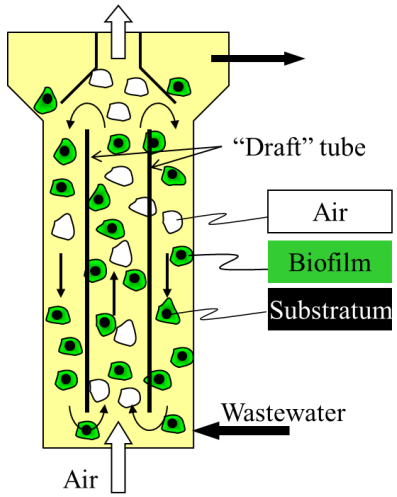
Mass transport processes in biofilms
Diffusive transport / Reaction

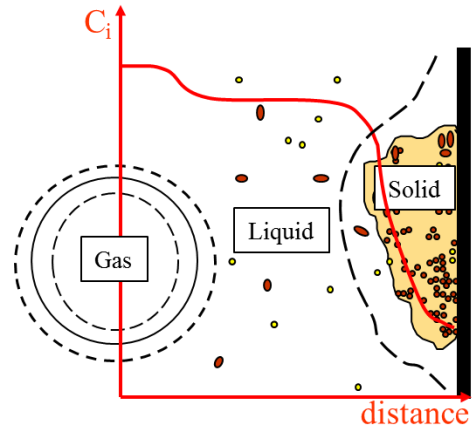


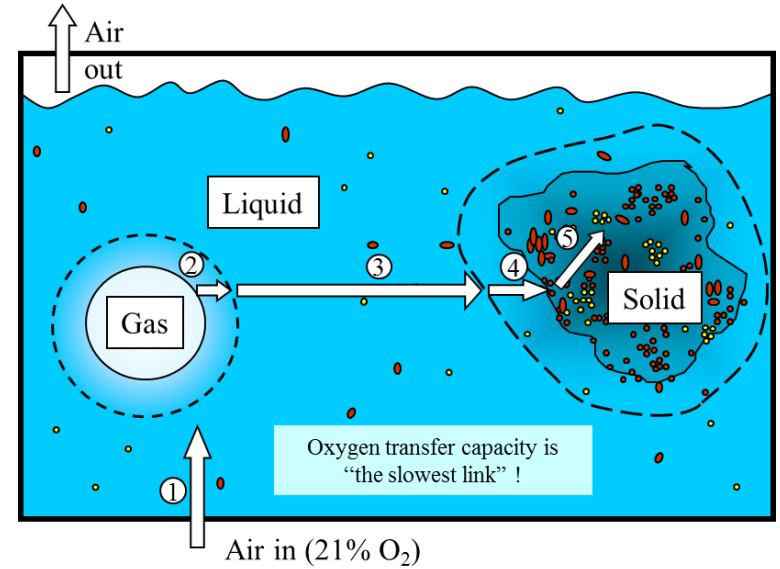
Advantages & Benefits

- **Higher biomass** concentration
- **Higher volumetric conversion capacity**
- **Less sludge** is produced
- **High settling velocity**
- Load and toxic **choc resistance**
- **C, N and P removal** (in same reactor/granule)

Biofilm ;-)

;-(

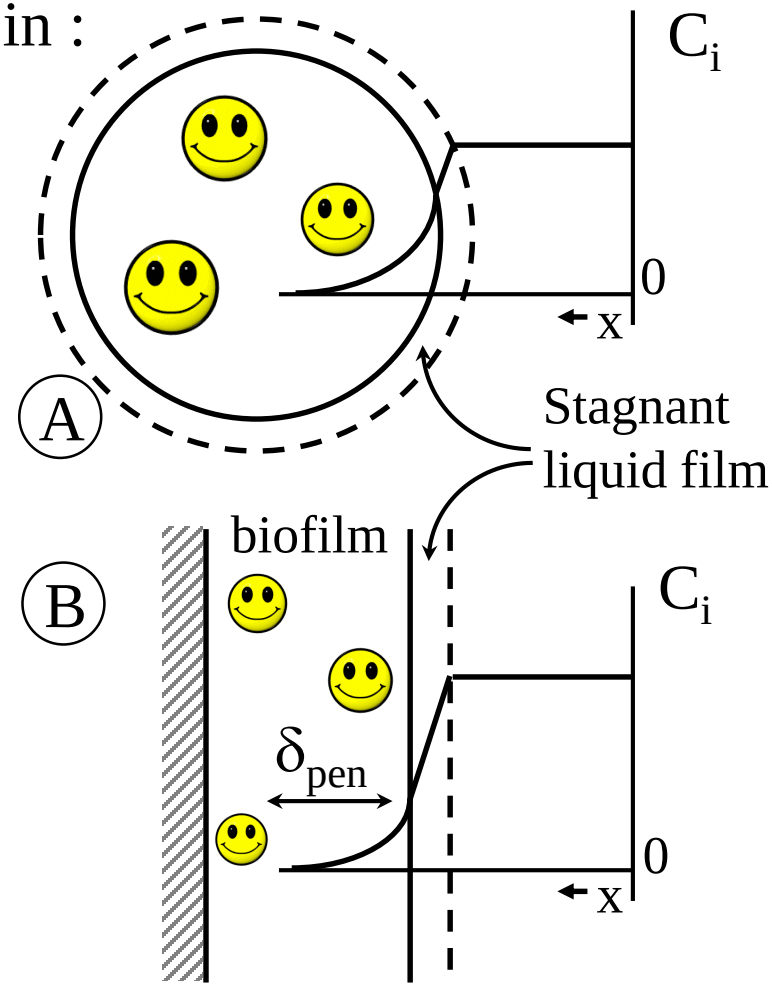




Diffusive transport / Reaction

Diffusive transport / Reaction processes occur in :

- Heterogeneous catalysis (A)
- Immobilized enzymes/cells (A)
- Biofilm with microorganisms (B)



→ Phenomenon :

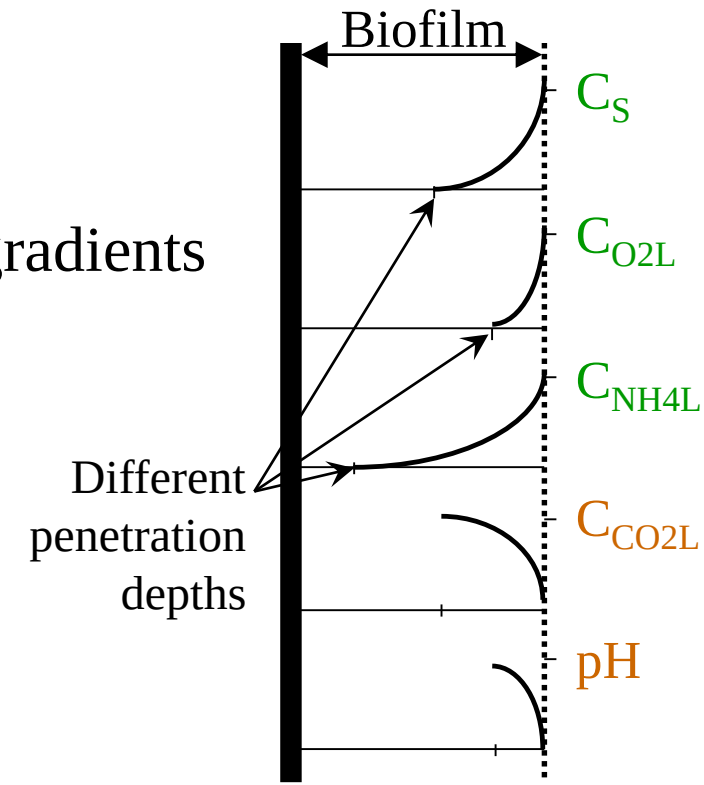
1. Gradient of concentrations for each compounds C_i
2. Concentrations become zero at δ_{pen} penetration depth
3. Expansion of biofilm with the growth of microorganisms

Microbial growth
→ Concentration gradients & Limitations

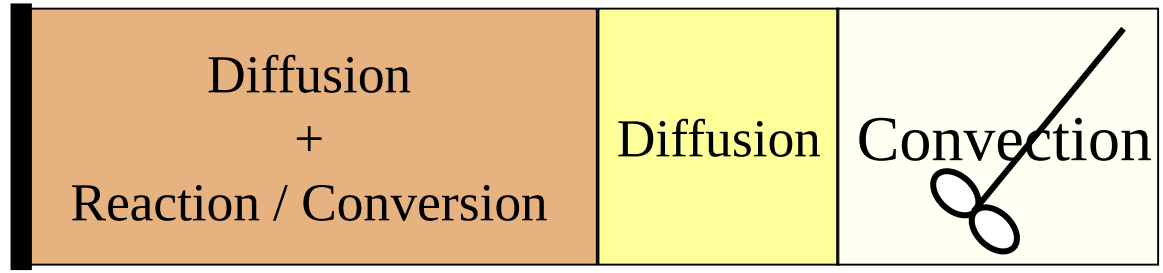
According microbial growth equation:

– 1 kg S – 0.5 kg O_2 – 0.1 kg NH_4^+ + 0.5 kg X
+ 0.8 kg HCO_3^- + (..)H_2O + (..)H^+

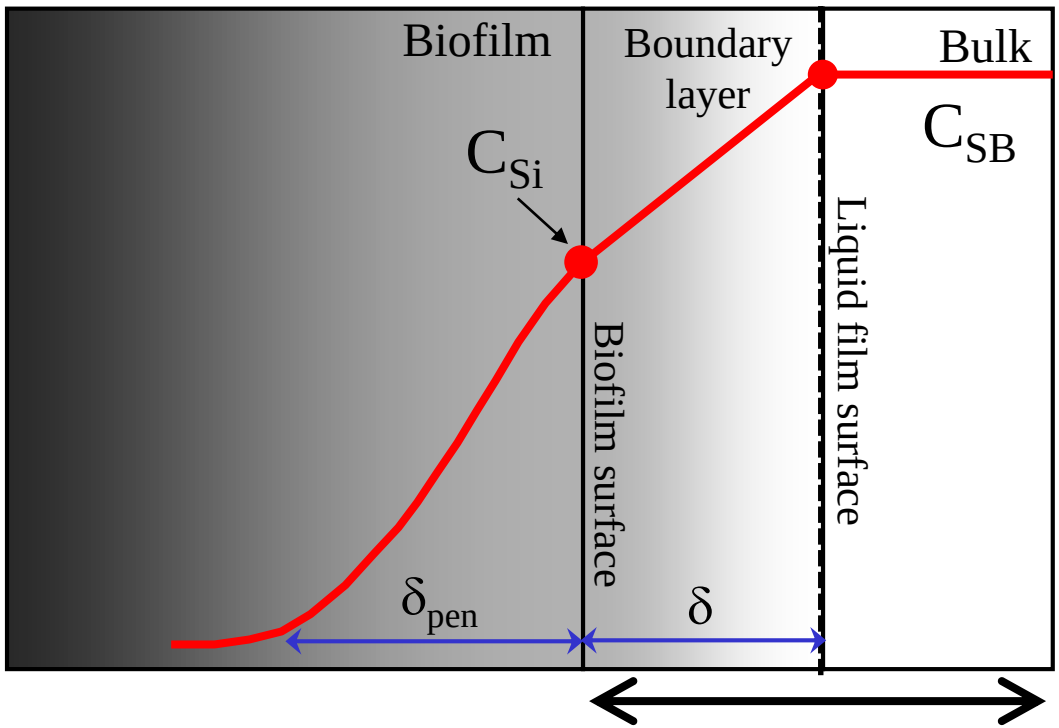
1. From diffusive transports and growth, gradients occur in biofilm, with different penetration depths :
   - Consumptions C_S, C_{O2L}, C_{NH4L} → DOWN gradients
   - Productions C_{CO2L}, pH, → UP gradients
2. Growth is limited by the least penetrating substrate/component



Flux exchanges Bulk ←→ Biofilm



Inside Biofilm:
Internal resistance to mass transport + conversions



Outside Biofilm:
External resistance to mass transport

→ Mass balance for each compound:

1. In boundary layer
2. In biofilm

1. Mass balance in Boundary Layer (1)

Assuming 1 Dimension:

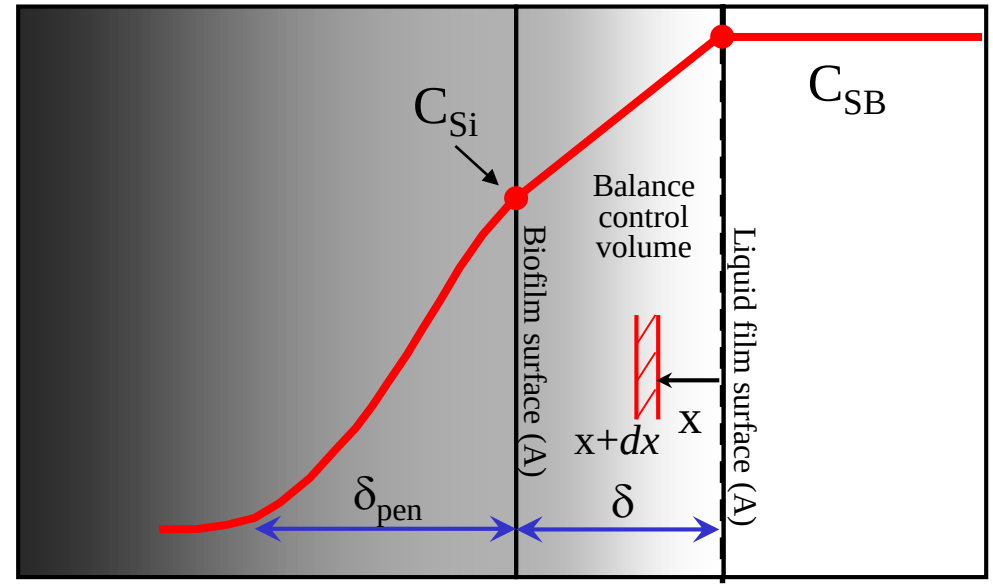
→ C_i drops at increasing x position!

Mass balance:

Acc. = in – out + conversions

In control volume:

V = A.dx (A: Biofilm area)



$$\frac{A.dx.\partial C_{i,(x)}}{\partial t} = J.A - (J.A + \frac{\partial J.A}{\partial x} dx) + r_i.A.dx$$

Liquid diffusion $J = -D\frac{dC_i}{dx}$

Assuming no biomass in liquid layer, $r_i = 0$

In 1 Dimension → A = Cst

$$\rightarrow \frac{\partial C_{i(x)}}{\partial t} = -\frac{\partial J}{\partial x} \rightarrow \frac{\partial C_{i(x)}}{\partial t} = D\frac{\partial^2 C_{i(x)}}{\partial x^2}$$

$$\frac{\partial C_{i(x)}}{\partial t} = \frac{\partial^2 C_{i(x)}}{\partial \left(\frac{x}{\delta}\right)^2} \quad \frac{1}{\left(\frac{\delta^2}{D}\right)}$$

time constant

1. Mass balance in Boundary Layer (2)

After $t >> \delta^2/D \approx 10^{-1}$ [s], a steady state is established, characterized by a stable constant gradient with $\partial C_{i(x)}/\partial t = 0$:

Integration of stagnant biofilm liquid layer mass balance equation:

$$\frac{\partial C_{i(x)}}{\partial t} = \frac{\partial^2 C_{i(x)}}{\partial \left(\frac{x}{\delta}\right)^2} \underbrace{\frac{1}{\left(\frac{\delta^2}{D}\right)}}_{\text{time constant } \tau} = 0$$

$$\frac{\partial^2 C_{i(x)}}{\partial \left(\frac{x}{\delta}\right)^2} = 0 \rightarrow \frac{\partial C_{i(x)}}{\partial \left(\frac{x}{\delta}\right)} = cst_a \rightarrow C_{i(x)} - C_{i(x=0)} = \frac{x}{\delta}.cst_a - (0) + Cst_b$$

For substrate C_S, at boundary conditions from x = 0 to δ:

x=0 $C_{i(x=0)} = C_{SB} \rightarrow Cst_b = 0$

x=δ $C_{i(x=\delta)} = C_{Si} \rightarrow Cst_a = C_{Si} - C_{SB}$

$$C_{S(x)} = \frac{C_{Si} - C_{SB}}{\delta}.x + C_{SB}$$

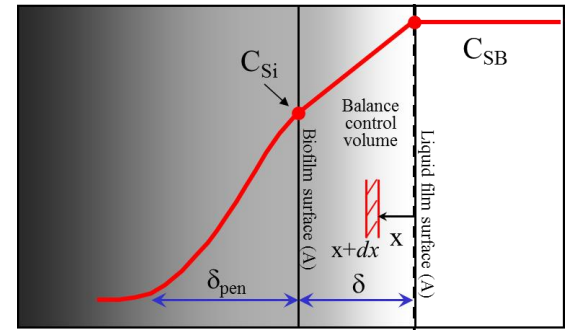
1. Mass balance in Boundary Layer (3)

At liquid boundary layer, the overall diffusion flux is:

$$Flux = J = -D\frac{\partial C}{\partial x}\left[\frac{amount}{m^2.h}\right] = -\frac{D}{\delta}(C_{Si} - C_{SB}) = Cst$$

with $\frac{D}{\delta} \underline{\underline{def}} \; k_L \; [m.s^{-1}]$

$$J_S = k_L (C_{SB} - C_{Si})$$



$$C_{S(x)} = \frac{C_{Si} - C_{SB}}{\delta}.x + C_{SB}$$

Biofilm liquid stagnant layer thickness
δ is known and k_L follows from various
mass transfer coefficient correlations:
$k_L \approx 10^{-4}$ m/s; $\delta \approx 10$ μm → Time constant is :

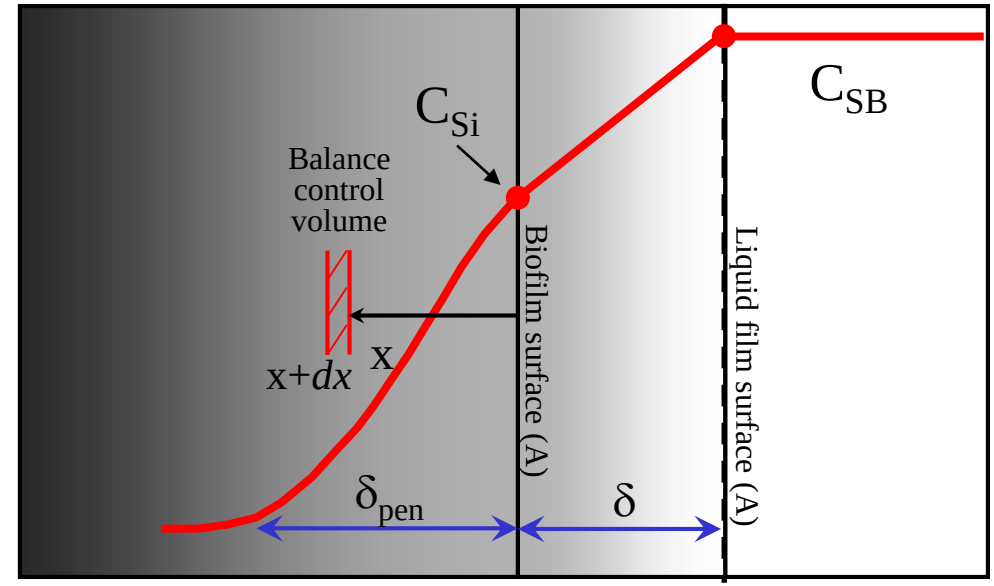
$$\frac{\delta^2}{D} = \frac{\delta}{k_L} = \frac{10^{-5}}{10^{-4}} = 10^{-1} \text{ sec. !!!}$$

Summary :

- According diffusion in boundary layer, **concentration decreases linearly** towards biofilm surface
- Steady state achieves quickly, in about 10^{-1} sec.

2. Mass balance in Biofilm (1)

Assuming 1 Dimension, mass balance in biofilm control volume,
V = A.dx (A: Biofilm area)
Acc. = in – out + conversions



$$\frac{A.dx.\partial C_{i,(x)}}{\partial t} = J.A - (J.A + \frac{\partial J.A}{\partial x}dx) + r_i.A.dx$$

$$\rightarrow \frac{\partial C_{i(x)}}{\partial t} = -\frac{\partial J}{\partial x} + r_i \quad with \quad J = -D\frac{dC_i}{dx}$$

$$\rightarrow \frac{\partial C_{i(x)}}{\partial t} = D\frac{\partial^2 C_{i(x)}}{\partial x^2} + r_i$$

$$\rightarrow \quad \frac{\partial C_{i(x)}}{\partial t} = \frac{\partial^2 C_{i(x)}}{\partial \left(\frac{x}{\delta_{pen}}\right)^2} \cdot \underbrace{\left(\frac{\delta_{pen}^2}{D}\right)}_{\tau\ diffusion} + r_i$$

2. Mass balance in Biofilm (2)

In biofilm, penetration depth δ_{pen} is about 1 mm.
Thus diffusive transport process time constant is:

$$\tau_{diffusion} = \frac{\delta_{pen}^{\ 2}}{D} = \frac{\delta_{pen}}{k_L} \approx \frac{10^{-3}}{10^{-4}} \approx 10^{+1}[s]$$

Concerning biomass conversion/reaction rates, time constant is:

$$\tau_{reaction} = \frac{C_i\ [kg/m^3]}{r_i\ [kg/m^3.hr]} \approx 5[s]$$

For time ~ minutes → $\partial C_{i(x)}/\partial t$ becomes small ≈ 0,
→ a **pseudo steady state** can then be considered:

$$\frac{\partial C_{i(x)}}{\partial t} = D\frac{\partial^2 C_{i(x)}}{\partial x^2} + r_i = 0$$

Assuming: **0 order** consumption kinetic $q_S = q_S^{max}$

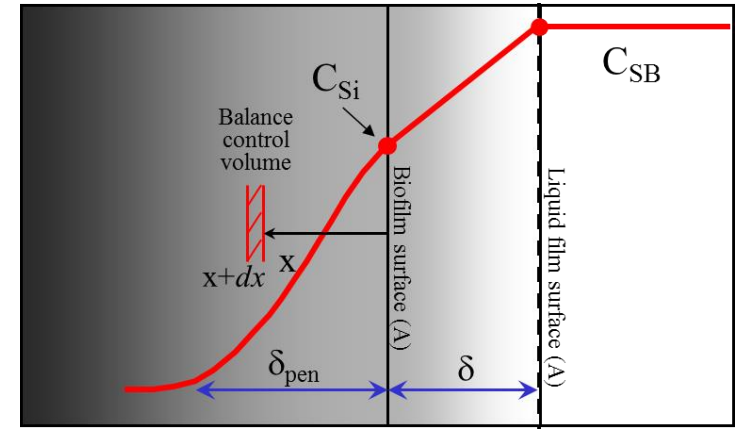
Biomass concentration in biofilm C_{Xf}

$r_S = - C_{Xf}\ q_S^{max}$

→ $$D.\frac{\partial^2 C_{(x)}}{\partial x^2} = q_S^{max} C_{xf}$$

2. Mass balance in Biofilm (3)

In biofilm, if: $D.\frac{\partial^2 C_{(x)}}{\partial x^2} = q_S^{max} C_{xf}$



Boundary conditions are:

x = 0 $C_S = C_{Si}$ (Biofilm interfacial concentr.)

x = δ_{pen} → No reaction. No transport.

→ $\partial Ci(x)/\partial x = 0$

Integration gives concentration penetration profile of compound C_i in the biofilm:

$$C_{Si} - C_{S(x)} = \frac{q_S^{max} C_{xf} \delta_{pen}^2}{D} \cdot \left[\frac{x}{\delta_{pen}} - \frac{1}{2} \left(\frac{x}{\delta_{pen}} \right)^2 \right]$$

Thus, δ_{pen} is given when :

x = δ_{pen} and $C_{S(\delta pen)} = 0$

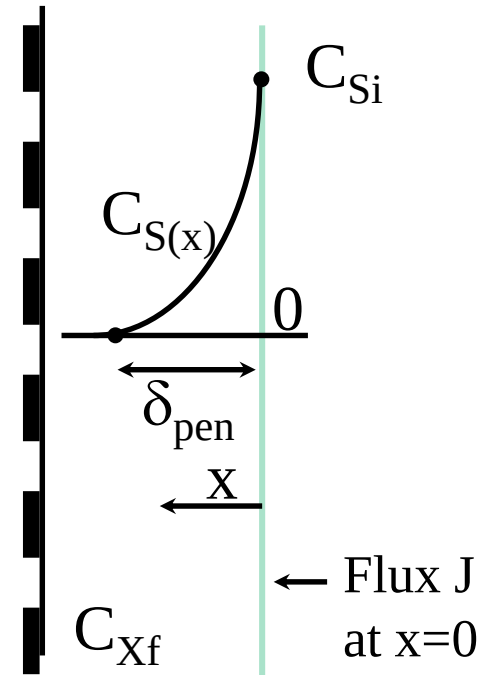
$$\delta_{pen} = \left(\frac{2 D C_{si}}{q_S^{max} C_{xf}} \right)^{0.5}$$

2. Mass balance in Biofilm (4)

By integration of: $D.\frac{\partial^2 C_{(x)}}{\partial x^2} = q_S^{\max} C_{xf}$

With $\partial Ci(x)/\partial x = 0$ when $x = \delta_{pen}$ $\quad \delta_{pen} = \left(\frac{2DC_{Si}}{q_S^{\max} C_{Xf}}\right)^{0.5}$

$$\rightarrow \frac{\partial C_S(x)}{\partial x} = \frac{q_S^{\max} C_{Xf}}{D}.x + \left(-\frac{q_S^{\max} C_{Xf}}{D}.\delta_{pen}\right) \qquad C_s(x) = C_{si} - \frac{q_S^{\max} C_{Xf} \delta_{pen}^{\ 2}}{D}.\left(\frac{1}{2}.\left(\frac{x}{\delta_{pen}}\right)^2 - \frac{x}{\delta_{pen}}\right)$$



At biofilm interface (surface), x = 0 where $C_{S(x=0)} = C_{si}$ the crossing substrate flux coming from boundary layer is given by:

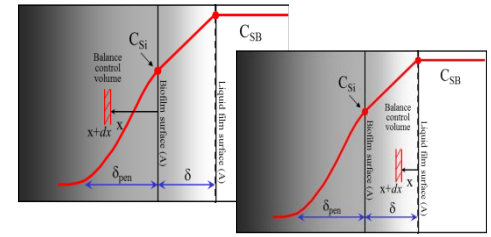
$$J_s = D\frac{\partial C_{S(x)}}{\partial x}\Big|_{X=0}^{X=\delta_{pen}} = D\left(\frac{q_S^{\max} C_{Xf}}{D}.x + \left(-\frac{q_S^{\max} C_{Xf}}{D}.\delta_{pen}\right)\right)\Big|_{X=0}^{X=\delta_{pen}} = \left(2q_S^{\max} C_{xf} DC_{Si}\right)^{\frac{1}{2}} : k_{0.5} = \left(2Dq_S^{\max} C_{xf}\right)^{0.5}$$

→ $$J_S = k_{0.5}.\left(C_{Si}\right)^{0.5} \quad with \quad k_{0.5} \overset{def}{=} \left(2.D.q_S^{\max}.C_{Xf}\right)^{0.5}$$

Flux at biofilm interface increases with reaction and diffusive transport.

Solving Biofilm & Liquid boundary layer (1)

From both sides of the biofilm/layer interface the mass flux J should be equal.



Liquid Stagnant layer **Biofilm**

$$J_S = k_L (C_{SB} - C_{Si})$$

$$J_S = k_{0.5} . \left(C_{Si}\right)^{0.5} \quad with \quad k_{0.5} \overset{def}{=} \left(2.D.q_S^{\max} . C_{Xf}\right)^{0.5}$$

Eliminating C_{Si} , J can be expressed as C_{SB}, D, q_S^{max} and C_{Xf}:

$$J_S = \left(\frac{0.25\, k_{0.5}^4}{k_L^2} + k_{0.5}^2 C_{SB} \right)^{0.5} - 0.5 \frac{k_{0.5}^2}{k_L}$$

This shows limitations:

k_L very small → External boundary layer transport limitation $C_{SB} > C_{Si} \approx 0$

→ $J = k_L C_{SB}$

k_L very large → Mainly limitation from biofilm diffusion $C_{Si} \approx C_{SB}$

→ $\mathbf{J = k_{0.5} C_{SB}^{0.5} = J_{KL=\infty}}$ (NO limitation of transfer by liquid boundary layer)

Solving Biofilm & Liquid boundary layer (2)

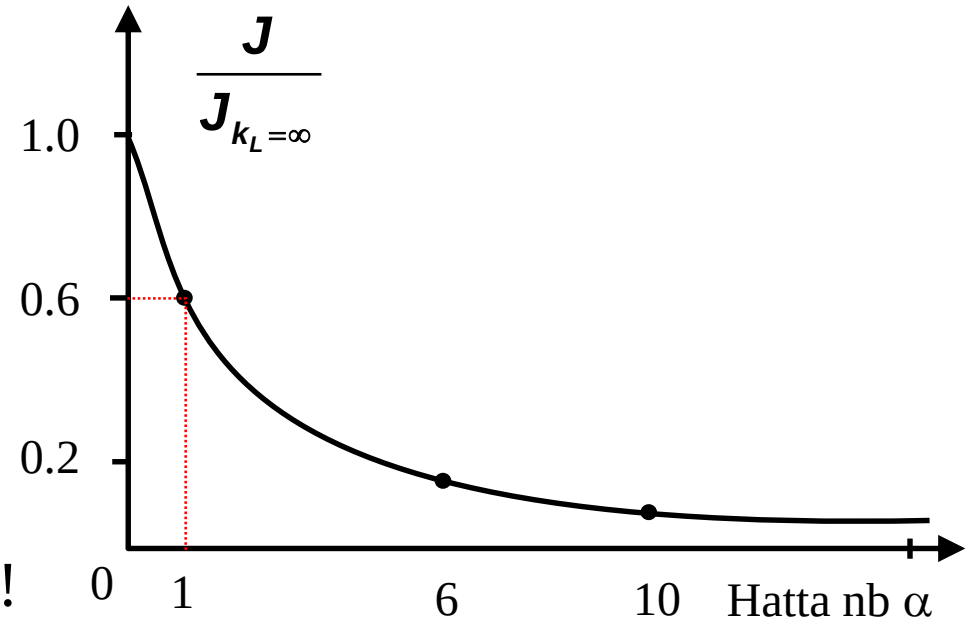
Thus, coupled Biofilm/Liquid boundary layer mass transfer can be compared with unlimited transfer at boundary layer $J_{KL=\infty}$.

Using Hatta Number, ratio of maximal biofilm conversion rate vs biofilm external transport rate

$$\alpha = \frac{max.\ internal\ conversion\ rate}{max.\ external\ transport\ rate} = \frac{k_{0.5}\left(C_{SB}\right)^{0.5}}{k_L C_{SB}}$$

To estimate Transport Efficiency, $J/J_{KL=\infty}$ expression is:

$$\frac{J_S}{J_{k_L=\infty}} = \left(1+0.25\alpha^2\right)^{0.5} - 0.5\alpha$$



One can then estimate external limitation!
For Hatta number $\alpha > 1$ → External mass transfer limitation is serious.

Numerical calculation example (1)

In Biofilm: Biomass: $C_{Xf} = 40$ [kg.m^{-3}]

Substrate: $q_S^{max} = 0.2$ [kgS.kgX^{-1}·h^{-1}]

Stoichiometry of growth (neglecting maintenance):

$$-1 \text{ kg S} - 0.5 \text{ kg } O_2 - 0.1 \text{ kg } NH_4^+ + 0.5 \text{ kg X} + 0.8 \text{ kg } CO_2$$

Kinetics of growth: $q_{O2}^{max} = 0.1$ [kgO_2.kgX^{-1}·h^{-1}]

$q_{CO2}^{max} = 0.16$ [kgCO_2.kgX^{-1}·h^{-1}]

In Bulk: O_2: $C_{B,O2} = 9 \cdot 10^{-3}$ [kg.m^{-3}]

Substrate: $C_{B,S} = 9 \cdot 10^{-3}$ [kg.m^{-3}] (?)

Given:

Diffusion coefficient (for O_2 and S): $D = 10^{-9}$ [m^2·s^{-1}] $= 3.6 \cdot 10^{-6}$ [m^2·h^{-1}]

Mass transfer coefficient: $K_L = 3 \cdot 10^{-5}$ [m.s^{-1}] $= 0.11$ [m.h^{-1}]

Which compound transport limits growth, O_2 or Substrate?

What are the respective penetration depths?

Numerical calculation example (2)

In Biofilm:

$$J_S = k_{0.5}.\left(C_{Si}\right)^{0.5} \quad with \quad k_{0.5} \overset{def}{=} \left(2.D.q_S^{\max}.C_{Xf}\right)^{0.5}$$

$k_{0.5,O2} = 5.36\ 10^{-3}$ [$kgO_2^{0.5}.\ m^{-0.5}.h^{-1}$]

$k_{0.5,S} = 7.59\ 10^{-3}$ [$kgS^{0.5}.\ m^{-0.5}.h^{-1}$]

In Stagnant layer. With no transport limitation, $\mathbf{J_{kL=\infty} = k_{0.5}C_{SB}^{0.5}}$

$J_{KL=\infty}$; $C_{SB} = C_{Si}$ and $C_{O2B} = C_{O2i}$

→ $J_{kL=\infty,O2}$ $5.09\ 10^{-4}$ [$kg.m^2.h^{-1}$] 0.509 [$g.m^2.h^{-1}$]

$J_{kL=\infty,S}$ $7.20\ 10^{-4}$ [$kg.m^2.h^{-1}$] 0.720 [$g.m^2.h^{-1}$]

Flux with transport limitation using Hatta number.

$$\alpha == \frac{k_{0.5}\left(C_{SB}\right)^{0.5}}{k_L C_{SB}}$$

$\alpha = 0.514$ for O_2

$\alpha = 0.727$ for Substrate

$$\frac{J}{J_{k_L=\infty}} = \left(1+0.25\alpha^2\right)^{0.5} - 0.5\alpha$$

$= 0.775$ for O_2

$= 0.7$ for Substrate

→ O_2: $J_{O2} = 0.775 \cdot J_{KL=\infty,O2} = 3.95 \cdot 10^{-4}$ [$kg.m^2.h^{-1}$]

Substrate: $J_S = 0.7 \cdot J_{KL=\infty,S} = 5.04 \cdot 10^{-4}$ [$kg.m^2.h^{-1}$]

Numerical calculation example (3)

Using $J_S = k_L (C_{SB} - C_{Si})$

Interfacial concentrations,
knowing k_L , C_{SB} and J_S from previous or from

$$J_S = \left(\frac{0.25\, k_{0.5}^4}{k_L^2} + k_{0.5}^2 C_{SB} \right)^{0.5} - 0.5 \frac{k_{0.5}^2}{k_L}$$

	Bulk C_B	Interfacial C_{Si}
C_{O2i}	$9 \cdot 10^{-3}$ [kg.m^{-3}]	$5.41 \cdot 10^{-3}$ [kg.m^{-3}]
C_{Si}	$9 \cdot 10^{-3}$ [kg.m^{-3}]	$4.41 \cdot 10^{-3}$ [kg.m^{-3}]

Penetration depth $\delta_{O2,pen} = 98 \cdot 10^{-6}$ [m]
$\delta_{S,pen} = 63 \cdot 10^{-6}$ [m]

$$\delta_{pen} = \left(\frac{2 D C_{si}}{q_S^{max} C_{xf}} \right)^{0.5}$$

Conclusion

From Substrate penetration → limitation by transport of Substrate with a transfer flux, $J_S = 5.04 \cdot 10^{-4}$ [kgS.m^{-2}.h^{-1}] at biofilm interface.
From stoichiometry yield: 0.5 [kgO_2.kgS^{-1}] → Thus, the O_2 flux required for respiration $J_{O2} = 2.52 \cdot 10^{-4}$ [kgO_2.m^{-2}.h^{-1}]

→ Only (63%) of $J_{O2} = 3.95 \cdot 10^{-4}$ [kgO_2.m^{-2}.h^{-1}] transfer potential is used. (why?)