CVEN 4474/5474 Haz Waste Outline

- Site Clean-up Methods:
  - I. In-Situ Vadose Zone Soil
    - Soil Vapor Extraction
    - Bioventing
  - 2. In-Situ Unconfined aquifer tmt
    - Air Sparging
  - 3. Ex-Situ contaminated gas treatment

Contaminated Gas Treatment

- Vapors extracted from the soil by SVE must be treated before release to the air
- Various industries also produce contaminated gas streams containing hazardous organic compounds which must be treated

Common Gas Treatment Methods

- Thermal Incineration
- Catalytic Oxidation
- Carbon Adsorption
- (Wet scrubbing or absorption)
- Biological Treatment

Thermal Incineration

- Destroys organic compounds
- Good for high concs of toxics in the gas
- High reliability and removal efficiency
  - 99.99% to 99.9999% “4 to 6 nines”
- Expensive due to energy cost

Incineration

- Goal: to convert organic compounds into inorganic compounds (CO₂, H₂O) by a high temperature environment with an oxidizing agent (O₂)
- Can be used for contaminated gases, soil, water
  - Widely used at Superfund sites for soil treatment (30 mobile incinerators; >2 million tons of soil
  - Example: Times Beach dioxin-contam. soil

Incineration Efficiency controlled by:

- Time
  - Retention time in the incinerator:
    - 0.5-1 sec for gas treatment (depends on temp)
- Temperature
  - 1200-1600°F, add fuel such as natural gas
- Turbulence
  - Mixing needed for combustion with oxygen
- Oxygen
  - 10-50% excess air added beyond O₂ req’d
Oxygen needs can be calculated by stoichiometry

- Toxic cmpd \((C_xH_yCl\text{?}N\text{?}O\text{?}S\text{?}) + O_2 + N_2\)
  \(\rightarrow CO_2 + H_2O + NO_2 + NO + HCl + SO_2 + N_2 + \text{heat}\)
- Ex: fuel \(CH_4 + _2O_2 \rightarrow _2CO_2 + _2H_2O\)
- TCE \(C_2HCl_3 + _2O_2 \rightarrow _2CO_2 + _2H_2O + _2HCl\)
- Design using a mass balance and heat balance

Catalytic Oxidation

- Converts toxic organics to \(CO_2, H_2O, \ldots\)
- Catalyst is a metal used to lower energy needed to combust organics
  - Must be periodically replaced (2-5 yrs); 
  - Lower temperature reaction (500-700°F)
  - Lower cost due to less fuel req’d
  - Efficiency 90-98%
    - \(\uparrow\) efficiency at \(\downarrow\) gas flowrate (\(\uparrow\) ret time)
  - Compared to incineration, better at lower toxic concs

Carbon Adsorption

- Pack granular form of carbon (GAC) into column or bed to treat gas
- Transfers contaminant to the solid phase (carbon)
- Must regenerate carbon when exhausted or dispose of the carbon ($)
- Best for low concs of toxics in the gas
- High reliability and removal efficiency –Up to 99%

Designing Carbon Adsorption

- Experimentally derived sorption values
  - Vary based on source material for carbon
  - Vary based on surface area of carbon
  - Higher surface area better
- Estimate based on relative affinity of compound for gas vs carbon sorption
  - \(Kac:a \sim Koc:H' = Coc/Cw / Ca/Cw = Coc/Ca\)

Carbon Adsorption

- Sorption isotherms describe equilibrium concs on carbon and in water
  - Const. temp. pH
- Freundlich: \(Csorb = K_f C_w^{1/n}\)
  - (App. A txt)
- \(log\ mass\ sorb / mass\ carbon\)
  \(x\ \ x\ x\)
  \(y\ \ \text{int}=\log\ K_f\)
  \(log\ Conc\ in\ Water\)
  \(slope=1/n\)
  Poor prediction at near saturation

Carbon Adsorption

- Langmuir: \(Csorb = q_m b C_w / (1+bC_w)\)
  \(slope=1/q_m b\)
  \(y\text{-int}=1/q_m\)
  \(\left(C_w\right)^{-1}\)

\(q_m = \text{max mass sorb/mass carbon (full saturation)}\)

Can estimate performance in air since at equilibrium \(H' = Ca/Cw; \text{substitute Ca/H' for Cw into isotherm equations}\)
Carbon Adsorption for Air Tmt

- Freundlich: \( C_{\text{Sorb}} = K_f C_w^{1/n} \)
- @ equilibrium \( H' = C_a/C_w \)
- Freundlich air: \( C_{\text{Sorb}} = K_f (C_a/H')^{1/n} \)
- Example: which compound most efficient to treat by activated carbon adsorption from air? Want highest \( C_{\text{Sorb}} \):
  - benz > 112TCA = pXylene @ Ca 10 mg/L
  - pXyl ~ benz > 112TCA @ Ca 1 mg/L

But real gas treatment is a dynamic system, not equilibrium

Example:

Design AC columns

Adsorption zone where Ca ~10-90% inlet conc
To design column dimensions use:

\[
\bar{V}_{\text{air}} = \frac{Q_{\text{g, col}}}{A_{\text{col}}} = \frac{q_{\text{max}} \cdot \text{slope} \cdot \text{depth AC}}{C_{\text{in}}}
\]

Slower air velocity in column will approach equilibrium

From a plot test:

\[
\frac{q_{\text{max}} \cdot \text{mg cont} \cdot \text{kg AC}}{\text{kg AC vol bed}} = \frac{C_{\text{out}}}{C_{\text{in}}}
\]

Optimal # colms in series

AZ depth = \[ \frac{\text{Col depth}}{1} = \frac{0.1 \cdot \text{slope}}{1} \]

Rounded to next highest whole number

Biological Treatment

- Can mineralize (to CO2, H2O) or transform some compounds
- May be more economical than alternative processes
- Reliability and removal efficiency variable
  - 90-99% removal possible for some organics
  - Must maintain live bacterial population without build-up of inhibitory metabolites

Types of Bioreactors

- Biofilter
  - bacteria on solid media
- Biotricking filter
  - Bacteria on solid media
  - Continuous liquid recirculation
- Bioscrubber
  - 2 reactors, bacteria suspended in liquid spray
- Suspended Growth bioreactor
  - Gas bubbled into liquid containing suspended bacteria

Biofilter

- Packed bed of soil, compost, etc. on which bacteria grow
- Solids supply nutrients or can add
- Poor control of redox (O2 availability)
- May plug over time due to excess biomass (bacterial cells plug pores of soil)
**Biotrickling filter**
- Engineered media (plastic, GAC, etc)
- Continuous liquid recirculation
  - Supplies nutrients (N,P)
  - Maintains optimal pH
  - Washes out inhibitory metabolites
- Higher cost due to both gas and liquid pumping
- May still have plugging problems

**Bioscrubber**
- 2 reactors: gas:liquid contactor (for mass transfer) & bioreactor (biodegrad)
- Fine spray of liquid containing bacteria contacts with bulk gas
- Contaminants are degraded in controlled bioreactor (to which nutrients, etc. can be added)
- Highest cost due to pumping liq & gas
- Bacteria can plug “spray” nozzle
- Least reliable approach

**Suspended Growth bioreactor**
- Contaminated gas is “sparged” or “bubbled” into bulk liquid containing suspended bacteria (similar to WW activated sludge)
- Good control of bacterial growth conditions and predictable mass transfer
- Rational design makes it most reliable to engineer
- Cost similar to trickling filter when shallow liquid depths (1 m) can be used