生物材料學 BIOMATERIALS

Swelling and Leaching

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Purpose of the Class

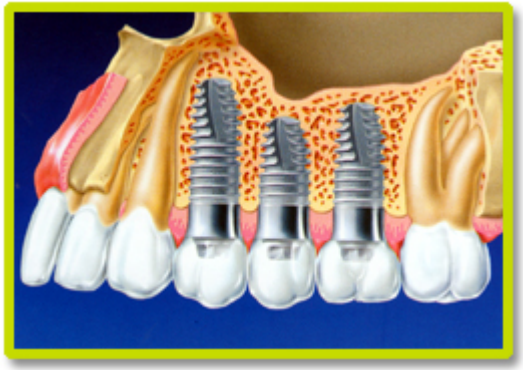
To develop in the students a familiarity with the uses of materials in medicine and with the rational basis for these applications.

Introduction

1. Introduction

- The *simplest* form of interaction between implant materials and biological environment

  → transfer of material across the material-tissue interface in the ***absence of reaction***



1. Introduction

- Two possible results:

1. ***Swelling***

   – If the substance (primarily fluid) moves from the tissue into the biomaterial

   → swelling in a fully dense material due to conservation of volume

   * Even in the absence of fluid uptake

   → the biomaterial may absorb some component or solute from the surrounding fluid phase

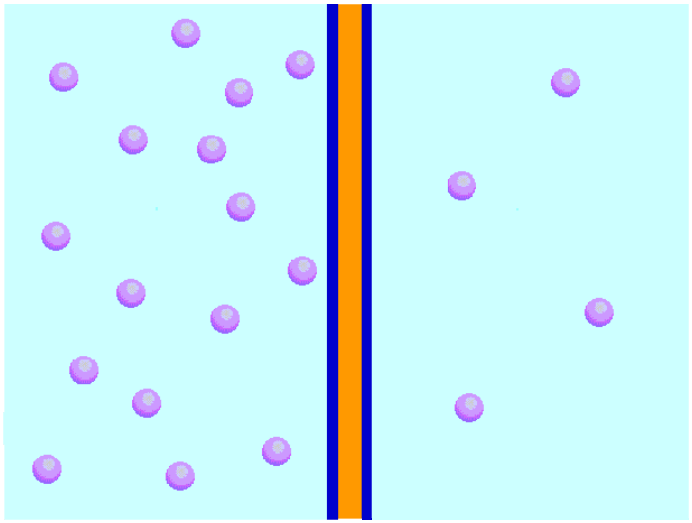
2. ***Leaching***

   – If the fluid moves into the tissue, or if one component of the biomaterial dissolves in the fluid phase of the tissue

   → material porosity

1. Introduction

- Both of these effects have profound influences on the behavior of materials despite the absence of externally applied mechanical stresses and obvious shape changes
- Swelling and leaching both result from the process of ***diffusion***



Fick's Laws of Diffusion

2. Fick's Laws of Diffusion

- **Diffusion** is defined by **Crank (1975)** as

'the process by which matter is transported from one part of a system to another as a result of *random molecular motion*'

2. Fick's Laws of Diffusion

- When a system contains two or more constituents whose ***concentrations*** **vary** from <u>one</u> position to <u>another</u>

  → a **natural tendency** for mass to be transferred

  → ***minimize*** the ***concentration differences*** within the system

  → ∴ the transport of the component from a region of ***higher*** to one of a ***lower*** concentration

  ⇒ called **'mass transfer'** (Welty, 1976)

2. Fick's Laws of Diffusion

- Mass transfer

  1. *Molecular* mass transfer

     – mass transferred by random molecular motion in *undisturbed* fluids

     (≈ conductive heat transfer)

  2. *Convective* mass transfer

     – mass transferred from a surface into a *stirred* fluid aided by fluid aided by fluid dynamic phenomena

     (≈ convective heat transfer)

2. Fick's Laws of Diffusion

- In order for microstructural changes or chemical reaction to take place in condensed phase

  → Atoms should be able to move about in the crystalline or noncrystalline solid

- There are a number possible mechanisms in a crystalline solid:

  1. *Direct exchange* of positions between two atoms, or more likely by a *ring mechanism* (a closed circle of atoms rotate)

2. Fick's Laws of Diffusion

2. The motion of atoms from a normal position into an adjacent *vacant* site

(↔ ***vacancy diffusion*** -- in the opposite direction)

→ energetically more favorable

→ the most frequent for generating atomic motion

* There are vacant sites in every solid at temperature > absolute zero

3. Atom moves from a regular site to an *interstitial* position (as in the formation of Frenkel defects)

↔ *interstitialcy mechanism*

(an ion moves from its interstitial site to a lattice site)

2. Fick's Laws of Diffusion

- Refractory corrosion, sintering, oxidation, and gas permeability are influenced by ***diffusion*** properties
- If we consider a single-phase (*isotropic*) composition in which diffusion occurs in one direction under conditions of constant temperature and constant pressure

  → the transfer of material occurs in such a way that

  concentration gradient (chemical potential gradients)

  are ***reduced***

2. Fick's Laws of Diffusion

- For such a system the mathematical theory of diffusion in isotropic substance is based on the hypothesis

-- the quantity of diffusion material which passes per unit time through a unit area normal to the direction of diffusion is proportional to its concentration gradient

and the fundamental relationship is:

$$J = -D\frac{\partial C}{\partial x} \qquad [1]$$

2. Fick's Laws of Diffusion

$$J = -D\frac{\partial C}{\partial x} \qquad [1]$$

where

J = flux (quantity per unit time per unit area, or rate of transfer per unit area)

D = ***diffusivity*** or diffusion coefficient -- $(\text{length})^2(\text{time})^{-1}$ or $\text{cm}^2\text{sec}^{-1}$

C = concentration of diffusing material

x = coordinate normal to cross section

'_' : diffusion occurs in a direction ***opposite*** to that of increasing concentration

This is called ***Fick's first law*** → diffusion that obeys this relationship is termed ***'Fickian*** or ***Type I* diffusion '**

2. Fick's Laws of Diffusion

- In this simple case, **D** depends only upon the material diffusing (the ***solute***) and the ***matrix*** through which it moves

  → ∴ D is *independent* of concentration, position, and time

  However, D does depend upon the ***type of diffusion process*** taking place → including ***surface***, ***grain boundary***, and ***volume diffusion*** → This dependence is given by

$$D = D_0 e^{[-Q/kT]}$$

  Q = energy of activation of the diffusion process

  → $Q_{volume} > Q_{grain\ boundary} > Q_{surface}$ **(4:3:2 or :1)**

  $D_0 = D_{0\ (surface)} > D_{0\ (grain\ boundary)} > D_{0\ (volume)}$

  ∴ a substance diffusing through a biomaterial

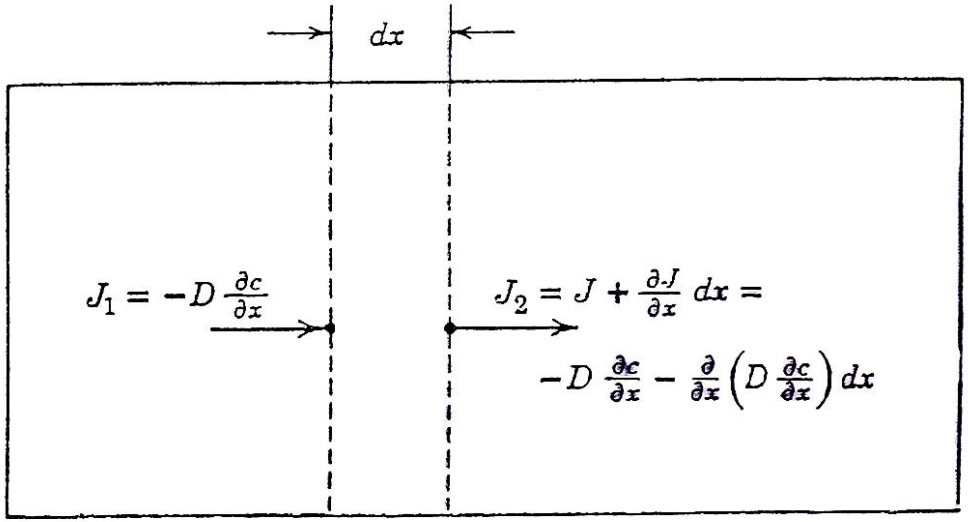
  → $D_{surface} > D_{grain\ boundary} > D_{volume}$

  ⇒ ***surface diffusion*** is favored at all temperatures

2. Fick's Laws of Diffusion

- The fundamental differential equation of diffusion in an isotropic medium is derived from equation [1]. The change in concentration at any point in time can be determined during a diffusion process by determining the difference between the flux into and flux out of a given volume

  → If two parallel planes are separated by distance ***dx*** as illustrated in the following figure:



2. Fick's Laws of Diffusion

- The flux through the first plane is

$$J = -D\frac{\partial C}{\partial x}$$

and the flux through the second plane is

$$J + \frac{\partial J}{\partial x}dx = -D\frac{\partial C}{\partial x} - \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)dx$$

and by subtraction of J

$$\frac{\partial J}{\partial x} = -\frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)$$

- The damage in flux with distance ($\partial J/\partial x$) is equal to $-\partial C/\partial t$ allowing derivative as follows:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)$$

2. Fick's Laws of Diffusion

- If D is constant and independent of the concentration, this equation may be rewritten as (*i.e.,* when Eq. [1] is applied to the problem of one-directional flow in an infinite medium, a differential equation of this form can be obtained):

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad [2]$$

- Equation [2] is usually called ***Fick's second law***

2. Fick's Laws of Diffusion

- The application of equations [1] and [2] to the different geometries, and to the initial and boundary conditions, of specific situations is sufficient to determine the distribution and mass transfer rate (*i.e.,* diffusivity, D) of diffusing materials in all cases:
  - If the flux is to be determined (in a steady-state diffusion with a fixed concentration gradient) → Fick's first law
- The solution of Fick's second law → a determination of the concentration as function of position and time, *i.e.,* C(x, t)

Absorption

3. Absorption

- The simplest case that results in ***swelling***

  → diffusion from a fluid with a fixed concentration (in the presence of perfect mixing) into an infinite medium

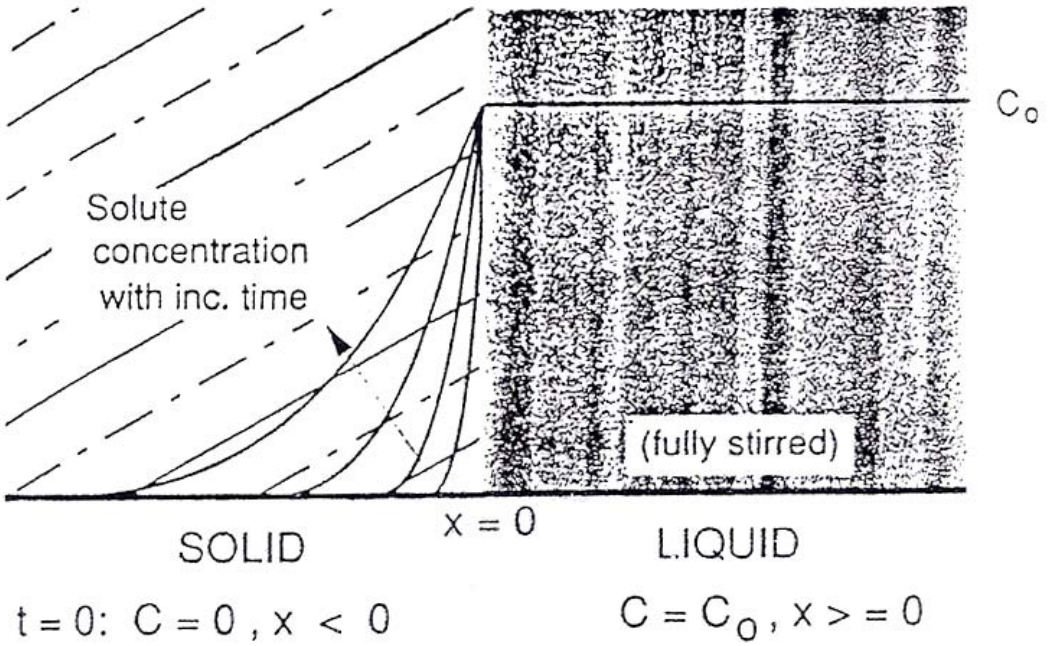
- This is the case for the early period of absorption in any geometric arrangement

- When the diffusing material is mostly near the surface

  → *geometric factors* have little effect

3. Absorption

- The arrangement, initial conditions, and change of concentration in the solid (biomaterial) phase with time are shown in the following figure:



3. Absorption

- The exact solution for the **concentration** at a given point, as a function of **time**, is

$$C = C_0 \left(\frac{x}{2 (Dt)^{1/2}} \right) \qquad [3]$$

where

C_0 = external concentration

x = distance perpendicular to the interface

3. Absorption

- Integration of equation [3] over distance for two values of time

  → the following relationship for the total mass transfer (M_t) across the boundary:

$$M_t = 2C_0 \left(\frac{Dt}{\pi}\right)^{1/2} \qquad [4]$$

3. Absorption

- The following conclusions follow directly from equations [3] and [4]:

1. The distance of penetration of any given concentration ('the diffusion front') increases in proportion to the square root of time ($t^{1/2}$)
2. The time required for any point to reach a given concentration is proportional to the square of distance (x^2) from the surface & is inversely proportional to the diffusivity
3. The total amount of diffusing material (M_t) entering the biomaterial through a unit area of interface increases as the square root of time ($t^{1/2}$)

3. Absorption

- The situation shown in above figure is correct for either volume or grain boundary diffusion (with appropriate diffusivities) when the liquid phase is ***well mixed***

(*e.g.*, fluid or solute uptake from arterial blood)

3. Absorption

- Two possibly complicated situations:

1. If the liquid phase is ***not well mixed*** (*e.g.*, interstitial fluid surrounding a soft tissue implant site) → more complex:

   - The simplest case occurs when ***a stagnation layer*** exists at the solid surface

   → this may be modeled as a third phase with a ***'resistance' to diffusion***

   → often expressed by reducing the fluid phase concentration by a multiplier, k (< 1)

   → ∴ the adjusted concentration C'_0 is given by:

$$C'_0 = kC_0$$

3. Absorption

2. Arising when the solid phase is able to absorb H_2O (or another solvent) as well as the solute under study

   → producing a steadily thickening solvated surface layer in which the solute can diffuse more readily than in the unsolvated solid

   ⇒ This has the effect of increasing the 1/2 power exponent in equations [3] and [4] to values closer to one (and similarly of altering conclusion 1-3 above)

   ⇒ Such a process is termed ***'non-Fickian'*** or ***Type II*** **diffusion**

Leaching

4. Leaching

- The simplest case that results in **leaching**

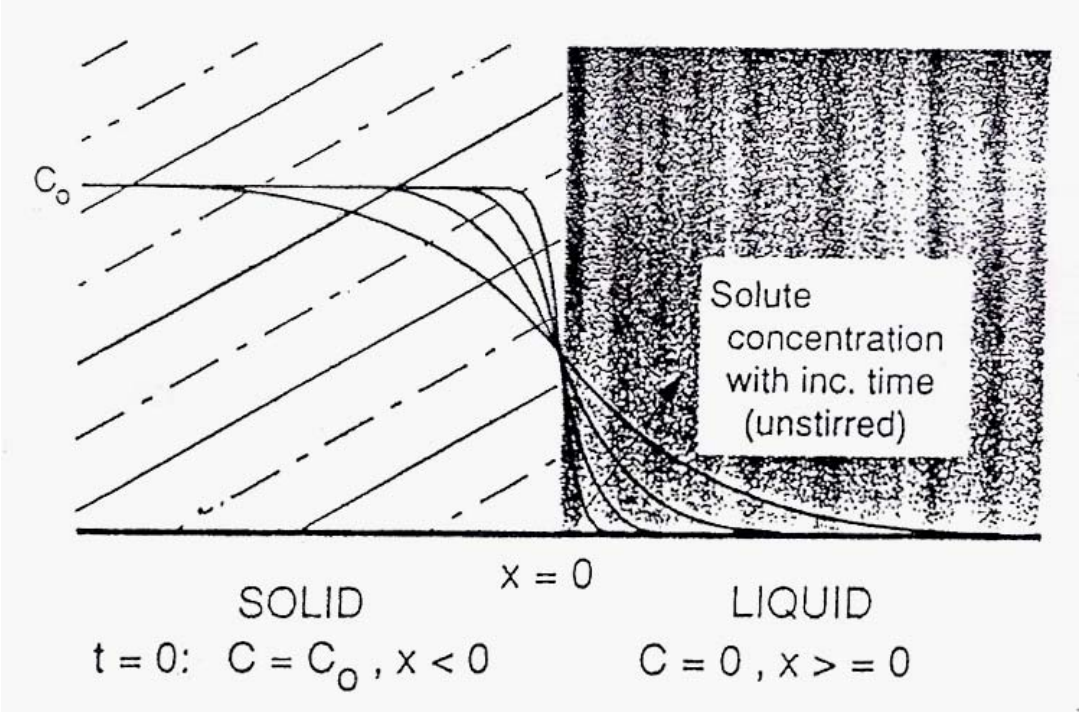
  → removal of diffusing material from the surface at a constant rate

- Solids dissolve in liquids with a **velocity** that is proportional to the difference between the actual and the saturated concentration of solute

- It is closely parallel to the *in vitro* situation of evaporation from a surface → the velocity may be determined by a diffusion mechanism or by what may be termed a spontaneous-escape mechanism

4. Leaching

- The arrangement, initial conditions, and change of concentration of the solute in the solid (biomaterial) phase with time are shown in the following figure:



4. Leaching

In most real situations, there is an additional condition:

- If the fluid medium is in motion but not fully stirred
  - → some rate of transfer must be assumed
  - → The simplest case: transfer rate is proportional to **surface concentration** at any moment
- **Transfer rate** is linearly dependent upon the difference between a surface concentration C_s and bulk concentration C_0:

$$-D\frac{\partial C}{\partial x} = \alpha (C_0 - C_s) \quad at \quad x = 0$$

4. Leaching

- Standard reaction kinetics theory for dissolution of a solid gives equation [5]:

$$C_t = C_\infty \left(1 - e^{-k_r S t / V}\right) \qquad [5]$$

where

C_t = the concentration of dissolved molecules at time t
C_∞ = the saturation concentration of solute molecules
k_r = the rate constant
S = the surface area from which dissolution occurs
V = the volume of solution

4. Leaching

- Equation [5] may be rewritten as equation [6] as:

$$M_t = M_\infty \left(1 - e^{-\alpha t^{\frac{1}{2}}}\right) \qquad [6]$$

where

M'_t = the solute dissolved value at a given value of $t^{1/2}$

M'_∞ = the saturated value of dissolved molecules

4. Leaching

- Equation [5] would be the same form as equation [6] if either k_r or S (or the two in combination) varied as $t^{-1/2}$

→ The result would be that the value of k_rSt would be proportional to $t^{1/2}$:

1. It is plausible that k_r could decrease with time as the setting process continued
2. The change in the real surface area (S) could also decrease with time if asperities were dissolved away

Effects of Swelling and Leaching

5. Effects of Swelling and Leaching

- There are adverse aspects to large deformations that may be caused by swelling and leaching

  → creep stress in the material

  → produce continual deformation and absorption (rather than the attainment of an equilibrium solute concentration)

5. Effects of Swelling and Leaching

1. Swelling

- reduces the elastic limit of a material
  (*i.e.,* the available strain to the elastic limit)
- lead to a mode of failure
  ⇒ static fatigue or 'crazing', especially in *brittle* materials

- Crazing
  – the development of microcracks that merge and can eventually result in fracture
- The principal effect of absorption of low molecular weight species → swell the matrix → moving the crystalline 'islands' further apart → thus weakening the already weak bonds between them

5. Effects of Swelling and Leaching

2. Leaching

- the reverse of swelling -- in real applications there is competition

- usually has a less pronounced effect on properties

- The primary undesirable aspects of unplanned leaching

  → local and systemic biological reactions to the released products

5. Effects of Swelling and Leaching

- Excessive leaching

  - (*e.g.*, intergranular leaching in metals)

  → a reduction in fracture strength

- The defects produced by leaching can coalesce into macroscopic voids

  → a possible significant percentage of the volume of rigid materials

  → elasic modulus ↓

Reference

- 自行編纂

Summary

- Biomaterials
- Biocompatibility
- Biological Environment
- Swelling and Leaching
- Interfacial-Dependent Phenomena in Biomaterials
- The Structure of Solids
- Characterization of Materials