicable.
[a] Shallow.
[b] Assumes ferrous metals to be present.
[c] Assumes metals to be present.
[d] Assumes no vapors present.

Note: Many site-specific conditions may dictate the choice of a method rated 2 or 3 in preference to a 1.

Magnetic detector

Source: Benson, 1988

Table 3-3 Applications of Selected Field Investigation Techniques for Waste Disposal Sites

	METHODS										
APPLICATIONS	SEISMIC	SEISMIC MONITORING	SONAR	GRAVITY	MAGNETIC	RESISTIVITY	ELECTROMAGNETIC	RADAR	TIME-DOMAIN REFLECTOMETRY	RADIOMETRICS	BOREHOLE LOGGING
DEPTH TO BEDROCK	●					○	○	●			
FAULT DETECTION	●				●		●				●
FRACTURES IN ROCK		○						○		○	●
BURIED CHANNELS	●			○		●	●	●			
GROUND WATER SURFACE	○					○	○	●	○		●
SOIL WATER CONTENT	○					○	○	●	●	●	●
WATER DEPTH			●					●			
SUB-BOTTOM STRATIGRAPHY	●		●					●			
SEA BED SCOUR			●								
ICE THICKNESS							○	●			
PERMAFROST MAPPING	●					●	●	●	○		
PEAT THICKNESS	○					●	●	●			
SOIL STRATIGRAPHY	●					○	○	●		○	●
SAND & GRAVEL MAPPING	○					●	●	●			
LEACHATE PLUMES						●	●	○		●	●
SALT WATER INTRUSION						●	●	○	○		○
BURIED DRUMS					●	○	●	○			
BURIED PIPES & CABLES					○		●	○			
BURIED CAVITIES & TUNNELS	●			○	○		●	●			
VOIDS AROUND PIPES		○						○			
SUBSIDENCE (SLOPES & TUNNELS)	●	●		○			○	●	○		
PHYSICAL PROPERTIES	●	○		○	○	○	○	○	●	●	●
ELECTRICAL GROUNDING						●	●				
RIPPABILITY	●										
RADIOACTIVE HAZARDS											

SOURCE: Modified From MultiVIEW Geoservices Inc.

● OFTEN APPLICABLE
○ SOMETIMES APPLICABLE

Figure 3-12 Summary geophysical techniques

8

Remediation

DNAPL REMEDIATION TECHNIQUES (& other NAPL Contaminants)

1. BIOLOGICAL PROCESSES
   1.1 Aerobic biodegradation
   1.2 Anaerobic biodegradation
2. Electrolytic Processes
   2.1 Electro Osmosis
   2.2 Electro Acoustic
3. Containment and Ground Modification
   3.1 Impermeable boundaries
   3.2 Stabilization and Solidification
   3.3 Permeable treatment walls
4. Soil Washing Processes
   4.1 Alkali Soil Washing
   4.2 Cosolvent Washing
   4.3 Surfactant Soil Washing
   4.4 Water flooding and groundwater extraction
5. Air Stripping
   5.1 Air sparging and vacuum extraction
   5.2 Vacuum vaporizer wells
6. Thermal Processes
   6.1 Contained Recovery of Oily Wastes
   6.2 In-situ steam enhanced extraction
   6.3 Radio frequency heating
   6.4 In-situ vitrification.

[8:1] Biological Processes

Aerobic biodegradation

Anaerobic biodegradation

1. BIOLOGICAL PROCESSES

- Organic compounds metabolized by micro-organisms
- Micro-organisms stationary – attached to surfaces or agglomerated
- Metabolism as aerobic or anaerobic.

Form of micro-organisms

1. Naturally present – Effectiveness enhanced by providing nutrients eg. O_2, nitrates, nitrogen, phosphorous
   – eg. Algae growing in ponds due to fertilizer usage.

2. Introduction of Exogenous Cultures –
   So far not shown successful.
   Injection of genetically engineered organisms prohibited by US law.

Requirements for Success (general)

- Adequate aquifer permeability $K > 10^{-4}$ cm/s
- Prior removal of free product
- Suitable microbial population
- Hydrodynamic control – contain plume
  – deliver amendments (nutrients)
- Monitoring system to define progress of the process

  Monitor:
  1. Changes in nutrients (oxygen, nitrate)
  2. Decrease in dissolved compound concentration
  3. Increased biomass, in situ.
  4. Increased CO_2 or Methane concentration
     – essentially circumstantial

1.1 Aerobic Biodegradation

Organic compounds metabolized by oxygen using organisms.
Applicable to compounds such as : TCE ⟶ Vinyl chloride

Field Processes

- Wellhead or infiltration gallery injection (nutrient + air)
- Similar to pump-and-treat methods
- Pulsed (cyclic) injection of amendments → prevent biofouling @ inj well
- Biostimulation may change aqueous chemistry, viscosity, and flow paths of media.

Sparged O_2

- Oxygen supplied to (usually) anaerobic subsurface
  - in water usual saturation ($O_2 \rightarrow DO = 8-12$ mg/L) Sparge → 40 mg/L
- Nutrients (nitrate) supplied in dissolved form (high solubility).
- Delivery to contaminated zone complicated by heterogeneity

Hyd. Peroxide

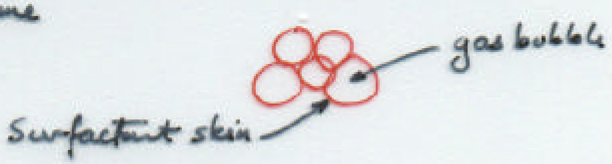
Hydrogen Peroxide (H_2O_2) may be used as an oxygen supply.

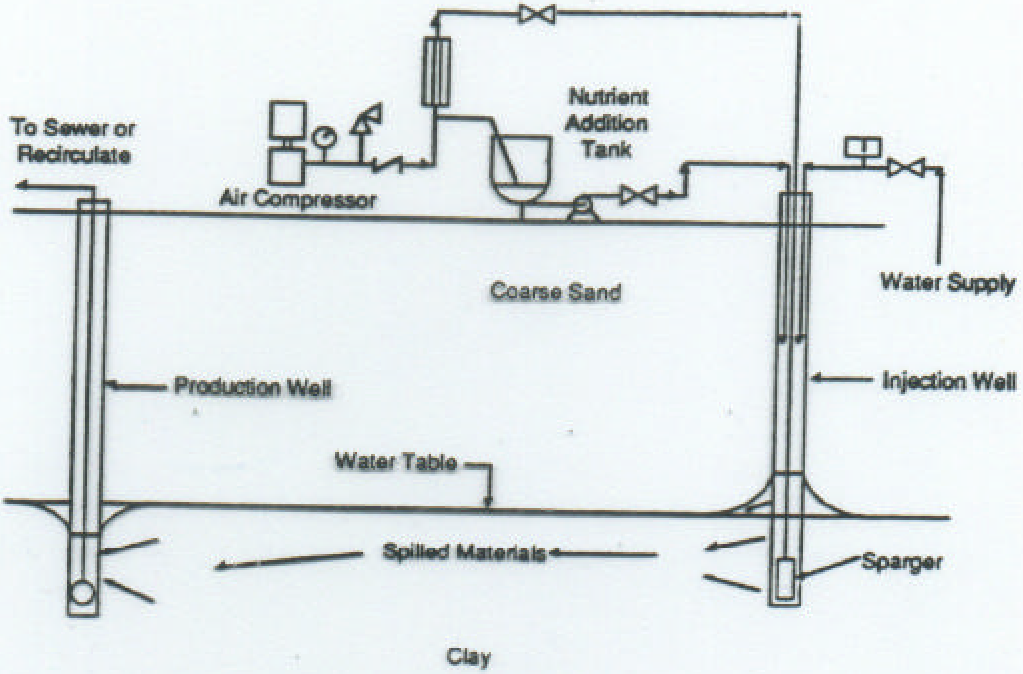
- Oxidizes some organic compounds directly.
- Increases mobility of lead and antimony

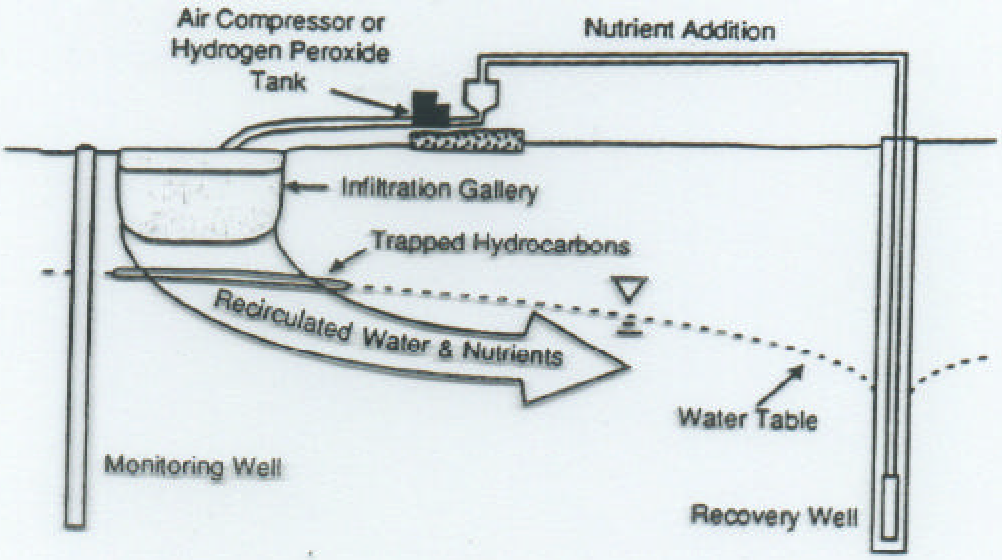
Colloidal Gas

Colloidal Gas Aphrons (CGAs) may deliver O_2.

- essentially a foam (colloidal microdispersion of O_2)
- 65% O_2 by volume




To Sewer or Recirculate
Air Compressor
Nutrient Addition Tank
Coarse Sand
Water Supply
Production Well
Injection Well
Water Table
Spilled Materials
Sparger
Clay


Air Compressor or Hydrogen Peroxide Tank
Nutrient Addition
Infiltration Gallery
Trapped Hydrocarbons
Recirculated Water & Nutrients
Water Table
Monitoring Well
Recovery Well

EXAMPLES

Moffett Field Naval Air Station, Mountain View, CA

- Anaerobic, shallow, confined sand-gravel aquifer
- Bromide tracer studies → flow field
  → capture efficiency
- Nutrient stimulation of TCE degradation.

Also applied to coal tar.

Applicability/Limitations

- Free phase → toxic to microbial populations (remove)
- Lab studies continue to exhibit biodegrability of
  DNAPLs believed non-biodegradable
- $K > 10^{-4}$ cm/s (nutrient delivery)
- Heterogeneity → inability to deliver nutrients
- Other treatability factors: Nutrient demands; cultures;
  pH; redox potential; moisture conds.
- Esp. useful for petroleum hydrocarbons
  10 – 100 years naturally ⇒ months to years

Cost and Availability

- Hardware and expertise available. Esp for petroleum hydrocarbons
- Pump and treat systems

– \$ 15 – 60/yd^3

1.2 Anaerobic Biodegradation

Non-oxygen using micro-organisms
Nutrients: Nitrates, Sulfates, CO_2, Ferric Iron, Metal oxides

Field Processes

Same as for aerobic but no O_2 added/needed ∴ no sparger
Subsurface usually anaerobic ∴ a natural method.

Demonstration Level

Naturally occurring degradation
Field studies: Creosote (St. Louis Park, NM)
Carbon Tet, TCA, Freon (Moffett Field, CA)
Especially in zone close to injection.

Applicability/Limitations

- Affects aqueous phase only (not free product)
- Sorbed products removed via aqueous phase (reversible)
- Intermediate transformation products may be toxic
  - eg. Vinyl chloride is a by-product that poses more hazard than the original product (TCE)?
  - This is reason why aerobic processes preferred

Cost and Availability

- In situ anaerobic is naturally occurring
- Full scale application – discouraged – toxic by-products
- \$15 – 60/yd^3

[8:2] Electrolytic Processes

Electro osmosis

Electro acoustic

2. ELECTROLYTIC PROCESSES

- Applied electric field to enhance contaminant removal
  - Electro-osmosis
  - Electro-acoustical methods

} primary interests.

	Gradient, X			
Flow, J	Hyd. Head	Temperature	Electrical	Chemical
Fluid	Darcy's Law	Thermo-osmosis	Electro-osmosis	Chemical-osmosis
Heat	Therm. advection	Fourier's Law	—	—
Current	Streaming current	—	Ohm's Law	Diffusion
Ion	—		—	Ficks (1st) Law.

- Electro-osmotic and chemical-osmotic effects important in fine-grained soils $K < 10^{-7}$ cm/s
- Also in clays the surplus of cations to balance negative charge of clay particles → hydraulic flow

- May mobilize – ionic species e.g. Heavy metals, radionuclides, charged organic compounds.

DNAPLs are typically non-charged
∴ not moved.

2.1 Electro-Osmosis

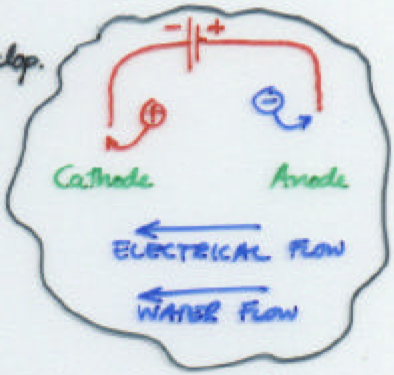
Main mechanism:
- Ionic migration of charged species (cations, anions) due to electrical potential
- Advection of neutrally charged species in the diffusive flow
- Osmotic and pH gradients may develop → reverse flows
- Desiccation due to electrode heat and soil fabric changes.

Process

Surplus of cations ⊕ ∴ net flow to cathode since more cations ⊕.
"Drag" water with them, net flow to cathode.

Influencing Factors

- Electrical and hydraulic gradients held constant but chemical gradients develop.
  - If these develop countercurrent then reverse flows due to advection.



- Electrode heating and pH changes.

Anode → pH 2
Cathode → pH 12 } ∴ acid front propagation towards cathode

Alkaline conditions may → desorb organics, pesticides, heavy metals and enhance removal.

Field Implementation

Apply electrodes and potential

Recover contaminants at electrodes (wells)

Dissolved contaminants pumped to surface → treated

Similar strategy to pump-and-treat using electrodes

eg. use high conductivity features etc.

Electrodes – e.g. Well casing (steel) @ injection & extraction wells.

Graphite electrodes – non wetting surfaces, corrosion resistance, reduce hydrogen gas formation.

Prevent consolidation @ anode and keep saturated by adding surfactants, salts and water

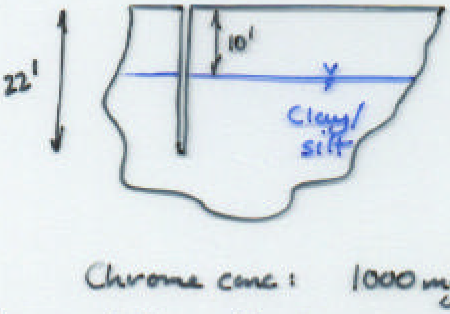
Dewatering applications. Electrode spacing 30 ft } DC potential
Contaminant removal 3–5 ft } 25–500V.

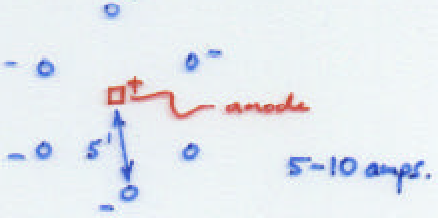
Demonstration level

Clay dewatering / landslide stabilization 1930s +

Only lab studies for organics such as TCE

Field studies: Chrome plating plant, Corvallis, Oregon.





Chrome conc: 1000 mg/L → 35 mg/L

Also applied to: lead, arsenic, acetic acid. Bench studies for TCE.

Applicability / Limitations

- Ionic species, radionuclides, heavy metals, polar organic compounds
- Fine grained soils with large clay content
- Desaturation, drying, desiccation } may effect efficiency
- Gas production & electrode corrosion }

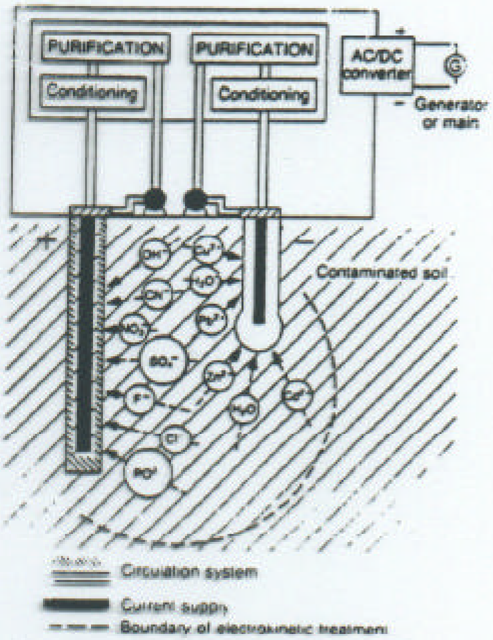
Cost and Availability

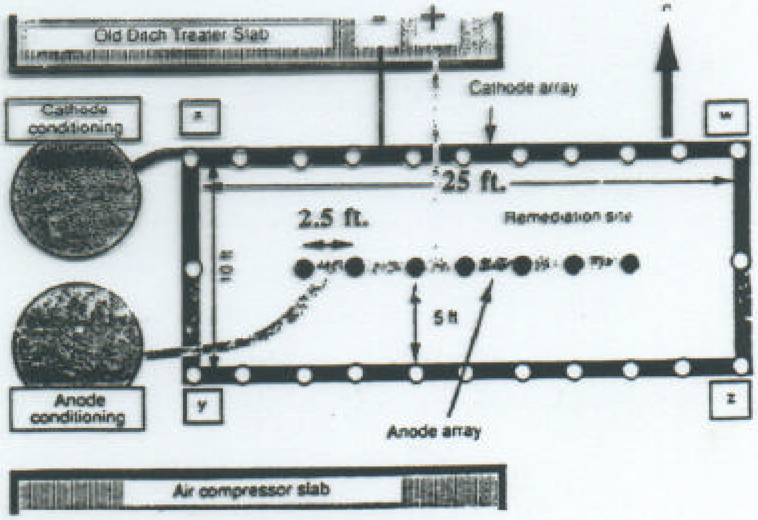
- Full scale. Geotech. and contaminant removal
  - Well established design criteria
    European patent - Geokinetics
    US Patent (1991) Probstein
  - No DNAPL field scale study (non-polar)

Long term treatment → $50/ton
Short term $400/ton
} electricity $2 - $20/ton.

↑ of remediated fine grained soils

Flow *J*	Gradient *X*			
	Hydraulic Head	Temperature	Electrical	Chemical
Fluid	Hydraulic conduction: Darcy's law	Thermo-osmosis	Electro-osmosis	Chemical-osmosis
Heat	Isothermal heat transfer	Thermal conduction: Fourier's law	Peltier effect	Dufour effect
Current	Streaming current	Thermo-electricity: Seebeck effect	Electrical conduction: Ohm's law	Diffusion and membrane potentials
Ion	Streaming current	Thermal diffusion of electrolyte: Soret effect	Electrophoresis	Diffusion: Fick's law



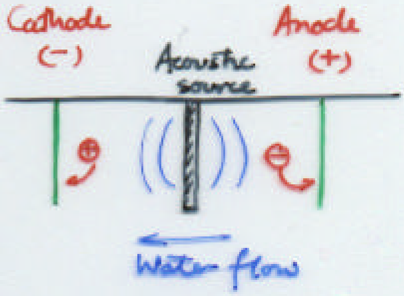


2.2 Electro-acoustic Soil Decontamination (ESD)

- Electrical gradient and acoustic "shaking" to enhance removal
- Similar to hybrid electro-osmosis & radio frequency heating but lower frequency (100–1000 Hz)
- Seismic waves { compressional waves – attenuate with distance as $1/r^2$
  shear waves – attenuate $\propto \omega^2$
- Mechanisms
  1. Shaking – rearrangement of particles → new channels
  2. Cavitation of pore fluids → bubble expulsion and frees pore trapped materials.
  3. Decreased fluid viscosities due to heating

Field Implementation

In development.



Level of Demonstration and Performance

Not yet implemented in field

Metals removed more effectively than, for example decane (non-polar)

Difficult to evaluate relative importance of electrical-vs-acoustical.

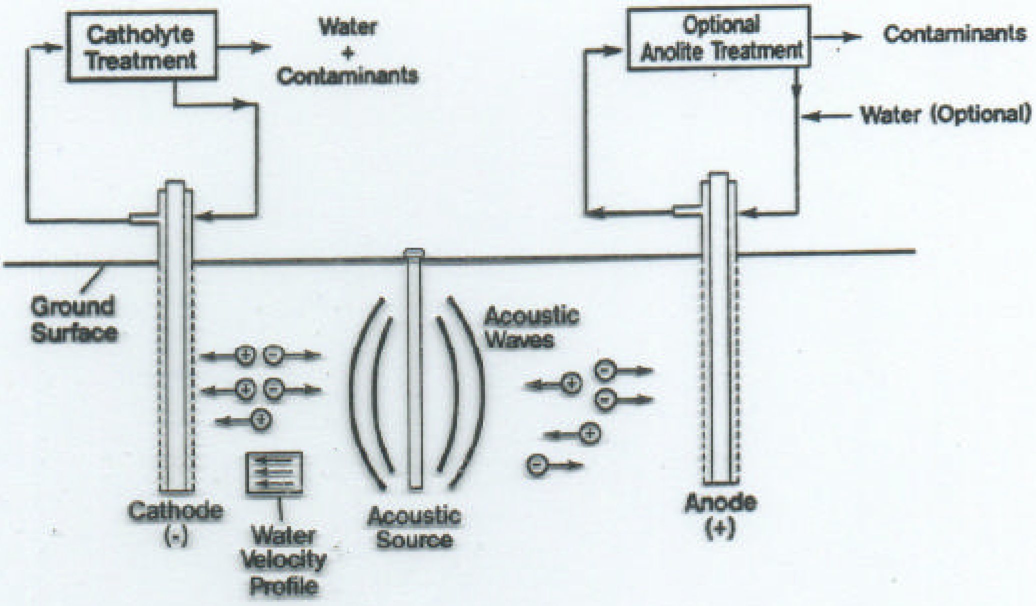
Applicability and Limitations

Same as electro-osmosis.

Cost and Availability

Lab demonstration only. Patented by Battelle

Probably not v. good for non-polar organics. RF heating ~ $40–100/ton.


Catholyte Treatment
Water + Contaminants
Optional Anolite Treatment
Contaminants
Water (Optional)
Ground Surface
Acoustic Waves
Cathode (-)
Water Velocity Profile
Acoustic Source
Anode (+)

[8:3] Containment and Ground Modification

Impermeable barriers

Stabilization and solidification

Permeable treatment walls

3. CONTAINMENT AND GROUND MODIFICATION

Retain source DNAPLs/LNAPLs immobile and prevent offsite migration.

3.1 ☐ Impermeable boundaries: Slurry walls, sheetpiles, jet grouting, pumping
3.2 ☐ Stabilization/solidification: Soil mixing, cementation, in situ vitrification
3.3 ☐ Permeable treatment walls: Treat evolving plume as it develops

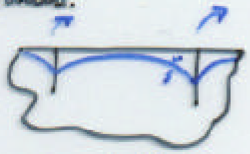
Impermeable boundaries & stabilization techniques proven @ field scale.
Permeable treatment walls under (strong) development.

3.1 Isolation and Containment

Theory

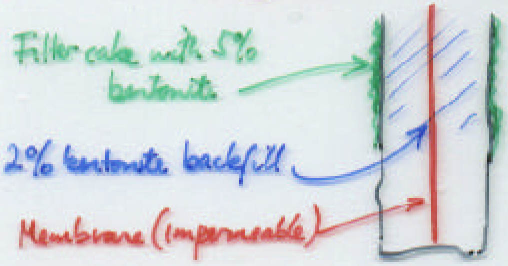
Passive systems – Impermeable boundaries, grout walls, slurry walls, jet grouting, sheet pile walls.

Active systems – Hydraulic controls – pumping



☐ **Slurry walls**

- **Bentonite-soil**
  - High plasticity ∴ resistant to fracture
  - Low conductivity. Low K with 5–7% bentonite
    4% bentonite ΔK × 1000
  - Low cost since soil used
  - Backfill typically 2% bentonite
  - Incorporation (sometimes) of sheetpiles/geomembranes/concrete cut-off.



- **Cement-bentonite** (brittle)
- **Polymers, resins, emulsions, asphalts.**

☐ Penetration and Jet Grouting

Pressure grouting to fill voids. Hole spacings 1–3m.

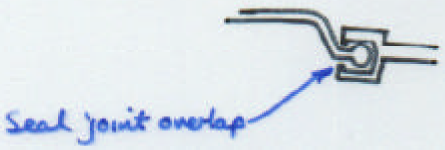
Pressure grouting to destroy initial fabric → mix soil–slurry

Hole spacing 0.3– 2 m

Overlap columns.

Grout sample conductivities 10^{-5}–10^{-8} cm/s. (Mix dependent.)

☐ Sealable joint sheet pile walls



Drive with piledriver

Seal joint with bentonite and polymers

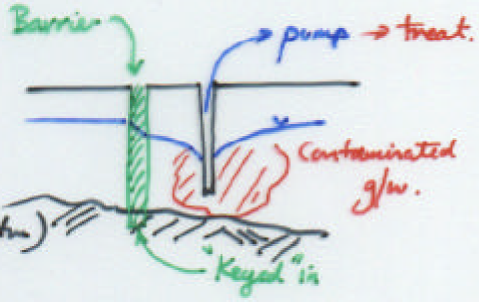
May crack aquicludes due to driving

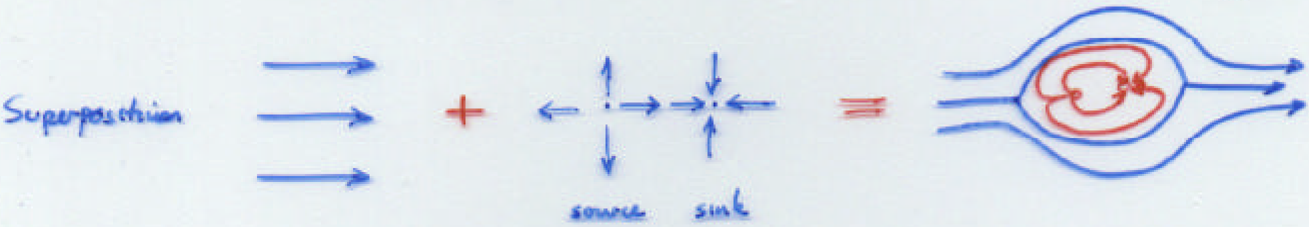
☐ Active groundwater controls

In addition to containment

Positive flux into cell

Hydraulic barriers need to cut-off (termination)





Field Implementation

1. Encompass DNAPL source area (volume) with barrier (complete containment)

or 2. Dissolved plume locally arrested with barriers.

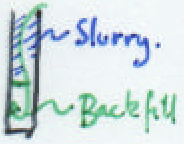
Slurry trenches – 2–3 ft deep

Max 400' deep – open for several weeks. 1000' long

Backfill – weathered shales, sand, clays, till

2–6" slump and

Backfill 15 pcf denser than slurry



Grouting – Particulate grouts – Clay, lime, flyash, cement

Chemical grouts – Bitumen, resins, silicates (low viscosity → ↑ penetration)

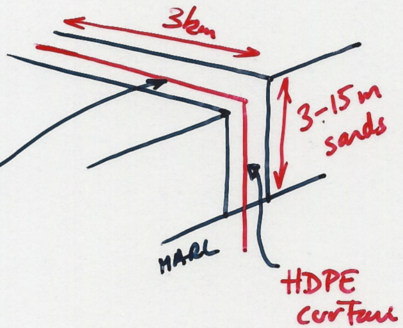
Jet grouting 1-2 rpm 1-2 ft^3/min 6000 psi injection pressures.

Level of Demonstration

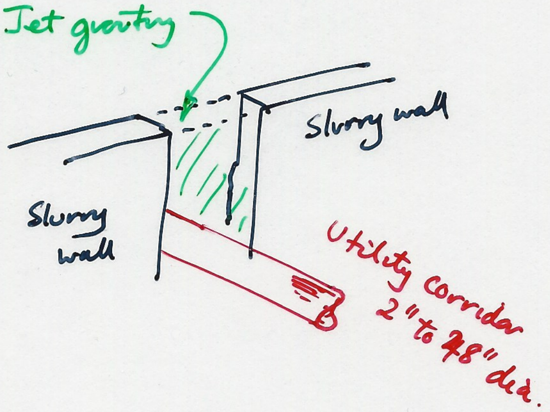
Liguria, Italy 3 km by 3-15 m deepwall

Containment of contaminants

Tongue and groove curtain



Testing → $K = 10^{-6}$ to 10^{-7} cm/s.



Jet grouting for complex heterogeneous areas.

Applicability – Limitations

- Generally to isolate and recover NAPLs

  Pump and flush within boundary – eg. Surfactants
- Durability of clays with acidic and organic compounds

  Reasonable resistance to organics

  Cements brittle but less susceptible to organics/acids
- Grouting – Fracture sealing – but complete seal?

  Verification difficult.

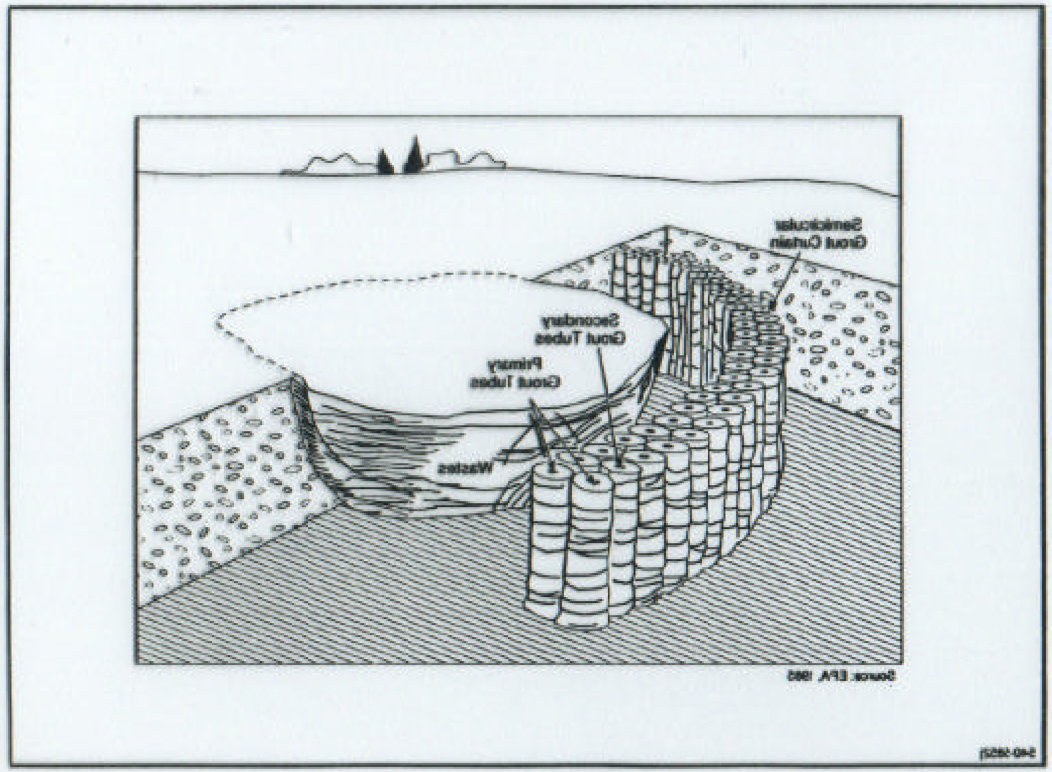
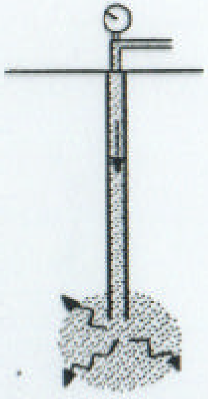
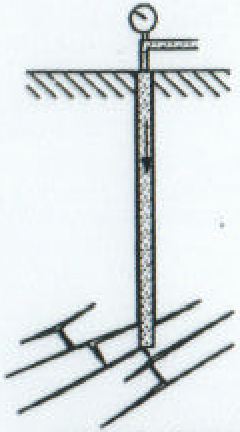


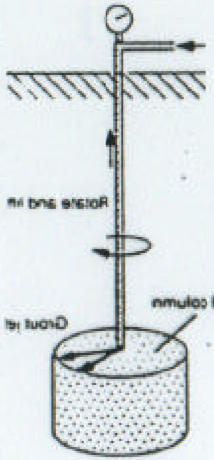
FIGURE 3-3 GROUT CURTAIN



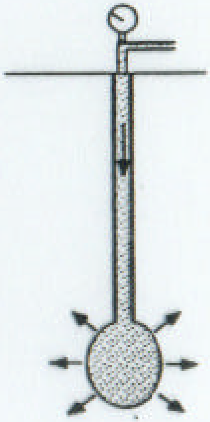
Penetration (permeation)



Penetration (intrusion)



Jet grouting
(displacement, replacement)



Displacement
(compaction grouting)

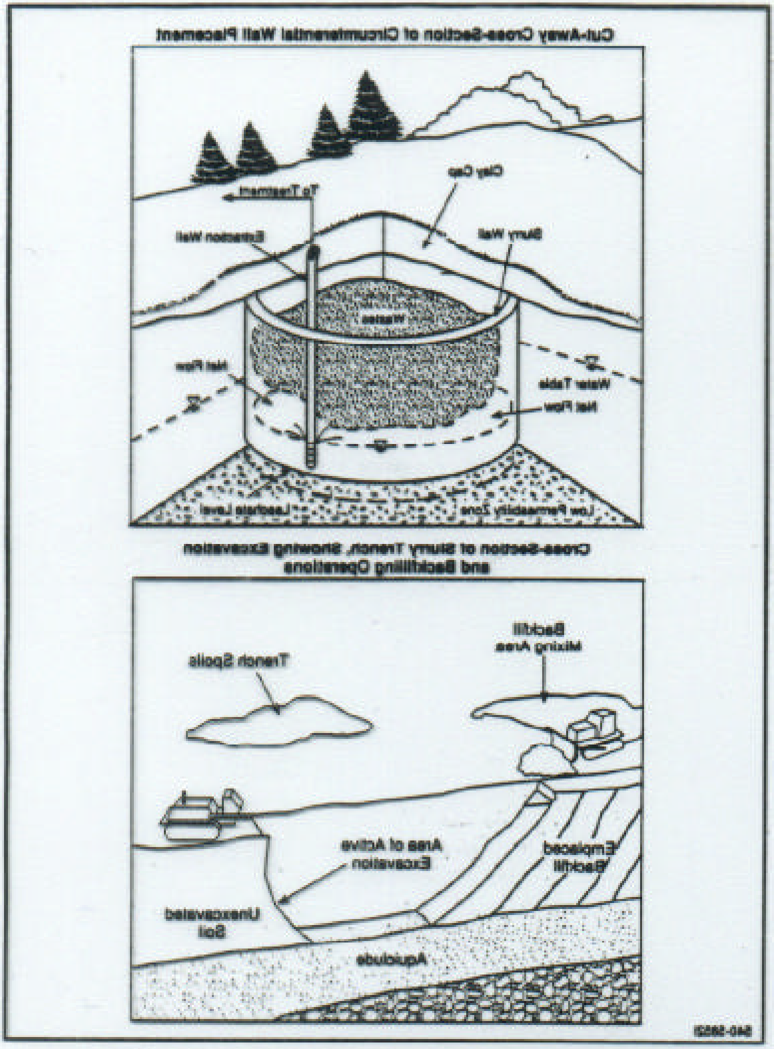


FIGURE 3-3 TYPICAL SLURRY WALL CROSS SECTIONS

Cost/Availability

Slurry walls and jet grouting offered by specialized contractors.

Usually cheaper than other contaminant systems

Slurry walls \$7-13/ft^2

Grouting \$60-100/yd^3

3.2 Stabilization and Solidification

Theory

Stabilization – in-situ neutralization – change toxicity or solubility

Solidification – encapsulation into monolithic solid

eg. sludges, liquids, lagoon sediments.

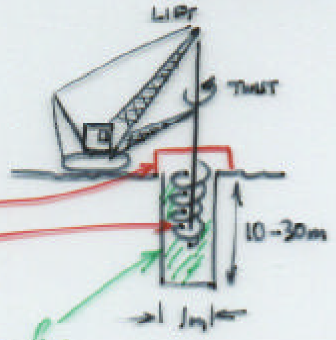
S/S reagent types:

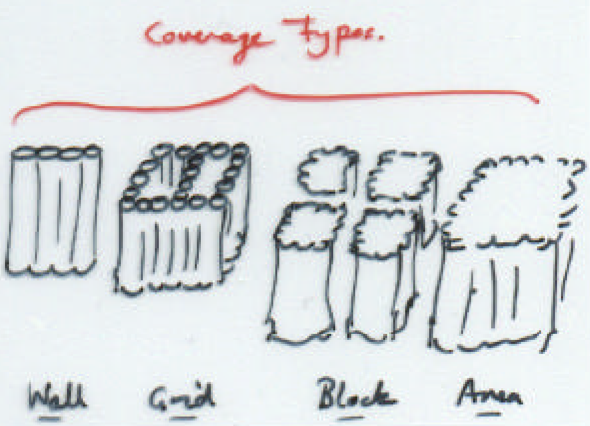
Organic – (polyethylene, asphalt) Thermoplastic encapsulation
– eg Radioactive wastes

Inorganic – (Cementing agents [lime, cement]; Bulking agents adsorption capacity)
eg flyashes, pozzolans.

Strength and Durability: ↑ with ↓ in voids
Also index properties: Suspended solids, pumpability
Density
Permeability
Strength/durability (wet/dry & freeze/thaw)
Contaminant leaching (EP Tox, TCLP)

Field Implementation





Level of Demonstration

Developed in 1950s

Applied in sand, silty clays $K = 2 \times 10^{-2}$ cm/s   PCBs to 1000 ppm

15 m deep soils contaminated

Reagent addition   .18 lb reagent / 20 lb dry soil

$K = 10^{-7}$ cm/s $q_u = 410$ psi

Volume ↑ 8.5%

TCLP tests ⟶ no PCBs in leachate

Applicability/Limitations

Well proven and effective remediation method

Good candidate for DNAPLs since thoroughly mixed.

– preventing migration from remediation zone.

Application to 25% by weight of organics

Will penetrate drums etc. but not large boulders.

Costs.

SSM and Deep SM – \$20-50/m³ and \$100-200/m³, respectively excluding reagent costs.

3.3 Permeable Treatment Walls

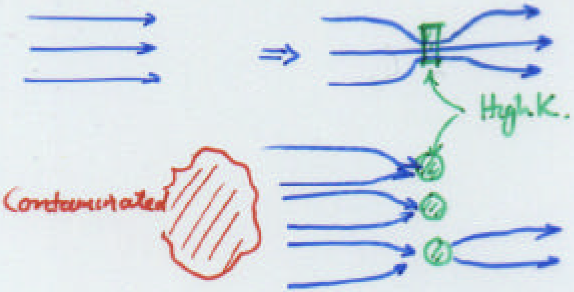
Theory

Installed using conventional slurry wall technology.

Granular backfill with reagents and reactive granular backfill.

- nutrients and bacteria → biodegradation
- redox controls and metal catalysts → metals precipitation and dehalogenation
- organic carbon → denitrification and
- other sorbents

Wall spans plume or directs flow through wall



Field Implementation

Slurry walls

Large diameter borings

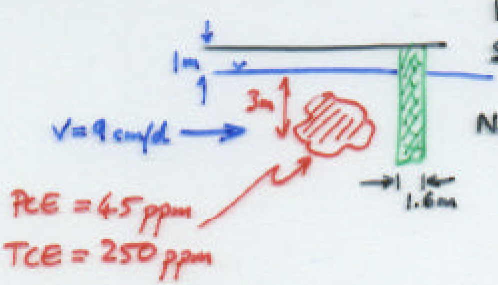
Automatic addition of aqueous/liquid or gaseous amendments.

Level of Demonstration

Field tests

Zinc and iron transform halogenated aliphatics (pH dependent)

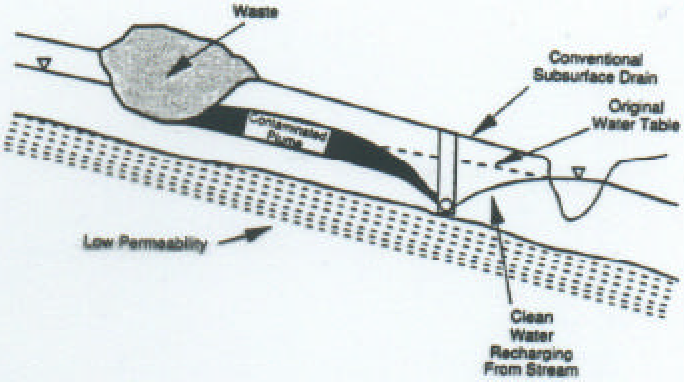
Pilot test (Borden)



Iron grindings 22% by wt
Sand 78% by wt

No plume. Chlorine conc.
↑ shows degradation.

41% reduced
95% reduced } 500 days.



Applicability/Limitations

Treatment of dissolved plume

Amendments must be non-Toxic

stationary (non-soluble)

Excessive biogrowth/precipitation may ↓ long term K and effectiveness

eg. No flow through wall.

No access to reagent particle surfaces

If dehalogenation incomplete → may form vinyl chloride

Cost/ Availability

Less expensive than pump and treat

Low maintenance solution (zero maintenance?)

WCGR owns patents.

- Fouling and oxidation of iron filings with time → slows effectiveness
- Acoustic stimulation (deep) for removal of surface coating.

Patent @ PNNL (Hanford)

1995-96 applications ~ $375K to $500K construction.

Ireland/Kansas/N. Carolina/ Colorado

– TCE mainly.

- Hydrofrac reagent injection

[8:4] Soil Washing

Alkali soil washing

Cosolvent washing

Surfactant soil washing

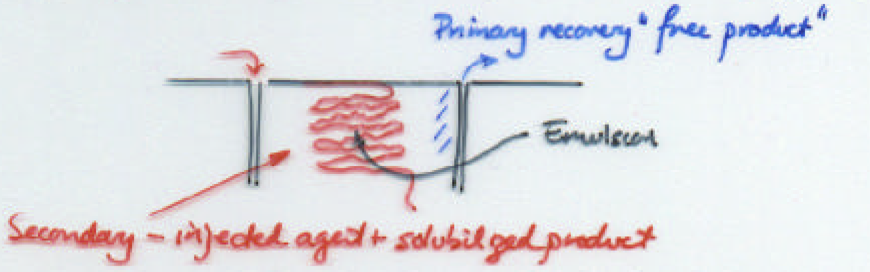
Water flooding and groundwater extraction

4. SOIL WASHING PROCESSES

Fluid-fluid displacement {Water / Alkalis / Surfactants / Co-solvents} ← {Physical displ. (reducing surface tension) / Solubility changes.

Effectiveness controlled by {Phase equilibria / Hydrodynamics eg. Heterogeneity/fluid props./aquifer geometry

Two forms of recovery



Isotropic media

Front stability

controlled by • Mobility ratio, $M = \frac{v_w}{v_{nw}} = \frac{\mu_{nw} k_w}{\mu_w k_{nw}}$ M<1 is good !!

• Gravity number, $N_g = \frac{N_B}{N_c} = \frac{\text{gravity forces}}{\text{viscous forces}}$ {Indicates gravity over-ride potential / Defines slope of advancing fluid front.

Bond No = $N_B = \frac{(\rho_{nw}-\rho_w) g k}{\sigma_{nw}} \doteq \frac{\text{buoyancy forces}}{\text{interfacial forces}}$ (vertical direction)

Capillary No. = $N_c = \frac{\mu_w v_w}{\sigma_{nw}} \doteq \frac{\text{viscous forces}}{\text{interfacial forces}}$ (horizontal direction).

Heterogeneous media complicate this issue.

Alkali: Enhance NAPL removal by "saponifying" the organic acids and produce natural surfactants → ↓ σ

Cosolvents: Creates plug of single phase water – cosolvent – DNAPL to move without surface tension effects

Surfactants: Reduce σ_{nw}

All EOR methods → not significant recovery.

4.1 Alkali Soil Washing

Inject { Sodium Carbonate Na_2CO_3
Sodium Hydroxide $NaOH$ ← strong alkali and ∴ good results

Removal mechanisms:

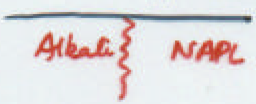
1. Creates natural surfactant – due to alkali–NAPL– reactions
2. Precipitate Ca and Mn salts ↓ water hardness ↑ interfacial activity
3. Reduces surfactant adsorption onto aquifer mineral materials
4. Changes NAPL wettability (change σ_{nw} by x1000)
5. Coalescence of NAPL ganglia into single bank and pump as single bank (phase)
6. Creates an emulsion of mixed material with <u>small</u> droplets

contradictory? (5, 6)

Processes:

Differs from surfactant flooding: { Alkali
Surfactant

processes operate @ front only.



Surfactant injection may be multiply pulsed.

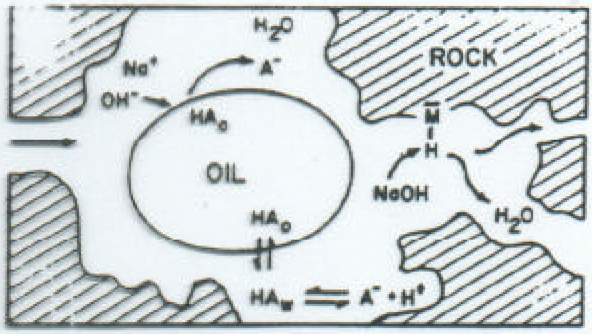
Applicability / Limitations

Most DNAPLs do <u>not</u> contain acidic components ∴ → no in situ saponification results ∴ surfactants must be supplied.

Decreasing σ may give downward vertical migration

Environmental applications – surfactants more toxic than DNAPL.
– not problematic for oil reservoirs.

Alkalis reduce water viscosity ∴ promotes unfavorable mobility ratios and prevents displacement processes.



Compatability issues (were alkali/cosolvent/surfactant used).

- interaction of alkali & soils or pore fluids by dissolution and attenuation of effect (esp. clays)
- pore clogging with dissolved precipitates

Ultimate pore fluids may have high pH and need treatment to neutralize.

Cost and Availability

Hardware readily available

Much experience in petroleum but few for envt. apps.

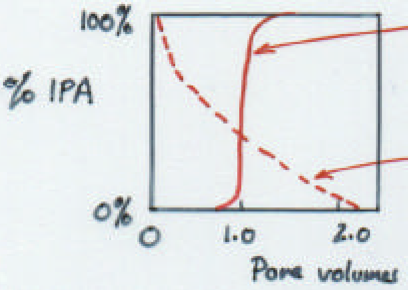
Successful application using surfactants and alkalies completed.

For DNAPL, use surfactants to augment lack of saponification

No envt. cost info available.

4.2 Cosolvent Washing

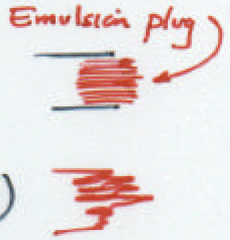
Hydrophilic organic compounds {alcohols, esters, ketones} solubility enhancement, reduces surface tension



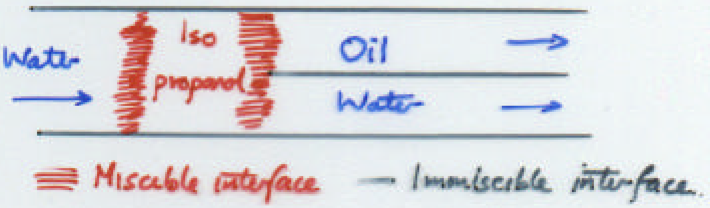
Isopropanol displ. Naptha $M = 0.27$ (Stable)

Creates miscible plug

Naptha displ. IPA $M = 3.69\,(1/.27)$ (Unstable)



Schematic



Field Implementation

1. Slug injection of cosolvent + 2. Injection of driving fluid (water)

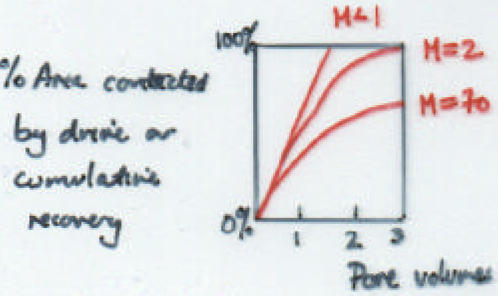
Consider stability of each front with $M < 1$

M may change as slug is attenuated {adsorbed to grains, expended at front}

No known field application — TCE pilot study @ R.S. Kerr Lab (EPA)

Level of Demonstration

Petroleum industry – 1-D column experiments, 2-D radial experiments $M<1$ ok } homogeneous



← Heterogeneous models (Habermann, 1960; Blackwell, 1959)

Boyd and Farley (1992) $H_2O \rightarrow IPA \rightarrow TCE$ 1-d column of glass beads.

v = 18 ft/day

Upflow, downflow and horizontal sweeps

Downflow most effective (front stable) with action of gravity

Experiments with 16% wt clays.

Small slug sizes gives poorer TCE recovery due to fines mobilization and clogging.

Applied to 2ppm PCB contaminated soils (lab) 2g/kg organic matter

Ethanol water solutions

PCB displ. effectiveness of 85-98% using ethanol-water of 47%-76%

Applicability / Limitations

- Solubility enhancement of hydrophobic hydrocarbons in soils well documented since 1980s.
- Interfacial instability ($M \geq 1$) for large differences in viscosity (5-200cp) causes deterioration of slug.
- May add alkali agents, surfactants, polymers, to improve M.
- Heterogeneities largely influence behavior
- Special well construction materials may be needed. Stainless steel.
- May result in desiccation for clays due to cosolvent reactions.

Cost and Availability

Used in petroleum industry

No widespread use for NAPLs in envt. but shows promise.

Density considerations (cosolvents are light) may make cosolvents applicable for LNAPLs rather than DNAPLs.

Heterogeneity is major issue.

No cost information.

4.3 Surfactant Soil Washing

Mechanisms:
1. Micellular solubilization of hydrophobic hydrocarbons.
2. Conversion into an emulsion
3. Reduce surface tension → ↑ mobility
4. Coalescence of ganglia into single bank

∴ similar to cosolvents and alkalis.

Two regions of interfacial tensions:

1. Low surfactant conc (.1-.2 wt%) two-phase system (oil/water)
2. High surfactant conc. (2-10 wt%) three-phase with micro-emulsion in equilibrium with (oil/water)

The emulsion will preferentially separate to the water or oil phase depending on:

1. Salinity: ✓1% NaCl conc → water
   × 3% NaCl conc → oil
2. Surfactant solution conc. (low conc → water)
3. Temperature ✓High temp → water

Best to have micro-emulsions between oil-water since low σ and removable under reasonable hydraulic gradients.

Field Implementation

Continuous low conc. (<1% wt) - continuous flush (~~pv~~ multiple p.V.)

Two strategies: (1) Solubility enhancement or (2) Displacement process

Keep M<1. Use conc. solution 10-40 wt% as finite slug.

Injection and production wells.

Sometimes horizontal.

Heterogeneities may affect results.

Level of Demonstration

Several decontaminations:

Volk Nat. Guard Base (WI)   TCA, TCE to 3 - 300ppm
Sandy soils with $f_{oc} = .015$ max
$K = 10^{-4} - 10^{-2}$ cm/s
Lab tests → 74 - 94% NAPL recovery in 12 pore volumes.
Field - @ 14 pore vols. 3 test holes clogged by 3rd day.

Laramie, Wyoming
Creosotes.   Isolation cell of pore volume 5000 gals.
Injection of 30,000 gal surfactant } recovered - 260 gal
14,000 gal waterflood } - 1600 gal
~ 95% concentration reduced.

Borden (1990) $K = 10^{-4}$ m/s   3 x 3 m cell.
231 l PCE released - migration for 2 months
48 l → pumping
52 l → excavation of upper 1m.
Backfilled with bentonite cap
12 l → Waterflood
62 l → 14.4 pore volumes of surfactant (1 pv = 2400 gal)
over 4 months
10 l → Soil samples reveal less than 10 l left.

184 l. of 231 l
~ 50 l missing

perhaps volatilization, @ sheetpile periphery,
or ↓ migration in fractures caused
by sheet piling.

Also used for PCBs
Carbon Tet.

Applicability/Limitations

Applicable to most DNAPL sites.
Toxicity and recovery of surfactant are key.
↓ σ may cause downward migration
Recovery strongly affected by heterogeneities

1. Sweep process (conc. > 10%) for high NAPL concentration at sites
2. Solubilization (Conc. ~1%) for low concentration of NAPL this controls fugitive DNAPL migration

Cost and Availability

Hardware available
Full scale application in ext. area completed.
Potential use with co-solvents.

No case information.

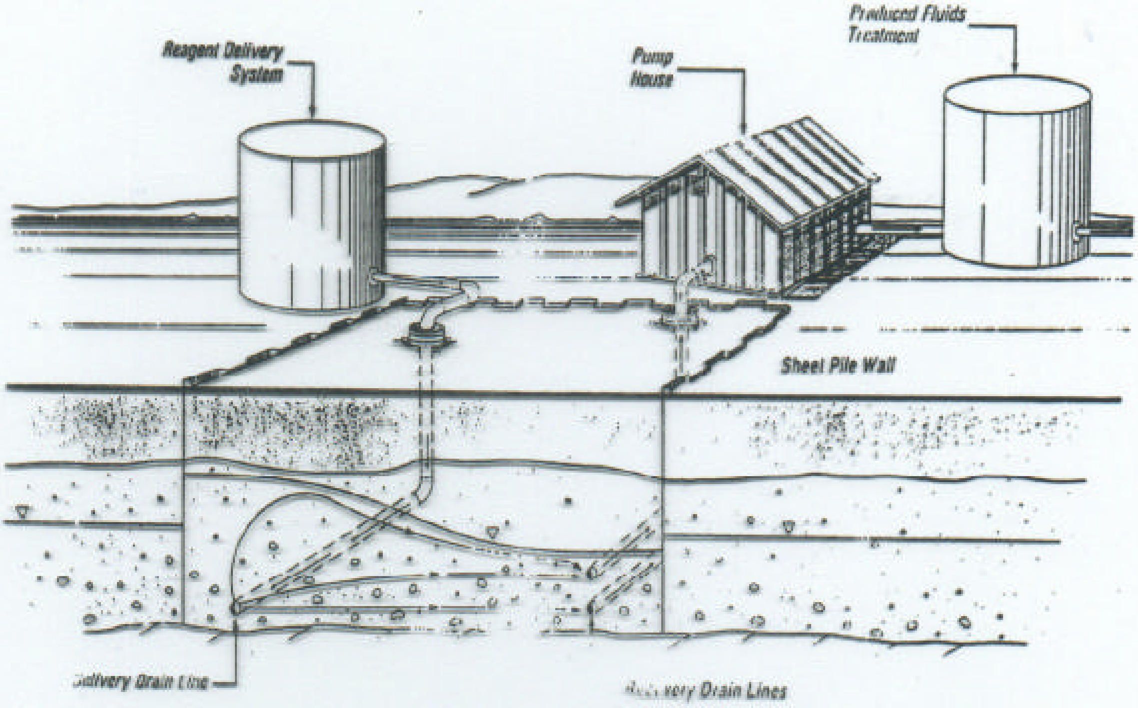


Figure 3.5.3.5 Schematic of dual drain line system for the 1988 field test using water and combined alkali/surfactant flooding of heavy oils [Sale et al., 1989].

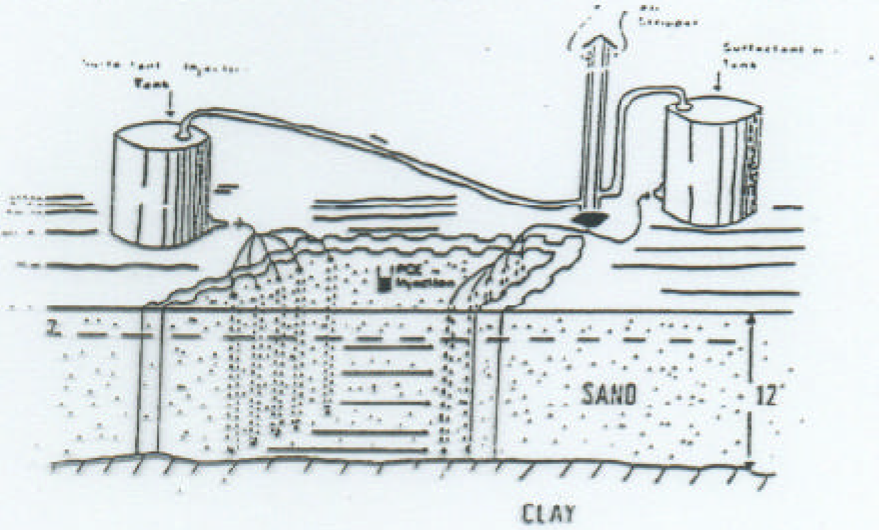


Figure 3.5.3.6 Schematic of field test using water and surfactant flooding for enhanced PCE recovery (Borden, Canada) [Fountain et al., 1990].

4.4 Water Flooding and Groundwater Extraction

Pump-and-treat.

Will only move free product with continuous phase (high contamination).

Upconing will result from pumping (reduce overlying pressure)

Maximize recovery using low pumping rates (reduces viscous/interface effects).

Field Implementation

Conventional wells, trenches, horizontal wells.

Install at base of DNAPL pool → maximize recovery
using "stratigraphic depressions".

Water recovery wells nested above DNAPL wells.

Pump water recovery wells continuously. Resume DNAPL
recovery when DNAPL detected in water wells.

Control DNAPL pumping to prevent "pinch-off".

Level of Demonstration

East Stroudsburg. Coal Tar pool 3-10' deep
35,000 gal pumped

Laramie, WY Waterflood in 5000 gal porespace
cell recovered 1600 gal wood treating
wastes.

∴ most applicable for high NAPL conc.

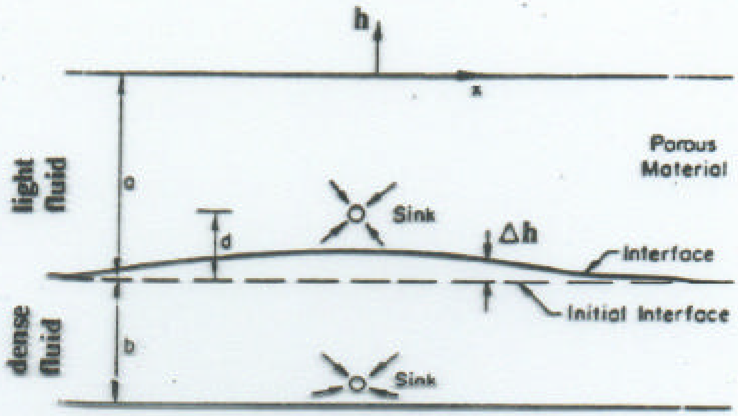


Figure 3.5.4.1 Schematic illustrating the upconing phenomena of a dense fluid phase to pumping stress in the overlying fluid phase [Wisniewski et al., 1985].

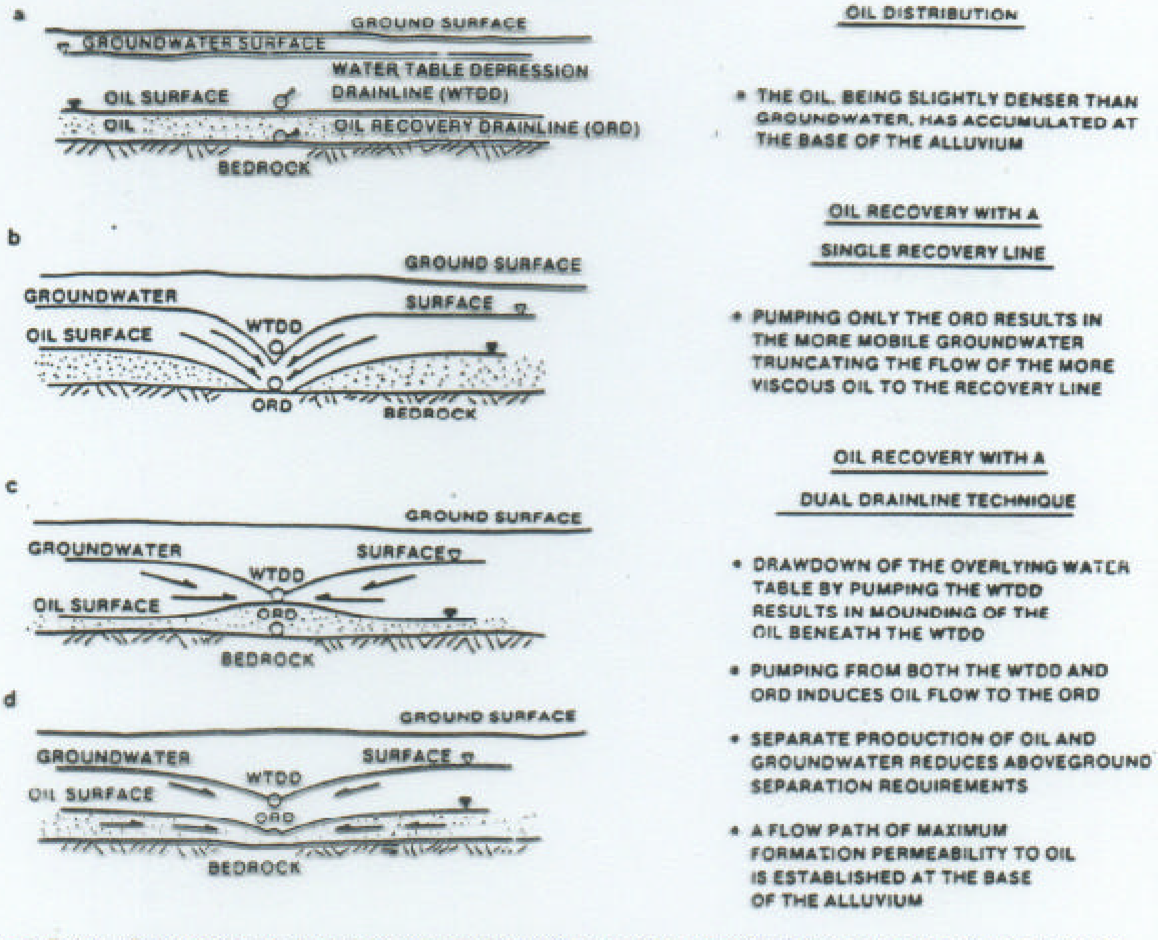


Figure 3.5.4.2 Schematic of dual drain line system for pumping of both light and dense fluid phase to enhance the recovery of the underlying, denser phase [Sale et al., 1988].

Applicability

Recovery from DNAPL pools – as initial treatment
- need secondary recovery to remove low residual conc. (5 - 20wt%)

Applied to low Specific Gravity DNAPLs (~1.1 SG)

Simultaneous pumping of water and DNAPL may reduce potential ex situ processing → volumes considerable
→ water reinjected.

Cost and Availability

Coal tar recovery $1000/month

Coal tar (17,500 BTU) sold as fuel supplement.

[8:5] Air Stripping

Air sparging and vacuum extraction

Vacuum vaporizer wells

5. AIR STRIPPING

Air circulation
- Air sparging – below g/w table
- Vacuum extraction – vadose zone

  work together
- Vacuum vaporizer wells (UVB)
  - strip within well
    - → vapor removed
    - → water to aquifer

Processes diffusion limited

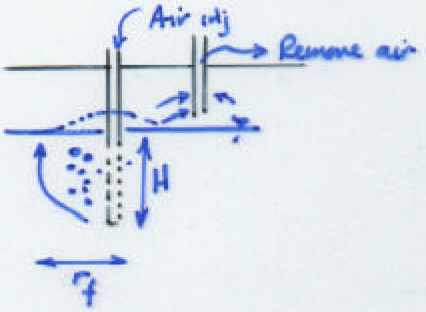
Volatile components only.

May also biostimulate as a beneficial by-product.

5.1 Air Sparging and Vacuum Extraction

Air sparging in sat zone.

Vacuum extraction in vadose zone.



Inject air

Bubbles ⇒ large surface area.

Gases partition across bubble skin.

— perhaps coalesce in channels

Heterogeneities may affect movement

Install spargers below contaminated zone.

Air entry pressure governs entry into soil

$\downarrow p_c \rightarrow$ larger radius of influence, r_I.

$\therefore$ reduce number of wells.

Less than soil fracturing pressure.

Effectiveness of sparger judged by:

1. Height of groundwater mounding
2. Pressure in vadose zone wells.
3. Rise in vapor concentration in neighboring wells
4. Concentration of dissolved O_2 in neighboring wells (monitoring).

$r_{inf} \sim 5-20$ ft coarse soils

$r_{inf} \sim 20-60$ ft stratified environments

Up to $r_{inf} \sim 300$ ft if geomembrane cover.

Vacuum extraction continuous or pulsed.

Bioremediation may be improved with excess O_2 (Aerobic).

Field Implementation

EPA - Soil Vapor Extraction Technology - Reference Handbook (1991).

Injection & vacuum wells 1-1.5" dia. PVC or stainless steel pipe.

Well points also used - Screen ~ 3ft max (reduce pump capacity and air only enters at screen top).

Vertical nesting used.

Dual use injection/recovery wells.

Level of Demonstration

Numerous sites in North America and Europe

PCE, TCE, TCA, BTEX compounds. 10-1000 ppb.

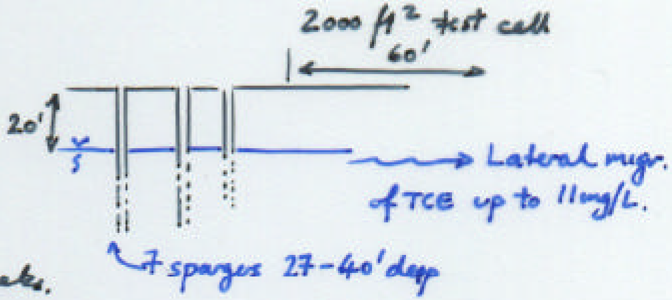
Mainly sands and coarse silts

CT study. 4 wk pilot study.

Extraction wells $15''-20''\ H_2O$

4 pounds VOCs removed.

Concentrations returned in 2 weeks.



Groundwater mounding 60' outside site

Lateral migration due to stratification

Off site VOC up to 150 ppm. ∴ pulsed injection

Applicability/Limitations

Contaminants with $H > 10^5$ atm.m^3/mole viable for removal.

i.e. volatile and semi-volatile compounds

For sufficient airflow $K > 10^{-3}$ cm/s.

Stratigraphic heterogeneities (gravel layers) strongly control behavior/success.

Lateral migration possible.

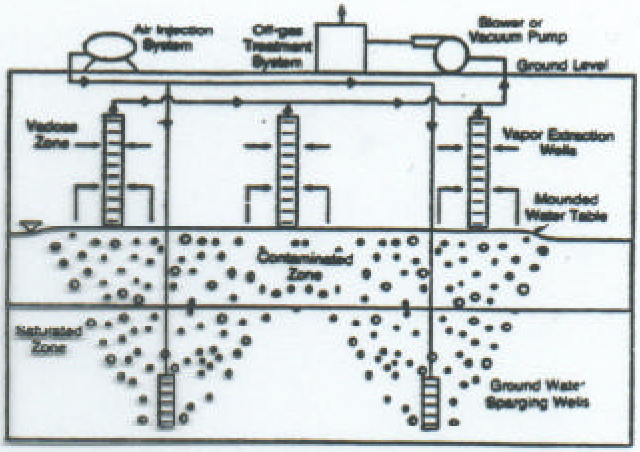
May mobilize free product due to movement up through NAPL.
May stimulate bioremediation (aerobic).

Cost and Availability

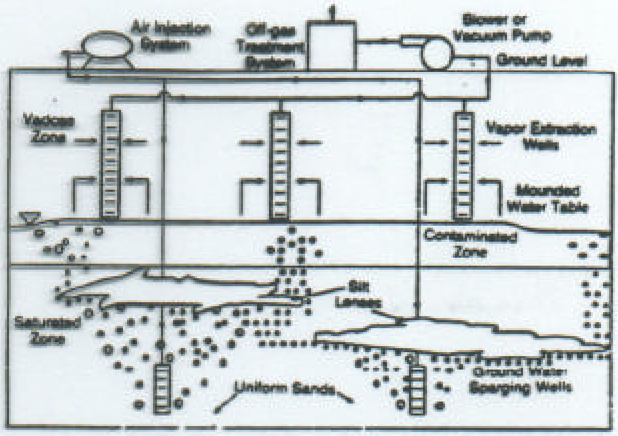
Used in US late 1970s to supplement bioremediation } well developed technology on hundreds of sites.
Used in Germany mid 1980s for VOC removal

Remediation of dissolved plumes (good candidates).
Hot-air injection → enhance stripping.
Potential remobilization of NAPL may be problematic

Costs site specific: Poorly reported
  Possibly $75-150/yd^3
  Collected gases passed through activated carbon.


Air Injection System
Off-gas Treatment System
Blower or Vacuum Pump
Ground Level
Vadose Zone
Vapor Extraction Wells
Mounded Water Table
Contaminated Zone
Saturated Zone
Ground Water Sparging Wells

(a)


Air Injection System
Off-gas Treatment System
Blower or Vacuum Pump
Ground Level
Vadose Zone
Vapor Extraction Wells
Mounded Water Table
Contaminated Zone
Silt Lenses
Saturated Zone
Uniform Sands
Ground Water Sparging Wells

(b)

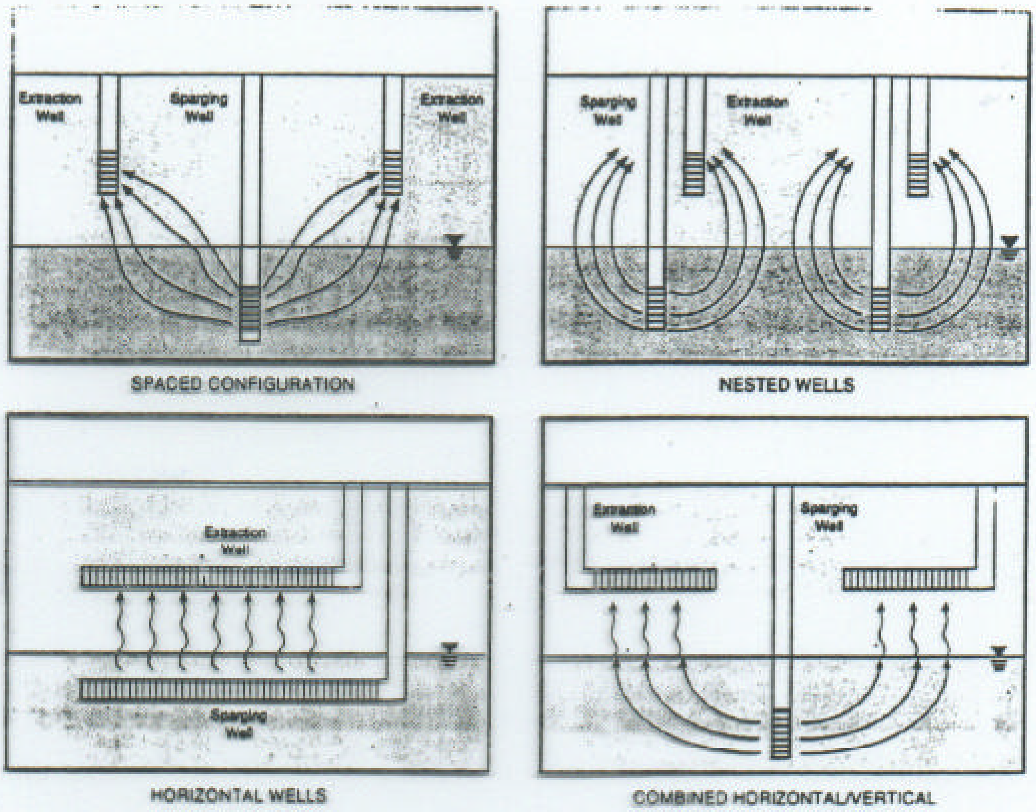


Figure 3.6.1.3 Possible air sparging well configurations [Loden and Fan, 1992].

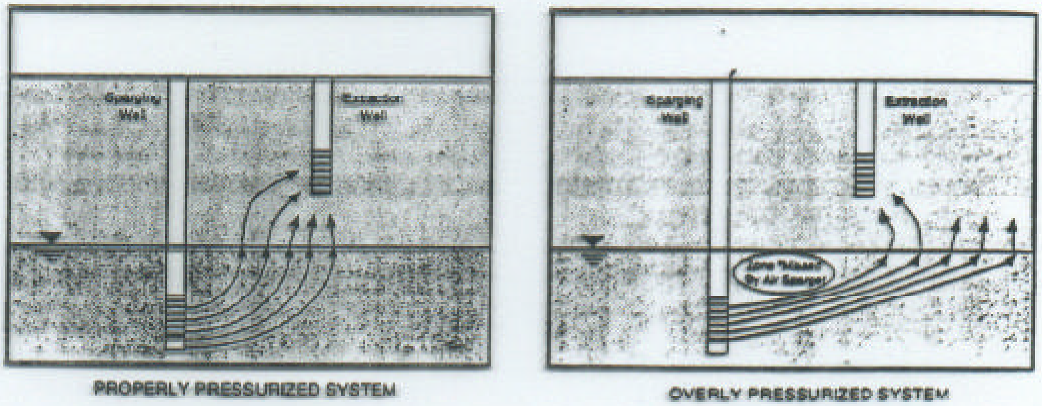
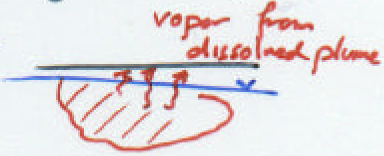


Figure 3.6.1.4 Effect of gas injection pressure on air sparging system [Loden and Fan, 1992].

5.2 Vacuum Vaporizer Wells

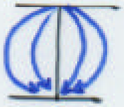
(UVB: Unterdruck Verdampfer Brunnen)

1. Direct in-well stripping-off of volatile NAPLs from groundwater, and
2. Passively by soil vapor extraction in vadose zone



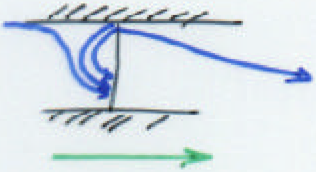
Effectiveness related to:

1. Solubility
2. Volatility
3. Recirculation of treated water in aquifer



No g/w flow

g/w flow →



- For horiz. flow velocities the form of the capture zone changes
- Overlap capture zones

Field Implementation

3. configurations

a) Two distinct regions "g/w extraction" and "stripping".

Clean air drawn into well

stripped water reinjected

Subatmospheric pressures in stripping region

b) No separation plate. Short-circuiting stopped by density differences

May counteract – also heat produced in process.

a) & b) subject to clogging Fe, Mn, Ca.

UVBs to 40m flow rates to 500 m^3/hr. – Fresh air & soil gas 180–320 m^3/hr.

May stimulate biodegradation

Level of Demonstration

60+ sites in Europe   PCE, TCE, TCA   10-1000 ppb

Sands and silty soils

Rhine-Ruhr steel plants. 10^{-1} cm/s   Sandy soil 40 m deep

Concentration to 5ppm

Recovery 120-300 mg/m³ vapor production

Daily removal 2.0 kg/d.

4000 hours operation 50 kg VOCs.

Applicability / Limitations

$H > 10^{5}$ atm/m³/mole

Aqueous phase contaminants

Not known if free phase NAPL will be mobilized.

Good site characterization to avoid cross contamination

K range so far. $10^{-1} - 10^{-4}$ cm/s.

Ambient groundwater velocities to 1 m/d.

Cost and Availability

$50-100/yd³.

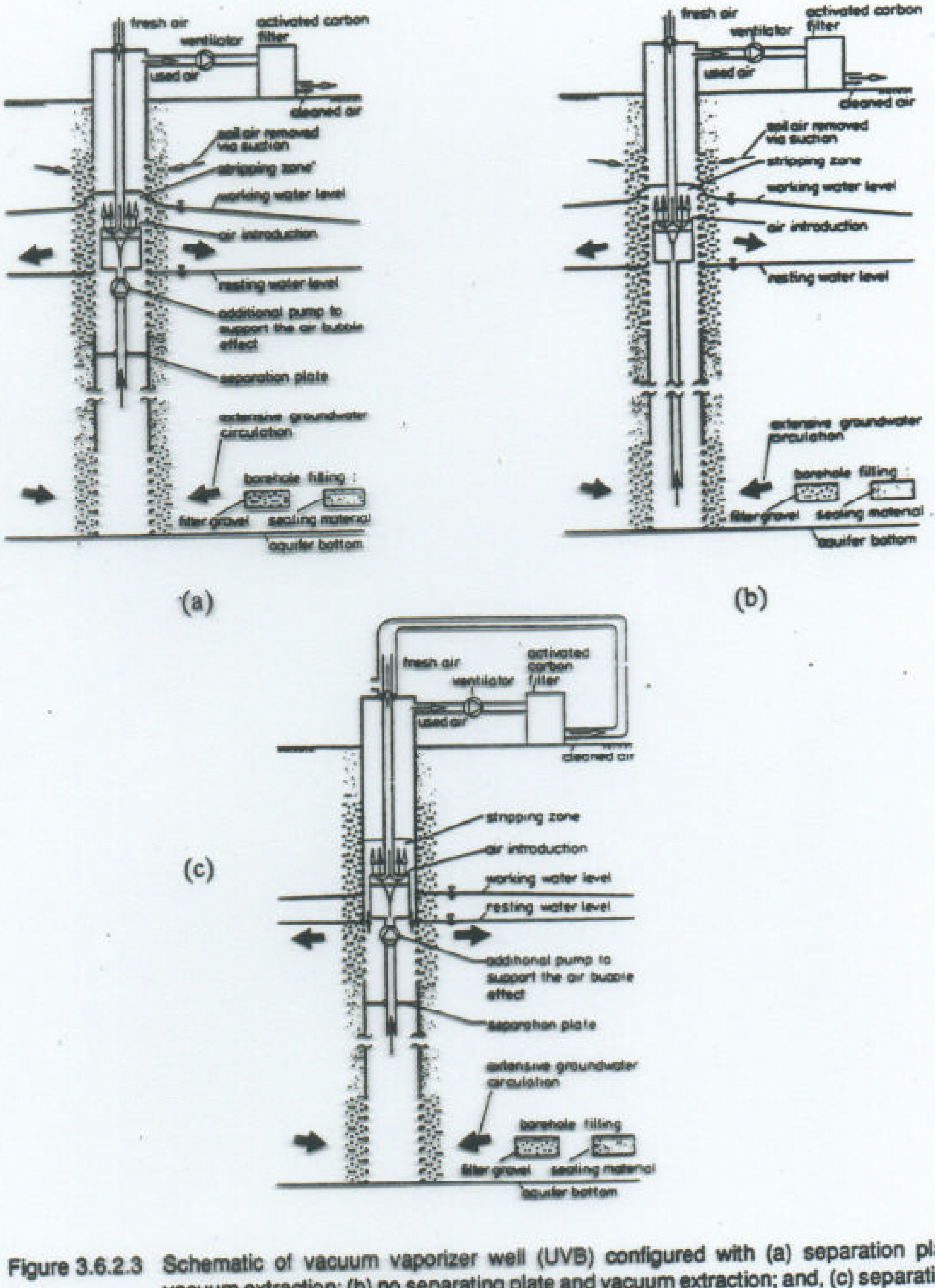


Figure 3.6.2.3 Schematic of vacuum vaporizer well (UVB) configured with (a) separation plate and vacuum extraction; (b) no separating plate and vacuum extraction; and, (c) separation plate and closed air recirculation. [Herrling et al, 1992a].

[8:6] Thermal Processes

Contained recovery of oily wastes (CROW)

In situ steam-enhanced extraction (SEE)

Radio frequency heating

In situ vitrification

6. THERMAL PROCESSES

Delivery of Thermal energy to subsurface:

1. CROW (Contaminated Recovery of Oily Waste) - Hot water/low quality steam
2. SEE (In situ Steam Enhanced Extraction) - High quality steam
3. Radiofrequency heating - microwaves &
4. In situ vitrification - electrical energy

Heats fluids & porous medium { Vaporize contaminants / Reduce viscosity / Reduce surface tension } Fluid/fluid displacement

Issues:
1. Heat transfer and heat adsorption by aquifer materials.
   large blocks
2. Heterogeneities and short circuiting
3. Influence of buoyancy forces (over-ride)

CROW & SEE from EOR industry

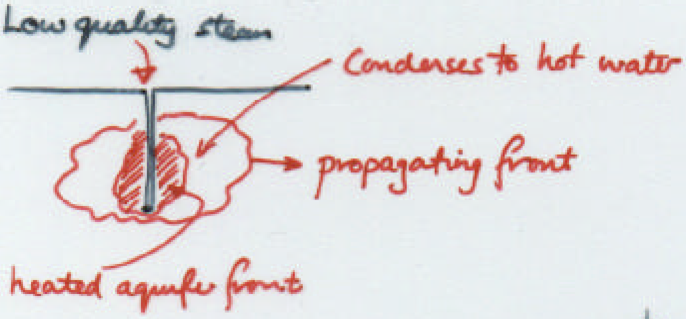
In situ Vitrification - Radionuclide containment

Incorporate as a glass.

6.1 Contained Recovery of Oily Water CROW©

Low quality steam:
1. Flotation of NAPL by ↓ρ
2. Reduced μ and increased mobilization
   - also surface tension changes.
3. Propagation of water front.

Secondary mechanisms:
1. Solubility enhancement of target NAPL
2. Enhanced in situ biodegradation.



Steam → condenses to water

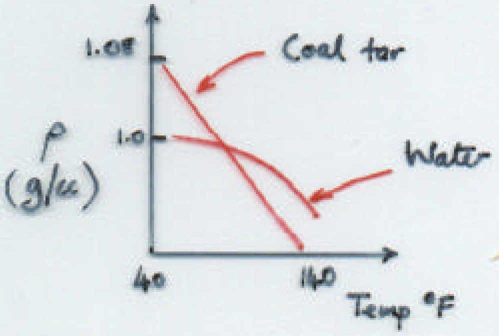
Water → (immiscible) plug displacement

Surfactants may be added.

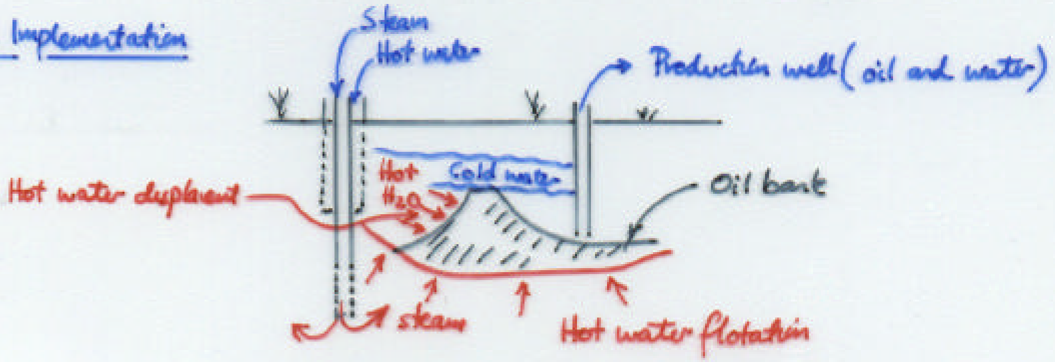
k_{rw} ↑ by hot water due to viscosity↓

$\mu \propto \frac{1}{\text{Temp}} \propto \frac{1}{\text{Kelvin}}$

Some DNAPLs may be transformed to LNAPL with temperature change



Field Implementation



Wells may inject: cold water } at different levels.
hot water
steam

remove: mixed water and NAPL → rinject water after treatment

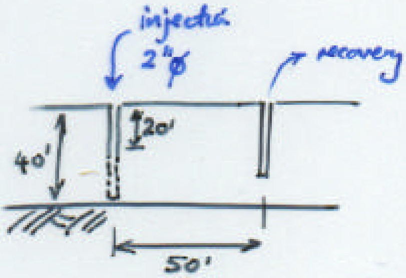
- float DNAPL to surface and horizontal displacement
- Concentrate NAPL in "oil bank" for displacement by water.
- ↓ S_{nw} due to ↓ interfacial tension
- Rear zone of solubilized NAPL due to hot water.

Cool water layer acts as confinement layer
May add surfactants to improve behavior.

Level of Demonstration

- Lab studies using columns (bead packs) for displacement } to determine
- Large reaction boxes 3×3×7ft } potential

Pilot studies



Wood treatment plant (creosote)
40 ft aquifer silty fine sands and gravels
30 day injection 4.5 gpm
147°F – 203°F
Uniform heating in 28 days.
Inject 193,000 gals; Extract 390,000 gals incl. 2000 gal NAPL

Samples of soil show: ~ 80% wt. reduction in hydrocarbons
after 20 pore vol. flushings.
~ PCP concentration 2100 → 3.6 ppm.

Applicability / Limitations

LNAPLs and DNAPLs. Densities within 10–15% of water @ 20°C

(since ΔT will float product).

Residual saturation of NAPL controlled by N_B and N_C (by passing/short circuit).

and residual of 0.1–5 wt% remains

∴ need additional movement mechanism

Significant S_{nw_0} reductions, mixing, oxygenation → useful augmenting technique to bioremediation.

Cost / Availability

Depth of treatment dictates cost.

Planned treatment @ Stroudsburg, PA. 20 ft aquifer.

Good candidate for DNAPL removal.

Soil treatability studies (2 × 55 gal drums) $20,000

Pilot study $300,000

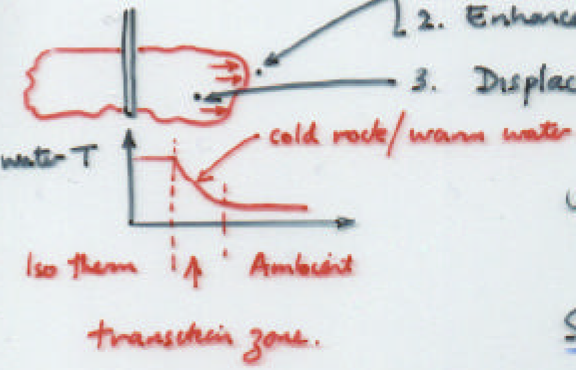
Full scale study $1.5–2.5M ← capital costs for installing equipment

↑ include in situ biological treatment.

Operating/maintenance costs $50K–$60K/year.

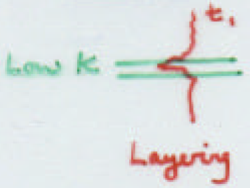
6.2 Steam Enhanced Extraction (SEE)

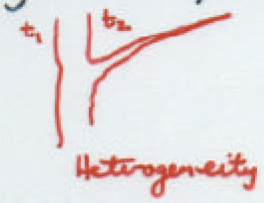
Mechanisms:
1. Vaporization of low b.p. liquids (b.p. <100°c)
2. Enhancement of evaporation of liquids b.p > 100°c
3. Displacement of contaminants by plug displ. condensation front.



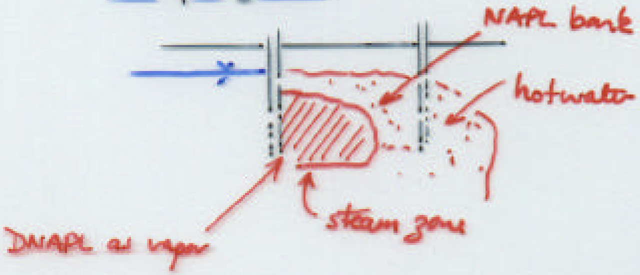
Unsat. zone: Gravitational forces negligible
∴ front ⊥ to flow movement

Sat. zone: Layering controls flow pattern





Multiple zones:



After steam breakthrough, vapors are recovered directly.

Desorption of organics enhanced due to thermal energy. Heat (due to steam) overcomes "latent heat of adsorption".
∴ partitioning to aqueous phase favorable.

Dead-end pore fluids also removed – heat + apply vacuum → induces boiling and vaporization → remove additional fluids.

Field Implementation

Steam injection well + condensate and vacuum extraction wells.
Low-carbon steel wells (temperatures).
Supersaturate steam to prevent condensation down b/h. (increase pressure).
100% steam @ b/h base.

Level of Demonstration

Lab desorption studies   eg. Diesel 1500 mg/kg → 19 mg/kg

Pilot studies (60 yd³)   BTEX (19,000 ppm)
TCE (1600 ppm)   } soil conc 2065 mg/kg → 12 mg/kg

763 lbs recovered in 140 hrs. { 29% due to vacuum
71% by steam

Steam injected @ 250 lb/hr @ 6 psig
5 ft well spacing (recovery).

Full scale treatment completed   Huntington Beach 135,000 gal diesel
in 40 ft aquifer
37 steam inj; 39 vacuum wells on 2 acres
5 months → 14,000 gals.
No offsite vapor migration.

Applicability/Limitations

Saturated and unsaturated zone
Petroleum & DNAPLs and mixtures.
Problems in delivery in silts and clays, but less
susceptible than other methods

Shallow application (low pressure & temp.) will → micro-organisms dormant
but flourish when ceased → bioremediation
Deep application (high T) → sterilization ∴ repopulation needed

Costs

$50–125/yd³ incl. treatment of waste ex situ.

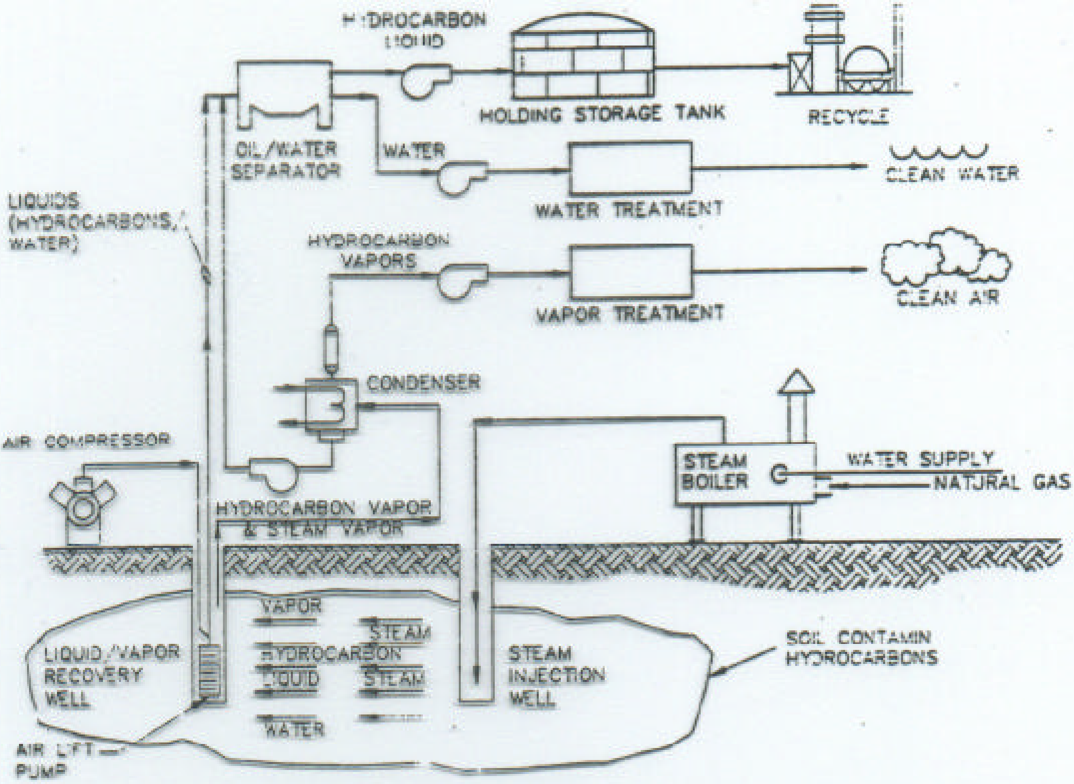


Figure 3.7.2.5 Schematic of in-situ steam enhanced extraction process [USEPA, 1992d].

6.3 Radio Frequency Heating

Electro magnetic energy → heating:

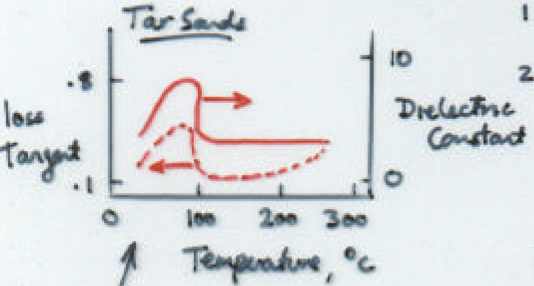
1. Vaporizes low b.p. liquids bp $< 100°C$
2. ↑ Evaporation rates for high bp liquids bp $> 100°C$
3. Displacement by propagating steam front
   + ↑k and ↓μ

Analagous to CROW

Microwaves distort physical (molecular) structure of polar compounds (water) → kinetic energy → heating.

Important parameters:

1. Dielectric constant (porous medium)
2. Loss tangent (ratio of apparent conductivity to change in frequency)



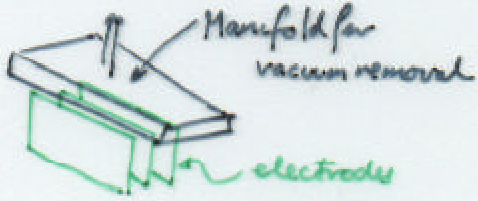
High loss of energy and low penetration in high ε soils. Water saturated → $\varepsilon_r \sim 80$

∴ low penetration of saturated soils

$\left.\begin{array}{l}\varepsilon_{NAPL} < 5\\ \varepsilon_{water} \sim 80\end{array}\right\}$ tar sand @ low water saturation

As fluid boils off the ε magnitude ↓ and coupling is more effective

Field Implementation



- Shield RF from humans (harmful) navigation etc.
- Triplate design
- Also used in EOR

Subsurface heating → vapors to perforated electrode - "vacuum" manifold
- removal to manifold
- produces natural draft

If soil temp < 100°c then hot water propagation front.

Level of Demonstration

Bitumen recovery from tar sands
20' long electrodes as triplate
Daily power 40-70 kW. Soil temp 200°c for 20d.
336 gals bitumen or 36% recovery

1 environmental application. Volk Field Air Nat. Guard Base, WI
Sandy soils. Hydrocarbons to 4000 ppm
6-8' deep triplate array 12' to water table
12d. temp to 150°c
Removal of volatiles (bp < 120°c) 99%
semi volatiles (bp 120-300°c) 95%

Applicability

- Low or high boiling point materials
- Applicable in unsat. zone

Not obvious if useful in saturated zone, or advantageous over SEEs
Not greatly affected by presence of clays
Likely sterilizes soil for biodegradation

Cost /Availability

Patent to IIT → Licensed to Roy F. Weston
$40-100/ton soil

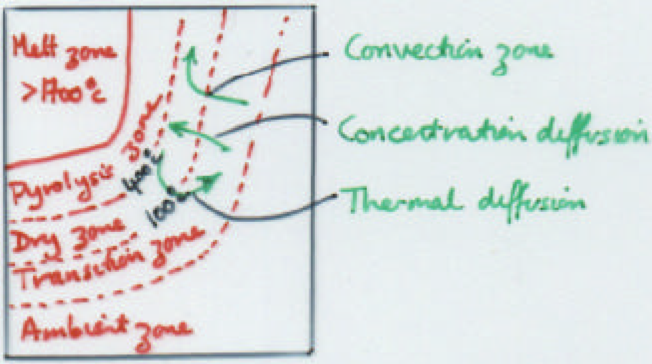
6.4 Vitrification

Joule resistance heating → melting → contaminant removal

Mechanisms: 1. Accelerated chemical reactions (melt and pyrolysis zone)
2. Organic vapor recovery in vacuum hood.
3. Pyrolysis of DNAPLs and vapors

1. Initial "starter" path of graphite added at surface between electrodes
2. Soil conductivity ↑ with melting (elec. cond.)
3. Soil temperatures 1600°c — 2000°c

Molten mass propagates ↓.



- DNAPLs boil as they transit the 100°c isotherm + dry.
- Dry zone acts as gas conduit
- Remaining compounds thermally decomposed in pyrolysis zone.

Cooled mass resembles obsidian. qu 5-10x concrete
high leach resistance.

Field Implementation

Molten soil mass – Heavy metals and radionuclides stabilized
DNAPLs pyrolized

50' dia. fugitive gas hood. Vacuum to ½ - 1" H_2O

Electrodes fixed or moved down with melt

Square electrode array. 35' separation (max)

Depth of 19 - 25'.

Backfill subsidence. Mobilization between sites ~ 16 hr.

Applicability / Limitations

Orignaly developed for radionuclides — high cost.

Also applicable to DNAPLs

Limitation. Groundwater vels in soil with $K > 10^{-4}$ cm/s will stop melt progress.

Applicable to vadose soils only, and clays saturated.

Could be used with dewatering / containment

Useful in very hetrogeneous soils.

Rule-of-thumb limitations:

- Metal concentration < 5–16% wt.
- No continuous metal traversing more than 90% of electrode spac
- Combustible organic concentration < 5–10% wt.
- Individual void volumes < 150 ft^3
- Drums and buried debris may short circuit (remaining at base of melt).

Hardware trailer mounted. Treat soil @ 10,000 lb/hr

Typical soils. 4 kW hrs/lb → 4000 kW per application

About same consumption as average-sized city hotel

Cost / Availability

No full scale ISV below w/t

US DoE has patent

Not applicable for DNAPL below w/t

Useful for mixed waste → $450/yd^3

Estimates $300–400 ton.

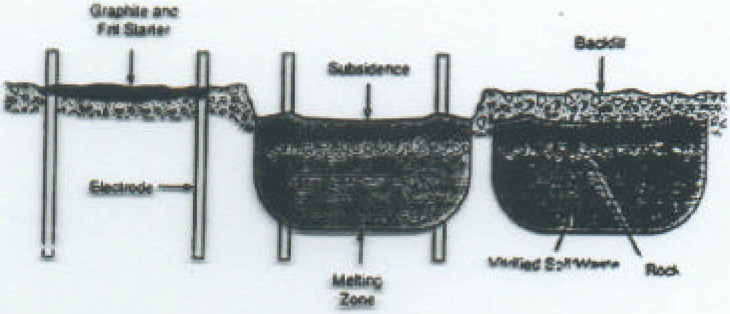


Figure 3.7.4.1 Schematic illustrating the in-situ vitrification (ISV) process [Smith and Hinchee, 1993].

TABLE 4.1.1. IN-SITU TECHNOLOGY COMPARISONS

IN SITU TECHNOLOGY	DESIGN BASIS	OPERATIONAL MECHANISM	APPLICABILITY	SCALE OF DEMONSTRATION	EXPECTED EFFICIENCY	COMMERCIAL AVAILABILITY	APPROX. COST RANGE ($/yd^3)
Aerobic Biodegradation	Theoretical	Treatment	Dissolved phase only	Pilot	Intermediate/High	Pilot/Available	15-60
Anaerobic Biodegradation	Theoretical	Treatment	Dissolved phase only	Pilot	Intermediate/High	Pilot/Available	15-60
Electro-Osmosis	Theoretical	Treatment/ Recovery	Dissolved phase only	Pilot	Low	Available	75-150
Electroacoustic Soil Decontamination	Empirical/ Theoretical	Treatment/ Recovery	Dissolved phase only	Laboratory	Low	Emerging	60-150
Slurry Walls	Empirical	Containment	Dissolved and separate phase	Full	High	Available	7-13/ft^2
Grouting	Empirical	Containment	Dissolved and separate phase	Full	Intermediate/High	Available	60-100
Hydraulic Gradient Control	Theoretical	Containment	Dissolved phase only	Full	Intermediate/High	Available	50-100
Stabilization/Solidification	Empirical	Containment	Dissolved and separate phase	Full	Intermediate/High	Available	SSM 26-65 DSM 130-260
Permeable Treatment Walls	Empirical/ Theoretical	Treatment	Dissolved phase only	Pilot	Intermediate/High	Pilot	50-100
Alkali Soil Washing	Theoretical	Recovery	Dissolved and separate phase	Pilot	Intermediate/High	Pilot/Available	75-125
Cosolvent Soil Washing	Theoretical	Recovery	Dissolved and separate phase	Laboratory	Intermediate	Emerging	75-125
Surfactant Soil Washing	Theoretical	Recovery	Dissolved and separate phase	Pilot	Intermediate/High	Pilot/Available	75-125
Water Flooding	Empirical/ Theoretical	Recovery	Dissolved and separate phase	Full	Low/Intermediate	Available	50-100
Air Sparging	Empirical	Recovery	Dissolved phase only	Full	Intermediate/High	Available	75-125
Vacuum Vaporizer Wells	Theoretical	Recovery	Dissolved phase only	Full	Intermediate	Available	50-100
CROW® Process	Theoretical	Recovery	Dissolved and separate phase	Pilot	Intermediate	Pilot	50-125
Steam Enhanced Extraction	Theoretical	Recovery	Dissolved and separate phase	Pilot	High	Pilot/Available	50-125
Radio Frequency Heating	Theoretical	Recovery	Dissolved and separate phase	Pilot (vadose zone)	Intermediate	Pilot	65-160
Vitrification	Empirical	Treatment/ Recovery	Vadose Zone only				400+

(see text for additional notes and explanations)