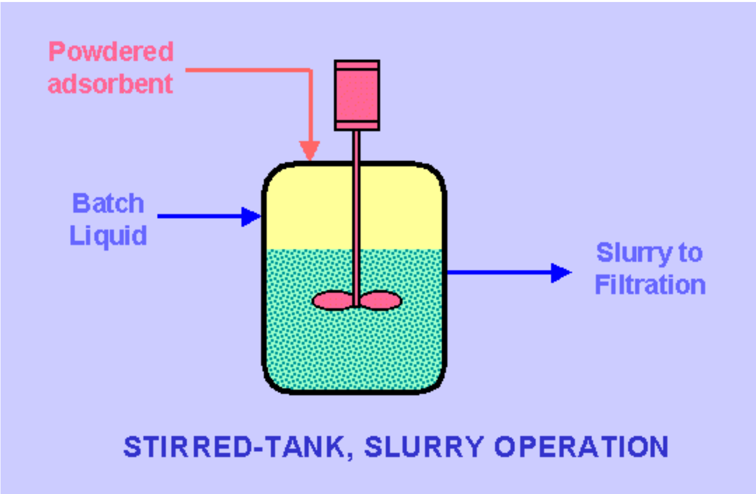
Lecture 8.
Slurry and Fixed-Bed Adsorption Systems

- Slurry Adsorption
  - Batch mode
  - Continuous mode
  - Semi-continuous mode
- Thermal-Swing Adsorption
- Pressure-Swing Adsorption

Slurry Adsorption

- Three modes of adsorption from a liquid in an agitated vessel
  - Batch mode: a batch of liquid is contacted with a batch of adsorbent for a period of time → followed by discharge of the slurry from the vessel, and filtration to separate solids from liquid
  - Continuous mode: liquid and adsorbent are continuously added to and removed from the agitated vessel
  - Semi-batch or semi-continuous mode: liquid is continuously fed, then removed from the vessel, where it is contacted with adsorbent, which is retained in a contacting zone of the vessel until it is nearly spent



Batch Mode

- The rate of solute adsorption, controlled by external mass transfer

$$-\frac{dc}{dt} = k_L a(c - c^*)$$

c^* : concentration in equilibrium with adsorbent loading, q
k_L : external liquid-phase mass-transfer coefficient
a : external surface area of adsorbent per unit volume of liquid

- By material balance (the adsorbent is initially free of adsorbate)

$$c_F Q = cQ + qS$$

Q : liquid volume (assumed to remain constant)
S : mass of adsorbent

- With appropriate adsorption isotherm, q = f(c*), the equations for c and q as a function of time can be solved
- For a linear isotherm, $c^* = q/k$

$$c = \frac{c_F}{\beta}\left[\exp(-k_L a\beta t) + \alpha\right] \qquad \beta = 1 + \frac{Q}{Sk} \qquad \alpha = \frac{Q}{Sk}$$

As contact time approaches ∞, $c\{t = \infty\} = \frac{c_F \alpha}{\beta}$

Continuous Mode

- As in a perfectly mixed reaction vessel (CSTR), concentration c throughout the vessel is equal to the outlet concentration, c_{out}

$$\frac{c_F - c_{out}}{t_{res}} = k_L a (c_{out} - c^*) \quad \rightarrow \quad c_{out} = \frac{c_F + k_L a t_{res} c^*}{1 + k_L a t_{res}}$$

t_{res} : vessel residence time

$$c_F Q = c_{out} Q + q_{out} S$$

- An appropriate adsorption isotherm relates c* to q_{out}
- For a linear isotherm, $c^* = q_{out}/k$

$$c_{out} = c_F \left(\frac{1 + \gamma\alpha}{1 + \gamma + \gamma\alpha} \right) \qquad \gamma = k_L a t_{res} \qquad \alpha = \frac{Q}{Sk}$$

$$q_{out} = \frac{Q(c_F - c_{out})}{S}$$

Semi-continuous Mode

- Adsorbent is retained in the vessel, but feed liquid enters and exits the vessel as a fixed, continuous flow rate
  - Both concentration, c, and loading, q, vary with time

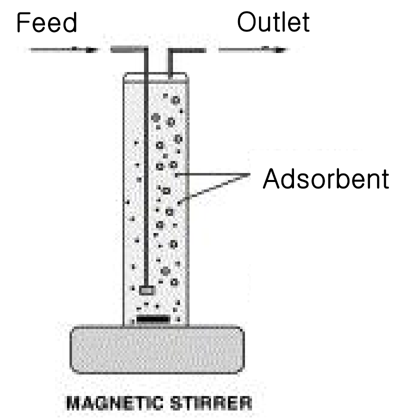
$$\frac{c_F - c_{\text{out}}}{t_{\text{res}}} = k_L a (c_{\text{out}} - c^*) \quad \rightarrow \quad c_{\text{out}} = \frac{c_F + k_L a t_{\text{res}} c^*}{1 + k_L a t_{\text{res}}}$$

- Variation of q in the batch of solids

$$S\frac{dq}{dt} = k_L a (c_{\text{out}} - c^*) t_{\text{res}} Q$$

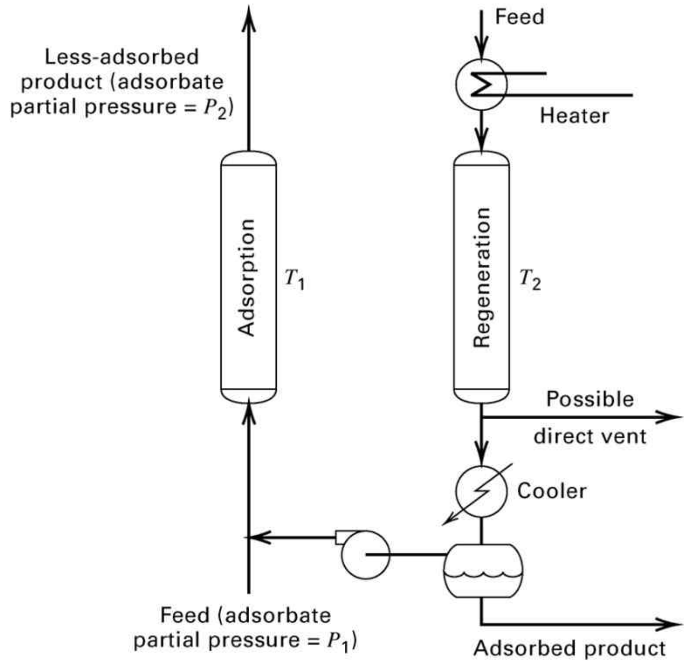
S : batch mass of adsorbent in suspension
Q : steady, volumetric-liquid flow rate

- An appropriate adsorption isotherm relates c* to q
- Using above two equations, q and c_{out} can be obtained as a function of time



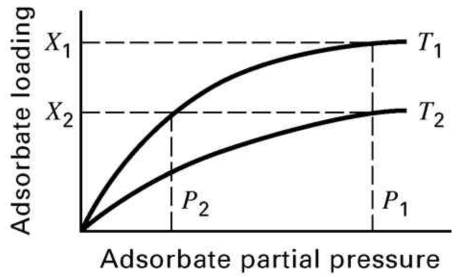
Thermal–Swing Adsorption (1)

- Thermal (temperature)–swing adsorption (TSA) is carried out with two fixed beds in parallel, operating cyclically
  - While one bed is adsorbing solute at near–ambient temperature, $T_1 = T_{ads}$, the other bed is regenerated by desorption at a higher temperature, $T_2 = T_{des}$
  - Although desorption might be accomplished in the absence of a purge fluid by simply vaporizing the adsorbate, some readsorption of solute vapor would occur upon cooling → it is best to remove desorbed adsorbate with a purge
  - TSA is best applied to removal of contaminants present at low concentrations in the feed so that nearly isothermal adsorption and desorption is achieved

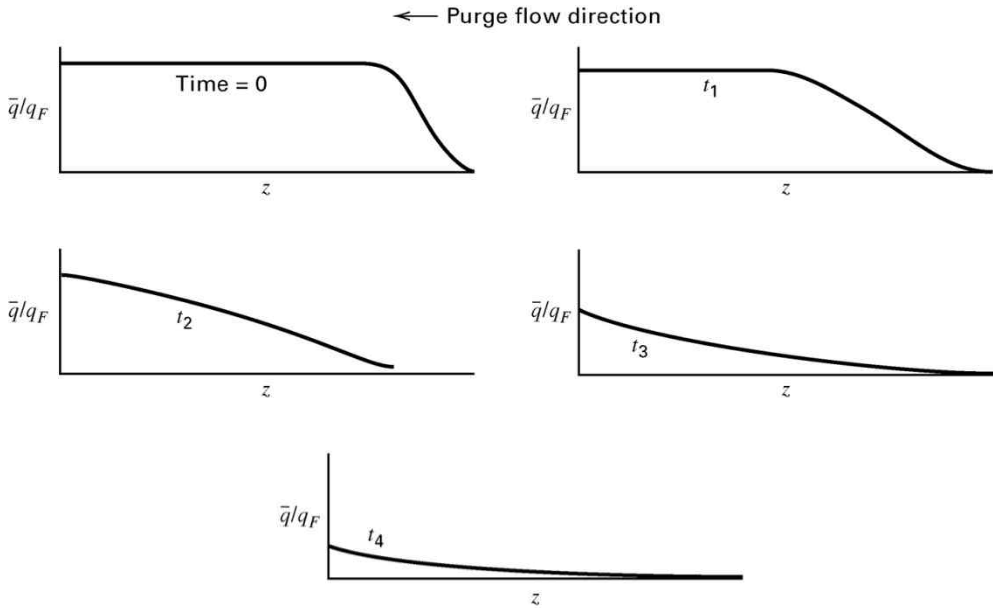


Thermal–Swing Adsorption (2)

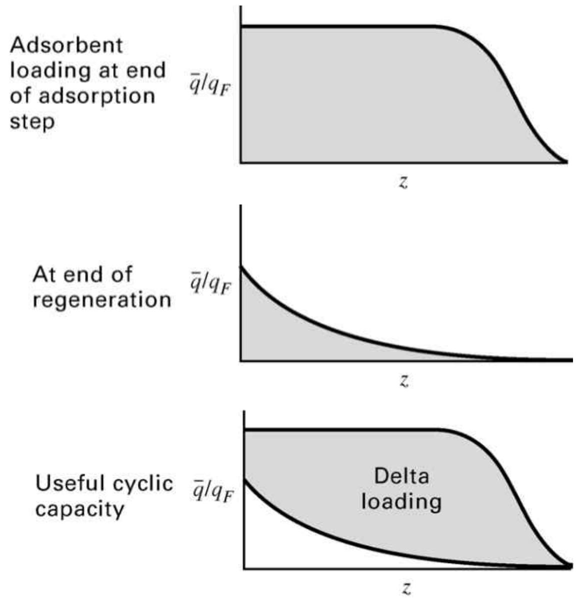
- An ideal cycle for TSA
  - (1) Adsorption at T_1 to breakthrough
  - (2) Heating of the bed to T_2
  - (3) Desorption at T_2 to a low adsorbate loading
  - (4) Cooling the bed to T_1



- Sequence of loading profiles during countercurrent regeneration

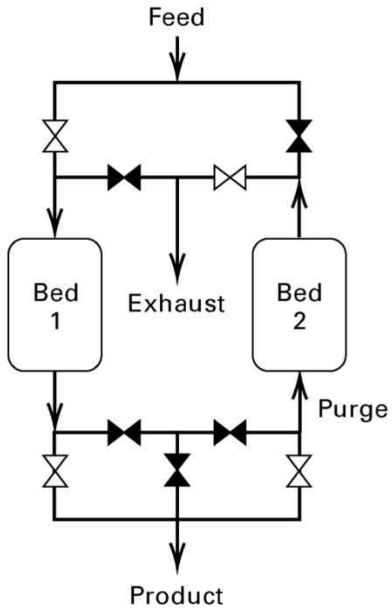


- Delta loading for regeneration step



Pressure-Swing Adsorption (1)

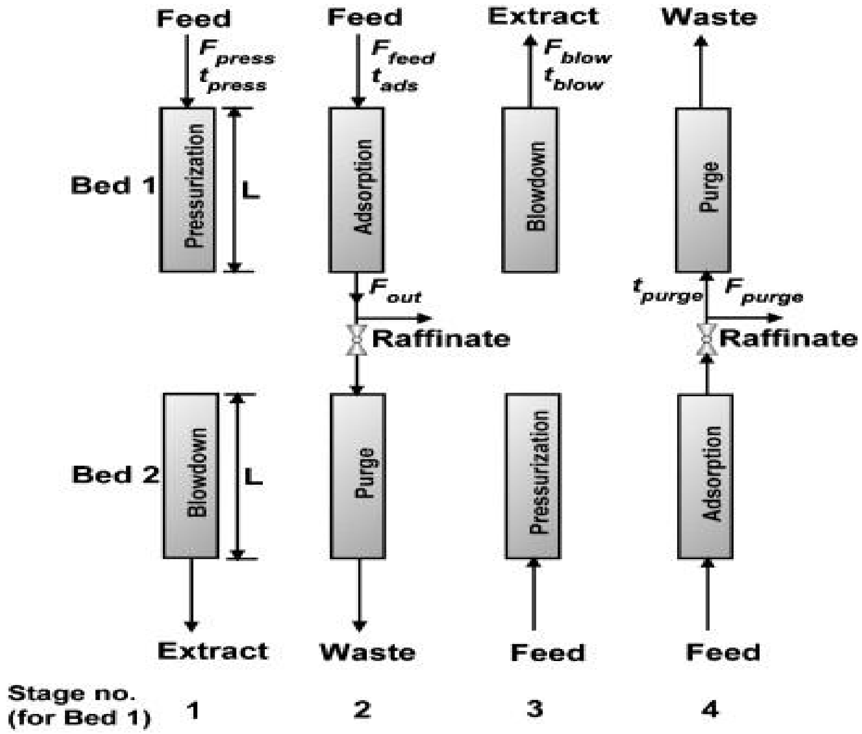
- PSA and VSA are carried out with two fixed beds in parallel, operating in a cycle
  - While one bed is adsorbing at one pressure, the other bed is desorbing at a lower pressure
  - Use mechanical work to increase pressure or create a vacuum
  - Process only gases, because a change in pressure has little or no effect on equilibrium loading for liquid adsorption
  - With valving, the cyclic sequence can be programmed to operate automatically



  - In 1960, PSA was originally invented and used only for purification, as in the removal of moisture from air
  - By the 1970s, PSA was applied to bulk separations, such as particle separation of air to produce either nitrogen or oxygen, and to removal of impurities and pollutants from other gas streams

Pressure–Swing Adsorption (2)

- Skarstrom cycle
  - Each bed operates alternately in two half-cycles of equal duration
    - pressurization followed by adsorption
    - depressurization (blowdown) followed by a purge
  - Feed gas is used for pressurization, while a portion of the effluent product gas is used for purge



- Modifications of Skarstrom cycle
  - Three, four, or more beds
  - A pressure-equalization step in which both beds are equalized in pressure following purge of one bed and adsorption in the other
  - Pretreatment or guard beds to remove strongly adsorbed components
  - Purge with a strongly adsorbing gas
  - Use of an extremely short cycle time to approach isotherm operation

Pressure-Swing Adsorption (3)

- Cyclic steady state
  - In TSA, following desorption, the regenerated bed is usually clean. Thus, a cyclic steady state is closely approached in one cycle
  - In PSA and VSA, complete regeneration is seldom achieved or necessary
  - At cyclic steady state, the difference between loading profiles after adsorption and desorption is equal to the solute in the feed
  - Starting with a clean bed, attainment of a cyclic steady state for a fixed cycle time may require tens or hundreds of cycles
  - Initial conditions for adsorption and desorption become the final conditions for desorption and adsorption of the previous cycle