ENV 504

Remediation of soils and groundwater
Final exam
May 10th 2022
9:15am-11:15am
Prof. Rizlan Bernier-Latmani

CORRECTION

Problem 1: SVE

ρ_{wb} = 2,000 kg/m^3
K_D = 0.003 m^3/kg
K_H = 2.08[-]
Soil porosity $\varepsilon = 0.3$
Soil moisture content $\theta = 5\%$
Q = gas flow rate = 100 m^3/s

Cylinder 50 m in diameter and 100 m tall.

Target concentration: $C_{S,benz,f}$ =25 mg/(kg dry soil)

1. Calculate the initial equilibrium concentration of benzene in the different phases

$m_{tot,benz,i} = 100{,}000\ kg$

$m_{tot,benz,i} = C_{aq,benz,i}V_L + C_{s,benz,i} * M_S + C_{G,benz,i} * V_G = C_{aq,benz,i} * (V_L + K_D M_S + K_H V_G)$

$$C_{aq,benz,i} = \frac{m_{tot,benz,i}}{(V_L + K_D M_S + K_H V_G)}$$

We need V_L, M_S, and V_G:

$$V_T = \frac{\pi H D^2}{4} = \frac{\pi * 100 * 50^2}{4} = 196{,}350\ m^3$$

$V_L = \theta V_T = 9{,}817\ m^3$

$V_L + V_G = \varepsilon V_T \rightarrow V_G = 49{,}087\ m^3$

$V_S = (1 - \varepsilon) * V_T = 137{,}445\ m^3$

$M_S = \rho_{wb} V_T - \rho_w V_L = 382{,}881{,}605\ kg = 3.83 * 10^8 kg\ dry\ soil$

We can calculate the initial partitioning of benzene in the different phases:

$$C_{aq,benz,i} = \frac{m_{tot,benz,i}}{(V_L + K_D M_S + K_H V_G)} = \frac{100{,}000\ kg}{(9{,}817\ m^3 + 0.003 \frac{m^3}{kg\ dry\ soil} * 3.83 * 10^8 kg\ dry\ soil + 2.08 * 49{,}087\ m^3} = 0.079\ \frac{kg}{m^3} => C_{aq,benz,i} = 79 \frac{g\ benzene}{m^3\ water}$$

$$C_{G,benz,i} = K_H * C_{aq,benz,i} = 2.08 * 0.079\ \frac{kg}{m^3} = 0.165 \frac{kg}{m^3} = 165\ \frac{g\ benzene}{m^3\ air}$$

$$C_{S,benz,i} = K_D * C_{aq,benz,i} = 0.003\ \frac{m^3 water}{kg\ dry\ soil} *\ 0.079\ \frac{kg\ benzene}{m^3 water} =\ 2.38 * 10^{-4} \frac{kg\ benzene}{kg\ dry\ soil}$$

2. Give the mathematical equation for the change in total amount of benzene over time during SVE assuming instantaneous equilibration for the change in benzene concentration.

$$\frac{dm_{tot,benz}}{dt} =\ -Q * C_{G,benz} =\ -Q * K_H * C_{aq,benz}$$

We know $C_{aq,benz}$ expression as calculated in the previous question:

$$\frac{dm_{tot,benz}}{dt} =\ -Q * K_H * \frac{m_{tot,benz}}{(V_L + K_D M_S + K_H V_G)}$$

We transform this as:

$$\frac{dm_{tot,benz}}{m_{tot,benz}} =\ -Q * K_H * \frac{dt}{(V_L + K_D M_S + K_H V_G)}$$

3. Using this relationship, how long would it take for the remediation to be completed?

By integrating we get the total amount of benzene removed:

$$\int_{t_{ini}}^{t_{fin}} \frac{dm_{tot,benz}}{m_{tot,benz,i}} = \int_{t_{ini}}^{t_{fin}} -Q * K_H * \frac{dt}{(V_L + K_D M_S + K_H V_G)}$$

$$\ln\left(\frac{m_{tot,benz,f}}{m_{tot,benz,i}}\right) =\ -Q * K_H * \frac{t_f}{(V_L + K_D M_S + K_H V_G)}$$

We need to calculate the final total mass of benzene:

$$Our\ goal\ is\colon C_{S,benz,f} = 25\frac{mg}{kg} = 0.025\frac{g}{kg}$$

$$C_{aq,benz,f} = \frac{C_{s,benz,f}}{K_D} = \frac{25\frac{mg}{kg}}{0.003\frac{m^3}{kg}} =\ 8{,}333\frac{mg\ benzene}{m^3 water} = 8.33\frac{g}{m^3}$$

$$C_{G,benz,f} = C_{aq,benz,f} K_H = 8{,}333\frac{mg}{m^3 water} * 2.08\frac{m^3 water}{m^3 air} =\ 17{,}333\frac{mg\ benzene}{m^3\ air}$$
$$= 17.33\frac{g\ benzene}{m^3\ air}$$

$$m_{tot,benz,f} =\ C_{aq,benz,f} V_L + C_{s,benz,f} M_S + C_{G,benz,f} V_G$$
$$= 8.33\frac{g}{m^3} * 9{,}817\ m^3 + 0.025\frac{g}{kg} *\ 3.83 *\ 10^8 kg + 17.33\frac{g\ benzene}{m^3\ air}$$
$$* 49{,}087\ m^3$$

$$m_{tot,benz,f} =\ 10{,}507{,}453\ g =\ 10{,}507\ kg$$

$$t_f = -\ln\left(\frac{m_{tot,benz,f}}{m_{tot,benz,i}}\right) * \frac{V_L + K_D M_S + K_H V_G}{Q * K_H}$$
$$= -ln\left(\frac{10{,}507\ kg}{100{,}000\ kg}\right) * \frac{9{,}817\ m^3 + 0.003\frac{m^3}{kg} * 3.83 *\ 10^8 kg + 2.08 * 49.087\ m^3}{100\frac{m^3}{s} * 2.08}$$
$$= 1.27 * 10^4 s = 3.8\ hour$$

4. Biodegradation of benzene with first order:

$$t_{biodegradation} = \frac{1}{k}\ln\left(\frac{C_{aq,benz,i}}{C_{aq,benz,f}}\right) = \frac{1}{0.005d^{-1}} * \ln\left(\frac{79\ g/m^3}{8.33\ g/m^3}\right) = 450\ days$$

5. Do you think SVE is a reasonable approach or do you recommend another?

Compared to biodegradation, SVE seems a reasonable approach: the cost is higher but the removal time is also much shorter.

Problem 2: Electrical resistive heating

$$C_{tot,TPH,i} = 2{,}000\frac{mg}{kg\ sediment}\ ; C_{tot,TPH,f} = 500\frac{mg}{kg\ sediment}$$

$$\rho_{wb} = 1{,}400\frac{kg}{m^3}$$
$$K_H = 2.08\ [-]$$

$$K_D = 0.03\frac{m^3}{kg}$$
$$k = 0.01\ d^{-1}$$

First, we need to calculate the new equilibrium at 60°C.

TPH desorbs due to the increase of T, the concentration in solids decreases of 80%, thus:

$$K_{D,60°C} = K_{D,25°C} * 20\% = 0.006\frac{m^3}{kg}$$

Let’s calculate the partitioning in the different phases (no gas phase since aquifer):

$$m_{tot,TPH} = C_{S,TPH}M_S + C_{aq,TPH}V_L$$

$$C_{aq,TPH} = \frac{m_{tot,TPH}}{V_L + K_D M_S} = \frac{V_T * \rho_{wb} * C_{tot,TPH}}{V_L + K_D M_S}$$

We have a linear relation between $C_{aq,TPH}$ and $C_{tot,TPH}$, so we can directly apply the first order kinetics:

$$t = -\frac{1}{k}\ln\left(\frac{C_t}{C_0}\right), with\ C_t and\ C_0\ the\ total, or\ aqueous, final\ and\ initial\ concentrations$$

$$t = -\frac{1}{k}\ln\left(\frac{1}{4}\right) = 138\ d$$

Problem 3: Desorption/degradation vs. bioventing

<u>Desorption/degradation</u>

CST reactor

1. Calculate the concentration of toluene in the aqueous phase of the slurry

<u>Considering 1 m³ of slurry</u>:

$$V_{T,slurry} = 1\, m^3 of\ slurry\ (no\ gas\ phase)$$
$$C_{ss} = 10 \frac{kg\ dry\ soil}{m^3 of\ slurry}$$

$$m_{tot,tol,i,slurry} = C_{aq,tol,i,slurry} V_{L,slurry} + C_{s,tol,i,slurry} M_{S,slurry}$$
$$= C_{aq,tol,i,slurry} * (V_{L,slurry} + K_D M_{S,slurry})$$

$$C_{aq,tol,i,slurry} = \frac{m_{tot,tol,i,slurry}}{V_{L,slurry} + K_D M_{S,slurry}}$$

We need V_L and M_S:

$$M_{S,slurry} = C_{ss} V_{T,slurry} = 10 * 1 = 10\, kg\ dry\ soil$$

$$V_{L,slurry} = V_{T,slurry} - V_{S,ylurry} = V_{T,slurry} - \frac{M_{S,slurry}}{\rho_S} = V_{T,slurry} - \frac{C_{ss} V_{T,slurry}}{\rho_S}$$
$$= 1 * \left(1 - \frac{10}{2{,}500}\right) = 0.996\, m^3$$

We also need the total mass of toluene in this volume of slurry (1 m³):

$$m_{tot,tol,i,slurry} = C_{S,tol,soil} * V_{S,slurry}$$

We need to calculate the concentration of toluene by kg of dry soil in situ:

$$m_{tot,tol,soil} = C_{aq,tol,soil} * (V_{L,soil} + K_H V_{G,soil} + K_D M_{S,soil})$$

$$V_{T,soil} = 50{,}000\, m^3$$

$$V_{L,soil} = \theta V_{T,soil} = 5{,}000\, m^3$$

$$V_{G,soil} = \varepsilon V_{T,soil} - V_{L,soil} = 7{,}500\, m^3$$

$$V_{S,soil} = 37{,}500\, m^3$$

$$M_{S,soil} = \rho_S V_{S,soil} = 93{,}750{,}000\, kg$$

- ➔ $C_{aq,tol,soil} = \frac{28{,}125}{5{,}000+0.41*7{,}500+0{,}02*93{,}750{,}000} = 0.0149 \frac{kg_{tol}}{m_L^3} = 14{,}900 \frac{g_{tol}}{m_L^3}$
- ➔ $C_{S,tol,soil} = K_D C_{L,tol,soil} = 298.7 \frac{mg_{tol}}{kg_{drysoil}}$

Thus, the initial mass of toluene in 1 m³ of slurry is:

$$m_{tot,tol,i,slurry} = C_{S,tol,soil} * V_{S,slurry} = 298.7 \frac{mg_{tol}}{kg_{drysoil}} * 10 \frac{kg_{drysoil}}{m^3_{slurry}} = 2{,}987 \frac{mg_{tol}}{m^3_{slurry}}$$

We can now calculate the initial concentration of toluene in the aqueous phase of the slurry:

$$C_{aq,tol,i,slurry} = \frac{m_{tot,tol,i,slurry}}{V_{L,slurry} + K_D M_{S,slurry}} = \frac{2{,}987}{0.996 + 0.02 * 10} = 2{,}497 \frac{mg}{m^3}$$

2. Calculate the residence time required for the degradation of the toluene to the target concentration.

For CSTR:

$$\frac{C_{out}}{C_{in}} = \frac{1}{1 + kt}$$

➔ $t = \left(\frac{C_{in}}{C_{out}} - 1\right) * \frac{1}{k}$

$C_{S,out} = 30 \frac{mg}{kg\ dry\ soil}$; So: $C_{aq,out} = 1{,}500 \frac{mg}{m^3}$

$$C_{aq,in} = 2{,}497 \frac{mg}{m^3}$$

Thus,

$$t_{batch} = \left(\frac{2{,}500}{1{,}500} - 1\right) * \frac{1}{0.5} = 1.33\ h \sim 80\text{min}$$

3. Estimate the amount of time required to treat the entirety of the 50,000 m^3 of contaminated soil by a slurry phase process.

Per batch:

$$M_{S,treated\ per\ batch} = V_{slurry\ in\ reactor} * C_{SS} = 2{,}000 * 10 = 20{,}000\ kg_{drysoil}$$

The number of batch to run to treat the entire soil is:

$$N = \frac{M_{S,soil}}{M_{S,treated\ per\ batch}} = \frac{93{,}750{,}000}{20{,}000} = 4{,}688\ batch$$

$$t_{tot} = N * t_{batch} = 260\ days$$

<u>Bioventing</u>

4. Calculate the volume of liquid and gas in the soil. What is the concentration of toluene in the aqueous phase of the soil?

Calculated in question 1.

5. What is the minimum amount of time it will take to reach the target concentration assuming toluene is oxidized to CO_2?

Toluene oxidation equation:

$$C_7H_8 + 9\ O_2 \rightarrow 7CO_2 + 4H_2O$$

We want to know in total how much toluene must be oxidized by doing a mass balance between the toluene initially and finally present in the <u>solid and aqueous phases.</u> For simplification, the gas phase is not considered. This a conservative assumption because toluene will also be lost by extraction of the gas phase during the bioventing.

$$C_{aq,tol,i,soil} = 14{,}900 \frac{mg}{m^3}$$

$$C_{S,tol,i,soil} = C_{aq,tol,i,soil}K_D = 298\frac{mg}{kg}$$

$$m_{tot,tol,i,soil} = C_{S,tol,i,soil}M_{S,soil} + C_{aq,tol,i,soil}V_{L,soil} = 28{,}079\ kg$$

$$C_{S,tol,f,soil} = 30\frac{mg}{kg}$$

$$C_{aq,tol,f,soil} = \frac{C_{S,tol,f,soil}}{K_D} = 1{,}500\frac{mg}{m^3}$$

$$m_{tot,tol,f,soil} = C_{S,tol,f,soil}M_{S,soil} + C_{aq,tol,f,soil}V_{L,soil} = 2{,}820\ kg$$

The mass of toluene to be removed is:

$$m_{tol,removed} = m_{tot,tol,i} - m_{tot,tol,f} = 25{,}259\ kg$$

$$n_{tol,removed} = \frac{25{,}259 * 1{,}000}{92.14} = 274{,}138\ mol$$

The amount of O_2 needed is:

$$n_{O_2} = 9 * n_{tol,removed} = 2{,}467{,}242\ mol$$

$$m_{O_2} = 32 * n_{O_2} = 78{,}742{,}088\ g = 78{,}952\ kg$$

6. The time for removal

From the oxygen utilization rate we can calculate the biodegradation rate:

$$k_B = \frac{k_O\varepsilon_a D_{O_2} C}{\rho_{wb}}$$

$$k_O = 0.005\ min^{-1}$$

$$\varepsilon_a = \varepsilon - \theta = 0.15$$

$$D_{O_2} = 1{,}330\frac{mg}{L} = 1.33\frac{kg}{m^3}$$

$$C = \frac{m_{C\ in\ toluene}}{m_{O_2\ to\ achieve\ mineralization}} = \frac{7 * 12}{9 * 32} = 0.29$$

$$\rho_{wb} = \rho_b + \theta\rho_{water} = 1{,}995\frac{kg}{m^3}$$

Thus,

$$k_B = \frac{0.5\ min^{-1} * 0.15 * 1.33\frac{kg}{m^3} * 0.29}{1{,}995\frac{kg}{m^3}} = 1.46 * 10^{-5}\ min^{-1}$$

Assuming first order kinetics:

$$t_{biodegradation} = -\frac{1}{k_B}\ln\left(\frac{C_{s,tol,f}}{C_{s,tol,i}}\right) = -\frac{1}{1.46 * 10^{-7}}\ln\left(\frac{30\frac{mg}{kg}}{300\frac{mg}{kg}}\right) = 110\ days$$

7. Which option is better?

According to the calculations above and with the assumptions (in particular that O_2 can be supplied fast enough to not limit the biodegradation of toluene), bioventing seems to be the better option. Also, it is an *in situ* option, which is preferable in general. We are also neglecting any soil vapor extraction that could happen with bioventing, which is a conservative assumption.