Environmental Quality: Monitoring and Analysis
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Lecture – 54
Application of Interphase Mass Transfer

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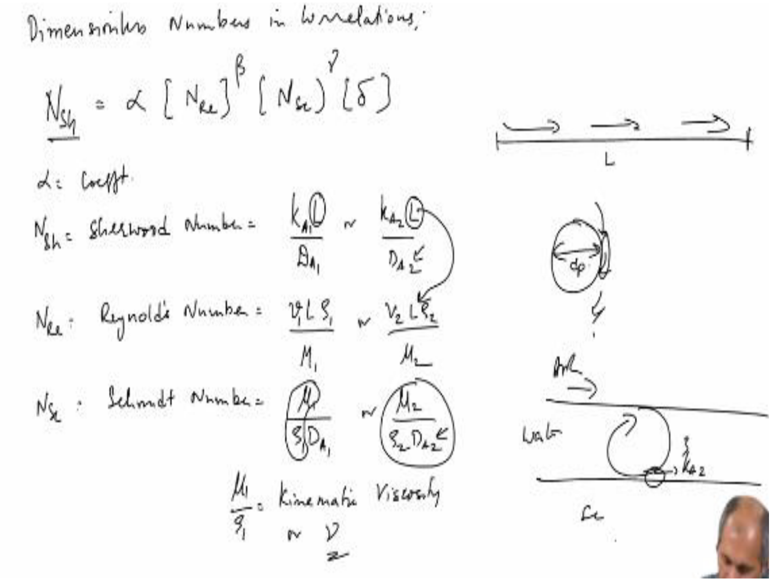

Dimensionless Numbers in correlations:

$N_{Sh} = \alpha [N_{Re}]^{\beta} [N_{Sc}]^{\gamma} [\delta]$

α: coeff

N_{Sh} = Sherwood Number = $\frac{k_{A_1} L}{D_{A_1}} \sim \frac{k_{A_2} L}{D_{A_2}}$

N_{Re}: Reynold's Number = $\frac{v_1 L \rho_1}{\mu_1} \sim \frac{v_2 L \rho_2}{\mu_2}$

N_{Sc}: Schmidt Number = $\frac{\mu_1}{\rho_1 D_{A_1}} \sim \frac{\mu_2}{\rho_2 D_{A_2}}$

$\frac{\mu_1}{\rho_1}$ = Kinematic Viscosity $\sim \nu$

A good correlation is usually a dimensionless in correlations. This has a lot of advantages in terms of unit that we use. So, normally for mass transfer coefficients, the nomenclature is in form of Sherwood number NSh equals, so in this correlation for example we have NSh equals

$$N_{Sh} = \propto [N_{Re}]^{\beta} [N_{Se}]^{\gamma} [\delta]$$

Nsh is called as a Sherwood number and this is defined as a mass transfer coefficient multiplied by some dimensional parameters.

$$N_{Sh} = \frac{k_{A1} L}{D_{A1}} \sim \frac{k_{A2} L}{D_{A2}}$$

So, it is usually L or D or whatever. So, in this case it could be L divided by the diffusion coefficient. I am not putting numbers there. So, this kA can be 1 or 2. So, depending on what goes D_A, if it is 1 here, this will also be 1. If it is 2 here, it will also be 2. These two are in the same phase, you cannot write kA1 and DA2 because they are related, so kA depends on the DA, so wherever you are doing this. The Reynolds number (N_{Re}), which is the other.

So basically a Sherwood number is the ratio of the convective mass transport to the diffusion mass transport, so it gives you the ratio of that, the magnitudes of that. Reynolds number here again is defined as a

$$N_{Re} = \frac{vL\rho}{\mu}$$

So here again depending on this, it could be

$$\frac{v_1 L\rho_1}{\mu_1} \sim \frac{v_2 L\rho_2}{\mu_2}$$

this is a medium. So this is inertial force, inertia as we know is function of the velocity the inertia and there is a density there which is mass volume. So inertial force divided by the viscous forces on this, the denominator is viscosity.

So, the Reynolds number essentially if the velocity is high, Reynolds number is usually high. So, that is the only thing that is changing dynamically in the system. So, you can have something at higher Reynolds number and then there is a third quantity called as Schmidt number (N_{Sc}) which is

$$N_{Sc} = \frac{\mu}{\rho D_A}$$

So, it is either

$$\frac{\mu_1}{\rho_1 D_{A1}} \sim \frac{\mu_2}{\rho_2 D_{A2}}$$

$\frac{\mu}{\rho}$ is called as the kinematic viscosity. So, this gives you some idea. So, if this exists in the correlation, this has this factor D_{A2} which will account for now the particular compound that is there, it is now scaled to that particular compound. There is also D_{A2} in the Sherwood number. So, it will also add to that, scaling of this particular compound. So, a good correlation takes into account everything, all factors are all there which means somebody has taken the pains to do the experiment for a wide set of compounds diffusion coefficient and then for a wide set of velocities and geometry, but this still geometry means what we are saying is this L here, the length scale, some length scale.

So, in this case, this L is the same L that is there in your Reynolds number. So, if you are talking about river, the interface of river, we are talking about the length of the water on which there is contact, the fluid is in contact with this length. If your Reynolds number is defined as this length parameter, the Sherwood number also has that same thing there. Sometimes, if there is mass transfer on the surface of a particle, Reynolds number is defined as in terms of the diameter of the particle and then there is the mass transfer on the surface of this particle is now defined with the same diameter.

So, wherever you will see some correlations sometimes, where we want to look at mass transfer between the suspended solid particle and water, in those conditions Reynolds number will be different, therefore Sherwood number also will be different. So, you have to watch out for the definitions. You cannot use length scale of one this thing and in Reynolds number and Sherwood number it will not match, it will be incorrect, you have to be careful about that.

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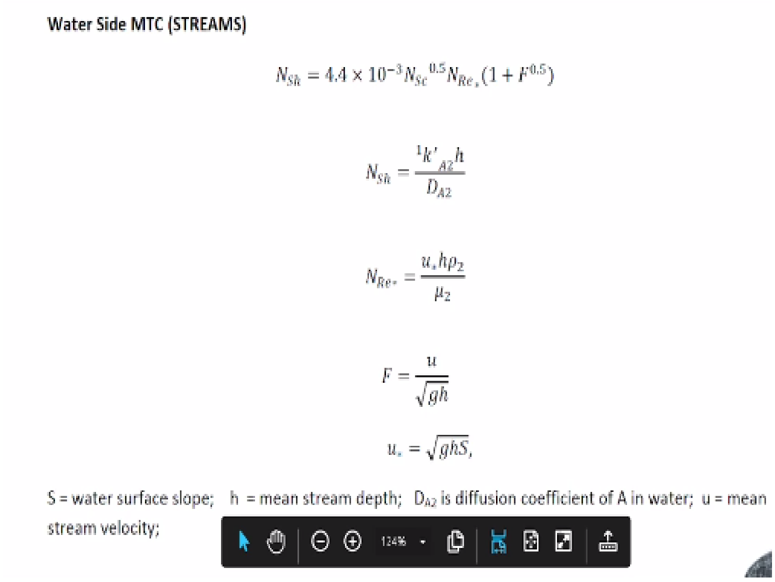

Water Side MTC (STREAMS)

$$N_{Sh} = 4.4 \times 10^{-3} N_{Sc}^{\ 0.5} N_{Re_*} (1 + F^{0.5})$$

$$N_{Sh} = \frac{{}^{1}k'_{A2} h}{D_{A2}}$$

$$N_{Re*} = \frac{u_* h \rho_2}{\mu_2}$$

$$F = \frac{u}{\sqrt{gh}}$$

$$u_* = \sqrt{ghS},$$

S = water surface slope; h = mean stream depth; D_{A2} is diffusion coefficient of A in water; u = mean stream velocity;

So, in this correlation, we have now different things. So they have given us something, so there is the parameter called F, F is defined as $\frac{U}{\sqrt{gh}}$ and then there is a term called u star, u star is defined as $\sqrt{ghS}$ and h is the mean stream depth, D_{A2} is the diffusion coefficient, u is the mean stream velocity and so on. So they have defined everything and you have to follow that quite simply.

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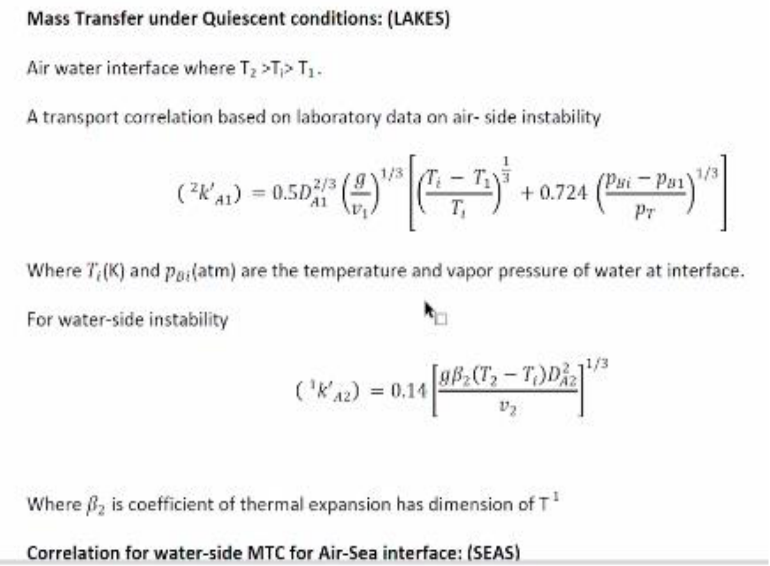

Mass Transfer under Quiescent conditions: (LAKES)

Air water interface where $T_2 > T_i > T_1$.

A transport correlation based on laboratory data on air- side instability

$$({}^{2}k'_{A1}) = 0.5D_{A1}^{2/3}\left(\frac{g}{v_1}\right)^{1/3}\left[\left(\frac{T_i - T_1}{T_i}\right)^{\frac{1}{3}} + 0.724\left(\frac{p_{Bi} - p_{B1}}{p_T}\right)^{1/3}\right]$$

Where T_i(K) and p_{Bi}(atm) are the temperature and vapor pressure of water at interface.

For water-side instability

$$({}^{1}k'_{A2}) = 0.14\left[\frac{g\beta_2(T_2 - T_i)D_{A2}^2}{v_2}\right]^{1/3}$$

Where β_2 is coefficient of thermal expansion has dimension of T^{1}

Correlation for water-side MTC for Air-Sea interface: (SEAS)

There is another coefficient people have measured mass transfer coefficient under quiescent conditions for lakes. Now when you have quiescent conditions for lakes, the only convection that is now is because of temperature, there is temperature difference.

$$({}^{2}k'_{A1}) = 0.5D_{A1}^{2/3}\left(\frac{g}{v_1}\right)^{1/3}\left[\left(\frac{T_i - T_1}{T_i}\right)^{\frac{1}{3}} + 0.724\left(\frac{p_{Bi} - p_{B1}}{p_T}\right)^{1/3}\right]$$

So, you see that Ti and T1, there is a temperature gradient that exists in the system where Ti, the temperature at the interface and air water interface where Ti is greater than T1. There is a gradient and this is the one which is causing. So the water is at higher temperature than the interface and air is at a higher temperature at this thing. So, therefore, there may be some differences based on that. So, density difference is there because the gradient is this direction that causes movement. So, for water side and air side, there is given this correlation in terms of the coefficient of expansion and all that.

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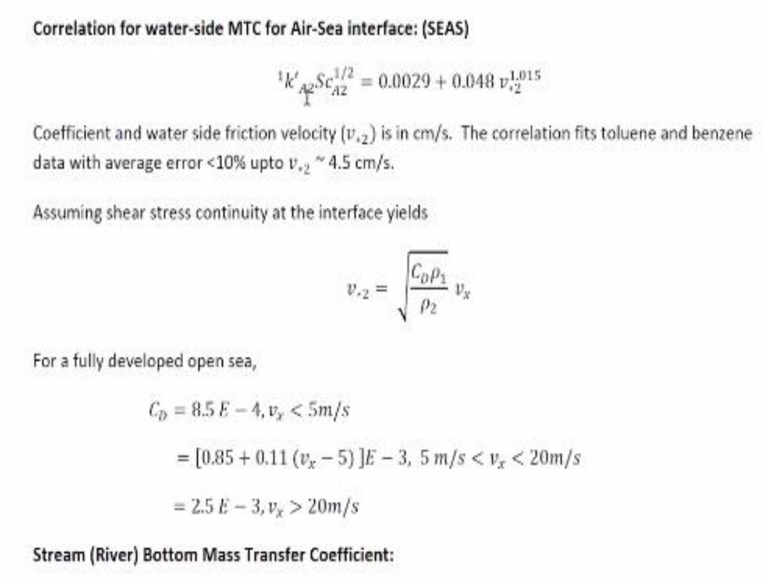

Correlation for water-side MTC for Air-Sea interface: (SEAS)

$${}^1k'_{A2}Sc_{A2}^{1/2} = 0.0029 + 0.048\, v_{*2}^{1.015}$$

Coefficient and water side friction velocity (v_{*2}) is in cm/s. The correlation fits toluene and benzene data with average error <10% upto v_{*2} ~ 4.5 cm/s.

Assuming shear stress continuity at the interface yields

$$v_{*2} = \sqrt{\frac{C_D \rho_1}{\rho_2}}\, v_x$$

For a fully developed open sea,

$$C_D = 8.5\,E-4, v_x < 5m/s$$

$$= [0.85 + 0.11\,(v_x - 5)\,]E - 3,\ 5\,m/s < v_x < 20m/s$$

$$= 2.5\,E-3, v_x > 20m/s$$

Stream (River) Bottom Mass Transfer Coefficient:

Correlation for water-side mass transfer coefficient at air-sea interface. Sea is huge, sea is different, sea is not like a lake okay, so very difficult to do experiments in sea and one sea measurements may not be the same as a different sea measurement, but if there is a reason for you to use a sea correlation, there are correlations that are there. So, there is a handbook of environmental mass transport in which there are different sections where these correlations are given, people have measured these correlations.

Whatever correlation is there, you have to find out how has this experiment been done, so that you can see if it fits your requirement okay. This is for mass transfer coefficient water-side mass transfer coefficient, which is ${}^1K_{A2}$.

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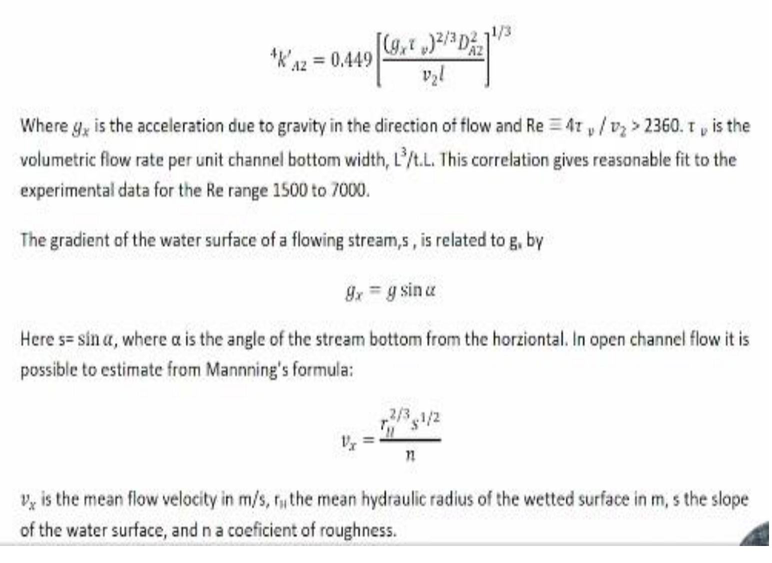

$${}^4k'_{A2} = 0.449\left[\frac{(g_x \tau_v)^{2/3} D_{A2}^2}{v_2 l}\right]^{1/3}$$

Where g_x is the acceleration due to gravity in the direction of flow and Re $\equiv 4\tau_v / v_2 > 2360$. τ_v is the volumetric flow rate per unit channel bottom width, $L^3/t.L$. This correlation gives reasonable fit to the experimental data for the Re range 1500 to 7000.

The gradient of the water surface of a flowing stream,s , is related to g_x by

$$g_x = g \sin\alpha$$

Here s= $\sin\alpha$, where α is the angle of the stream bottom from the horziontal. In open channel flow it is possible to estimate from Mannning's formula:

$$v_x = \frac{r_H^{2/3} s^{1/2}}{n}$$

v_x is the mean flow velocity in m/s, r_H the mean hydraulic radius of the wetted surface in m, s the slope of the water surface, and n a coeficient of roughness.

Stream river bottom mass transfer coefficient. Experimental measurement of the rate of solutions. Here again is mass transfer coefficient at the bottom of the lake. So, this is the sediment. This is the coefficient we are talking about at the beginning of this class, so we will look at $^4K_{A2}$ which means that it is in contact with whatever is there on the sediment bed but it is in water you have to look at that and then there is velocity.

So you have to be careful, I mean this v2 is velocity here, there it is ν (nu), so it is different things, viscosity, velocity and that, you have to make sure the signs are all correct.

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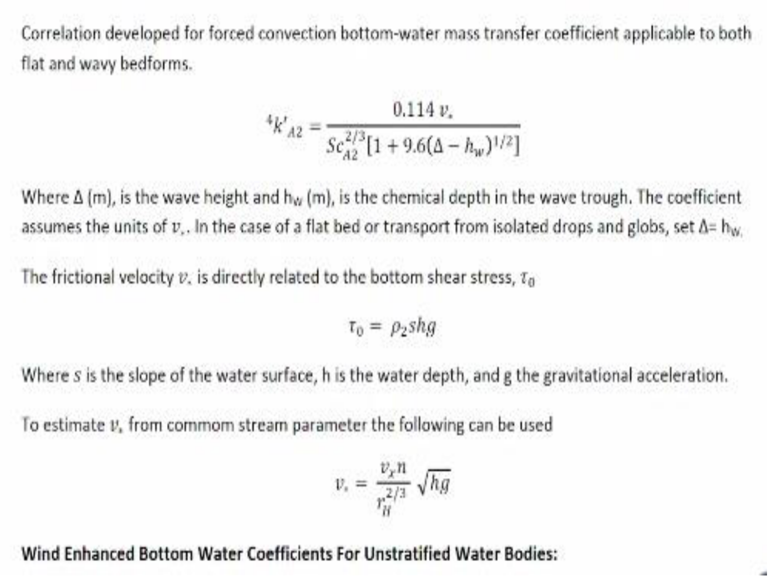

Correlation developed for forced convection bottom-water mass transfer coefficient applicable to both flat and wavy bedforms.

$$^4k'_{A2} = \frac{0.114\, v_*}{Sc_{A2}^{2/3}[1 + 9.6(\Delta - h_w)^{1/2}]}$$

Where Δ (m), is the wave height and h_w (m), is the chemical depth in the wave trough. The coefficient assumes the units of v_*. In the case of a flat bed or transport from isolated drops and globs, set Δ= h_w.

The frictional velocity v_* is directly related to the bottom shear stress, τ_0

$$\tau_0 = \rho_2 shg$$

Where s is the slope of the water surface, h is the water depth, and g the gravitational acceleration.

To estimate v_* from commom stream parameter the following can be used

$$v_* = \frac{v_x n}{r_H^{2/3}} \sqrt{hg}$$

Wind Enhanced Bottom Water Coefficients For Unstratified Water Bodies:

There are other correlations that are developed for similar kind of systems.

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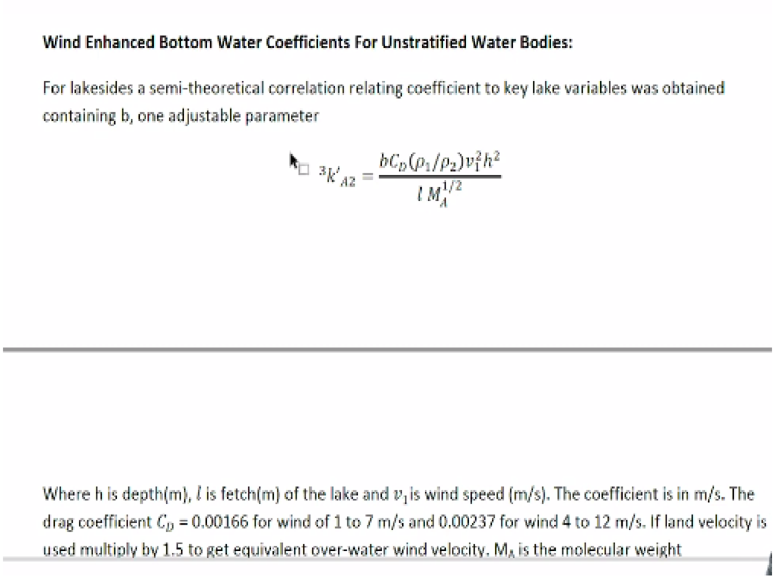

Wind Enhanced Bottom Water Coefficients For Unstratified Water Bodies:

For lakesides a semi-theoretical correlation relating coefficient to key lake variables was obtained containing b, one adjustable parameter

$$^3k'_{A2} = \frac{bC_D(\rho_1/\rho_2)v_1^2h^2}{l\, M_A^{1/2}}$$

Where h is depth(m), l is fetch(m) of the lake and v_1 is wind speed (m/s). The coefficient is in m/s. The drag coefficient C_D = 0.00166 for wind of 1 to 7 m/s and 0.00237 for wind 4 to 12 m/s. If land velocity is used multiply by 1.5 to get equivalent over-water wind velocity. M_A is the molecular weight

Then we have wind induced water coefficients for unstratified water bodies which means there are no temperature gradients, but it is wind induced turbulence. So, this is for if you notice it is ${}^3K_{A2}$, which interface is this? It is a sediment water interface. So, this is only applicable where it is wind-induced sediment water interface because there is no flow, unstratified water bodies, which you will see that there is one parameter that is there in this is the velocity of air. The velocity of air is causing enough churning, strong enough to cause large scale circulations that it is affecting the ${}^3K_{A2}$ at this interface. It is causing a turbulence there and that is the correlation, so it is a correlation So, you can write whatever you want, however you want you can develop this correlation. It has to be based in some physical observations of that system.

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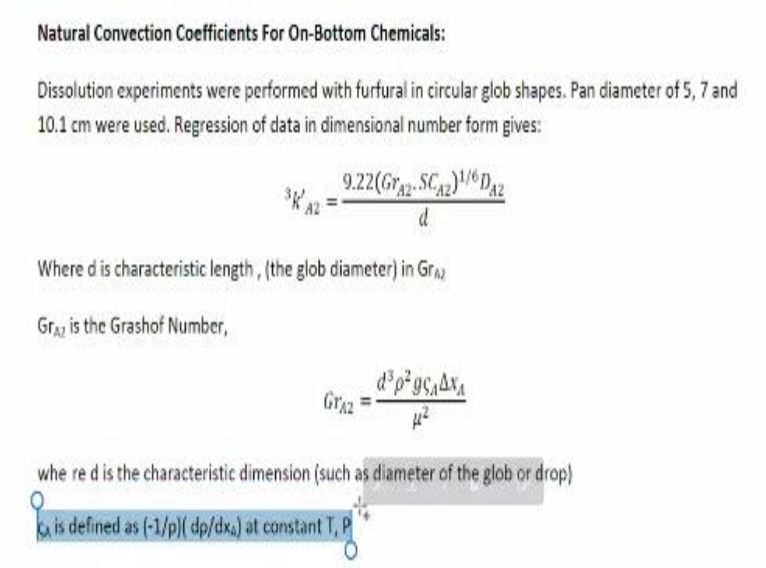

Natural Convection Coefficients For On-Bottom Chemicals:

Dissolution experiments were performed with furfural in circular glob shapes. Pan diameter of 5, 7 and 10.1 cm were used. Regression of data in dimensional number form gives:

$$ {}^3K'_{A2} = \frac{9.22(Gr_{A2}.SC_{A2})^{1/6}D_{A2}}{d} $$

Where d is characteristic length , (the glob diameter) in Gr_{A2}

Gr_{A2} is the Grashof Number,

$$ Gr_{A2} = \frac{d^3\rho^2 g\varsigma_A \Delta x_A}{\mu^2} $$

whe re d is the characteristic dimension (such as diameter of the glob or drop)

ς_A is defined as (-1/p)(dp/dx$_A$) at constant T, P

We have natural convection which is again a density difference, density driven thing okay. So, this density difference is defined as this bottom here.

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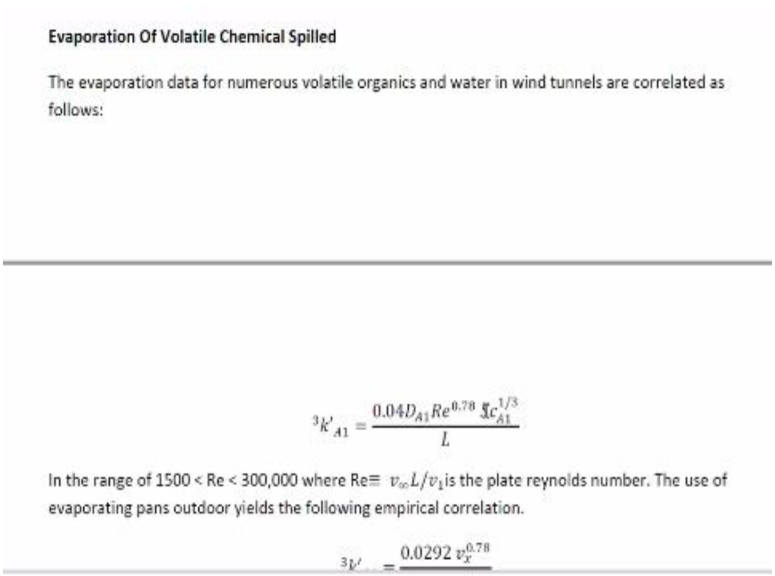

Evaporation Of Volatile Chemical Spilled

The evaporation data for numerous volatile organics and water in wind tunnels are correlated as follows:

$${}^{3}k'_{A1} = \frac{0.04 D_{A1} Re^{0.78}\, Sc_{A1}^{1/3}}{L}$$

In the range of 1500 < Re < 300,000 where Re≡ $v_\infty L/v_1$ is the plate reynolds number. The use of evaporating pans outdoor yields the following empirical correlation.

$${}^{3}k' = \frac{0.0292\, v_x^{0.78}}{}$$

We have evaporation of volatile chemical spills, which means it is ${}^{3}K_{A1}$. ${}^{3}K_{A1}$ will be the air and some solid interface, air and land, air and soil, something like that on the air side and so you see again that correlation has Schmidt number, it has Reynolds number, it has diffusion coefficient, so it is like a Schmidt number which is all rearranged here, but they have conditions, the range of Reynolds number is between 1500 and 300,000 and definition of Reynolds number is there and so on.

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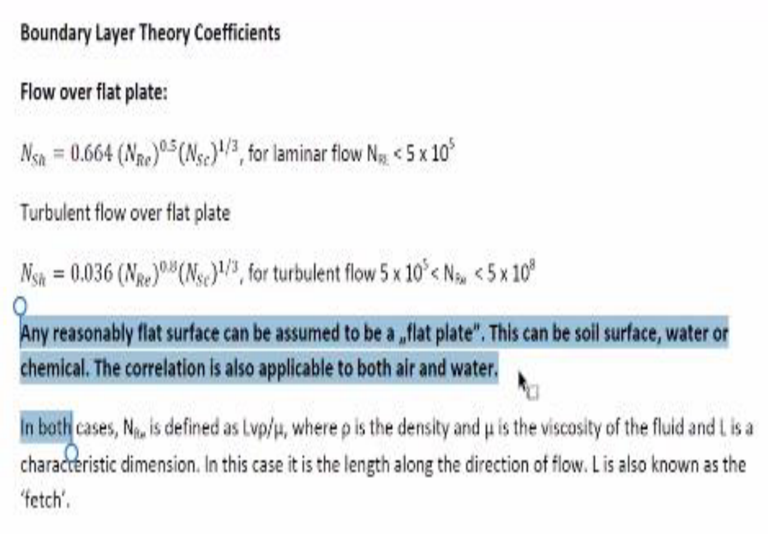

Boundary Layer Theory Coefficients

Flow over flat plate:

$N_{Sh} = 0.664\,(N_{Re})^{0.5}(N_{Sc})^{1/3}$, for laminar flow $N_{RL} < 5 \times 10^5$

Turbulent flow over flat plate

$N_{Sh} = 0.036\,(N_{Re})^{0.8}(N_{Sc})^{1/3}$, for turbulent flow $5 \times 10^5 < N_{Re} < 5 \times 10^8$

Any reasonably flat surface can be assumed to be a „flat plate". This can be soil surface, water or chemical. The correlation is also applicable to both air and water.

In both cases, N_{Re} is defined as Lvρ/μ, where ρ is the density and μ is the viscosity of the fluid and L is a characteristic dimension. In this case it is the length along the direction of flow. L is also known as the 'fetch'.

In addition to this, there are a large number of theories for mass transfer. One of them is called as a boundary layer theory for flat plate, for turbulent and laminar flow. So, for laminar flow, this is the laminar flow boundary layer theory, this Sherwood number is 0.664, Reynolds number into this, for Reynolds number less than 5 10 raise to 5. So, this is a very useful correlation, this is very well tested, it is developed derived from first principles which means it is from the Navier-Stokes equation you can derive this for flat plate, and I have written this here. Any reasonably flat surface can be assumed to be this.

Now, it is your discussion. So, reasonably flat plate means the plate is rigid, the surface is rigid. So, I can use this for air land, air water I have to be a little careful because water is not exactly rigid, water moves, but if I have nothing else to go for water, I can use this, for you have to take it with a bit of this thing. So, in all these correlations, there is a length scale for rivers and lakes and all that, this length scale is known as fetch, if it is the length along a river.

For example, these correlations is in this case the Sherwood number has a length scale, N_{Re} is defined as $\frac{vL\rho}{\mu}$ where L is the characteristic dimension, the length in the direction of flow, air or water flow. So you can apply this both, you can also apply this to water, but it is more applicable to air across on surfaces of solid or surfaces of water. It is less applicable for water on sediment because there is a finite layer, it is not flat plate.

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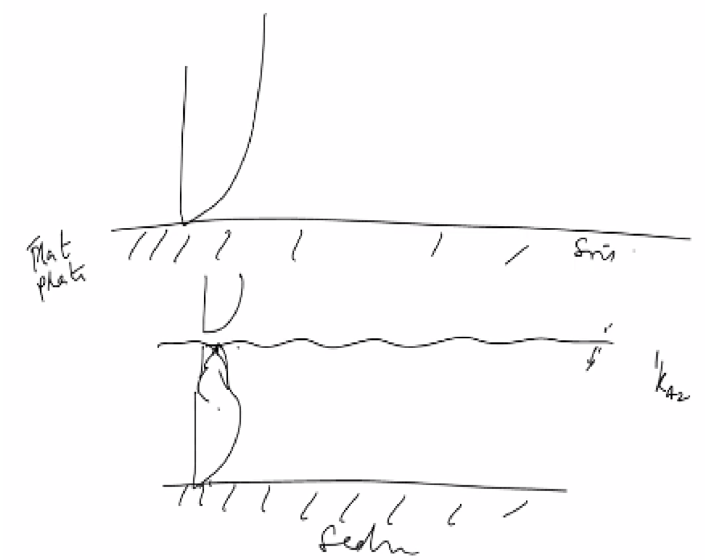

The basic assumption of a flat plate correlation is that it is flat and the boundary layer is kind of infinitely extending into atmosphere, there is no. This is flat plate, but if I have water, my surface, this is fine, this bottom surface is sediment and this is soil. If I have water here, I have another surface here. So, there may be a boundary layer here and then there may also be a boundary layer on this side, which I do not know exactly. This is not the same as this, but it may not extend fully, this boundary layer maybe, it is not a free surface.

It is not a free medium. There is a boundary here. So, the correlation may not exactly be the same flat plate, but if you do not have anything else you can use this, but fortunately there are correlations for stream, waterside coefficients, so you can use that. The only problem, only place where you do not have enough correlations is the waterside coefficients for streams in the air water interface. So, there are very few correlations that you will see for this KA21 for streams. So, then you have to use whatever is available okay.

Especially like the ones we saw the first beginning of this class, it is a bad correlation, but that is the only thing available you just have to use it, there is nothing else you can do.

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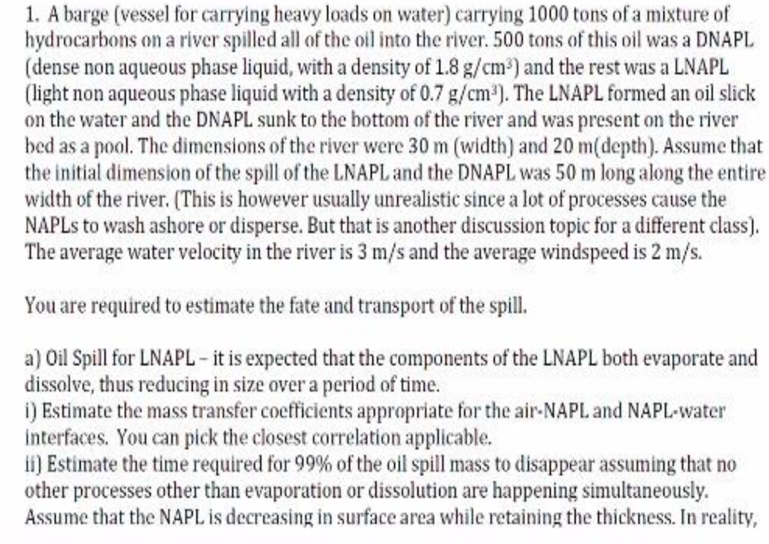

1. A barge (vessel for carrying heavy loads on water) carrying 1000 tons of a mixture of hydrocarbons on a river spilled all of the oil into the river. 500 tons of this oil was a DNAPL (dense non aqueous phase liquid, with a density of 1.8 g/cm^3) and the rest was a LNAPL (light non aqueous phase liquid with a density of 0.7 g/cm^3). The LNAPL formed an oil slick on the water and the DNAPL sunk to the bottom of the river and was present on the river bed as a pool. The dimensions of the river were 30 m (width) and 20 m(depth). Assume that the initial dimension of the spill of the LNAPL and the DNAPL was 50 m long along the entire width of the river. (This is however usually unrealistic since a lot of processes cause the NAPLs to wash ashore or disperse. But that is another discussion topic for a different class). The average water velocity in the river is 3 m/s and the average windspeed is 2 m/s.

You are required to estimate the fate and transport of the spill.

a) Oil Spill for LNAPL – it is expected that the components of the LNAPL both evaporate and dissolve, thus reducing in size over a period of time.
i) Estimate the mass transfer coefficients appropriate for the air-NAPL and NAPL-water interfaces. You can pick the closest correlation applicable.
ii) Estimate the time required for 99% of the oil spill mass to disappear assuming that no other processes other than evaporation or dissolution are happening simultaneously. Assume that the NAPL is decreasing in surface area while retaining the thickness. In reality,

So, there are a lot of problems, there are a couple of problems that I have put in a tutorial. So, you can have any kind of scenario. So I will say there’s a barge of vessel, you have lots of problems, scenarios, case studies in this okay. There is barge of vessel carrying heavy loads on water at 1000 tons of a mixture of hydrocarbons, 500 tons of this oil is a dense NAPL, yeah and the rest is a light NAPL and it spills okay. What will happen? So it is quickly, this problem is very easily found.

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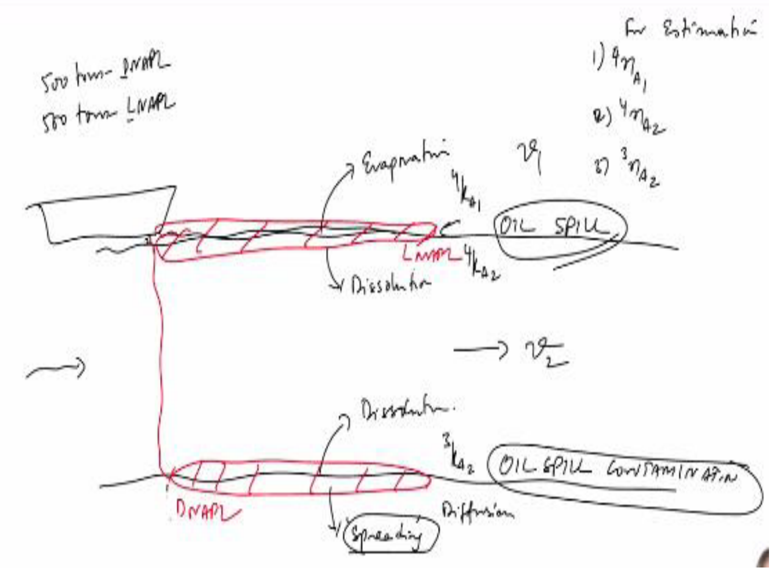

There is a barge. There is sediment and what is the system I am talking about here, it is a river. So it is a river, it is flowing and it spills it says 500 tons DNAPL and 500 tons LNAPL, dense and light, which means when it spills out, one portion of it is going to sit here. There is one large portion that is going to sit on the surface of water and there is another large portion that is going to go down and sit on the bottom of the river. So, this is the DNAPL, this is the LNAPL. Now in this problem, what will be your risk assessment?

What will be the risk assessment here, several things. One, there is processes that are happening are evaporation, dissolution. Here also something is happening, what is happening here? This is also spreading into the sediment and this is a process we will discuss now after finishing this set of examples. This is also spreading here inside, we will call it a spreading for the time being, it is contamination spreading downwards, so it is going below. So, all these processes.

So you have several interfaces at play here. One is $^4K_{A1}$, this is $^4K_{A2}$, this is $^3K_{A2}$, this is something else, there is no convection on this side, it is diffusion-based process. So, this is mostly diffusion inside the sediment. There is no mixing here. There is no convective force at all, so it has to be diffusion based, yeah. So, there is a velocity of the water, there is velocity of air, all these things come into play, yeah. So, I can make this problem as complicated as I want in terms of what I am looking for.

So, I can quickly calculate what is the steady state things I can calculate. I can calculate $^4n_{A1}$, I can calculate $^4n_{A2}$, I can calculate $^3n_{A2}$, these are the 3 steady state fluxes I can calculate. What we mean by steady state fluxes, I am assuming that the concentrations are all fairly constant during that period of calculation. If I know that they are changing, I cannot use steady state calculation, I have to use an unsteady state balance, that will change depending on what is the system I am taking and the time period and initial conditions and all that.

So, you have to go back to the mass balance and reapply, redo your problem. So, for the purposes of this class, we will not go there, at least, unless we have some more time. We will just look at this as the main this thing. So, this is very common. This is an oil spill on a surface. This is an oil spill contamination of sediments. What we call as oil spill is, oil is a very generic term, oil can be anything. It is a mixture of hydrocarbon, paraffins, naphthalene, anything, all kinds of petrochemicals.

Anything is a chemical spill for all this thing, but a lot of material that is transported on water is usually oil, so that is why generic term given for oil spills and this also again undergoes other processes. So, as we looked at the oil spill, on the surface, for example, this one can undergo spreading, it can undergo breakage dispersion, it can undergo a dispersion means one large spill may become several small spills and then it will carry forward.

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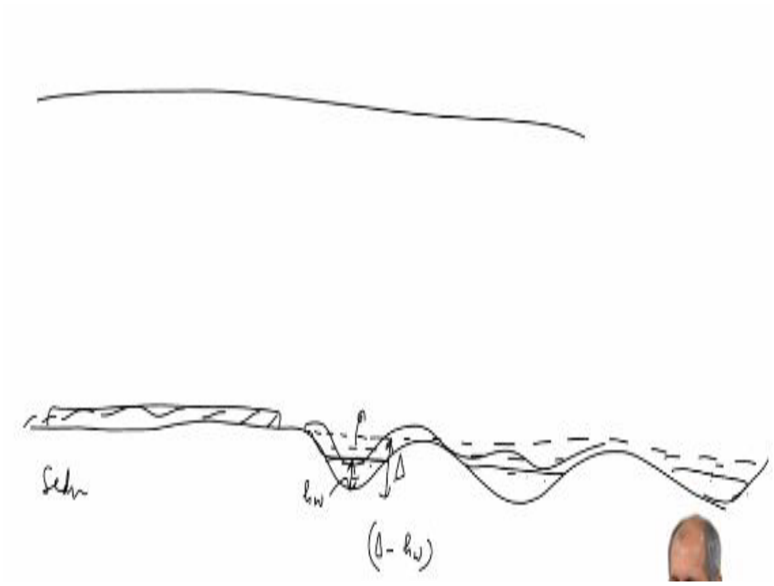

So, in the sediment side here, the oil spill can manifest itself as several this thing. So, it can appear depending on the bed, the sediment if it is smooth, oil will just sit on the surface of it like this right, but very often the oil spill is not very smooth. It is in the form of some waves you can see. So, in this case if you have this kind of waves, what will happen is, so if I exaggerate these waves and these things, it can fill up, the chemical can fill up the place here.

So, this looks like a flat surface, but, as dissolution occurs and depending on the amount of this thing, the oil can also, the chemical can also occupy something like this. So, people have developed correlations for this. So, one of the correlations that you see here in terms of the waterside this thing is this one, so this correlation here $^4K_{A2}$, there is a term here it says delta minus hw, so delta is the wave height, if this accounts for the wave, there is no wave.

So, the wave height is delta minus hw is the chemical depth in the wave trough, so wave height. So what it says is, this is delta and this is hw. So, the delta minus hw is a factor in your thing. So, if delta equals hw, this will become 0, which means that then this entire thing will go away only KA2 by 0.114 v star by SA2 stands, but if there is a if this is smaller, which means that the delta is bigger than hw, means there is a small pool of liquid here, then it will influence the mass transfer coefficient okay.

Because the mass transfer coefficient, now it has to come through, the liquid has to come through, the structure of the liquid is not the same anymore. The flow will change because it has to go through the wavy this thing okay and so on. So, there are examples of how people try to calculate the mass transfer coefficient through correlations and apply it. So, my suggestion to you is to quickly like the dispersion thing this will be there, we will go through these again later when we finish up the complete discussion of this or you can start looking at some of the cases here, yeah.

So, very quickly identify many problems that you can have in environmental this thing and see which is the appropriate mass transfer correlation in terms of nomenclature that you would use and if there are any special conditions along that.

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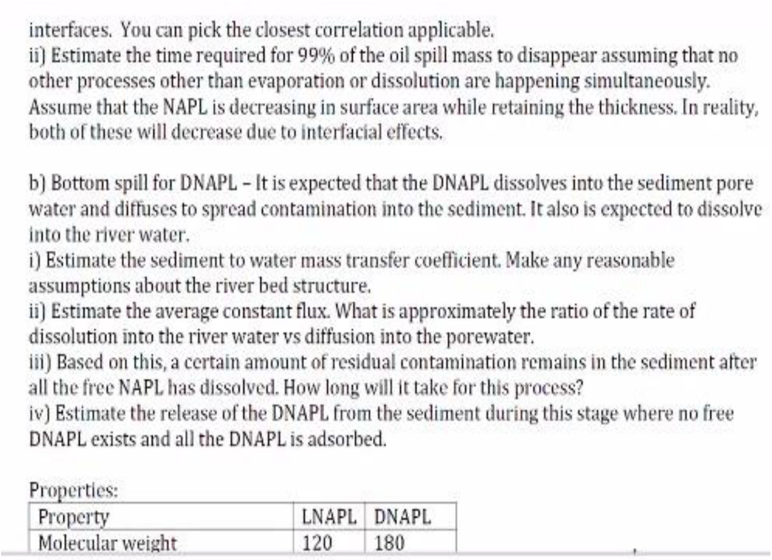

interfaces. You can pick the closest correlation applicable.
ii) Estimate the time required for 99% of the oil spill mass to disappear assuming that no other processes other than evaporation or dissolution are happening simultaneously. Assume that the NAPL is decreasing in surface area while retaining the thickness. In reality, both of these will decrease due to interfacial effects.

b) Bottom spill for DNAPL – It is expected that the DNAPL dissolves into the sediment pore water and diffuses to spread contamination into the sediment. It also is expected to dissolve into the river water.
i) Estimate the sediment to water mass transfer coefficient. Make any reasonable assumptions about the river bed structure.
ii) Estimate the average constant flux. What is approximately the ratio of the rate of dissolution into the river water vs diffusion into the porewater.
iii) Based on this, a certain amount of residual contamination remains in the sediment after all the free NAPL has dissolved. How long will it take for this process?
iv) Estimate the release of the DNAPL from the sediment during this stage where no free DNAPL exists and all the DNAPL is adsorbed.

Properties:

Property	LNAPL	DNAPL
Molecular weight	120	180

So, in this case the second problem again bottom spill, yeah. So, tomorrow we will discuss the sediment part of the spreading and more importantly after the spreading is done the release again, rerelease into the water, which is what we will talk about, which constitutes as historically contaminated sediment which means it takes several decades for that to happen because the process is based on diffusion.

So, this will give you a very good idea of what we call as fate and transport because fate and transfer occur over a long time and it is not a quick thing that happens, and the reason why people are interested in it is because it goes on for several decades and whether we can assess the risk okay.