# *In situ* physicochemical remediation
# Passive and active barriers

Lecture 9

# Learning outcomes

- Physicochemical treatments:
  1. Stabilization/solidification
  2. Heating technologies:
     - *A.* *In situ* thermal desorption
     - B. Electrical resistance heating
  3. *In situ* chemical oxidation
  4. Electrokinetic separation
  5. Pump-and-Treat
- Barriers
  1. Passive barriers
  2. Active barriers

# 1. Stabilization/solidification

# Stabilization vs. solidification

- Stabilization: process by which additives are mixed in the waste or soil to minimize contaminant migration from the waste
- Solidification: process by which the physical nature of the waste or soil is altered (solidified)
- Both are widely used in:
  - Land disposal (stabilization prior to landfill disposal)
  - **Site remediation**
  - Solidification of industrial wastes
- Both are often selected for source control treatment
- Often considered together S/S

# Stabilization

**Table 3-1. Effectiveness of Solidification/Stabilization on General Contaminant Groups for Soil and Sludges**

| Contaminant Group | Effectiveness |
|---|---|
| ***Organic*** | |
| Halogenated Volatiles | ▲ |
| Non-halogenated Volatiles | ▲ |
| Halogenated Semivolatiles | ■ |
| Non-halogenated Semivolatiles and Non-volatiles | ■ |
| Polychlorinated Biphenyls | ■ |
| Pesticides | ■ |
| Dioxins/Furans | ● |
| ***Inorganic*** | |
| Non-volatile Metals | ■ |
| Radioactive Materials | ■ |

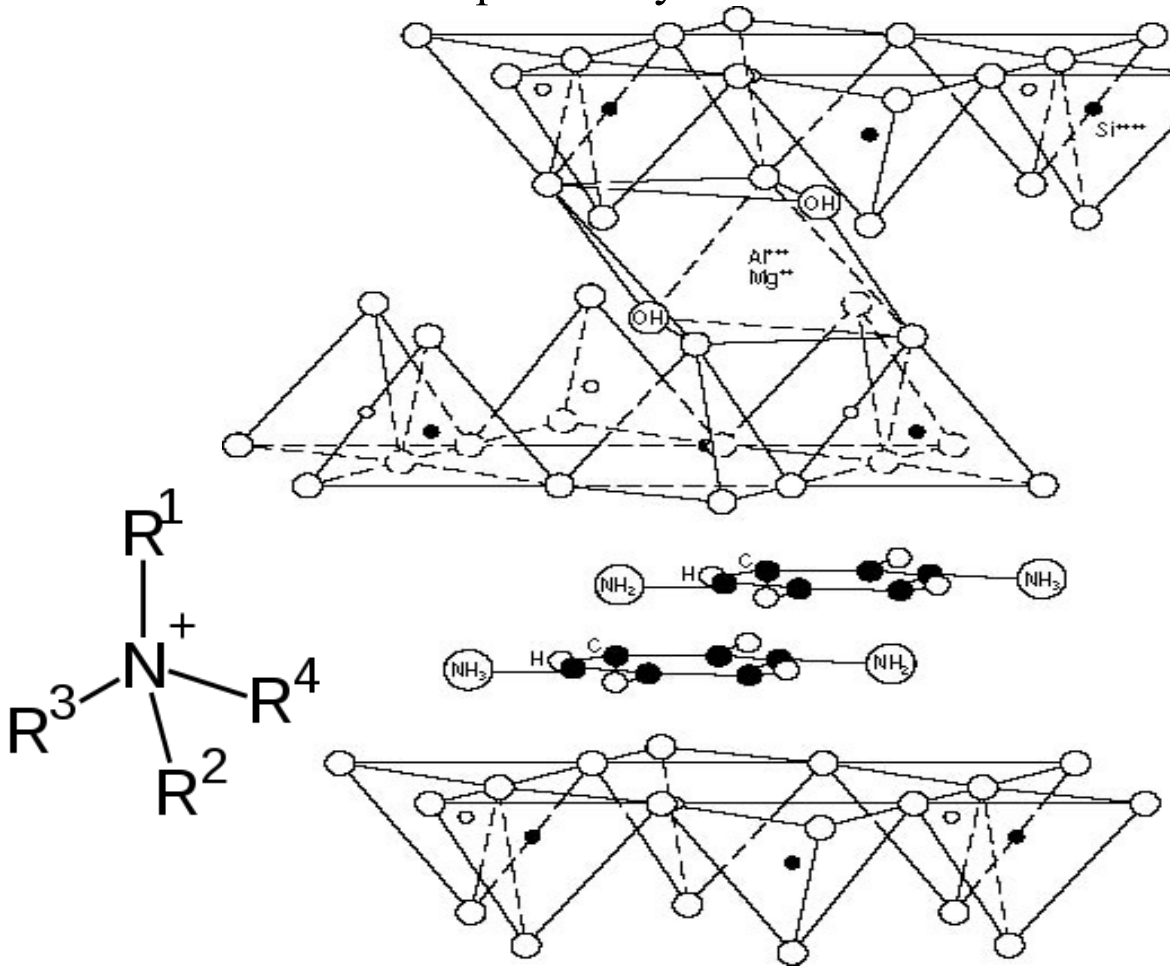
■ = Demonstrated Effectiveness ▲ = No Expected Effectiveness ● = Potential Effectiveness

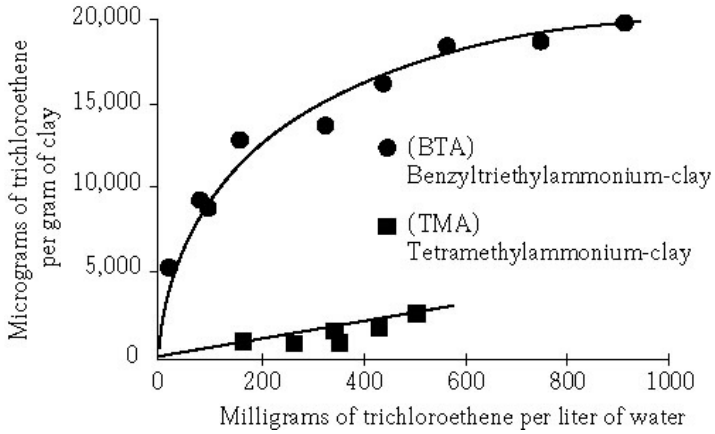
# Types of additives for stabilization

- **Binder** = reagent that contributes to the strength gain associated with stabilization
- **Sorbent** = reagent primarily contributes to retaining contaminants in matrix
- The material we will consider here is **clay**

# Organically-modified clays

- Used in conjunction with other additives to trap organic fraction of the waste and allow cement hydration process
- Replace the inorganic cations present in between clay platelets with organic quaternary ammonium cations
- Organic cations readily adsorb other organic species
- Nature of the quaternary ammonium ion used impacts binding of organics



# Solidification

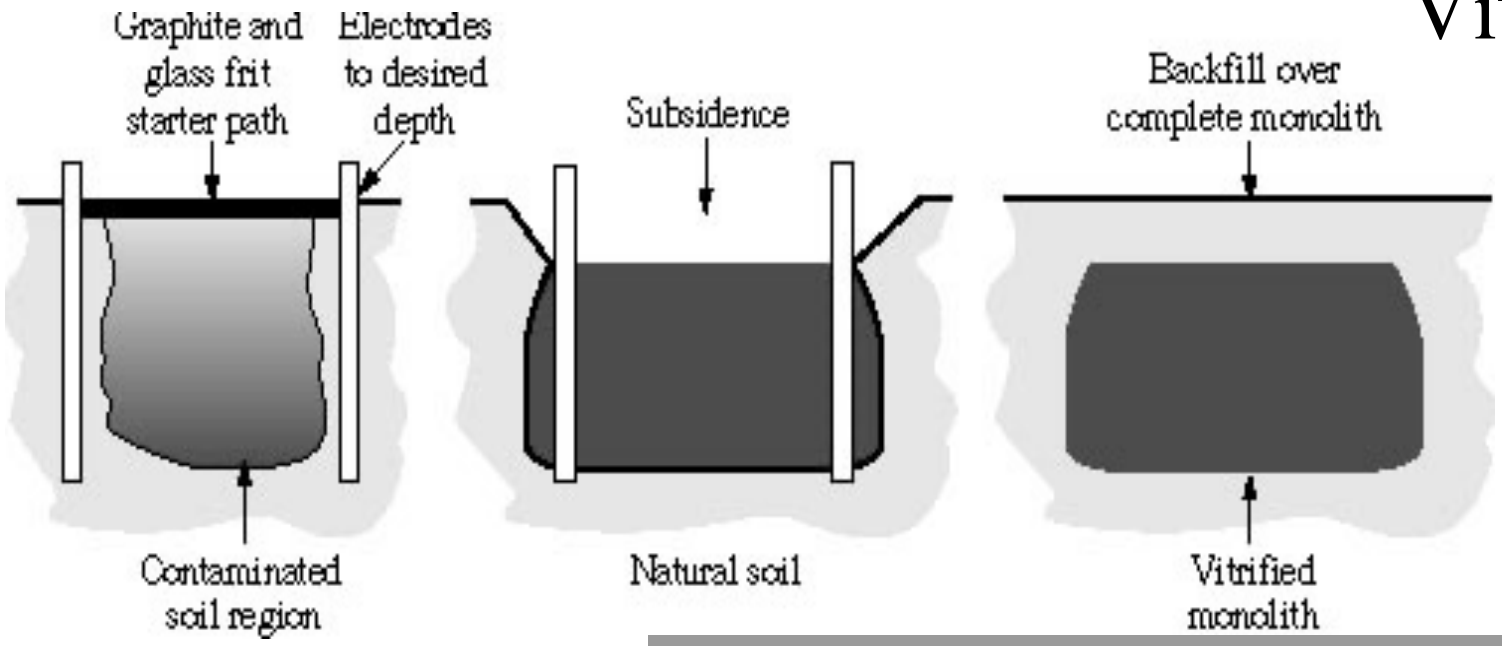
# Cement

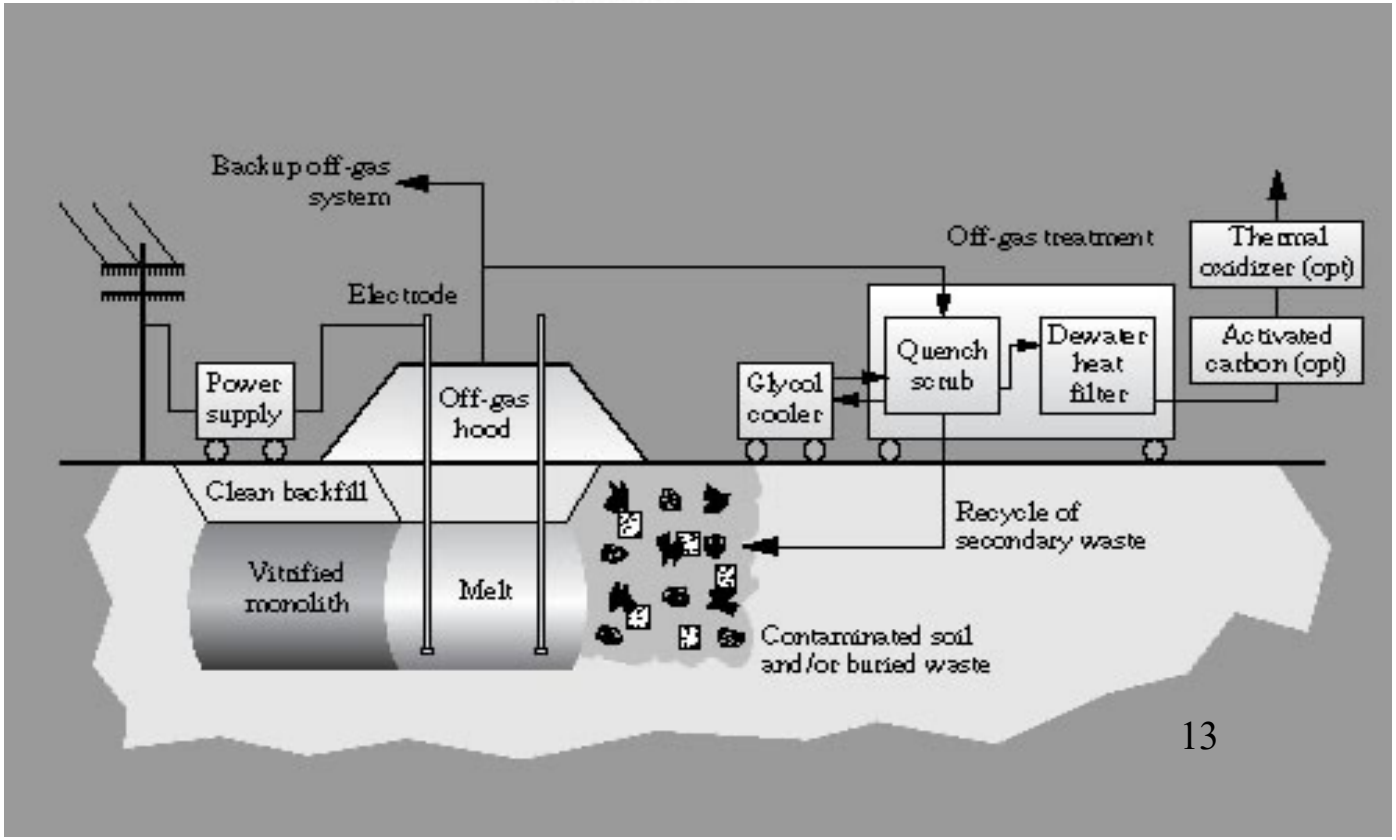
- Most common cement is Ordinary Portland Cement (limestone and clay in a kiln at high temperature)
- Powder that contains calcium, silicate, aluminum and iron oxides
- Waste materials mixed with powder and water is added (if needed)
- Hydrated cement forms a crystalline calcium aluminosilicate
- Best suited for inorganic wastes- organic contaminants interfere with hydration process
- Can compensate organic interference by adding clays

# Vitrification

- Vitrification does not involve the addition of reagents
- Melting and fusion of materials at >1,600 ºC followed by rapid cooling into noncrystalline form
- Solidification technique
- *In situ* vitrification:
  - available commercially
  - Application of electric current via electrodes
  - As current flows, heat builds up, causing the soil to melt
  - As the soil melts, it becomes more conductive and the molten mass transfers heat, allowing itself to grow
  - Use surface layer of graphite and glass
  - Electrodes maximum ~8m apart in a rectangular pattern
  - Soil melts 3-6 tons/hr
  - Organic contaminants: vaporize- capture gas emission and treat if needed
  - Volume reduction by 25-50% as pore space disappears

# Vitrification



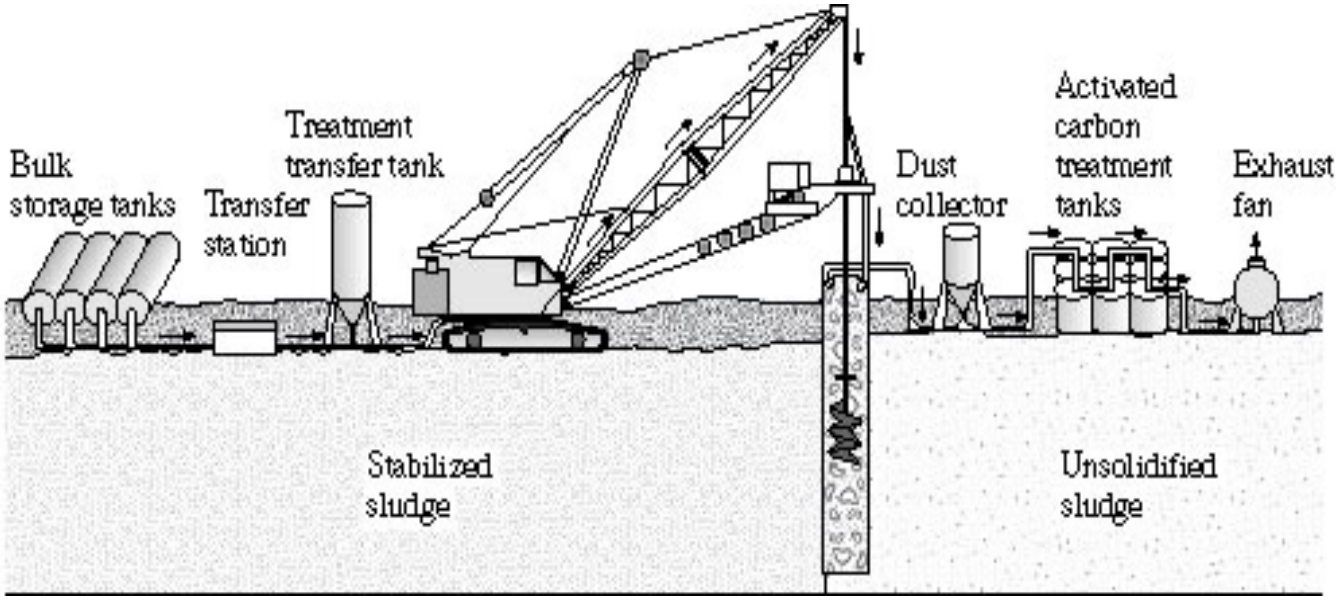



# Extraction and leaching tests

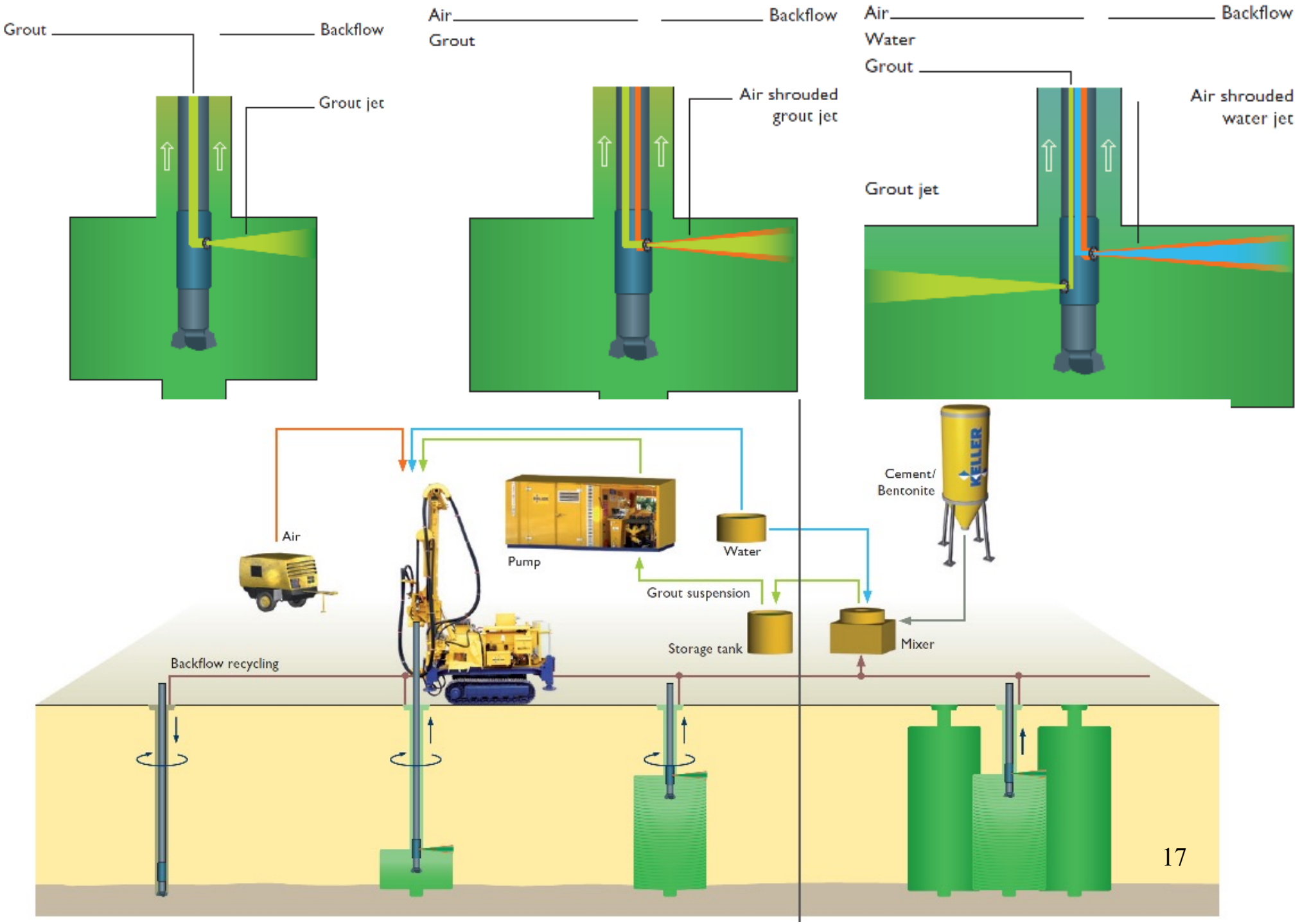
- A reduction of the rate at which contaminants can migrate into the environment is the major criterion in determining the success of a stabilization effort
- Over time, rainwater may percolate into the stabilized zone and release contaminants
- To evaluate how much pollutants could be released, use leaching tests
- Many different kinds of leaching tests using various ‘leachants’
- Purpose of tests varies:
  - Regulatory tests: basis for consistent decision-making- use highly reproducible test
  - Predictive tests: generate data to use in real-world modeling
  - Investigatory tests: study basic binding mechanisms of pollutant

# Field implementation

- Most widely implemented method (*in situ*)
- Mechanical ways of mixing improve on a regular basis
- Question about the thoroughness of mixing *in situ*
- **Modified augers**: allow mixing at depth
- **Jet grouting system**: rotating high pressure jet to excavate and mix in situ materials with injection fluid- first drill to desired maximum depth, uniform rotation and lifting from the bottom up
- **Batch mixing on site**: use a mechanical mixer at the surface- used fixed amount of waste material and additive- ensures better mixing

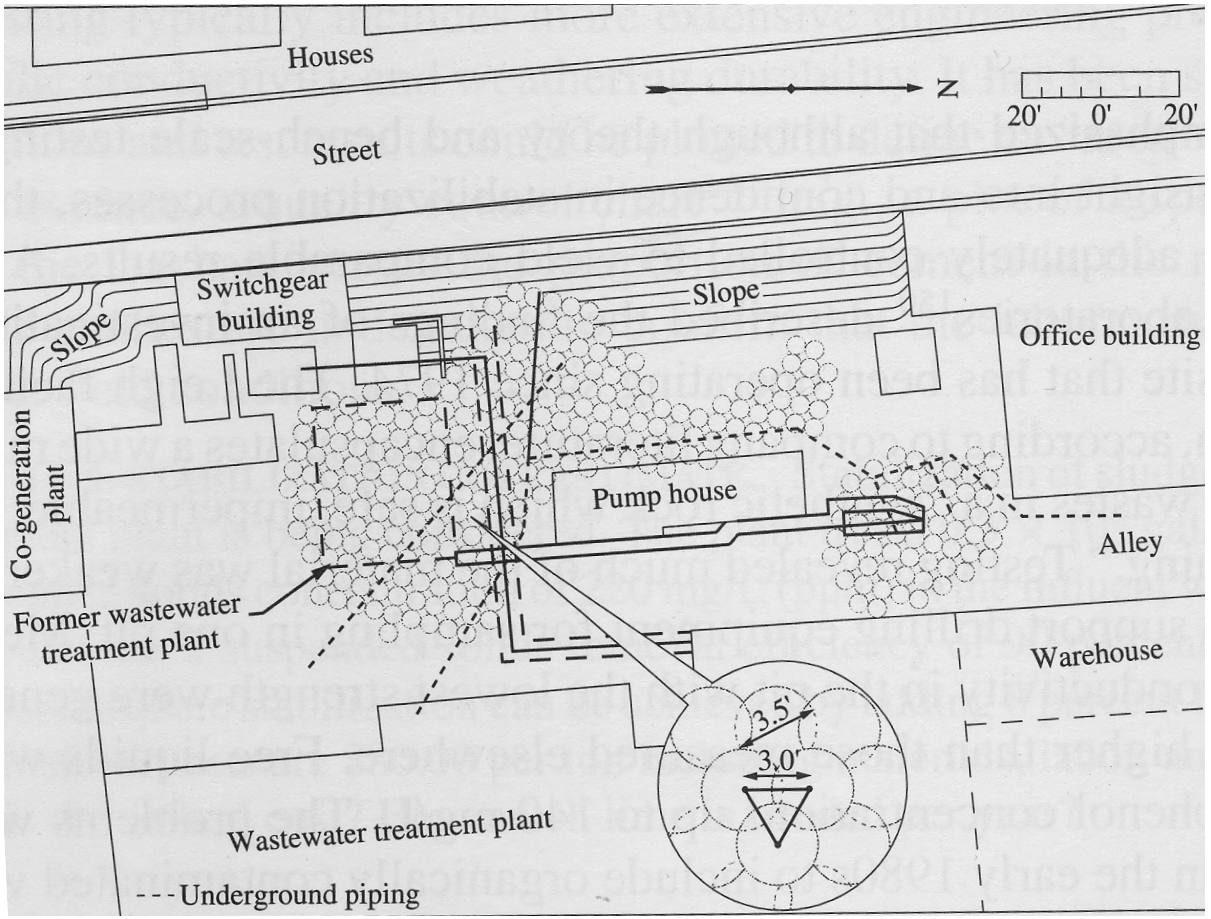


# Field implementation: Jet grouting systems



# Example: Sandy soils contaminated with Cd

- Dense sand and gravel soil: 130 mg/L of Cd
- Laboratory studies considered various stabilization strategies
- *In situ* jet grouting because needed to work around underground facilities



# 2. Heating technologies

# *In situ* thermal approaches

Types of thermal treatments:

- **Electrical resistive heating** (ERH)
- **In situ thermal conduction** (ISTD)
- Steam-enhanced extraction
- Large diameter auger soil mixing combined with steam/hot air injection
- Radio-frequency heating

Impact of heating on organic contaminants:

- Vapor pressure increases
- Adsorption coefficients decrease
- Water solubility increases

Thus, removal of contaminant is enhanced in the following ways:

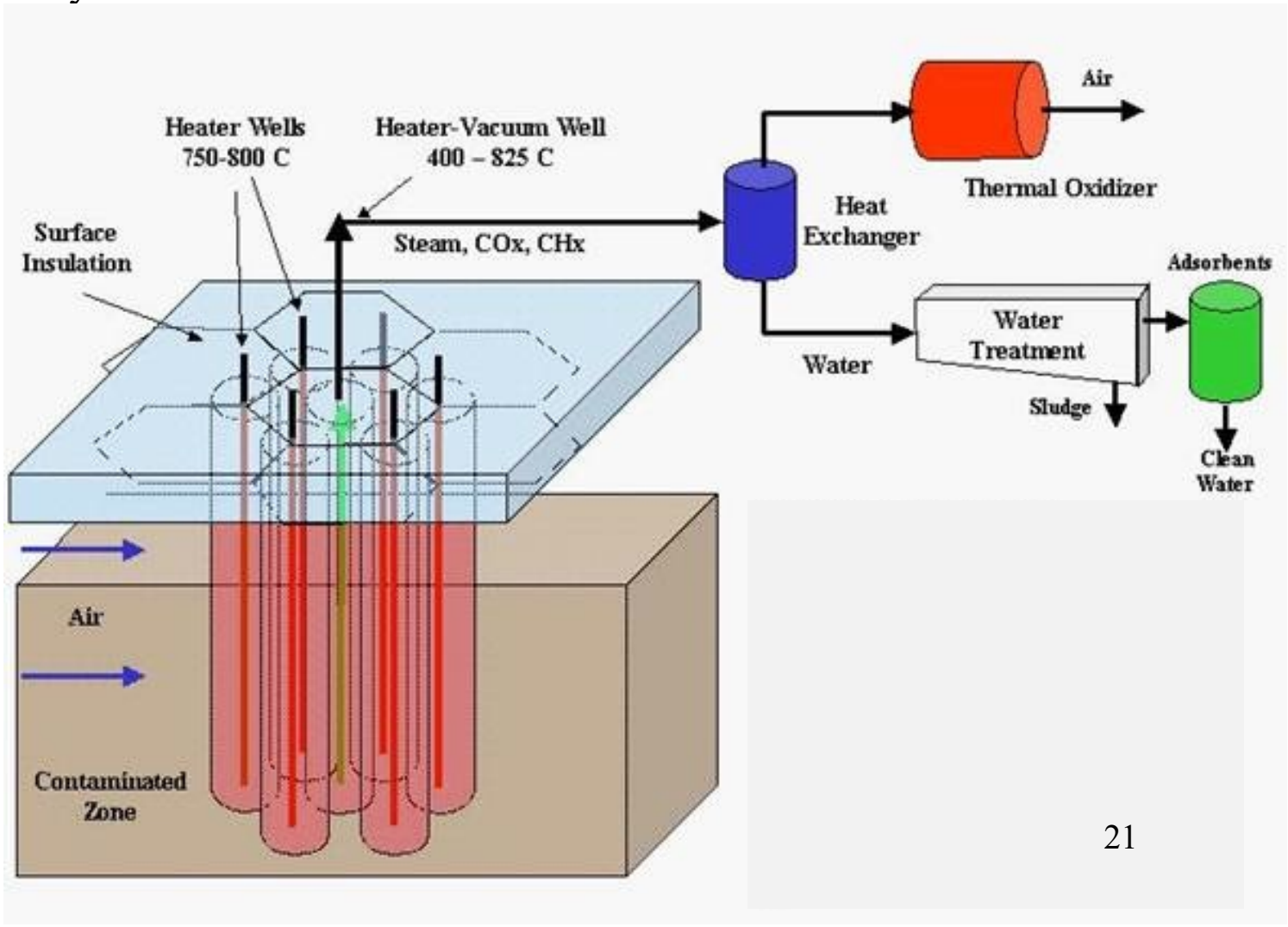
- By extraction with pumped groundwater
- By vaporization and extraction in the vapor phase
- By dissolution and desorption and removal with extracted water.
- By enhanced microbial mineralization
- By hydrolysis

Main disadvantages:

- Cost
- Not applicable near occupied areas
- Require sophisticated design
- Could enhance mobility of contaminant and migration off-site
- Post-treatment soil temperature can remain high for months to years

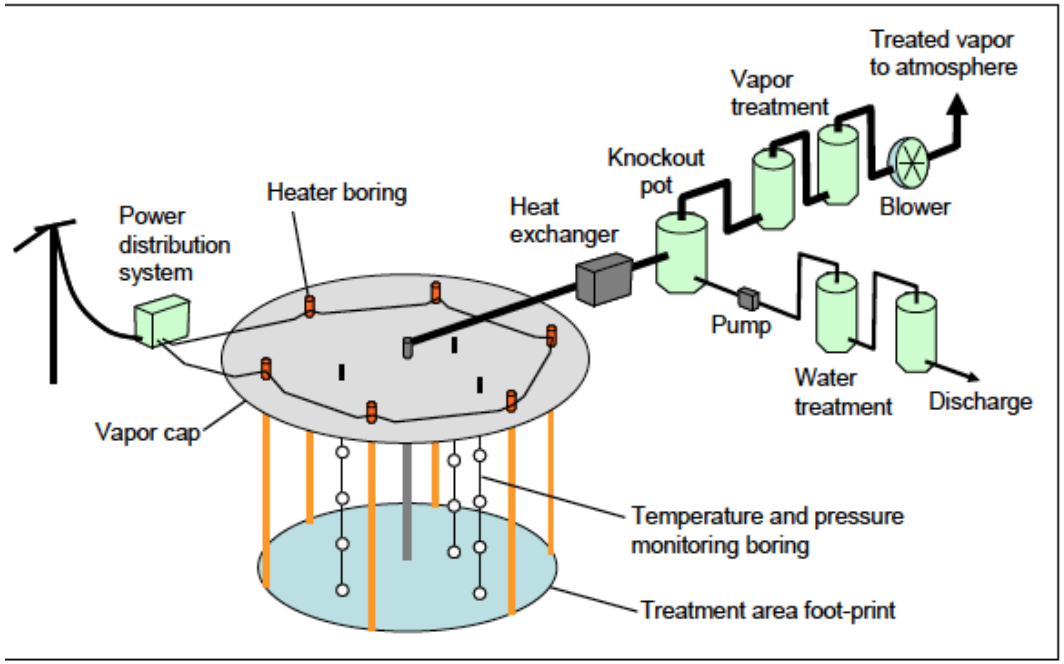
# *In situ* thermal desorption (thermal conduction heating)

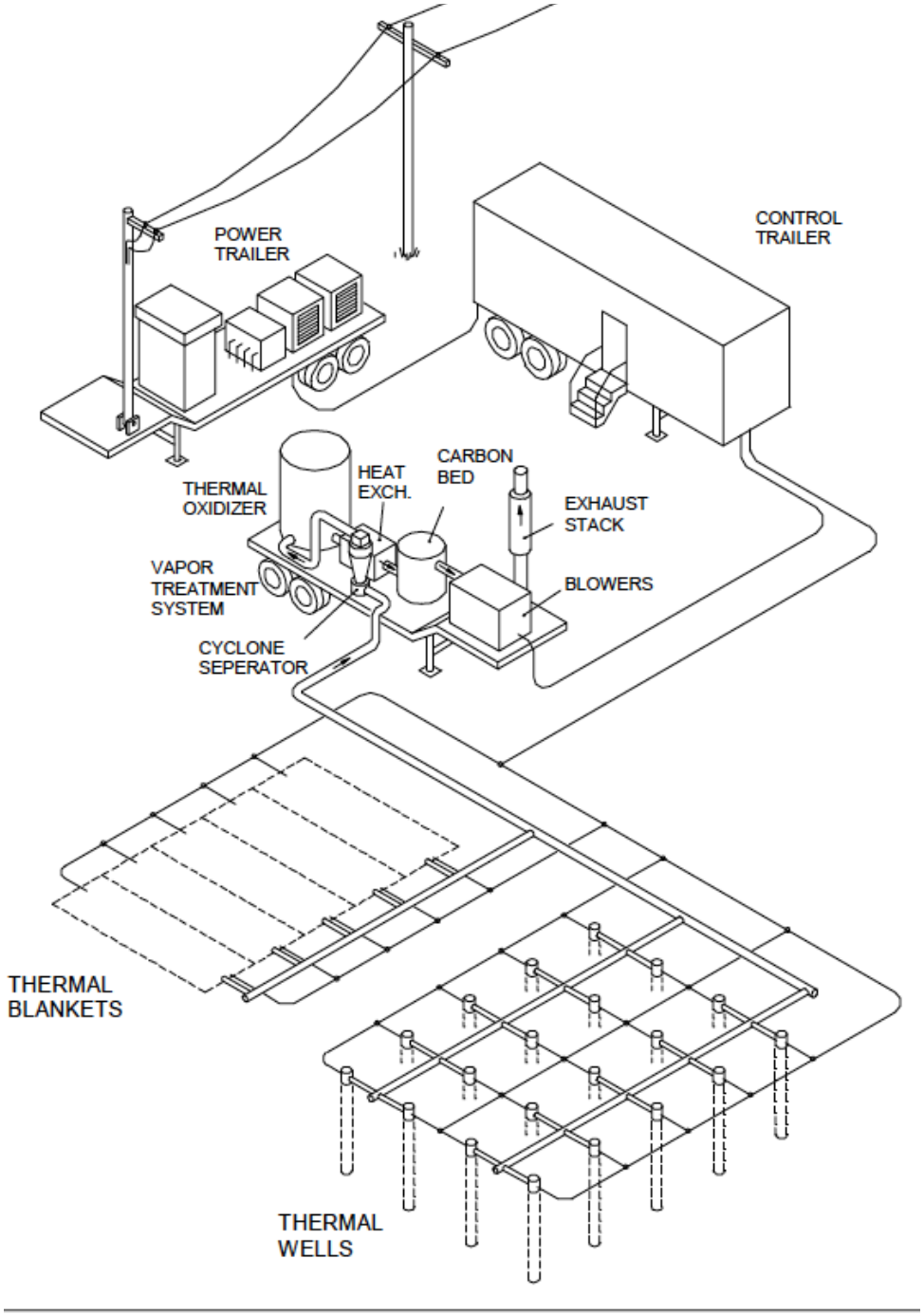
- Heater elements are hung in vertical wells to heat the subsurface
- Vapors generated are captured by vacuum wells
- Target temperature is around the boiling point of water (in between heaters)
- Heat front moves through the soil by thermal conduction
- Vapor cover to prevent infiltration, provide thermal insulation and a vapor seal
- Off-gas can be treated by GAC

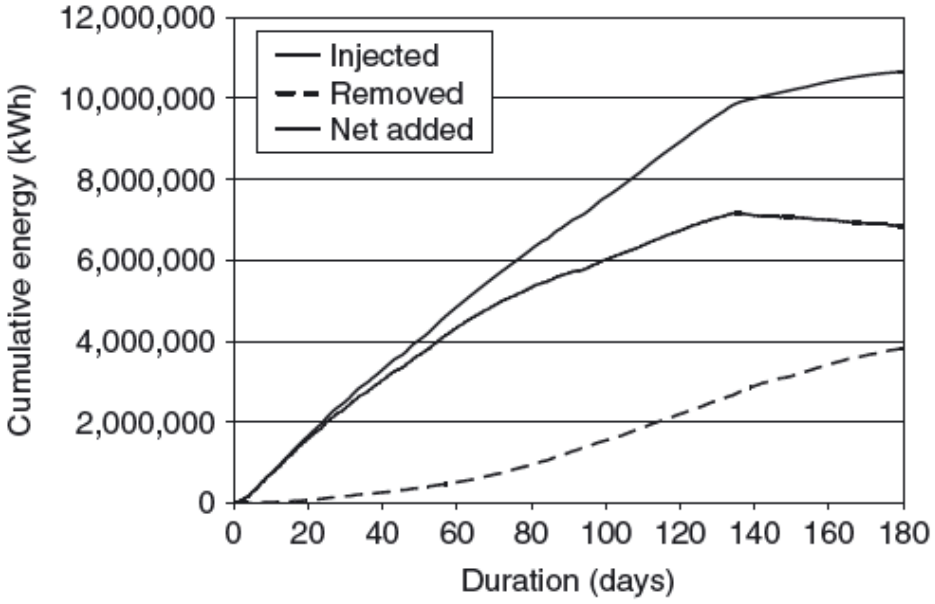


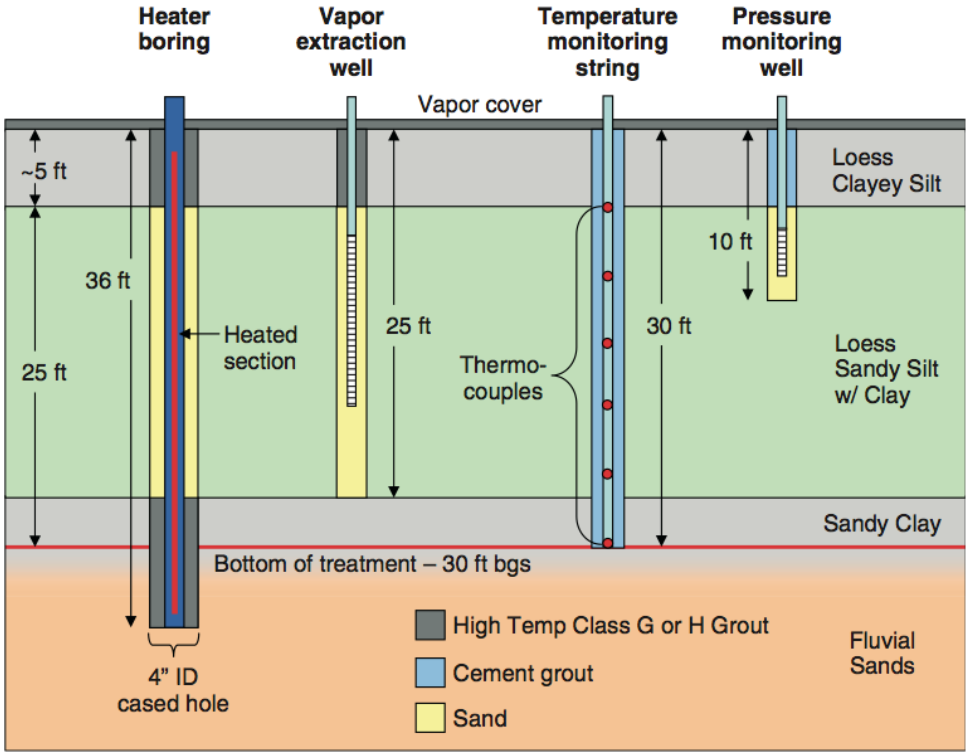
# *In situ* thermal desorption

- Can use thermal blankets for shallow contamination (≤1 m)
- In-well resistive heating element
- A feature is the creation of high temp. zone (500 ºC) where contaminant is destroyed
- Time required proportional to the square of spacing
- Wells usually placed in hexagonal configuration

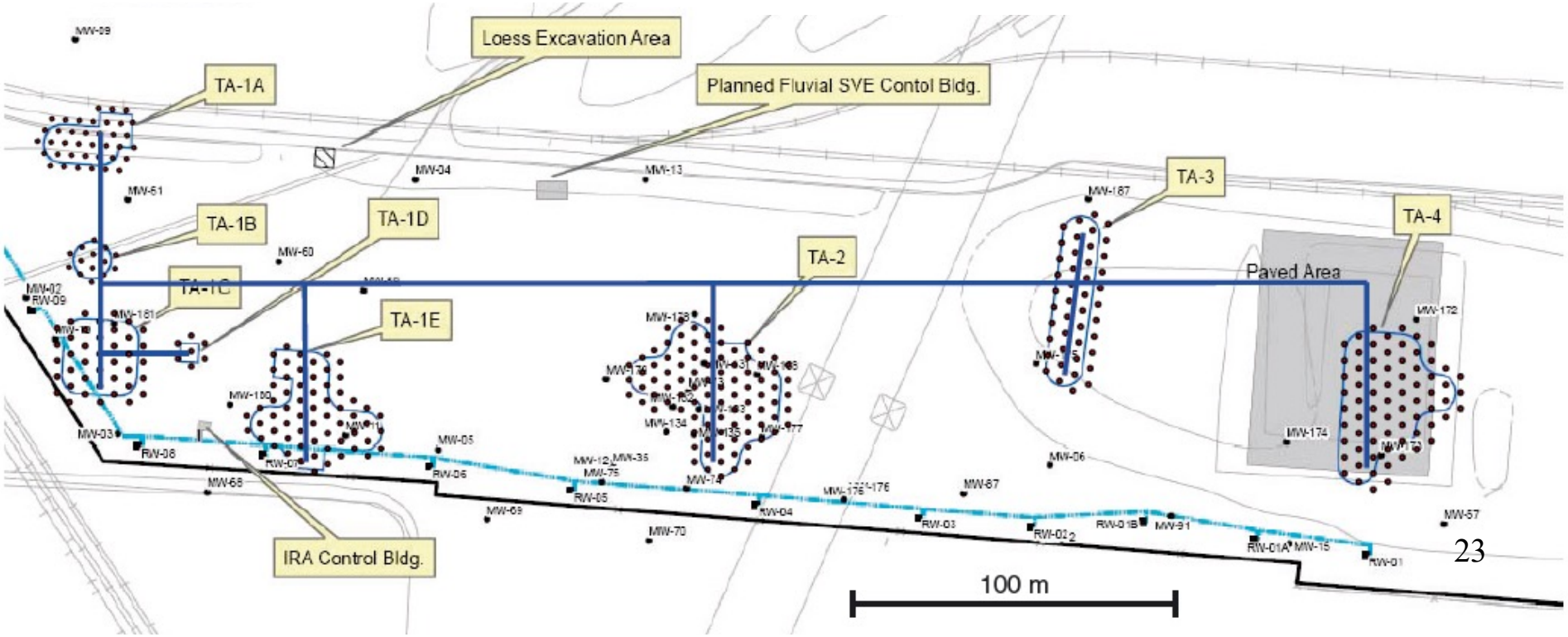


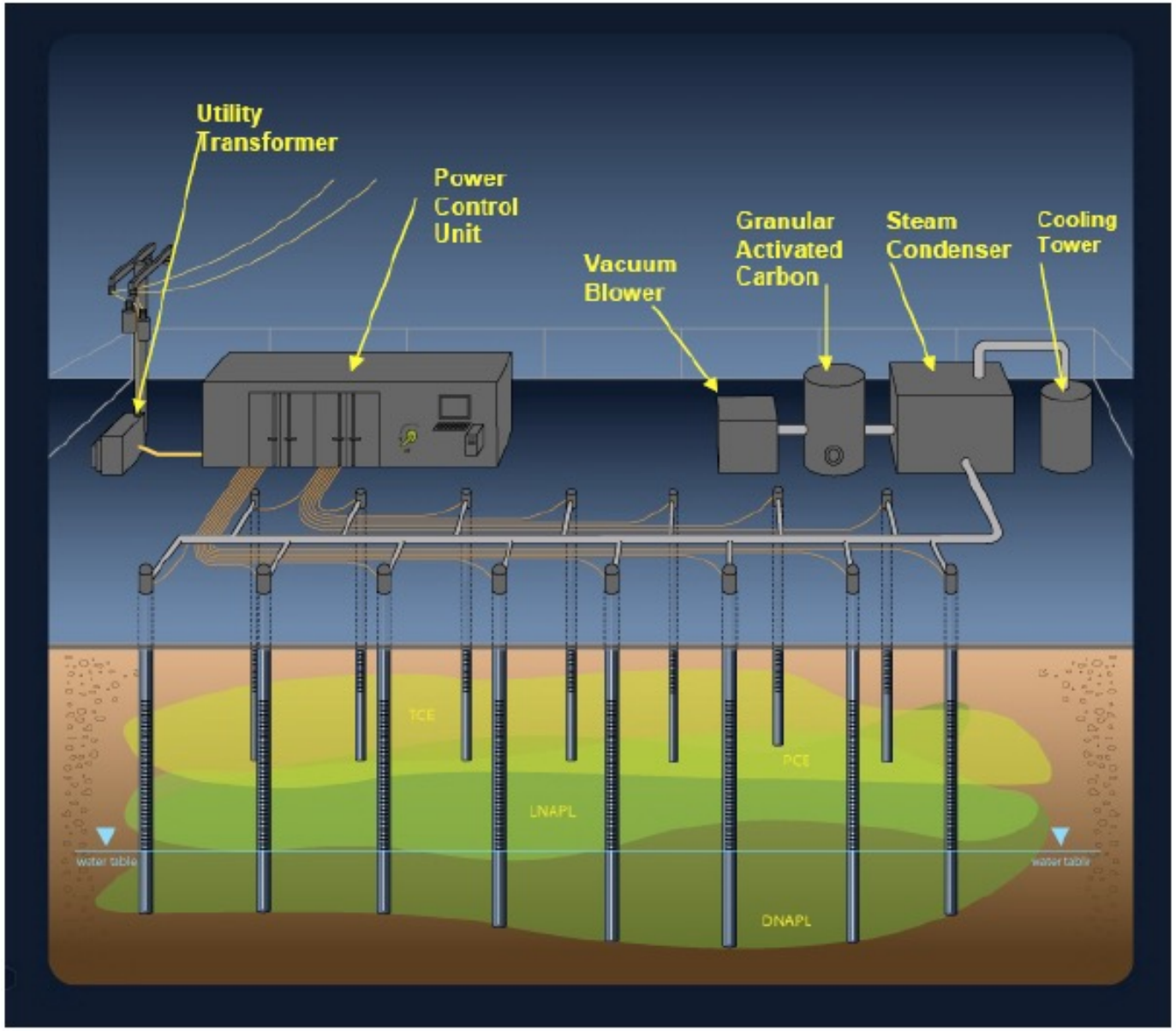



Example of contaminated soil in Tennessee



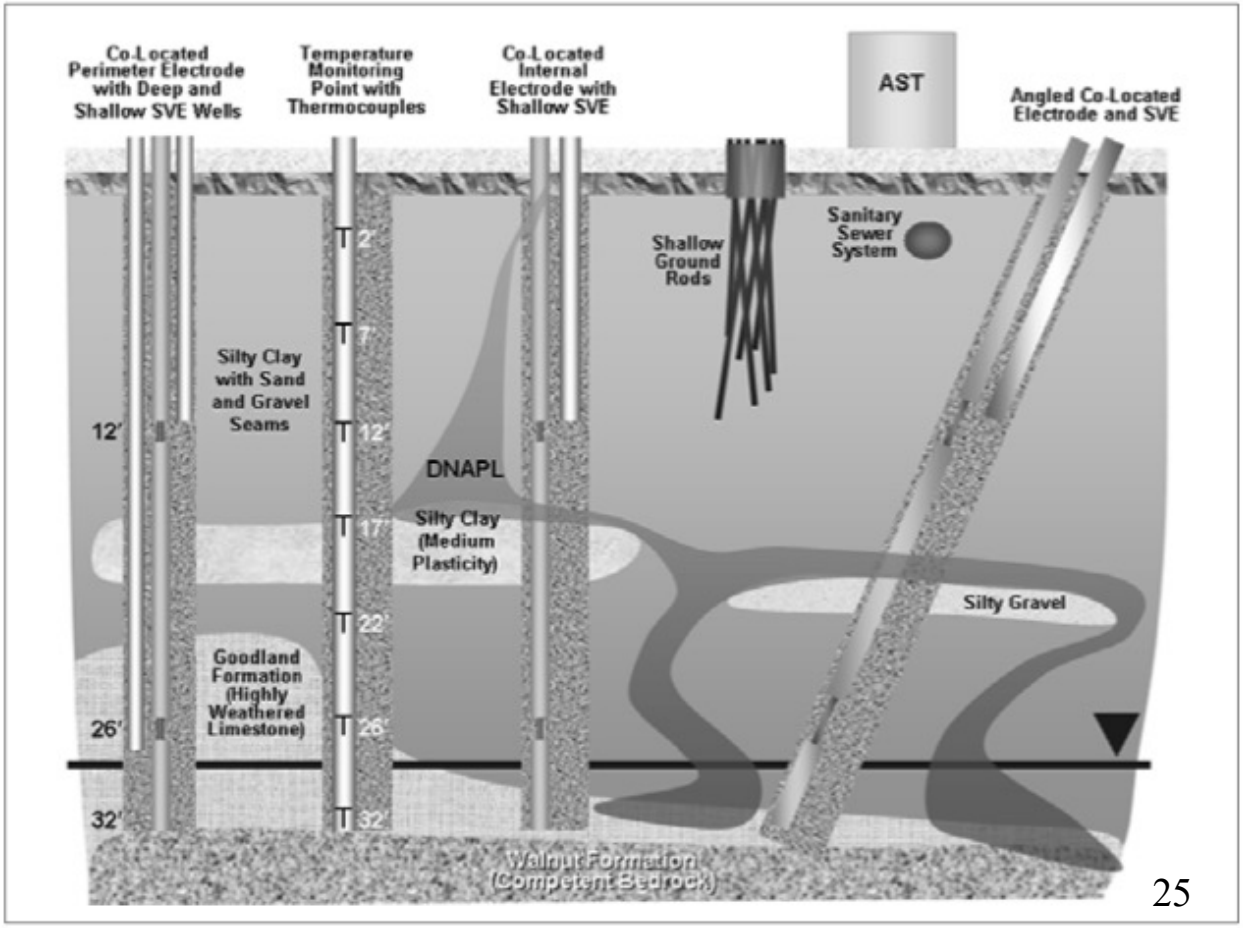
# Electrical resistance heating



# Electrical resistance heating (ERH)

- Soil and groundwater are heated by the passage of electrical current through soil between electrodes
- Resistance to the flow of electrical current results in increased temperatures
- Applied to the boiling point of contaminant and contaminant-water mixture
- Target a wide variety of organic contaminants

- Electrodes constructed of steel pipe or copper plate to treat distinct zones of subsurface
- At depths where ERH is not desired, use insulators
- Vapor recovery is carried out using standard vapor extraction
- Power control unit used to step-down standard line voltage
- Add potable water immediately surrounding electrodes to prevent soil from drying out (and becoming nonconductive)
- Typically 2-8 weeks to reach boiling point



# ERH vs. ISTD

| | ERH | ISTD |
|---|---|---|
| Mode of action | Electrical current into soil | Heat transfer to the soil |
| Electrode/heater | Electrode does not get hot | Heater can reach temp. >500 ºC |
| Temperature of soil | Up to boiling point of water | Variable as a function of distance from heater |
| Treatment of recalcitrants | No | Yes |
| Saturated vs. unsaturated | both | Best for unsaturated zone (need to dewater aquifer) |
| Enhanced bioremediation | Yes | Not as well |
| additions | Add water | No additions |
| Electrical needs | Lower | Higher |
| Number of boreholes | Fewer | More |

# 3. *In situ* chemical oxidation

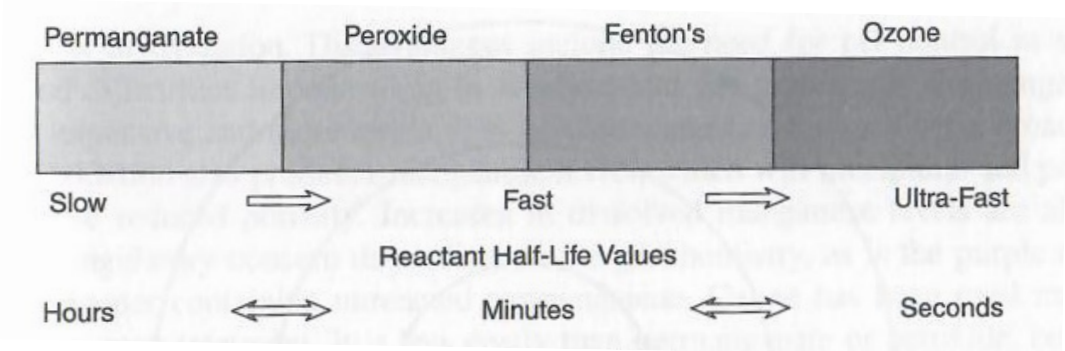
# *In situ* chemical oxidation

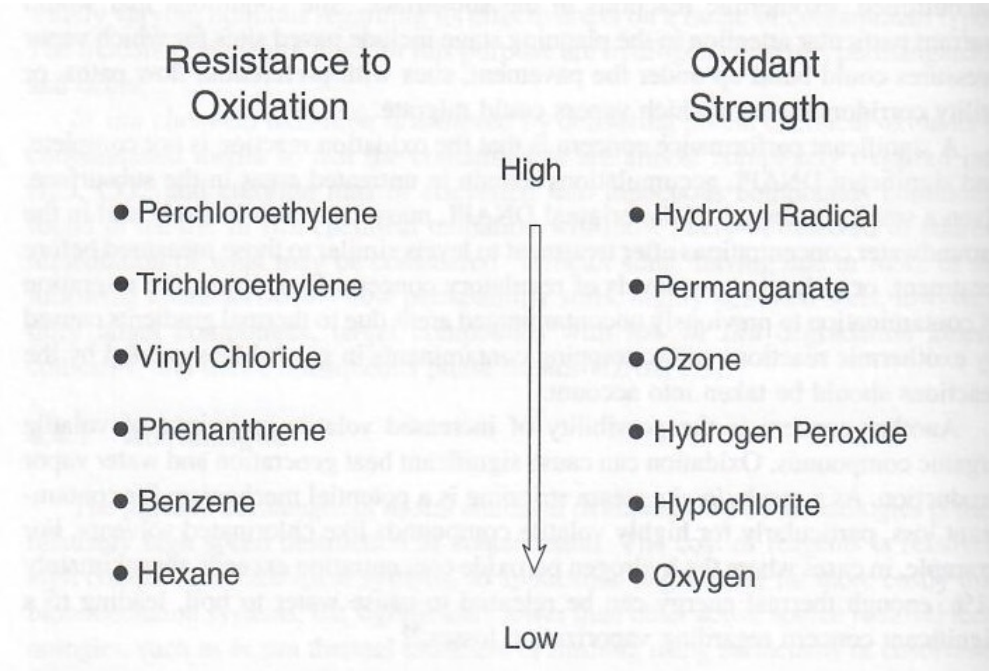
- Involves subsurface delivery of a chemical oxidant to destroy organic contaminants of concern
- Under the right conditions, oxidants yield reactive species that can transform many organics contaminants
- Delivery of oxidant through
  - permeation by vertical direct-push injection probes
  - flushing by vertical wells
  - Horizontal wells
  - Infiltration galleries (surface)
  - Soil mixing
  - Hydraulic fracturing
- Types of oxidants used

| Oxidant | Oxidant chemical | Commercial form | activator | Reactive species |
|---|---|---|---|---|
| Permanganate | $KMnO_4$ or $NaMnO_4$ | Powder, liquid | none | $MnO_4^-$ |
| Hydrogen peroxide | $H_2O_2$ | liquid | none, Fe(II), Fe(III) | $OH^\bullet$, $O_2^{\bullet-}$, $HO_2^\bullet$, $HO_2^-$ |
| ozone | $O_3$ (in air) | gas | none | $OH^\bullet$, $O_3$ |
| persulfate | $Na_2S_2O_8$ | powder | None, Fe(II), Fe(III), heat, $H_2O_2$, hi pH | $S_2O_8^{2-}$, $SO_4^{\bullet-}$ |
| *peroxone* | *$H_2O_2 + O_3$ (in air)* | *Liquid, gas* | *$O_3$* | *$OH^\bullet$, $O_3$* |
| *percarbonate* | *$Na_2CO_3.1.5H_2O_2$* | *powder* | *Fe(II)* | *$OH^\bullet$* |
| *calcium peroxide* | *$CaO_2$* | *powder* | *none* | *$H_2O_2$, $HO_2^-$* |

# *In situ* chemical oxidation

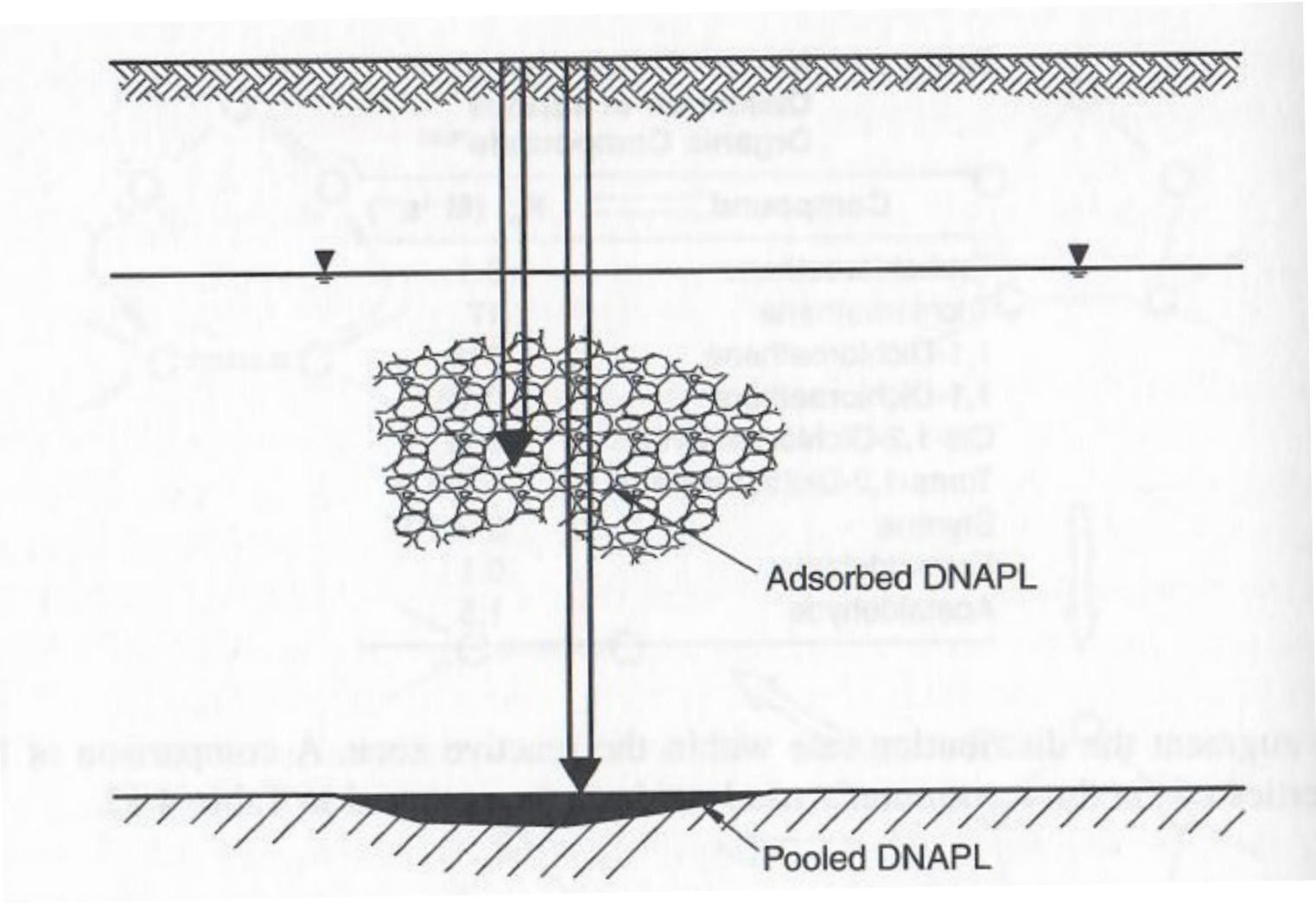
- Used for chlorinated solvents
- PCE and TCE are more reactive than TCA (due to double bonds being more reactive)
- Most commonly used: $H_2O_2$, $KMnO_4$ and $O_3$
- $KMnO_4$ more expensive than $H_2O_2$ but effective over a broader range of pH values
- $O_3$ is the strongest oxidant but is a gas



# Application: NAPL persistence

Targeted application of *in situ* chemical oxidation effective



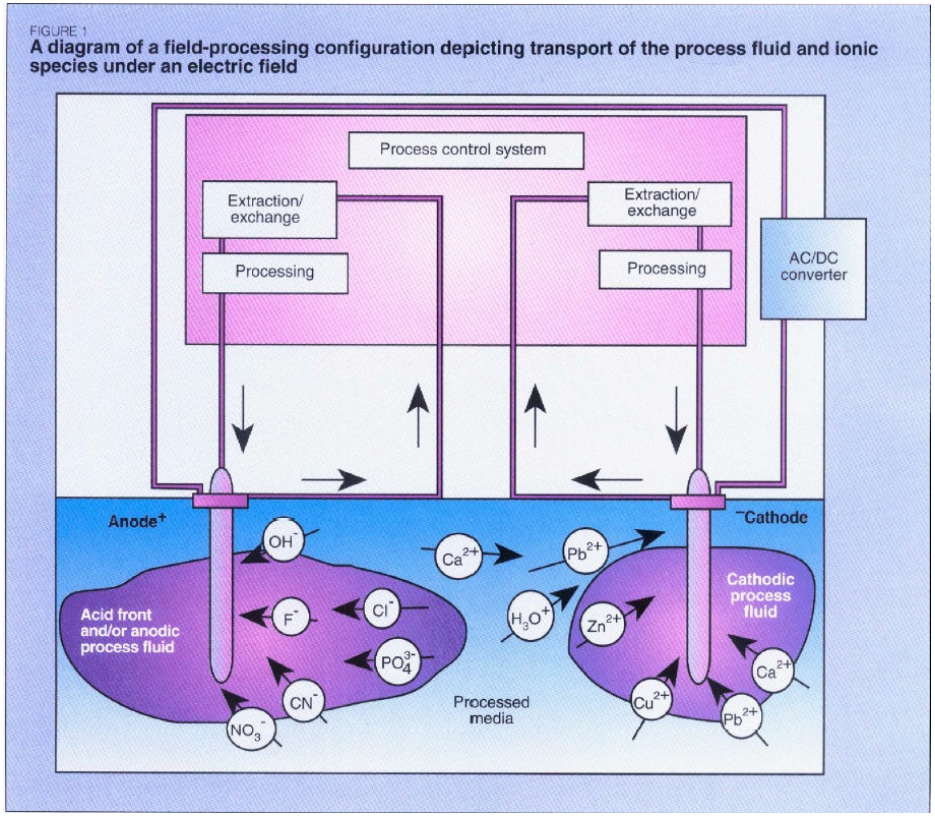
# *In situ* chemical oxidation

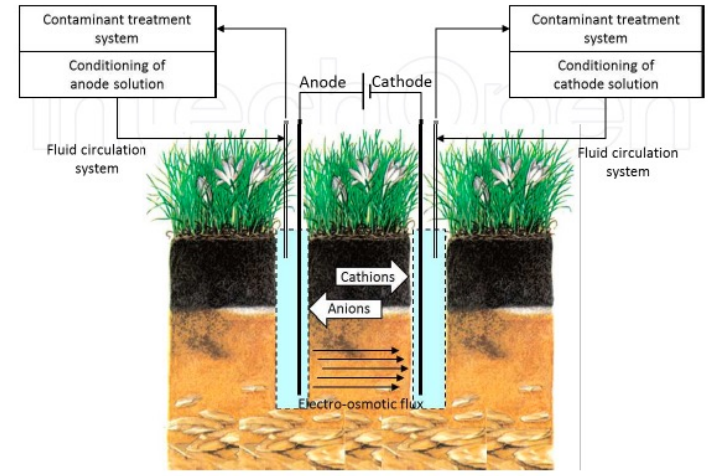
How much potassium permanganate is needed to oxidize all the tetrachloroethylene in the aquifer with the following characteristics?
Areal extent of the plume: 20 $m^2$
Thickness of the plume: 2 m
Average aqueous PCE conc. : 400 mg/L
Aquifer porosity $\varepsilon = 0.35$
Organic content fraction $f_{oc}=0.02$
Dry bulk density $\rho_b = 1.6$ g/$cm^3$
Organic carbon-liquid partitioning coefficient for PCE $K_{oc}=1.55 * 10^2$ L/kg
$MW_{PCE}= 166$ g/mol; $MW_{KMnO4}= 158$ g/mol

# 4. Electrokinetic separation

# Electrokinetic remediation

- Low-level direct current (DC) of a few mA/cm$^2$ of cross sectional area between electrodes
- Electric potential difference of a few volts per cm across electrodes
- Groundwater or supplied fluid provide conductivity
- Fluid flows in porous medium
- Species transport by conduction phenomena
- Electrolysis occurs at electrodes

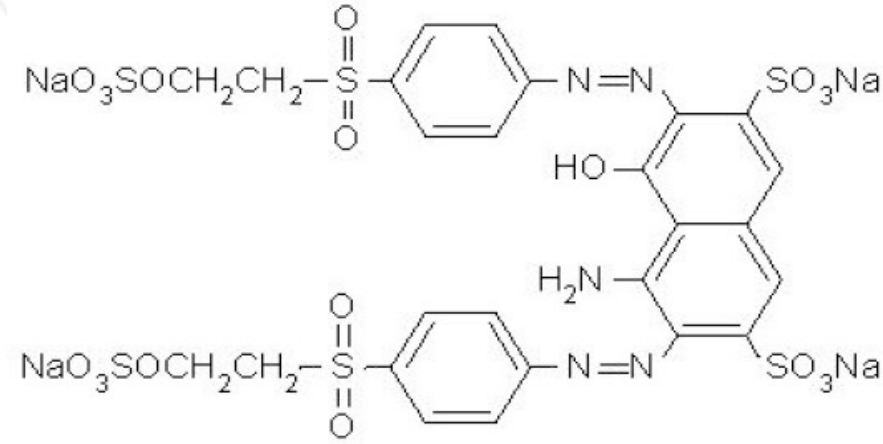


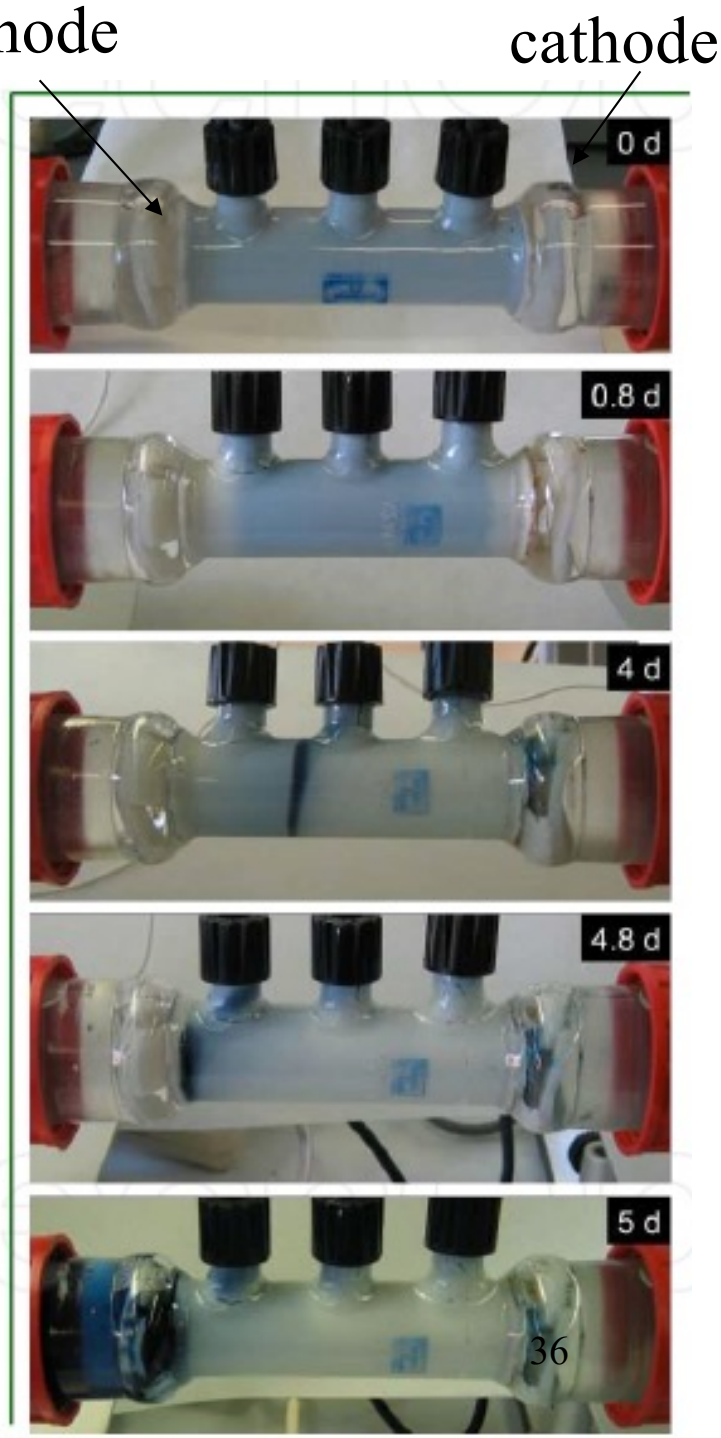




- Combined with chemical oxidation (transport oxidant)
- Combined with PRB (transport contaminant)
- Combined with bioremediation (transport cells)

# Example: Reactive Black 5

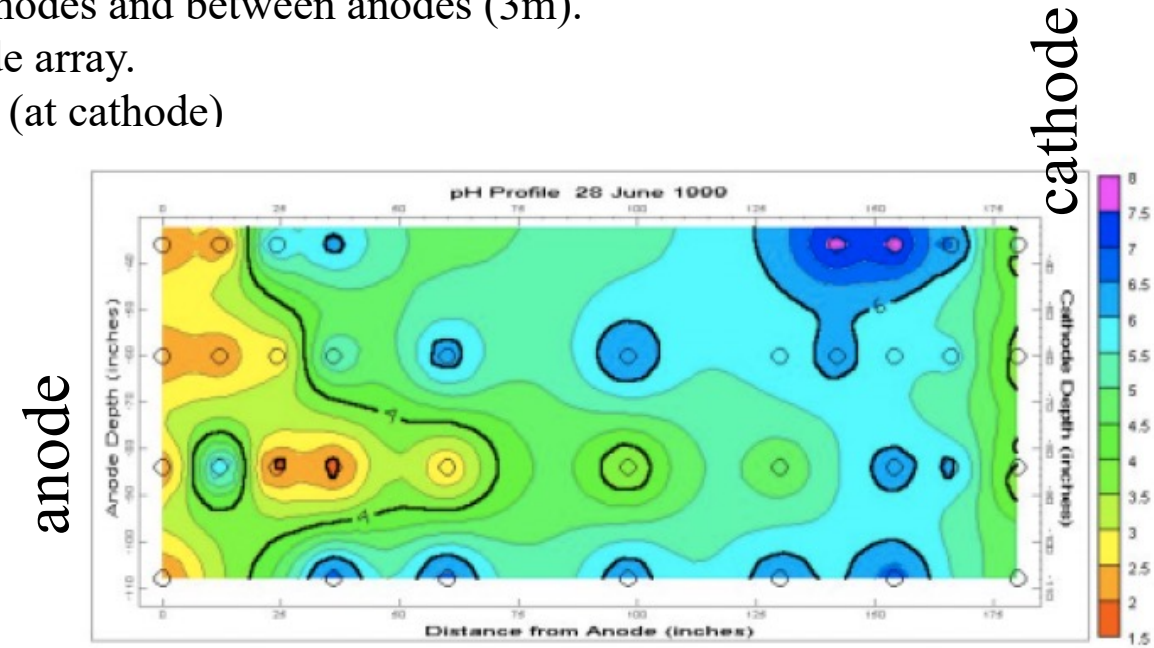
- Complex organic molecule difficult to biodegrade in the environment
- Reactive black 5 is soluble, but adsorbs readily
- The molecule can be ionized at alkaline pH forming an anion with 4 negative charges.
- Under these conditions, reactive black 5 can be transported by electrokinetics toward the anode, but only if the molecule is in solution.
- The desorption of the molecule can be achieved using potassium sulfate as flushing solution in the anode and cathode chambers.
- Advance of the Reactive Black 5 toward the anode by electromigration.
- Completely removed from the soil in 5 days.
- The pH was controlled in the anode at a value below 7 and
- The alkaline front electrogenerated at the cathode advances through the soil favoring the dissolution and electromigration of reactive black 5.

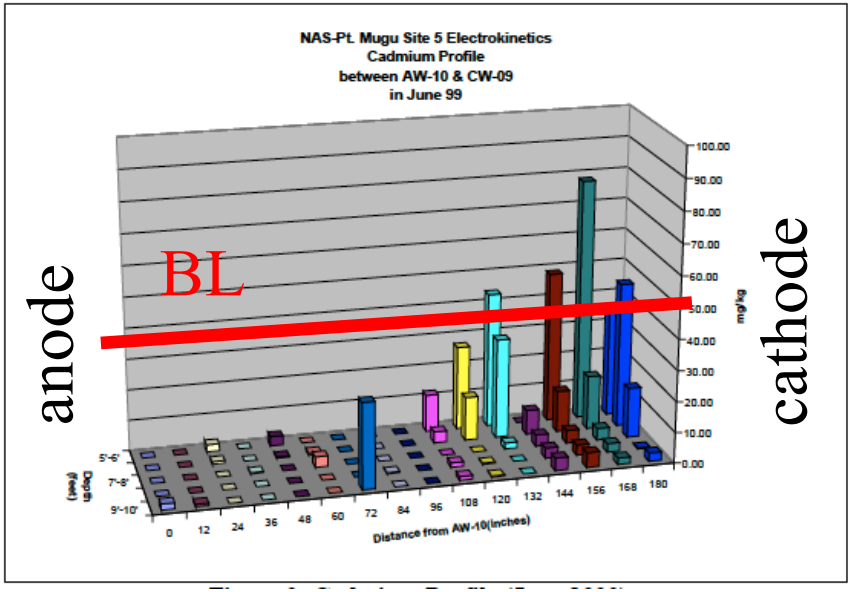


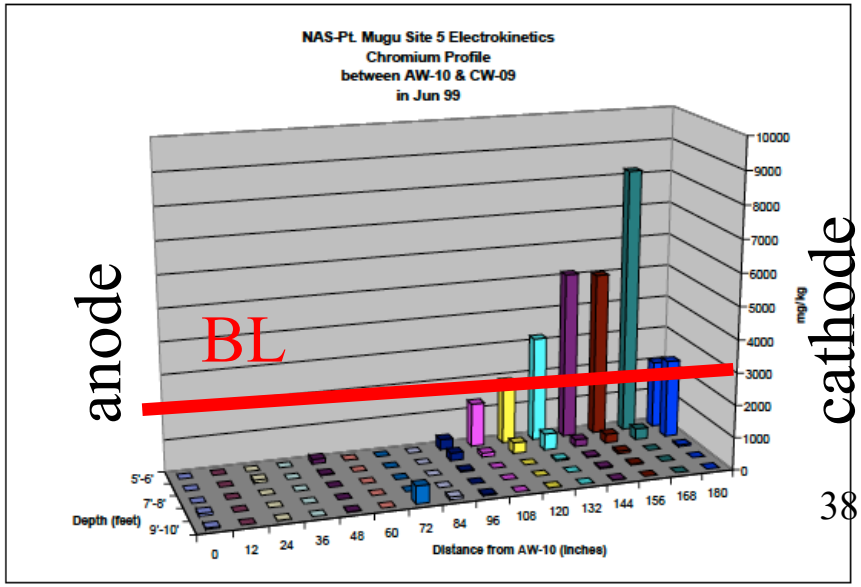



# Electrokinetic remediation- field example

- Metal-contaminated site (Cr, Cd)- vadose zone
- 14 feet (~ 7m) between anodes and cathodes and between anodes (3m).
- Applied 45 V ( max. 333 A) to electrode array.
- Add citric acid to help mobilize metals (at cathode)
- ~1 year
- Gas emissions (chlorine)
- Trihalomethane production
- Issue with chloride at site



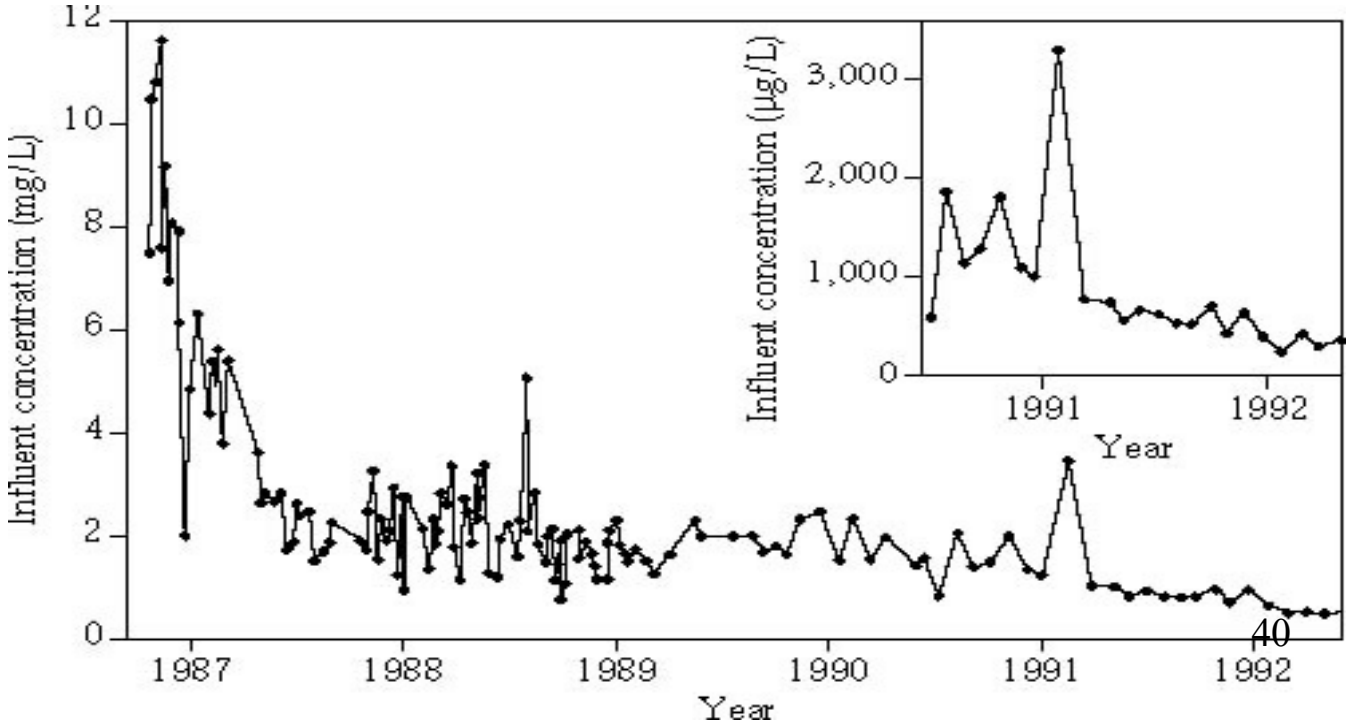



# 5. Pump-and-treat

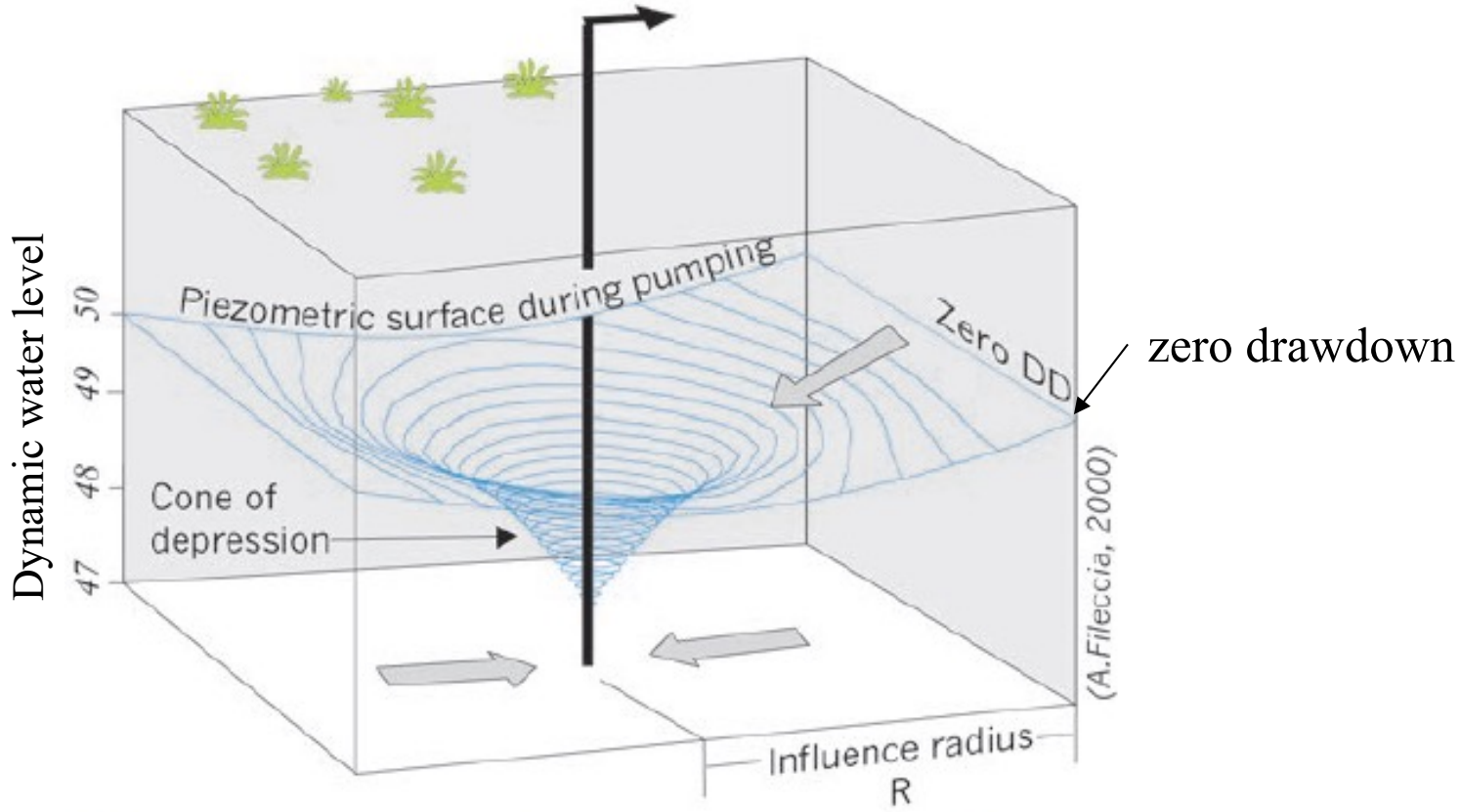
# Pump-and-Treat

- Common approach to remediate contaminated groundwater
- Water is extracted and treated above-ground
- Thus two objectives: (1) hydraulic containment of contaminated groundwater and (2) removal of chemical mass from the groundwater
- Treatment involves air stripping, carbon adsorption or biological degradation
- Major limitation of pump-and-treat: initial rapid decrease in chemical concentration but decreased rate of chemical removal at later stages- leads to long term treatment
- Another limitation is rebound of chemical concentration once wells are shut down: due to diffusion and desorption processes



# Groundwater pumping

- When pumping groundwater out, a cone of depression forms



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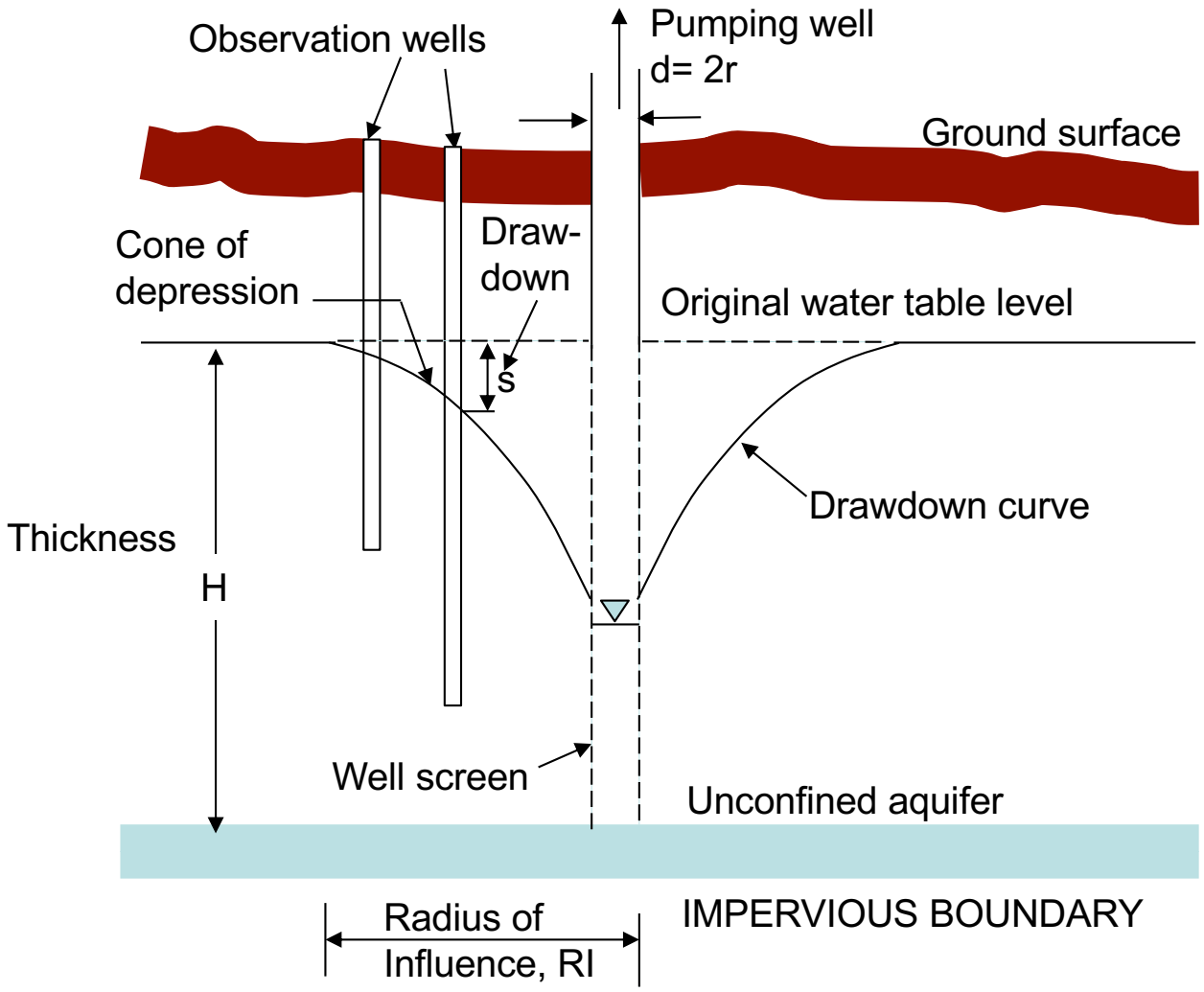
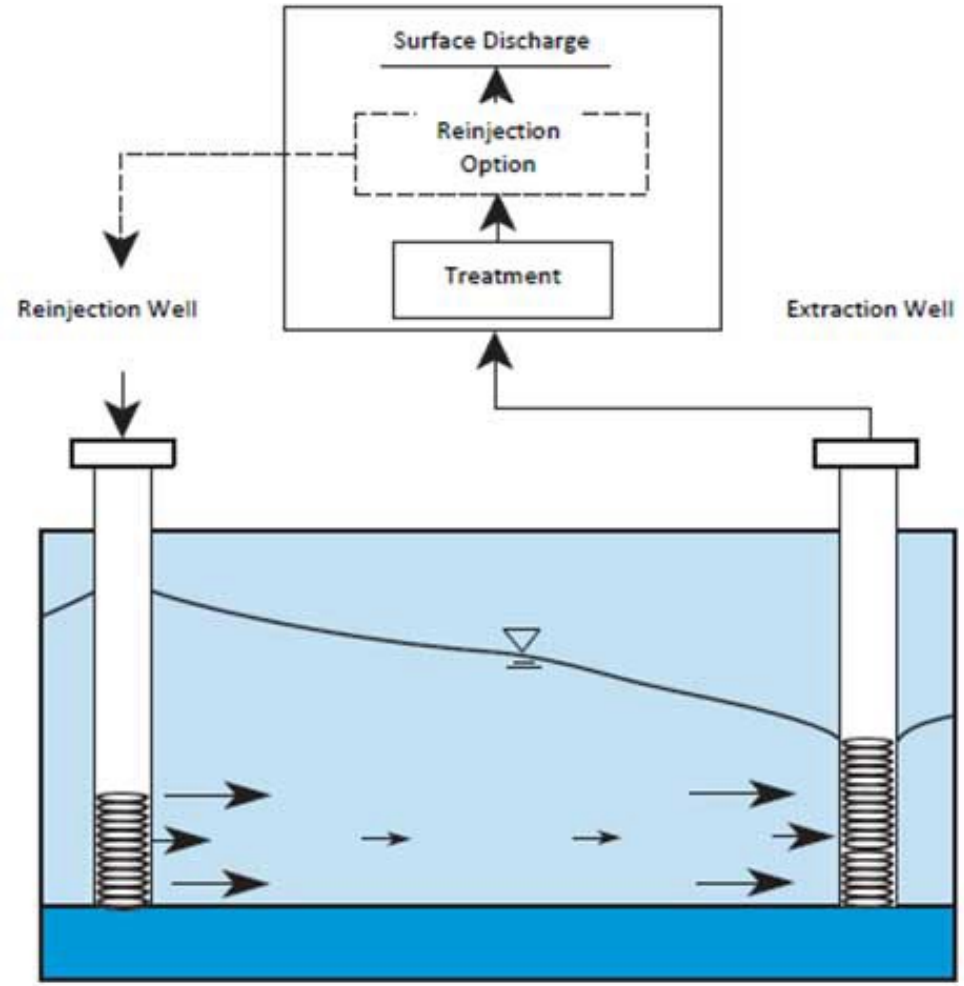
# Groundwater pumping

- When pumping groundwater out, a cone of depression forms
- It results in a lower water level up until a distance corresponding to the radius of influence



# Pump-and-treat



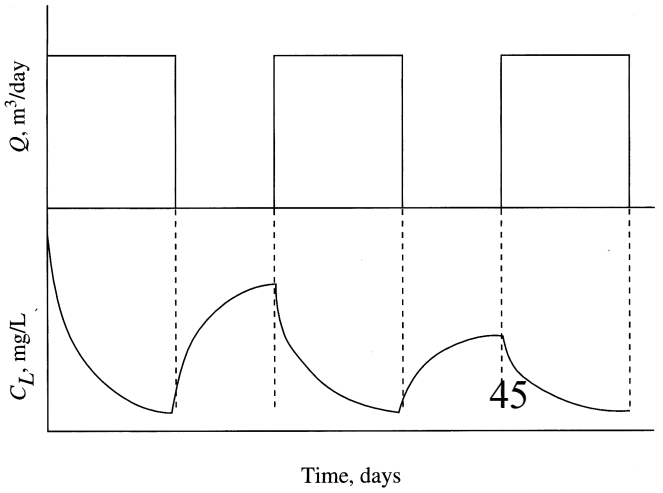
# Pump and treat (and reinjection)

- Groundwater pumped from the contaminated zone
- Treated at surface
- Re-injected (regulatory problems) or discharged above ground (sewer, land fill)
- Containment of plume is important parameter for pumping rate and location(s)
- Reinjection of water stimulates *in situ* bioremediation as well
- Requirements: (a) contain plume, (b) include monitoring wells and (c) include a sampling program.
- Need to: (a) determine local conditions, (b) estimate nutrient and $O_2$ requirements, (c) estimate concentration of contaminant in pumped water and (d) estimate time needed for bioremediation

# PT&R

- Contaminant mass estimation:
  - Depends on mass of contaminant in aquifer, the volume of contaminated zone and distribution coefficient.
  - Difficult to get accurate estimate of total mass of contaminant

- Pumping rate:
  - Many systems operate over decades so costly if high pumping rates
  - Unfavorable distribution of contaminants between soluble and solid phases- low soluble contaminant conc.
  - Desorption rate very slow typically
  - Intermittent pumping may be appropriate

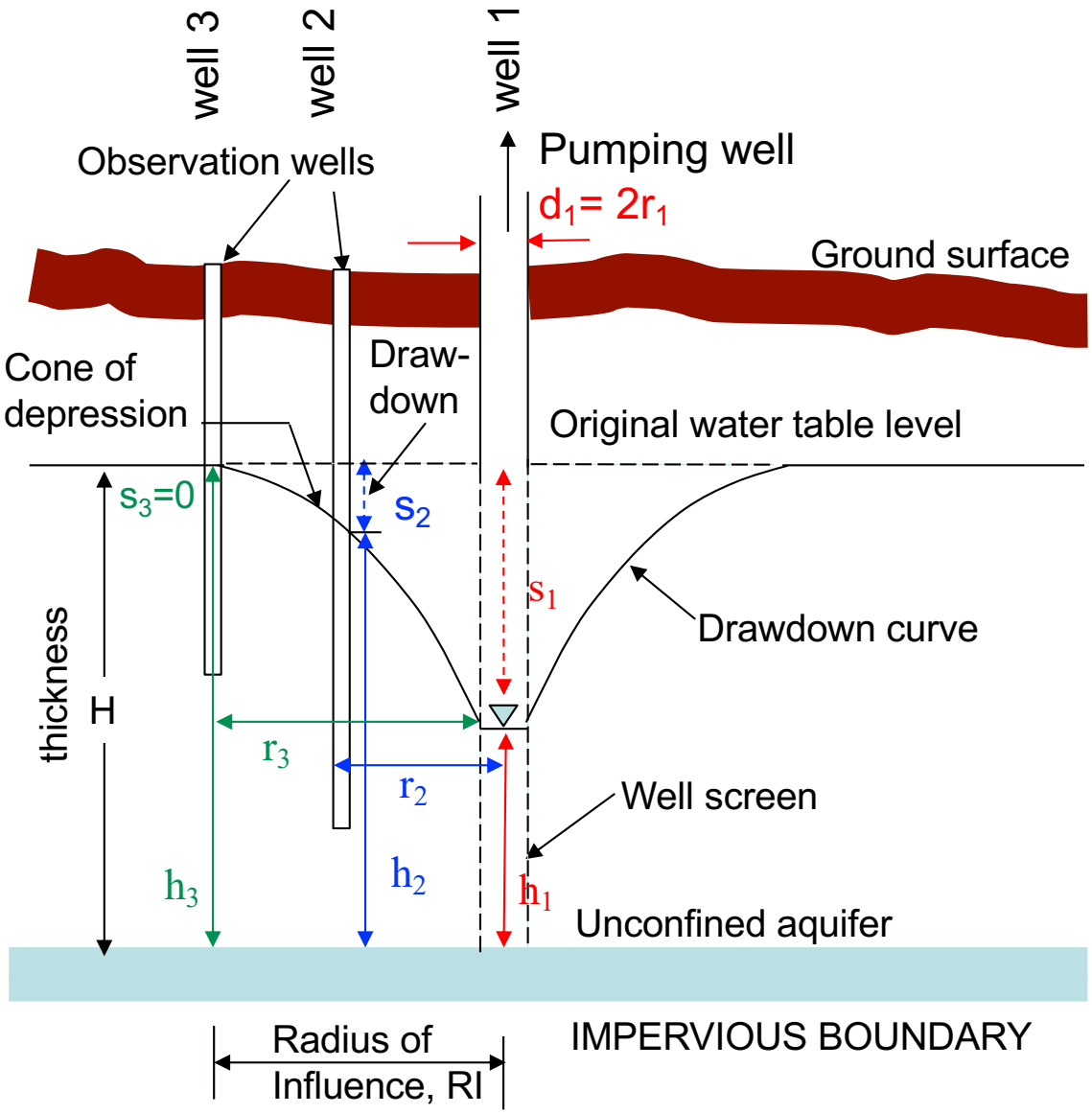


# PT&R

- Advantages:
  - Minimal disturbance during treatment
  - Equipment needed inexpensive

- Disadvantages:
  - Long treatment times
  - Running costs can be high (continuous or semi-continuous pumping)
  - Hydrophobic (sorbed) contaminants not treated except when desorb (slowly)
  - Difficulty in controlling flow patterns during reinjection (may spread plume)
  - Biological fouling of injection area
  - Regulations may not allow reinjection

## Steady-state flow from an unconfined aquifer




$$Q = \frac{\pi * K\ (h_2^2 - h_1^2)}{\ln(r_2/r_1)}$$

Where Q=pumping rate (length$^3$/time);
K=hydraulic conductivity (length/time);
H=aquifer thickness (length);
$h_1$ = height of water surface above bottom of aquifer at perimeter of well (length)
$h_2$, $h_3$= height of water surface above bottom of aquifer at distance $r_2$ or $r_3$ from well centerline (length);
$r_1$= radius to water surface at perimeter of well (i.e., radius of well) (length);
$r_2$, $r_3$= radius to water surface whose height is $h_2$ or $h_3$ above the bottom of the aquifer (length);

# Example

An unconfined aquifer is 12.2 meters thick. Groundwater is being extracted from a well that has a diameter of 0.1m.
The extraction rate is 0.15 $m^3$/min and the aquifer conductivity is 8.2 m/day. A steady state drawdown of 1.5 m is observed at the monitoring well 3m from the pumping well.

What is the drawdown at the pumping well?
What is the radius of influence of the pumping well?

# Passive and active barriers

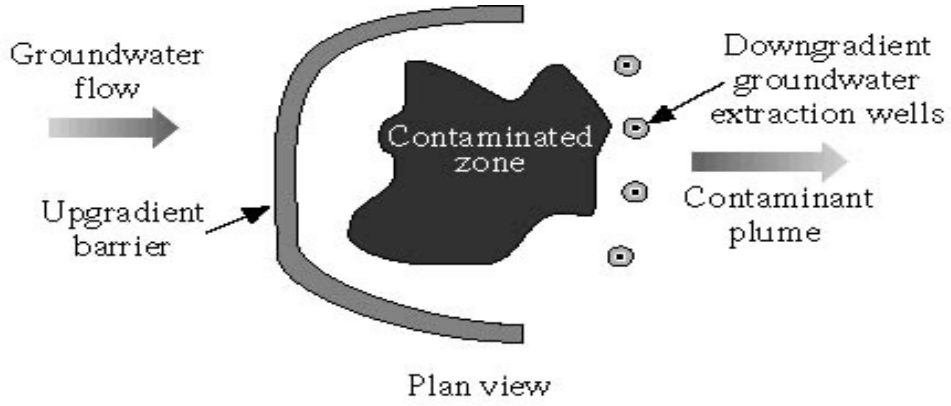
# Subsurface barriers

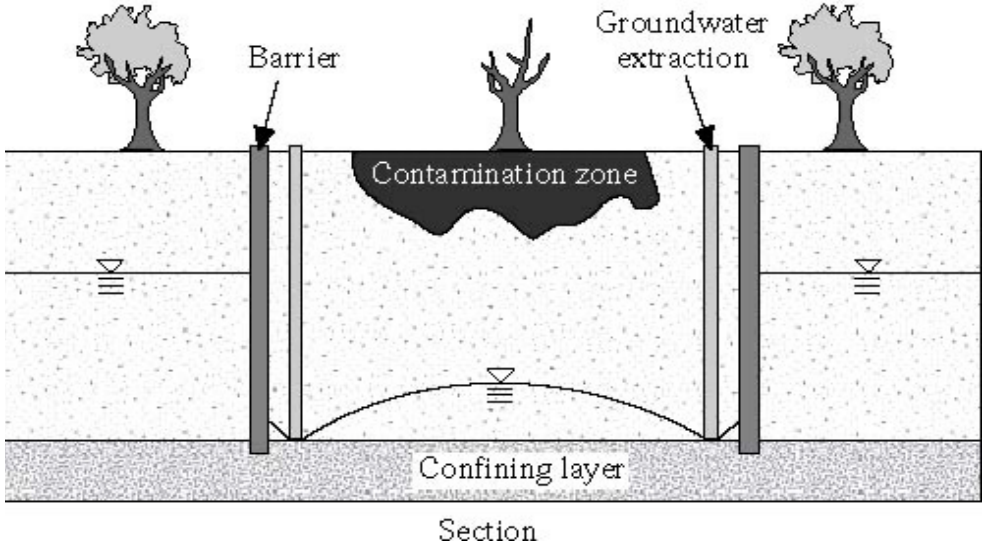
# Subsurface barriers

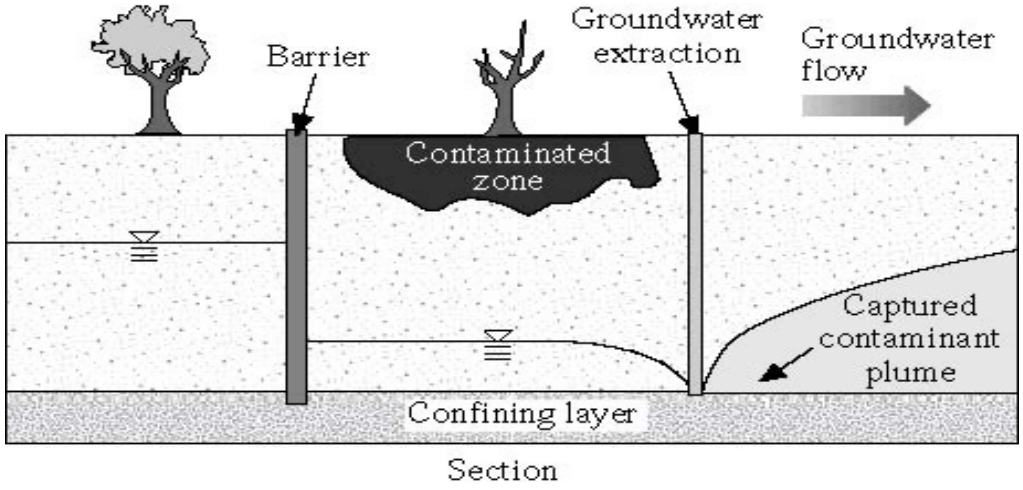
- Subsurface barriers come in several types:
  - Vertical barriers for groundwater control
  - Horizontal barriers for groundwater control
  - Permeable reactive barrier for treatment of contamination

• Employed to contain contaminants and redirect groundwater flow
• Several types:
  • Slurry trench cutoff walls
  • Grout curtains
  • Deep soil mixed walls
• Slow the rate of contaminant migration in places where horizontal hydraulic conductivity (HC) in higher than vertical HC
• Used in conjunction with pump-and-treat to limit pumping rates
• Inhibit flow of clean groundwater into the site to limit the increase in total volume of water to treat
• Most common configuration is circumferential (surrounding the contaminated zone)
•Up-gradient and down-gradient vertical barriers:
  • Up-gradient: cut-off to control influx of clean water
  • Down-gradient: coupled to pump-and-treat
• Vertical barriers typically keyed (embedded) into low permeability material

# Vertical passive barriers

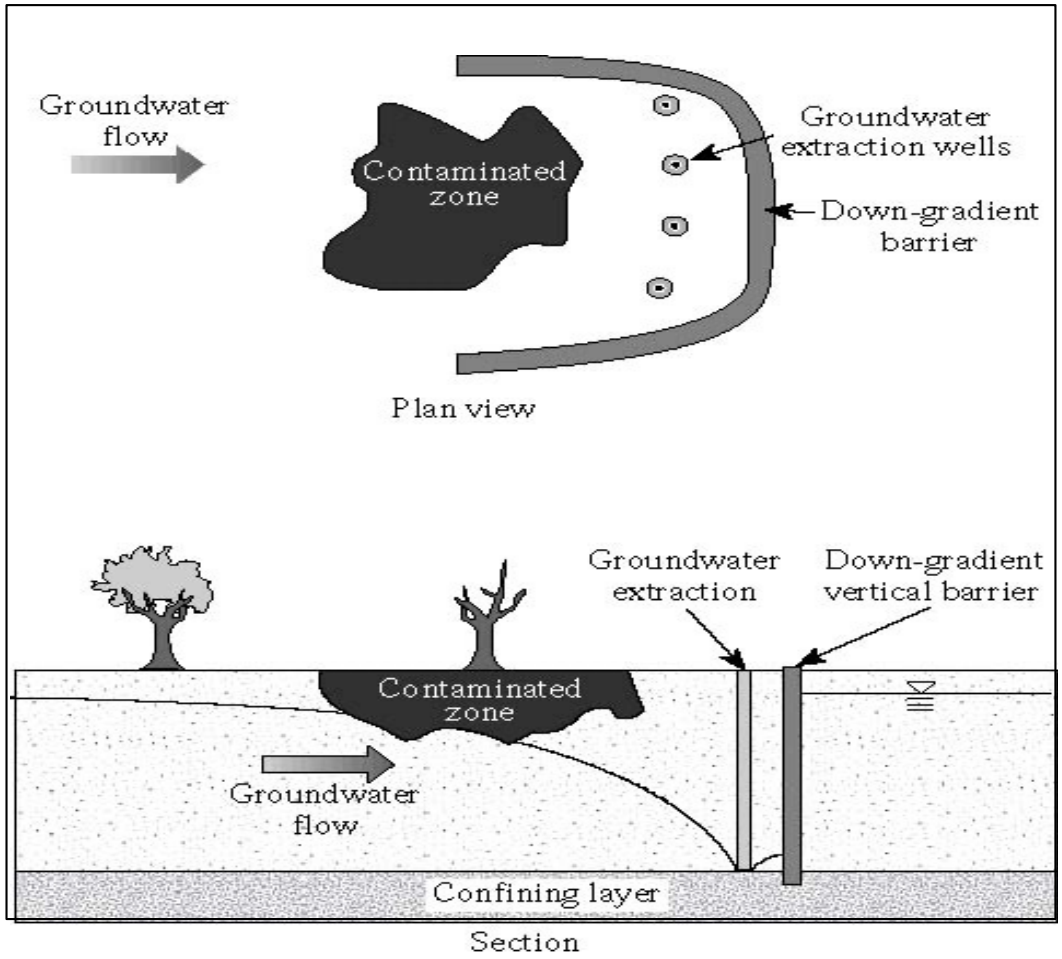




Circumferential configuration

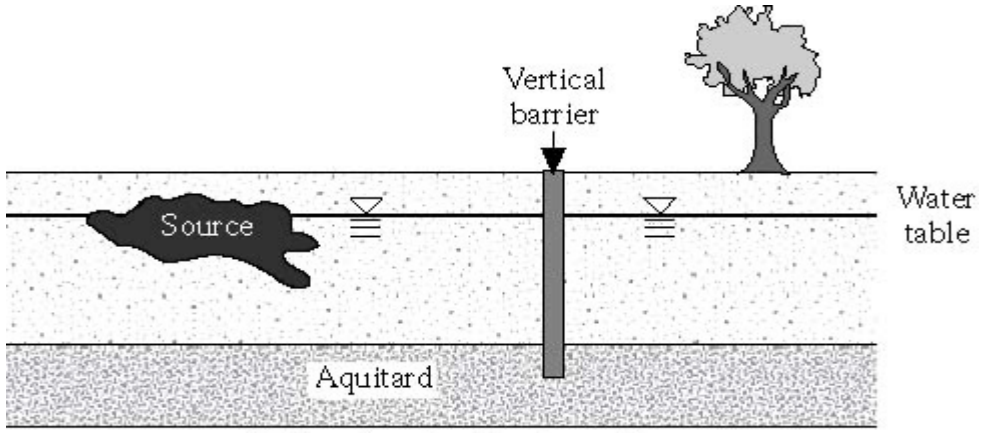
Upgradient configuration

# Vertical passive barriers

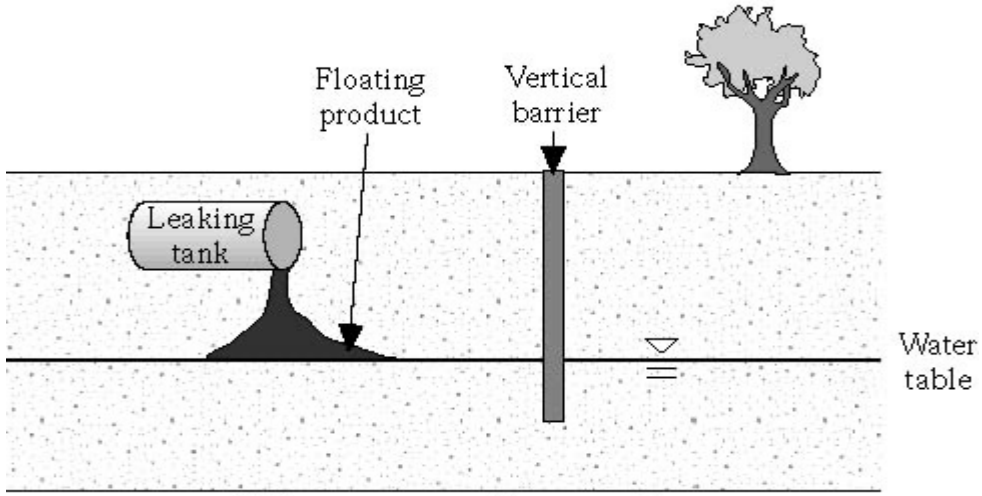



Downgradient configuration

# Vertical passive barriers: embedded ('keyed') into aquitard or 'hanging'



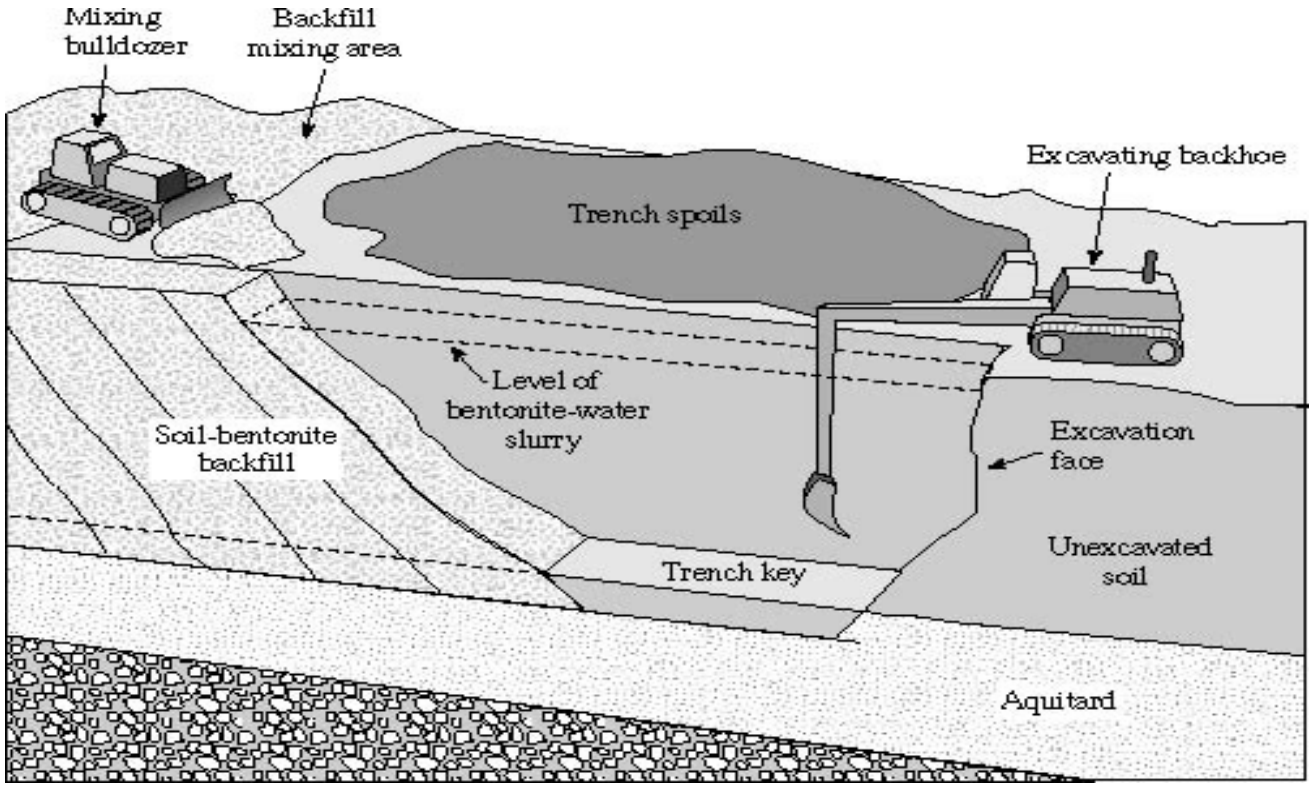

(a) Keyed vertical barrier wall



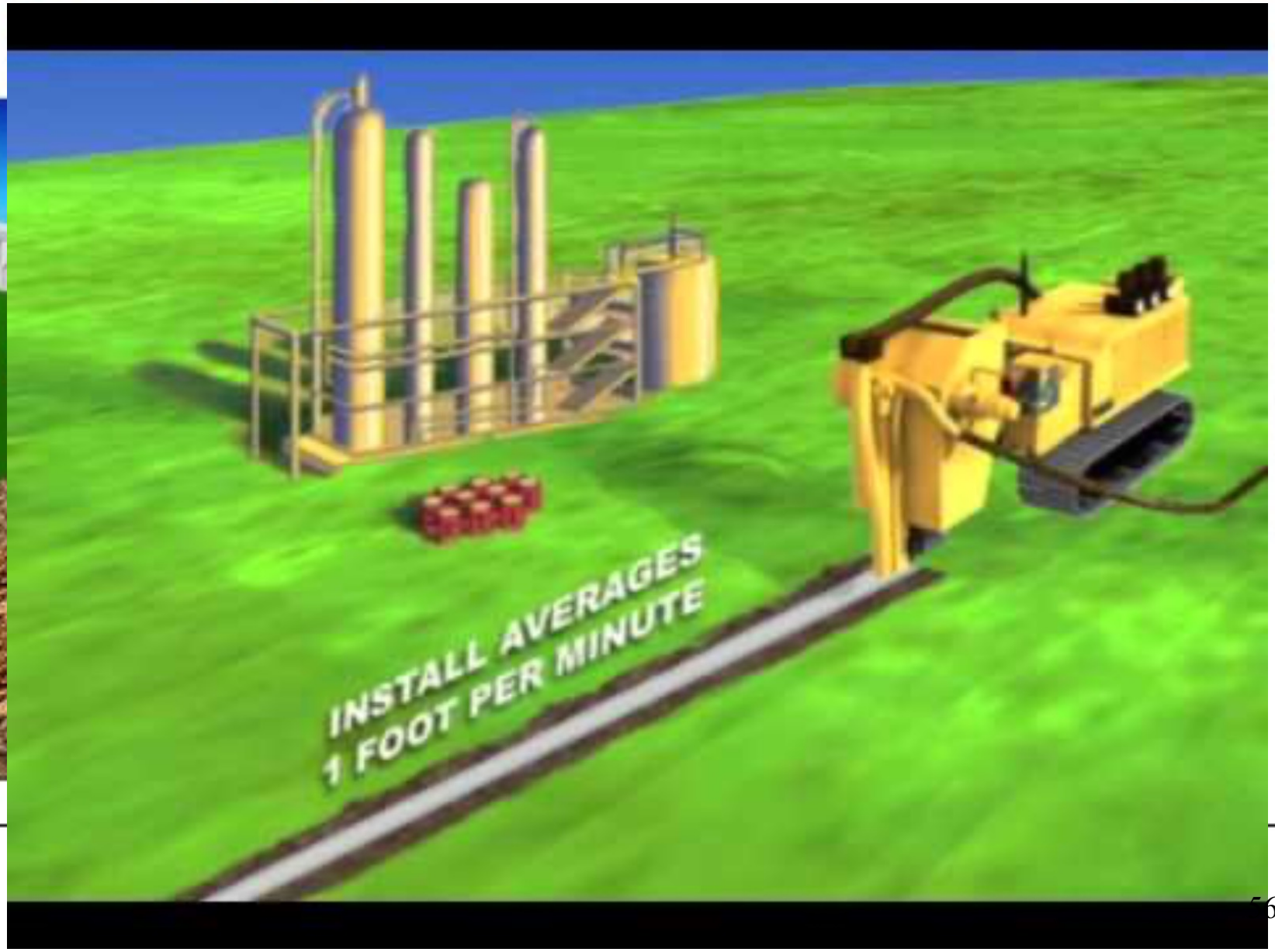

(b) Hanging vertical barrier wall

# Vertical passive barriers

- Soil-bentonite slurry trench cutoff wall
  - A trench is excavated and water-bentonite slurry is used to maintain trench stability
  - Slurry is ~ 95% water and 4-6% bentonite by weight (density 1.03-1.12 g/cm$^3$)
  - Backfilled with soil-bentonite mixture
  - soil-bentonite mix is low permeability (bentonite can be as low as 1%) ($10^{-7}$ to $10^{-8}$ cm/s)
  - Permeability dependent on kind of soil used
  - Can dig trenches down to 30m this way

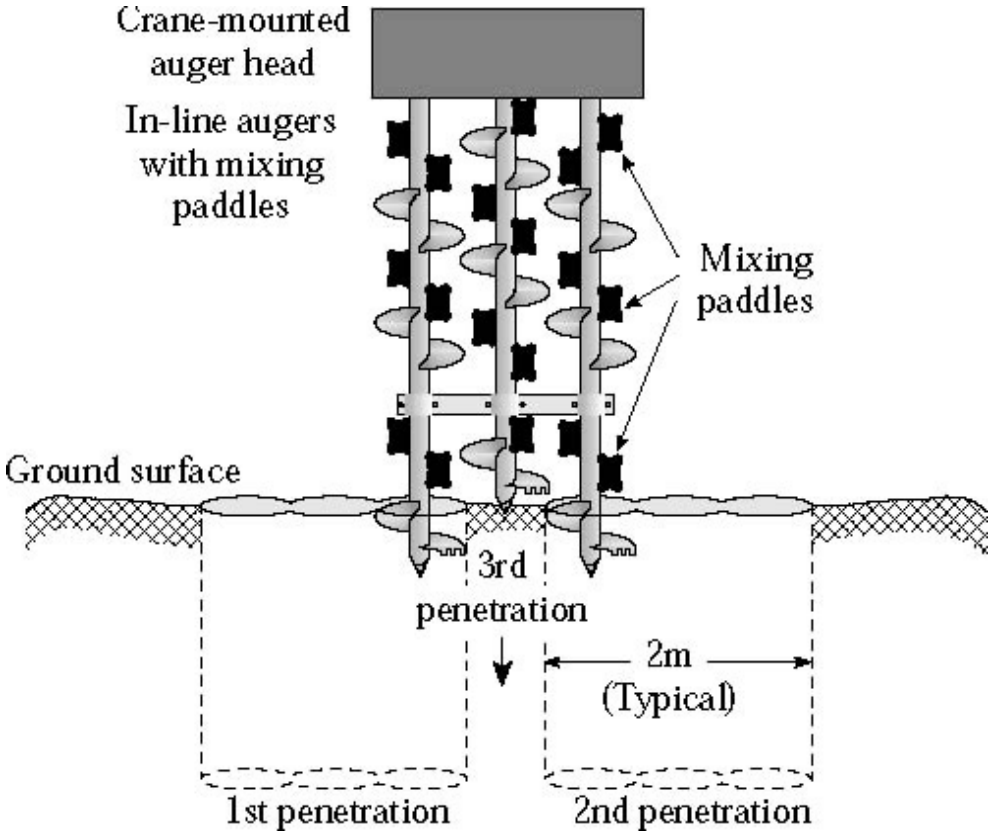



# Continuous one-pass trenching



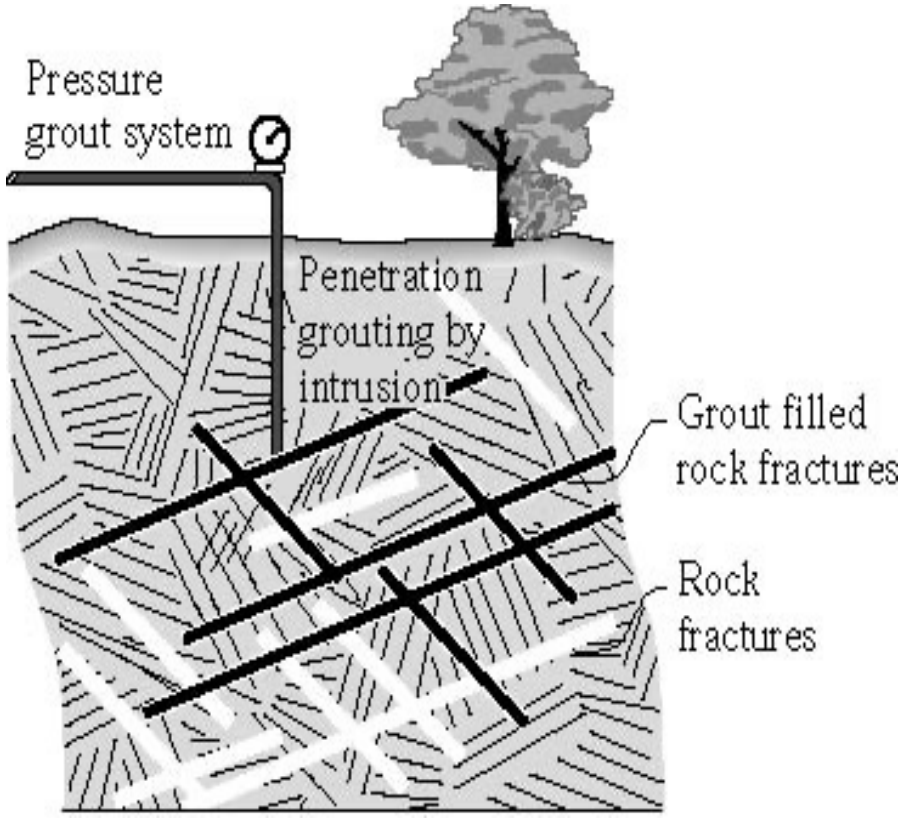
# Vertical passive barriers

- Deep soil mixed walls
  - Specially designed auger mixing shaft rotated into the ground while injecting slurry of bentonite (and cement) and water
  - Continuous wall can be obtained by overlapping penetrations
  - Bentonite (max 1%)
  - Advantages:
    - health and safety risks minimized (no need to excavate materials)
    - Wide walls can be built
    - Hydraulic conductivity at most $10^{-7}$ cm/s

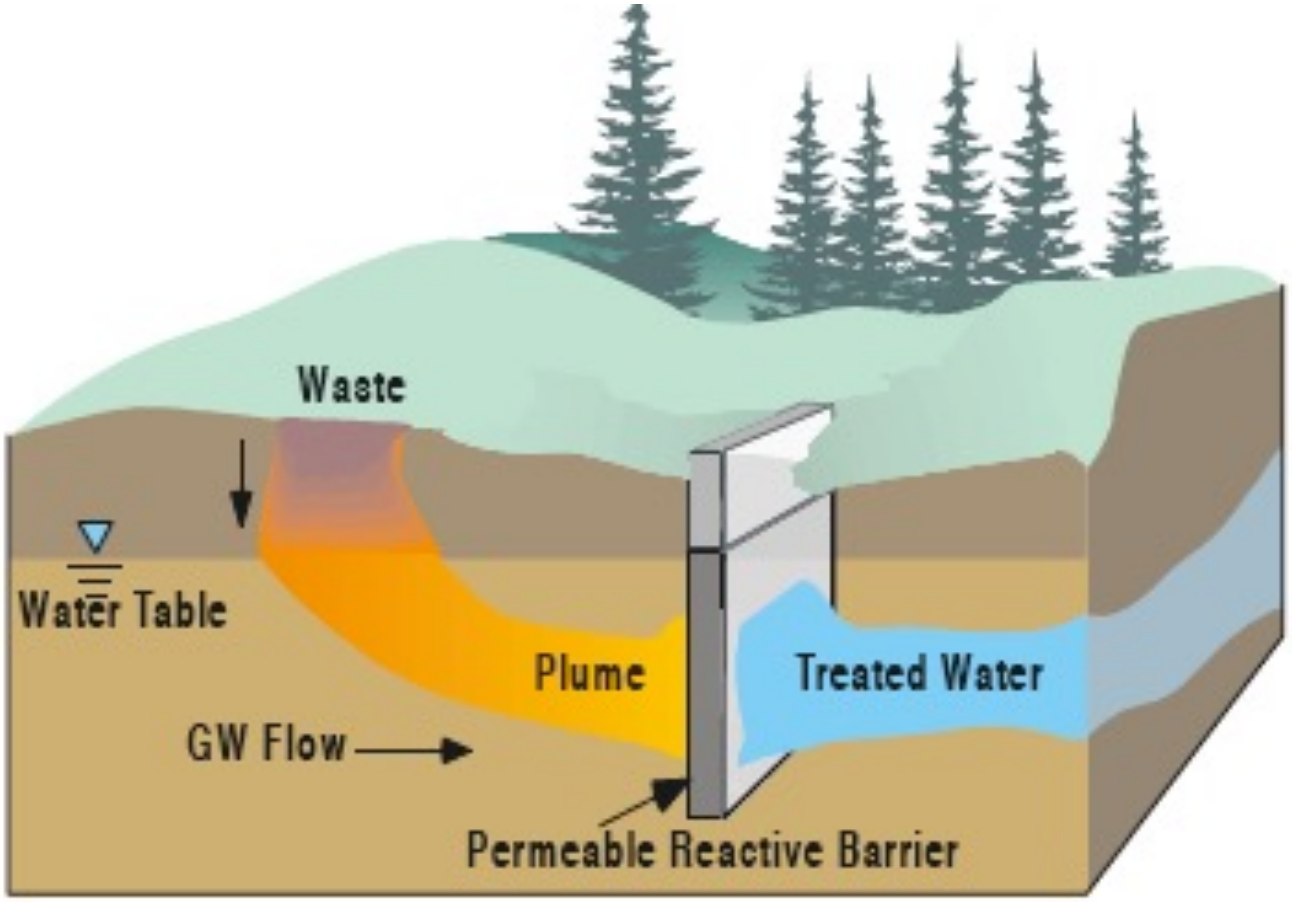



# Vertical passive barriers

- Grout curtains
  - in material that cannot be excavated (e.g., rock), grout curtains can be used
  - installed through pressure injection of pumpable material into fractures and pores
  - grout gels or sets in place lowering the hydraulic conductivity
  - can be made of cements, silicates, pozzolans
  - issue can be resistance of grout to degradation by contaminant



# Permeable reactive barrier



| Organic Compounds | | Inorganic Compounds | |
|---|---|---|---|
| Methanes | tetrachloromethane<br>trichloromethane<br>dichloromethane | Trace Metals | Chromium<br>Nickel<br>Lead<br>Uranium<br>Technetium<br>Iron<br>Manganese<br>Selenium<br>Copper<br>Cobalt<br>Cadmium<br>Zinc |
| Ethanes | hexachloroethane<br>1,1,1-trichloroethane<br>1,1,2-trichloroethane<br>1,1-dichloroethane | Anion Contaminants | Sulphate<br>Nitrate<br>Phosphate<br>Arsenic |
| Ethenes | tetrachloroethene<br>trichloroethene<br>cis-1,2-dichloroethene<br>trans-1,2-dichloroethene<br>1,1-dichloroethene<br>vinyl chloride | | |
| Propanes | 1,2,3-trichloropropane<br>1,2-dichloropropane | | |
| Aromatics | benzene<br>toluene<br>ethylbenzene | | |
| Other | hexachlorobutadiene<br>1,2-dibromoethane<br>freon 113<br>N-nitrosodimethylamine | | |

Compounds treatable by PRB:
Chlorinated solvents
BTEX
Inorganic contaminants

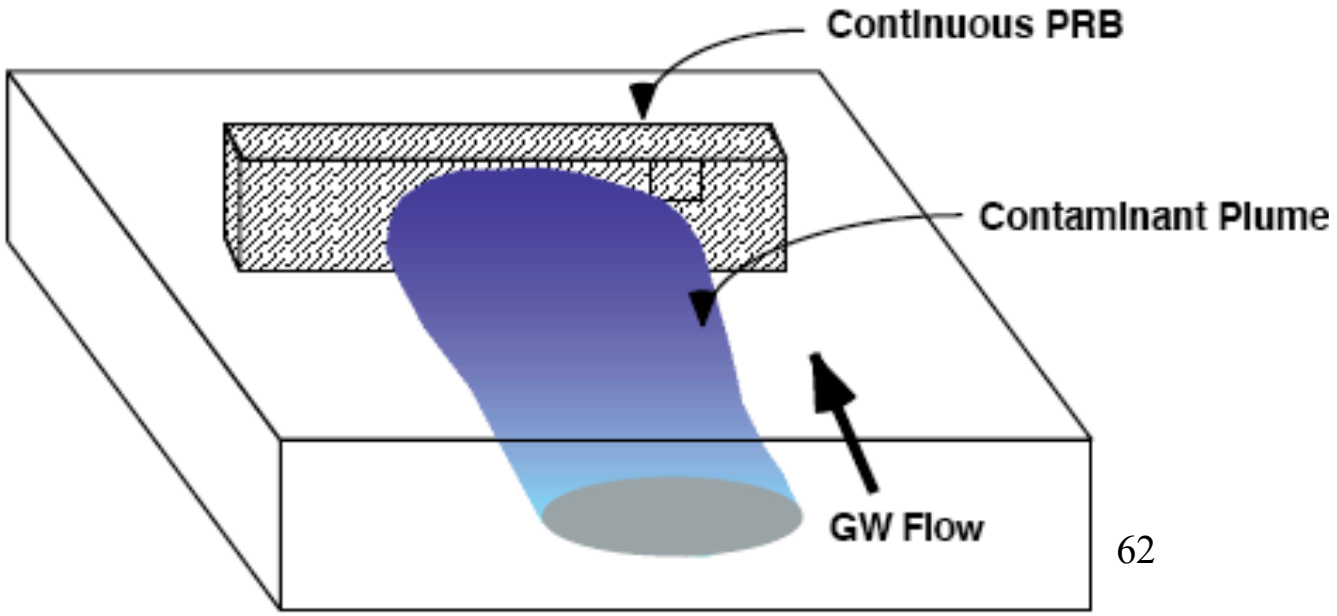
# Fe(0) [zerovalent iron=ZVI] PRB

| | | |
|---|---|---|
| $Fe^0 \rightarrow Fe^{2+} + 2e^-$ | Anodic Reaction | (1) |
| $RCl + 2e^- + H^+ \rightarrow RH + Cl^-$ | Cathodic Reaction | (2) |
| $Fe^0 + RCl + H^+ \rightarrow Fe^{2+} + RH + Cl^-$ | Net Reaction | (3) |

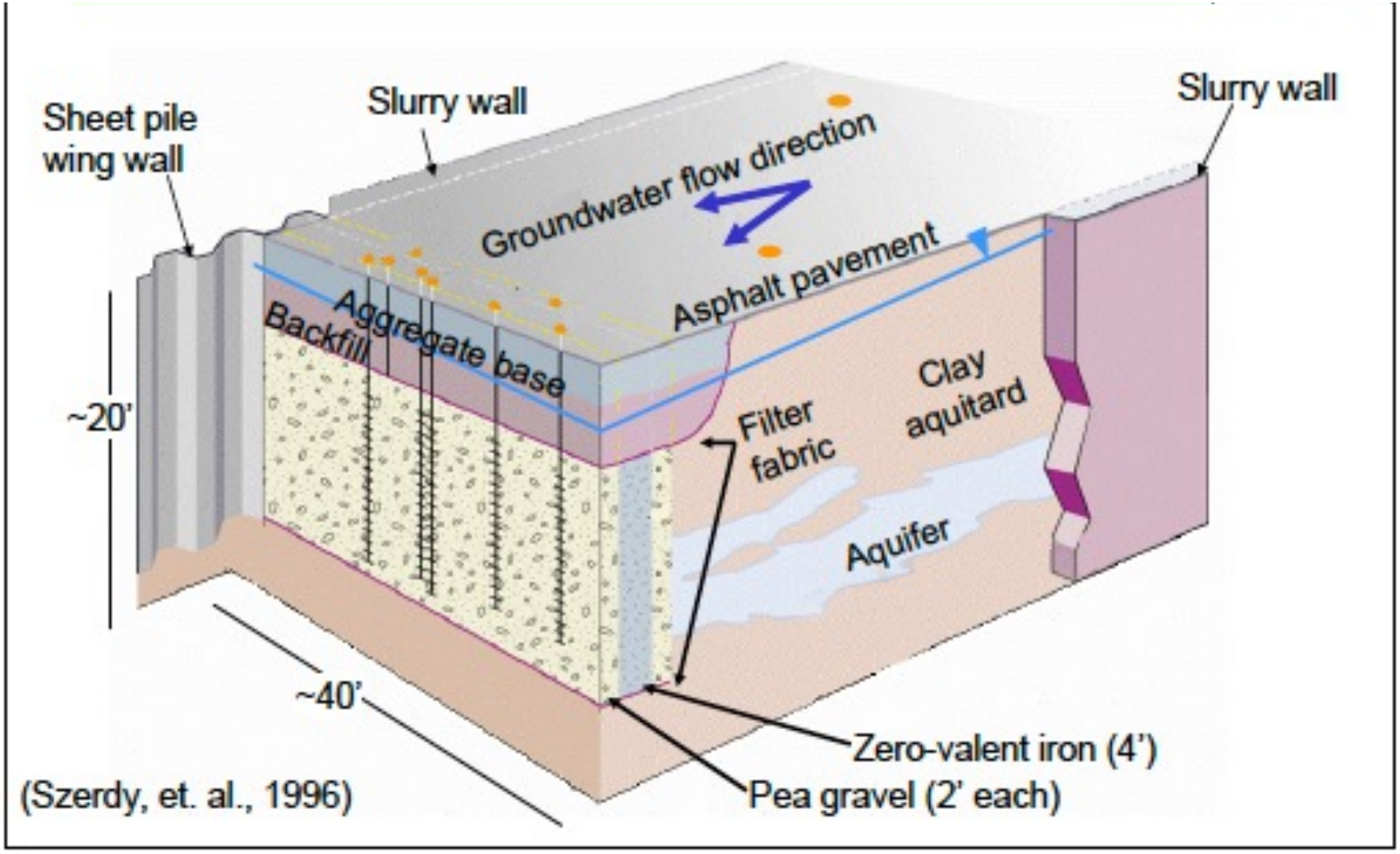
- Overall reaction is the sum of the anodic and cathodic reactions occurring at Fe(0) surface
- Transformation rate is a function of surface area of ZVI
- Commonly used material for PRB

# Continuous PRB

- Minimal impact on natural groundwater flow
- Typically a trench excavated and filled with material (ZVI, organic C, etc..)
- Need to cover an area comparable to cross-sectional area of the plume
- Hydraulic conductivity of PRB must be higher than that of aquifer
- Preferable to put the bottom of the PRB into impermeable strata so no flow under the PRB: "key" into impermeable layer
- Difficulty with placing a trench in saturated material (e.g., collapse of trench walls)
- Removal of aquifer material and emplacement of reactive material rapidly
- Use trenching device

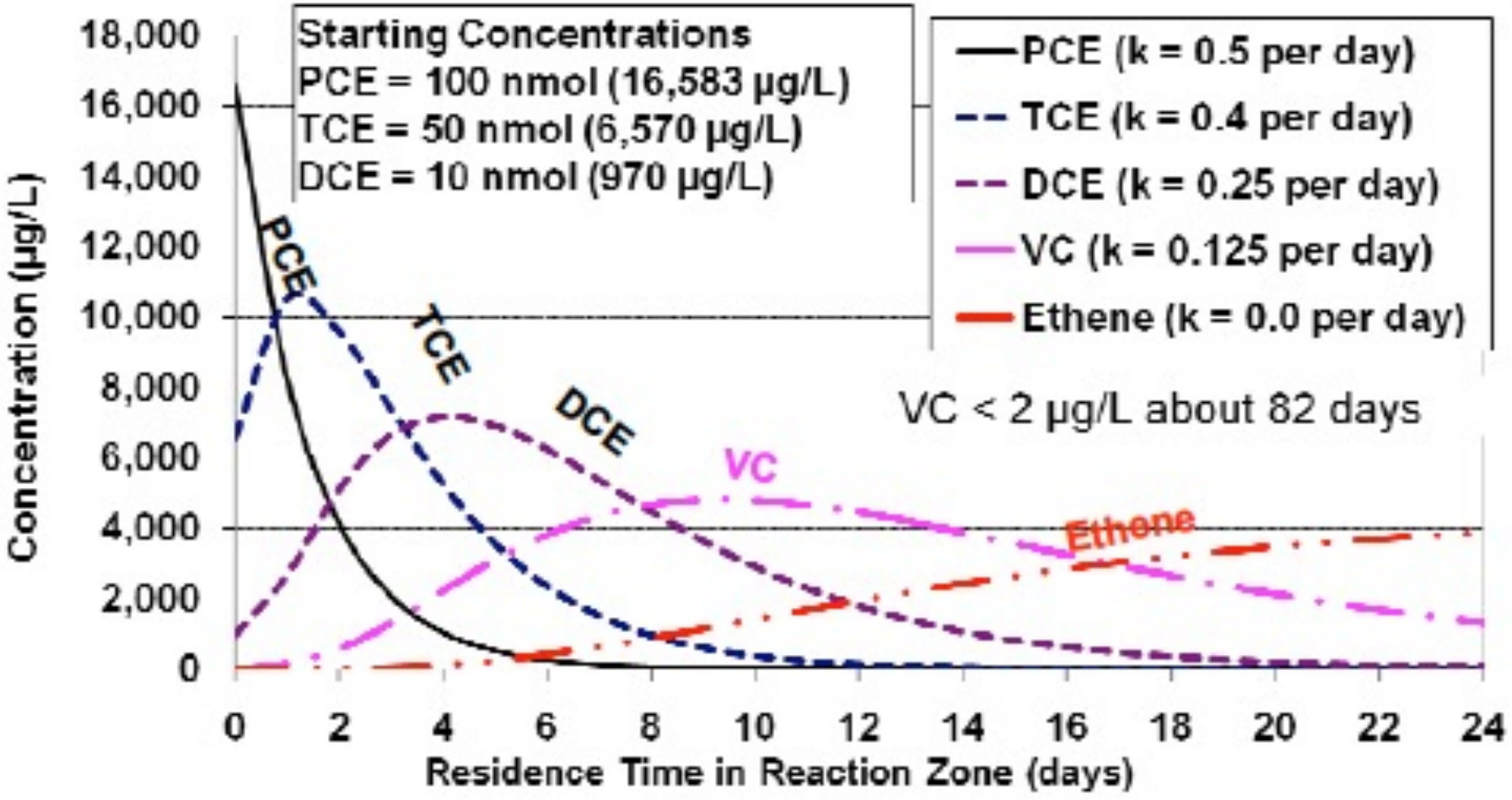


# Layout of a conventional PRB

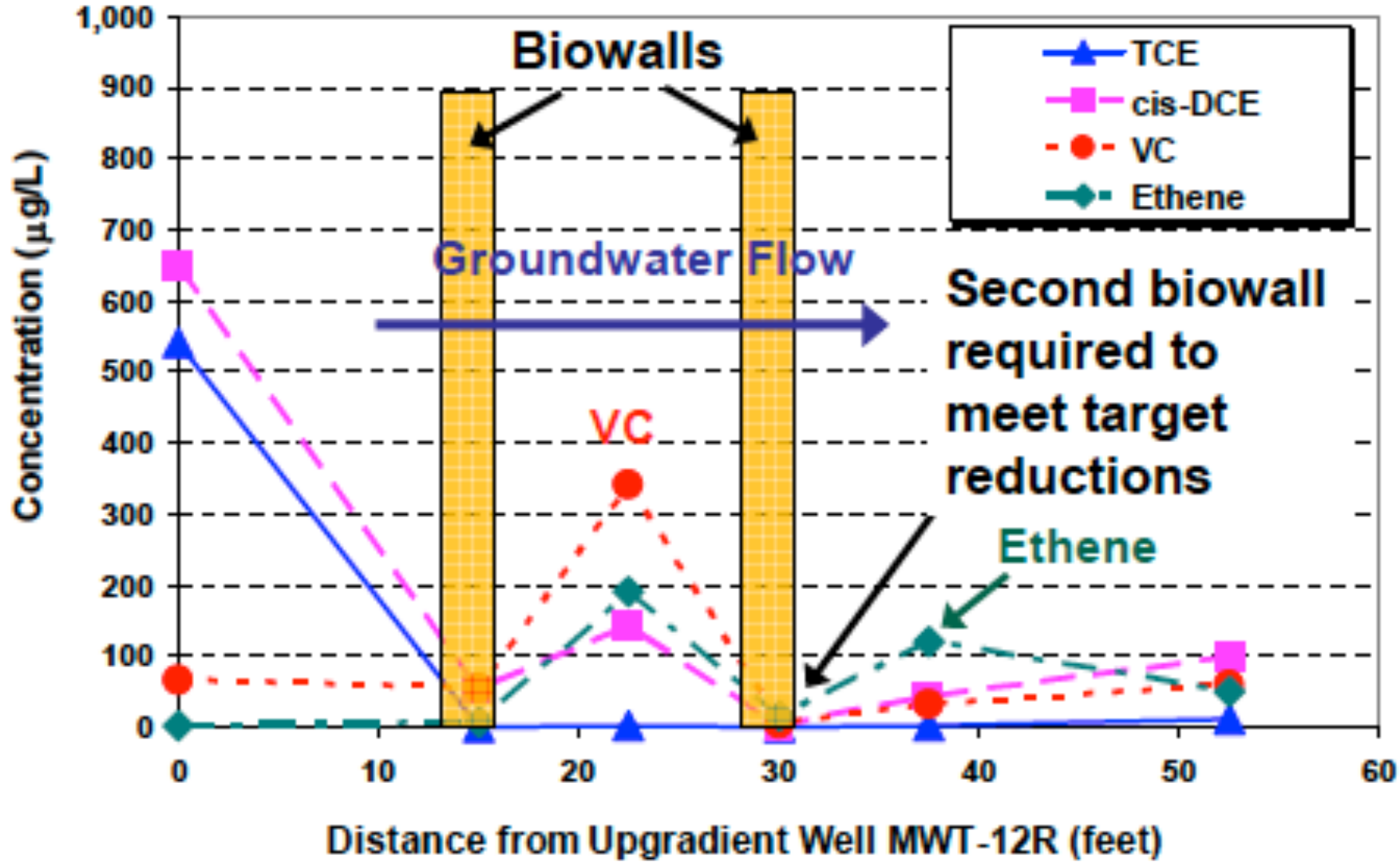


# Residence time needed

Residence time may be estimated from reasonable first-order rate constants and maximum contaminant concentrations



# Multiple PRBs

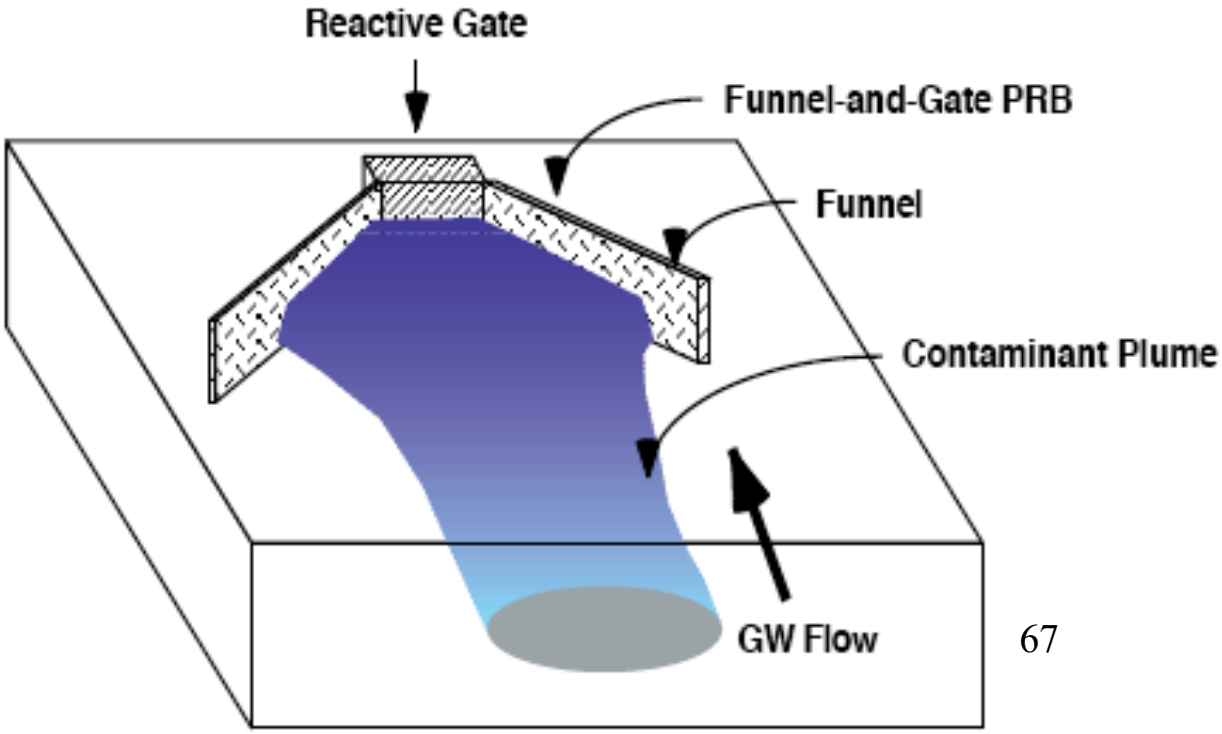


# Construction

- Conventional trenching methods
  - Conventional excavators to 7-9 meters
  - One-pass trenchers to 10-12 meters
  - Biopolymer slurry installation >15 meters
- Injection methods
  - Pneumatic and hydraulic fracturing
  - New materials may require new injection methods
- Alternate methods
  - Deep soil mixing
- Other considerations
  - Permitting
  - Emplacement verification

# Funnel and gate PRB

- Low permeability funnels direct GW toward reactive barrier
- Funnel typically made out of sheet pilings keyed into impermeable layer
- Groundwater velocities through gate faster
- Enough residence time through the gate for full reaction
- Water passing through the gate needs to be redistributed across similar cross-sectional area to avoid mounding past the gate



# Design parameters for permeable reactive barriers

• The thickness of the PRB wall is given by

$$b = v * t_{res} * SF$$

Where b= wall thickness (length)
ν = groundwater velocity (length/time) in the PRB
$t_{res}$= required residence time (time)
SF= safety factor

• ν is given by

$$v = \frac{K.i}{\varepsilon_{prb}}$$

where K= hydraulic conductivity (length/time)
i= hydraulic gradient across PRB [-]
$\varepsilon_{prb}$= porosity of reactive media in PRB [-]

• $t_{res}$ is given by

$$t_{res} = \left[ \frac{-\ln(\frac{C_f}{C_0})}{k} \right]$$

Where $C_f$= concentration downgradient of PRB (mass/volume)
$C_0$= contaminant concentration entering the PRB (mass/volume)
k= first-order reaction rate ($time^{-1}$)

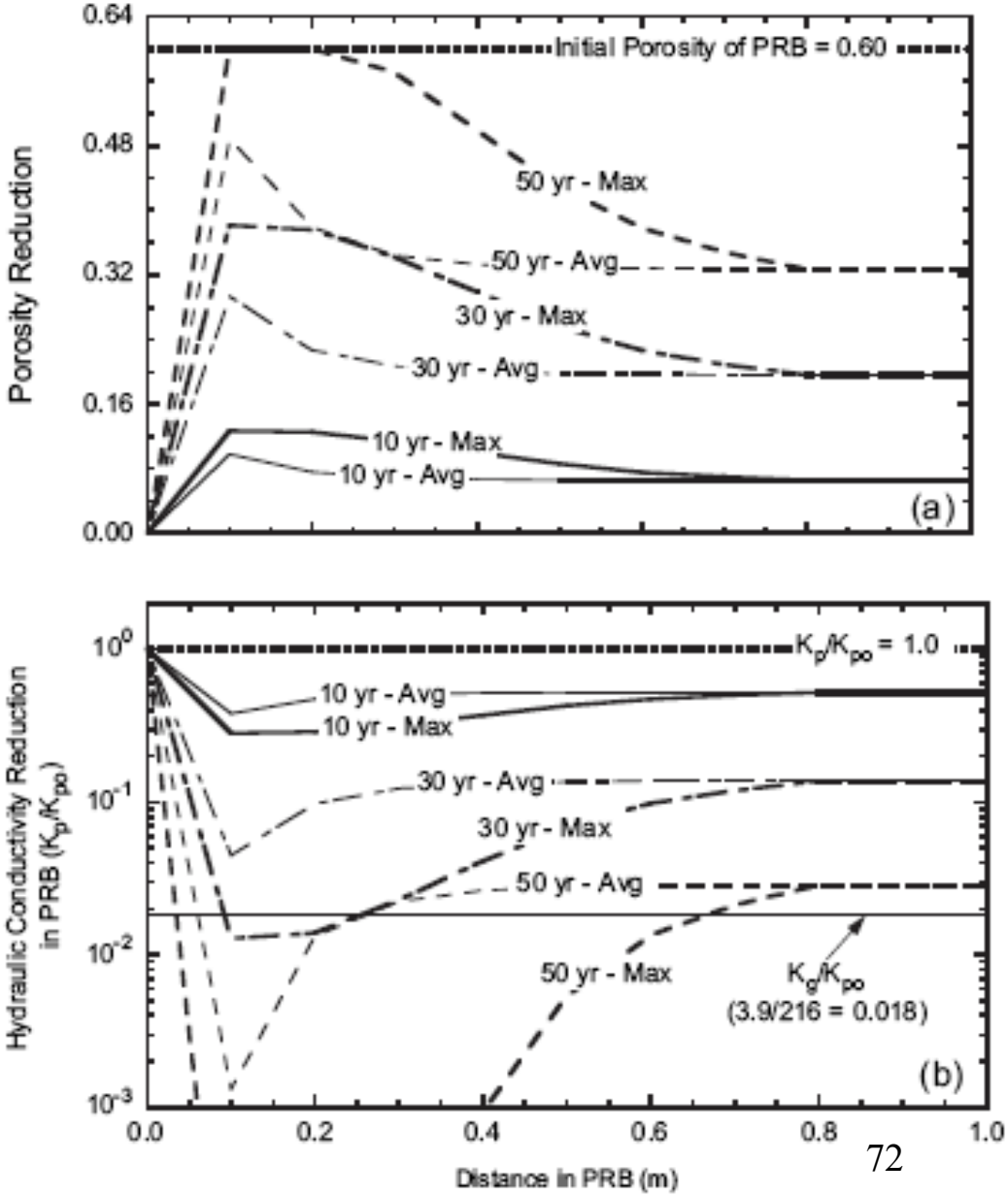
# Example PRB

Chromate reduction is considered with a PRB filled with ZVI.
The PRB thickness needs to be calculated.
Hydraulic conductivity of the aquifer K=2m/d=2 m/d
Hydraulic gradient across the PRB i=1.2 [-]
PRB porosity $\varepsilon$= 0.3 [-]
Rate of reduction k= 0.5 $h^{-1}$
$C_{aq,initial}$= 2 $\mu$M
$C_{aq,final}$= 0.2 $\mu$M

What is the required thickness for the PRB?

# Limitations of PRB

- Biggest issue is fouling
- Due to mineral deposition (Fe oxide, carbonates)
- Due to biomass clogging the barrier (if growth too rapid can decrease porosity)




$CaCO_3(s) \leftrightarrow Ca^{2+} + CO_3^{2-}$ Aragonite/calcite

$FeCO_3(s) \leftrightarrow Fe^{2+} + CO_3^{2-}$ Siderite

$Fe(OH)_2(am) \leftrightarrow Fe^{2+} + 2OH^-$ Ferrous hydroxide