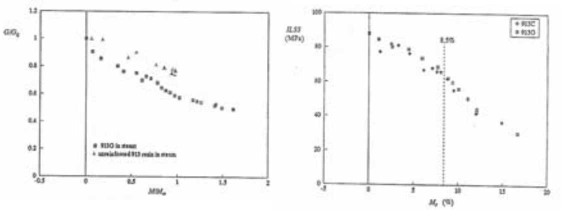
Class 6 & 7: Diffusion in FRP



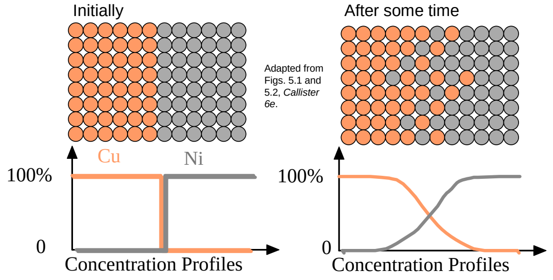
Left: Percent change of shear modulus with percent change in weight due to moisture
Right: ILSS (interlaminar shear strength vs percent moisture content.

R.D. Adams, M.M. Singh, "The Dynamic Properties of Fibre-Reinforced Polymers Exposed to Hot, Wet Conditions" , *Composites Science and Technology,* **56**, 977 (1996)

PRIME Modules
Project-based Resources for Introduction to Materials Engineering

Diffusion describes the mixing of a species into another

Diffusion is the mixing of two species due to a driving force, usually a concentration gradient



Adapted from Figs. 5.1 and 5.2, *Callister 6e.*

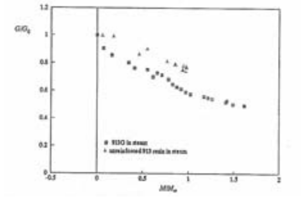
Slide adapted from Callister

Diffusion of water in FRP contributes to degradation of composite over time

Over time, there is a diffusion of water into the polymer matrix of FRP composites.

As the moisture content increases, shear strength decreases

The diffusion of the moisture into the composite is Fickian. This describes a mathematical function for the flux that is very common in materials science.



Percent change of shear modulus with percent change in weight due to moisture

R.D. Adams, M.M. Singh, "The Dynamic Properties of Fibre-Reinforced Polymers Exposed to Hot, Wet Conditions" , *Composites Science and Technology,* **56**, 977 (1996)

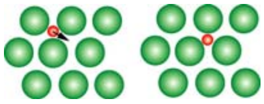
Diffusion in crystal structures occurs via interstitial or vacancy mechanisms.

Atoms can move into a crystal lattice as point defects
•Substitutional/ vacancy mechanism
•Interstitial Mechanism

Atoms can also diffuse along bulk defects such as grain boundaries and surfaces

In polymers, the diffusion mechanism is along the gaps in the polymer structure (space between the chains)

Substitutional/ Vacancy Mechanism



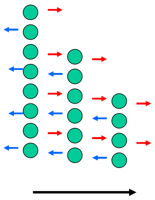
Interstitial Mechanism

Diffusion is a net motion made up of random jumps.

A driving force (such as a concentration gradient) is needed to result in a net flux of atoms in one direction.

This is because all the mechanisms are random (the atom is just as likely to jump in one direction as the other).

A concentration gradient means more atoms are jumping from one side than the other, resulting in a greater net motion.

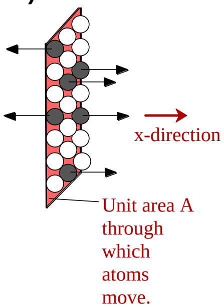


Net Flux, J

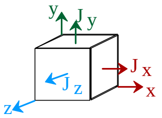
Flux is in units of atoms/ (cm^2 s)

Flux is the motion of atoms crossing a cross sectional area per unit time

$$J = \frac{1}{A}\frac{dM}{dt} \Rightarrow \left[\frac{kg}{m^2 s}\right] \text{ or } \left[\frac{atoms}{m^2 s}\right]$$



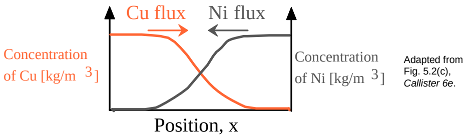
Flux is a directional quantity. In this class we only talk about 1-D, J_x



Slide adapted from Callister

Flux results from the concentration gradient

Concentration Profile, C(x): [kg/m³] or [atoms/m³]



Adapted from Fig. 5.2(c), *Callister 6e.*

- Fick's First Law:

flux in x-dir. [kg/m²-s]

Diffusion coefficient [m²/s]

$$J_x = -D\frac{dC}{dx}$$

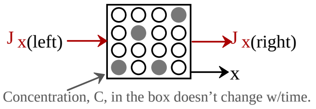
concentration gradient [kg/m⁴]

- The steeper the concentration profile, the greater the flux!

Slide adapted from Callister

In steady state diffusion, there is a constant flux and the concentration profile is constant

In steady state, the concentration profile doesn't change with time. The flux in equals the flux out.



Steady State:

$J_{x(left)} = J_{x(right)}$

Apply Fick's First Law: $J_x = -D\frac{dC}{dx}$

If $J_x)_{left} = J_x)_{right}$, then $\left(\frac{dC}{dx}\right)_{left} = \left(\frac{dC}{dx}\right)_{right}$

Result: the slope, dC/dx, must be constant (i.e., slope doesn't vary with position)!

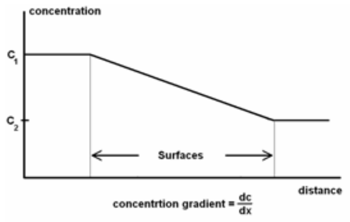
Slide adapted from Callister

In summary, in steady state diffusion the profile is constant with time.

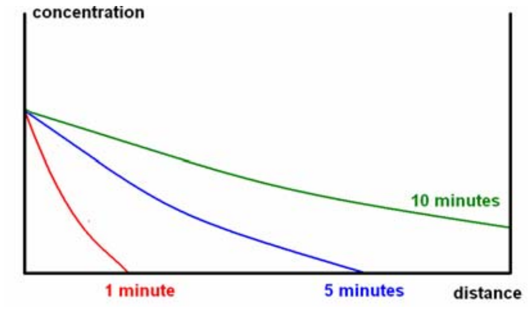
In Steady-state J does not change with time.

dc/dx does not change with time.

Concentration at a given point does not change with time.



In non-steady state diffusion, the concentraino changes with time.

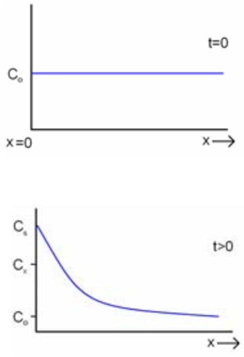


An FRP has non-steady-state diffusion of water

In an FRP, the amount of water in the polymer matrix builds up over time due to exposure to moisture in the environment.

The concentration of water in the polymer is always increasing (and the mechanical properties go down).

To describe this absorption of water over time, a mathematical model for non-steady-state diffusion is needed: Fick's second law



In non-steady state diffusion, the flux in and out are NOT equal

In non steady state diffusion, the flux in and out are not equal.

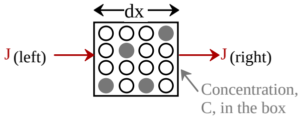
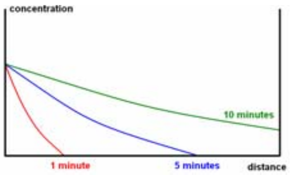


Figure from Callister

This results in accumulation or depletion in the sample.

The concentration profile changes with time.



Fick's Second Law describes non-steady state diffusion

The accumulation/ depletion is dC/dt

Fick's 1st Law

$$\boxed{\frac{J(\text{right}) - J(\text{left})}{dx}} = -\frac{dC}{dt} \qquad J = -D\frac{dC}{dx} \quad \text{or}$$

$$\boxed{\frac{dJ}{dx}} = -\frac{dC}{dt} \qquad \boxed{\frac{dJ}{dx}} = -D\frac{d^2C}{dx^2}$$

(if D does not vary with x)

equate

This gives Fick's Second Law

$$\boxed{\frac{dC}{dt} = D\frac{d^2C}{dx^2}}$$

Slide Adapted from Callister

The flux increases with temperature because D increases with temperature

Remember that the diffusion coefficient increase with temperature based on the Arrenhius equation

$$D = D_o e^{\frac{-Q_D}{RT}}$$

Fick's 2nd Law is a complex second order differential equation

Fick's second law is a complex, 2nd order partial differential equation.

To solve it exactly requires numerical simulation.

It can be solved analytically (with a mathematical equation) if assumptions are made.

The assumptions are known as boundary conditions.

There are many solutions to Fick's second law that apply for a specific set of boundary conditions

$$\boxed{\frac{dC}{dt} = D\frac{d^2C}{dx^2}}$$

An erf solution to Fick's 2nd Law can model diffusion in an FRP

To find an analytical solution to Fick's 2nd Law relative to FRPs, we assume:

The moisture in the environment maintains the water concentration at the polymer surface at the solubility limit (C_s)

The FRP is infinitely long relative to the diffusion (water doesn't build up at the back surface).

$$L > 10\sqrt{Dt}$$

Concentration of water at depth x

Initial concentration of water

$$\frac{C_x - C_o}{C_s - C_o} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

Surface concentration of water

Error function

The math can be simplified if you are just altering process conditions.

Solution of the problem can be simplified if you want the same concentration, but want to switch conditions (different time, different depth, etc.):

$$\frac{x^2}{Dt} = \text{constant}$$

What equations are needed to solve these examples?

Given constant flux, D, and the concentration at the surface, what is the concentration at some depth?

→ **Fick's 1st Law**

You are given time, temperature, concentration, and depth. If I change the treatment time, at what depth do I get the same concentration?

$$\rightarrow \frac{x^2}{Dt} = \text{constant}$$

An initial uniform concentration is exposed to a gas. What is the concentration at a certain depth after a certain time?

→ **Fick's 2nd Law Solution**

Aging of FRP Composites, Revisited

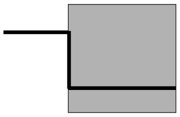
Aging: The process of degradation of properties over TIME.

How much time does it normally take for a material to age in the field?

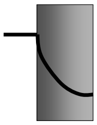
With proper maintenance and no “random events”, aging can take lifetimes.

So how do we measure the aging life of a material?

We monitor the diffusion rate of water in the polymer and solve Fick’s Second Law.



$$\frac{\partial C}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$



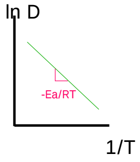
Polymer structure changes at high temperatures (glass transition temperature)

The only complication in understanding aging of FRP is that the polymer structure changes with temperature.

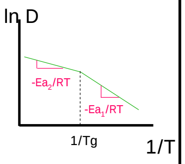
At high temperatures, polymers go through a glass transition. They lose there semi-crystalline nature, becoming more amorphous.

Diffusion in these structures occurs at a different rate than in the semi-crystalline structures

Single diffusion mechanism.

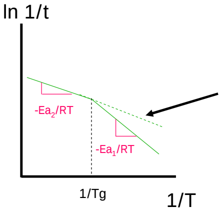


Change in mechanism at Tg.



If the change in mechanism is not factored in, the lifetime will be underestimated.

The lifetime at low temperatures (below Tg) would be less than predicted by extrapolating higher temperature models



Lifetime is underestimated!

In summary, diffusion of moisture in an FRP can be modeled with Fick’s 2nd Law

Non steady state diffusion results in an accumulation or depletion in the sample.

This change in concentration is modeled with Fick’s 2nd Law

The erf approximation of Fick’s 2nd Law can be used to model the diffusion of water in an FRP

$$\frac{c_x - c_o}{c_s - c_o} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)$$