Environmental Remediation of Contaminated Sites
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Lecture – 19
Remediation of Contaminated GW
Design of Permeable Reactive Barriers

Hello everyone welcome back to the latest lecture session. Again a quick recap of what we have been up to. So in the context of remediating groundwater we were talking about or discussing a relevant aspect let us say and that was permeable reactive barriers right and we discussed that in some detail and today we are going to look into the design of the relevant PRB design in the sense that typically we need to be able to calculate the thickness of the PRP right.

So that is something we are going to look into, but obviously before I go into that particular aspect let us say the relevant aspects with respect design we need to also look at the applications of let us say how to apply those particular mass balance for a particular control volume. So some of you might have been or might be familiar with the relevant aspects of mass balance and applying them to different kinds of systems.

But again we are going to spend maybe 15 to 20 minutes on this particular mass balance because that is the key aspect and you know in this particular design and also maybe throughout other aspects in the course right. So again why do I need to look at this mass balance, so think of this now. You have the groundwater coming in this direction and I have my PRB here right.

And the groundwater flows through the PRB, the relevant reactions occur inside the PRB let us say right and then you have the treated, relatively treated groundwater leaving the system now right. So now I want to be able to estimate or predict what happens inside this particular PRB right. So only then can I decide what is the thickness of the PRB right or let us say if I conduct some pilot-scale study let us say right to check for the relevant feasibility.

Or such of the system right and I want to scare it up again I need to be able to look at the relevant aspects with respect to scaling, again I need to come back to mass balance right. So in that context we are going to look at mass balance right. So what is this mass balance about? Again some people might have some background in this area, but again very much work you know going over this again yes.

So let us say I am in a room and let us say an entirely closed system right, I mean no windows, no doors or you know the doors are locked and so on. So there is no flow of any fluid coming in or going out right and let us say if there is some particular contaminant that is released here let us say toxic compound that is released here right and let us say all the fans in this particular room are turned on let us say right.

And then I want to be able to calculate let us say the relevant concentration or change in concentration of the relevant compound in this room with time right, so that I can know when will I be affected or because let us say I know the concentrations at which I will be affected let us say right or let us say if I know that let us say for compound X, if I am exposed to 10 ppm concentration for 10 minutes I am going to have some adverse effects or response let us say right.

And let us say in this context I want to be able to calculate when the concentrations will reach such a value right. How do I do that again I am going to consider this particular room as my control volume right. Apply the relevant mass balance equation and then look at how the concentration changes with time right and then calculate the relevant aspects right. So in this aspects let us look at what we are up to.

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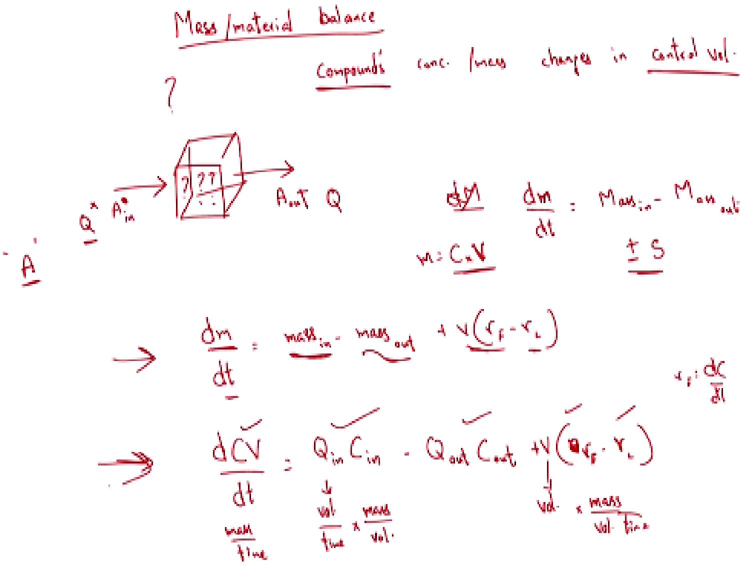

So typically when I look at or try to understand mass or material balance let us say, material balance right. What am I looking at? I am looking at trying to understand how a particular compound's concentration or it is mass let us say changes in a given control volume let us say, right, so obviously what do I need to identify? I need to be able to identify the compound upon which I am applying the mass balance obviously right.

So I am going to first identify the compound upon which I am applying the mass balance and then I am going to identify the control volume. So obviously identifying the relevant compound is relatively simple, but identifying the relevant control volume let us say is sometimes tricky and we are going to look at some of the minor aspects in that regard I guess right.

So for example let us say you know consider this to be a 3D box let us say hopefully, okay I seem to have gotten the hang of this. Again let us say some flow is coming in, in this direction X and again living here right and I have a relevant compound let us say right that is again coming in A0 or A in, let us call this A in, and A out and the flow is Q, let us say, Q coming in, Q going out.

And let us say, now I want to be able to understand what is the concentration of the relevant compound A inside this particular control volume that we have here right. So again we are going to try to apply this to microscopic scale systems so that you know you can either apply to microscopic scale systems itself or you know try to understand that or extrapolate that to macroscopic systems right.

Again so what is it that we have here? I want to understand what is happening to the relevant compound inside this particular control volume and what is my compound? This is compound A. So what am I concerned with? So DM or mass let us say, let me use this small m, dm/dt, what will it be equal to, it will be equal to let us say if you can understand it, mass coming in minus mass going out right.

So change in mass or mass is nothing but concentration of the compound into volume right. So if the volume is constant this will be dc/dt but for now we are going to say that we are looking at change in mass of the relevant compound with respect to time and obviously what is that going to be equal to in this particular system so you have some mass going in and you have some mass going out let us say yes.

So if there is a difference in either the flows or some such aspects let us say or relevant aspects let us say right obviously you are going to have accumulation of what do we say the relevant compound or you know greater loss compared to what is coming in right or degradation or degradation let us say the opposite of accumulation if I can say so yes.

So in this context obviously what do I need to know I need to know the mass that is coming in or the flux of the compound that is coming in and again flux of the relevant compound that is leaving the system right. So obviously in this case keep in mind that we are only looking at X direction for a simple case, but for complex systems let us say groundwater or such you can have mass fluxes in X, Y and Z directions right.

But here obviously we are looking at only the X direction for now anyway, right. So other than that let us say if I have any other reactions occurring within the particular system here we only considered the flow coming in or flux of the relevant compound coming in and leaving the system, but let us say you can also have some other chemical process inside the control volume let us say that can either lead to formation of the compound or loss of the compound right.

So there let us say, does not need to look at any other sources or sinks right and if it is relevant to the relevant, if I need to apply that for the relevant reactions forming the compound or any reactions leading to loss of the compound, so I will have to say it is plus volume into rate of formation minus rate of loss. Again the unit should be such that its mass of the relevant compound per time right.

So you know that is something that we need to look at right. So again these are the units more or less, so again this units too should be per time the way we write that here right. So if I look at this for microscopic systems it is going to be relatively tricky or slightly tricky. So let us try to understand this for a macroscopic system ideas right and here how can I transform that into let us say instead of mass I am going to now say dCV/dt = mass coming in.

Mass coming in is nothing but the flow rate Q in times concentration coming in right what are the units of Q, volume of the fluid per time and what are the units of this concentration? Mass of the relevant compound per volume right. So what are the units they are mass per time right again units here too are mass per time right. So again Q in, C in - mass going out similarly Q out, C out + volume * rate of formation – rate of loss.

Pardon me, I should have the volume term outside. So it is rate of formation of the compound – rate of loss of the compound, again let us look at the units here. So here you have volume right and what are the units of rate let us say, they are change in concentration with time, typically obviously let us say if you are trying to come up with some particular equation or trying to check let us say.

If the relevant variables you wrote down make sense right. One of the ways obviously is to look at the units, obviously all the units need to be the same and in this case we are trying to look at mass per time units right. So here let us say volume units and rate of formation, rate of formation is nothing, but dC/dT right. Typically, I am looking at how is the concentration changing with time similarly rate of loss right.

And in this context the units are going to be for concentration its mass per volume and per time right. So again you see the units are mass per time here. So for all the 4 sets of or 5 sets of variables we see that the units are mass per time in in the way that we have written this equation right, but one aspect as I mentioned is that we wrote down the equation for macroscopic systems.

In that sense what I typically mean is that you know the control volume that I have here let us say, you know in that context typically when can we apply this particular equation when the concentration of the compound inside the relevant volume is same throughout the volume on the reactor right, so but obviously when you have microscopic systems let us say right you have concentration changing with distance yes. Let us try to understand what we have, let me write this equation again.

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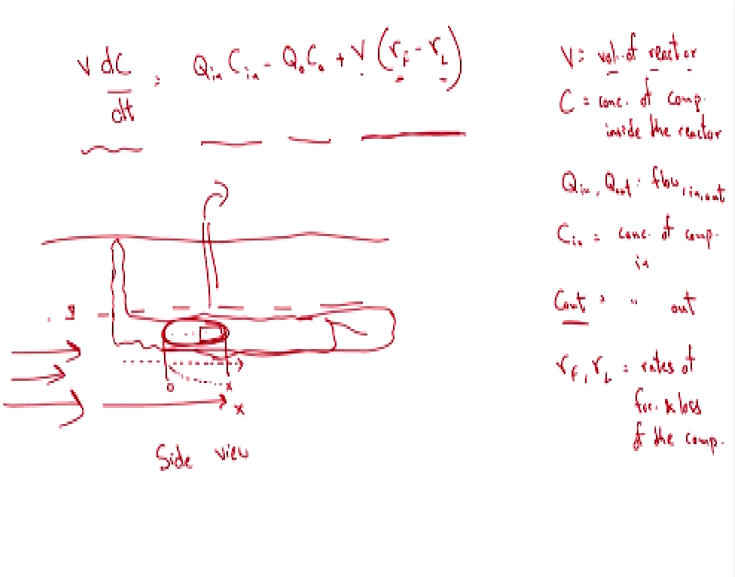

So assuming that the volume is constant it is going to be vdC/dt = Q in C in – Q out C out + volume * rate of formation of the compound – rate of loss of the compound right. So V is the volume of the system or the reactor right. Volume of reactor or system and C is the concentration of compound inside the reactor, concentration of compound inside the let us say I will write this as volume of reactor.

So concentration of compound inside the reactor alright. So obviously now as you see here we you know fundamental assumption maybe is that they are not maybe that is apparent is that, the concentration within the reactor is the same throughout the reactor right that is what you see here. You know the concentration is only changing with time not with space here right, so that is one aspect again we will come back to that later.

So Q in and Q out are the flow coming in and out. Flow is coming in and out of the relevant fluid right. C in is the concentration coming in of the relevant compound right, coming in. C out is the one that is going out concentration of the compound and the flow that is leaving the system. Volume here again is the volume of the reactor. Rate of formation and rate of loss right. Rates of formation and loss of the compound let us say right.

Again that is what we have again what do we have we are looking at change in mass or with the concentration with time that is equal to the mass coming in, mass going out and any mass that is being or the material that is being either formed or lost due to the relevant reactions right. So that is the fundamental, not fundamental, it is the mass balance equation you can use for or apply to macroscopic systems right.

But let us say in ground water what is the scenario though right. So let us look at this, so this is my ground surface and let us say this is my ground water her or water table here and let us say containment has been released and it reaches the ground water and the groundwater is flowing in this direction and now due to this particular groundwater flow I am going to have a net flow of fluid particularly in one direction.

So let us say I am going to have the plume to be spreading right. So this is the side view obviously, side view right. So here when I look at my particular system let us say if I am considering this particular case as in let us say there is a well here that is drawing water out okay. So I am concerned with a particular control volume let us say right. So here let us say as you can see the concentration changes from one point inside the relevant reactor to the other right.

Again if I take this to be the X direction right as you can see due to the effects of advection and dispersion and any other rates of loss of the relevant compounds or such, as the compound you know moves in this direction let us say, the concentration of the relevant compound changes right. The concentration is different from this point let us say 0 to x let us say right.

The concentration is changing like this let us say, yes, so in that case obviously I cannot apply this particular equation to my system right again when is that the case when let us say the concentration is changing inside your particular volume let us say right. So obviously what do I need to look at? I need to look at a microscopic scale let us say of the relevant control volume in which I will consider that the volume is relatively, not relatively, the constant within the control volume right and then apply the mass balance right.

So again in that context, I want to be able to what do you say communicate the fundamental mass balance equation here.

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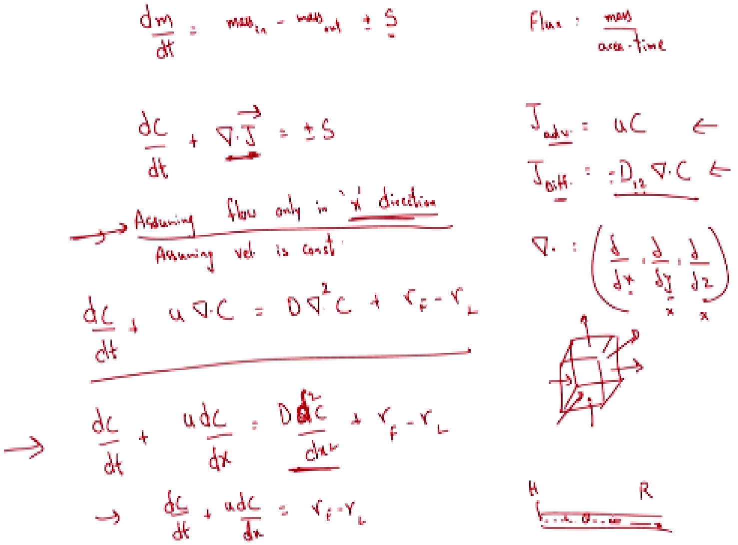

$$\frac{dm}{dt} = \text{mass}_{in} - \text{mass}_{out} \pm S$$

$$\text{Flux} = \frac{\text{mass}}{\text{area} \cdot \text{time}}$$

$$\frac{dc}{dt} + \nabla \cdot \vec{J} = \pm S$$

$$J_{adv} = uC \leftarrow$$

$$J_{diff} = -D_{12} \nabla \cdot C \leftarrow$$

$$\nabla \cdot = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$$

→ Assuming flow only in 'x' direction

Assuming vel. is const.

$$\frac{dc}{dt} + u \nabla \cdot C = D \nabla^2 C + r_F - r_L$$

$$\rightarrow \frac{dc}{dt} + \frac{u\,dc}{dx} = \frac{D\,d^2c}{dx^2} + r_F - r_L$$

$$\rightarrow \frac{dc}{dt} + \frac{u\,dc}{dx} = r_F - r_L$$

I will just briefly touch up on that right typically you know understanding the basics is always what do we say, good way to go about analyzing problems let us say. Let us say some of you are trying to understand system in greater detail let us say. These aspects are going to be relevance, but I will just spend a few minutes, not a lot of time in this regard. So what do we have?

We have let us say change in mass with time = mass coming in per time and mass going out per time right +/- sources or sinks which typically are the relevant reactions leading to formation or loss of the compound right. So in this case and if I can transform this and such with respect to flux. So I have used the term flux. Flux, what does that mean? mass coming in or going out depending upon what you are looking at per area per time let us say right.

So if I can transform this it transforms into let us say right it is going to transform into plus the del product of the flux right = +/- sources and sinks okay. So again this is the flux, flux can be due to advection. Flux can be due to diffusion or dispersion in the context of groundwater right. So again advection, what do I mean by advection let us say. If there is net flow of fluid in one particular direction let us say and the contaminant is then transported by that fluid, I would call that particular kind of transport to be advection.

So diffusion let us say is typically driven by the concentration gradient and it is random, yes and you have different kinds as in molecular diffusion let us say as in right now in this room there are no fans turned on and an example I typically look at or give out is I have a scent bottle I open that up and it will take some time or after some time it will certainly reach the person sitting at the back of the room right even when there are no fans turned on.

Why is that again there is a concentration gradient between this particular location and there and over time let us say the system will want to move in such a direction such that the potential of the particular control volume or let us say in this case the concentration of the particular compound inside the entire room is the same right. So but if I turn on the fans obviously the guy sitting at the back of the room will be able to sense the relevant compound faster right.

So the first case when there are no fans it would, the transport is going to be due to molecular diffusion and when the fans are turned on the conditions are turbulent right, but again keep in mind that there is no net flow of fluid in any particular direction right. So it is a turbulent case and you have your, you are going to have turbulent diffusion which is typically faster than molecular diffusion right.

So that is something to keep in mind, so advection it is going to be given by the velocity of the fluid, U is the velocity of the fluid, times the concentration and diffusion is going to be minus the diffusion coefficient of the relevant compound in the relevant media, 1 refers to the compound in media for example let us say compound X will have different diffusion coefficient in air and the same compound will have a particular diffusion coefficient in water right.

So obviously diffusion coefficient is depend upon both the compound and the media times the dell product of concentration let us say, why minus because you know the concentration or the diffusion drives the system such that concentration what we say or the compound tries to move from a location of higher concentration to a lower concentration right. Again cent bottle higher concentration to lower concentration.

So that is what we have, again I would not spend more time in this regard. So the flux is due to both advection and diffusion and I plug them in and so on and so forth and also assuming that assuming that let us say what is it now that there is flow only in the x direction, x direction let us say and before I go further del product, vector to scalar converter let us say and that will give me an idea about dou/dou x.

Or how is the relevant variable changing with space let us say right. So when I say the del product I am referring to the change of let us say in this context flux with respect to x, y and z directions right. What is that again, so I have this particular control volume right. So when I say the del product of flux I am concerned with flux going out x direction flux coming in in x direction and again y direction let us say and then z directions right.

So again I am unable to draw a pretty good picture. So the del product will give me an idea about all the flux and the 3 dimensions let us say going out and coming in right. So that is what I am trying to look at here. So again I just apply these aspects and assuming that the flow is only in X direction so that y and z; I am going to neglect them right. So it is going to transform as dc/dt + and also assuming that assuming velocity is constant.

Velocity of that particular fluid is constant, so I am going to have u del product of c = I am going to take the diffusion term onto the right hand side = the diffusion coefficient times right +/- sources or sinks and in our case they are rates of formation and rates of loss right. So I will simplify this further according to what I have here right. So dc/dt + what do I have here u dc/dx because I am saying that or assuming that flow is only in x direction similar to the groundwater flow or groundwater condition.

And then the diffusion coefficient or the dispersion coefficient let us say right, again second derivative let us say right + rate of formation – rate of loss right. So this is the equation that you can typically apply let us say for microscopic systems to. So if you have more complex system wherein let us say you also have flow along y and z directions then obviously you need to take that into account.

But typically in the systems that we are concerned with typically we do not read we as in environmental engineers are most environmentally nears anyway are concerned with we typically have flow in only one direction. For example, let us say I have Haridwar upstream and Roorkee downstream and there is a Ganga canal flowing through from Haridwar to Roorkee right and that is more or less what does that relate to, you have fluid flow in one particular direction.

So the compound is typically transported by advection and when you have advection typically you can neglect diffusion right. So if I am trying to apply it to the compound being transported from Haridwar to Roorkee how will this equation further transform into. So dc/dt + udc/dx, I can neglect the diffusion term because whenever I have what do we say advection, typically diffusion is relatively negligible right.

But that would not be the case obviously in ground water because the velocity of the flow of that particular fluid is pretty less, but in surface waters the velocity of flow of that or velocity of that particular fluid is relatively high right thus you can neglect diffusion, but not in the case of groundwater, but let us say the case of a compound you know in Haridwar and this is Roorkee and I have the Ganga canal compound is released here.

And it travels till Roorkee and any other reactions might occur in this particular canal. So how do I model that you know obviously by this particular reaction. What are the key aspects in this particular non reaction pardon me equation? What are the key aspects in this equation? First you see that we are assuming that the system is not at a steady state or that concentration changes with time right.

And the second variable or set of variables what does this tell you that C changes with X as in the concentration of the compound changes as the compound traverses from Haridwar to Roorkee right. So keep in mind that the concentration is changing with distance dc/dx right, what does that tell you, that the system, not the system pardon me, the concentration of the compound is changing with distance yes and now let us move on to the relevant aspects or let me write that mass balance down.

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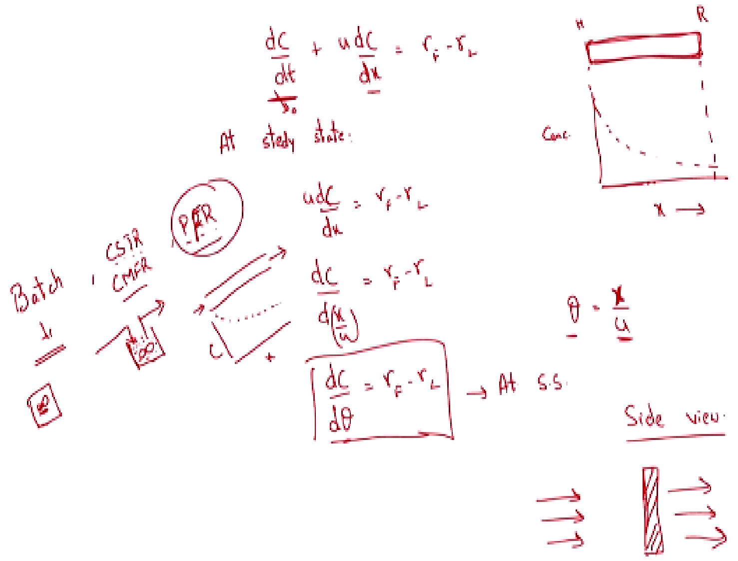

So dc/dt + u dc/dx = rate of formation of the compound - rate of loss of the compound right. So again what does this give me an idea about, how the concentration is changing with time inside my reactor right, my reactor can be now Haridwar to Roorkee, the entire Ganga canal stretch let us say right and here as I mentioned c is changing with x as in if this is my graph and this is x let us say and this is concentration of the compound.

So c is changing with distance here right. So c is changing with distance here that is what you see. Keep in mind that c is changing with distance and not with time as some people can say so when I am talking about changing with time what do I need to do? I need to sit only in Haridwar or at the same point in space right and then measure how is the concentration changing with time.

Why I reiterate this is that some people think that if I travel from Haridwar to Roorkee, you know and then take the concentration of the relevant compound and if it changes people think that it changes with time not really. So when you are looking at change in time you need to keep all the other variables constant including space right. So here when you are traveling from Haridwar to Roorkee you are measuring the change in concentration with distance not with time right.

So at steady state how does this particular equation transform into steady state means there is no change in any variable with respect to time, so this particular equation or this term will be = 0, so I just have udc/dx = rate of formation - rate of loss right or dc/d derivative of x/u =

rate of formation - rate of loss and that is dc/d theta = rate of formation - rate of loss and what is theta?

Theta is nothing but x/u right, u is constant, x is the distance that the relevant compound has traveled. What is theta obviously it is the hydraulic retention time right. So what does that give an idea about? It gives an idea about the average time let us say the relevant compound or the pardon me, the water molecule or in this case compound stays in that particular system right, hydraulic retention time.

How much time does the relevant compound stay in that particular system right? So here dc/d theta = rate of formation - rate of loss obviously this is at steady-state right. So why is this particular aspect important let us try to understand our PRP here right. So this is the side view, this is the side view okay as in this is my PRB, the thickness of the PRP let us say and I have ground water coming in let us say right.

And then leaving the system too right and now I need to model what is happening or try to predict what is the behavior of the relevant compound inside this particular PRP right. So obviously what kind of a system will that be similar to now right. As in most people are familiar with 3 kinds of systems, one is batch, the other is CSTR or completely stirred tank reactor or completely mixed flow reactor or plug flow reactor right.

Plug flow as in flow through a particular, similar to flow through a particular pipe or you know flow through a particular channel or such right. So batch reactor what does that mean? I have a system and I have no flow coming in, no flow going out but it is continuously stirred, I am using this symbol to say that the system is continuously stirred. So the concentration of the relevant compound inside the reactor is the same.

CSTR what does that mean? or what does that refer to? you have flow coming in, you have flow going out right and it is again continuously stirred right. So it is open system, but again the aspect is that the compound concentration within the reactor is the same and plug flow reactor. So similar to what we just discussed, we can just let us apply it to the Ganga canal case.

So at Haridwar flow coming in and again I am looking at the case in Roorkee, flow going out and the concentration here changes with distance here right. Concentration changes with distance here right. So again keep in mind that the concentration of the relevant compound is not same throughout the reactor, but is changing with distance here. So we come across batch CSTR and plug flow.

So batch reactors typical applications let us say have you looked at this room or any experiments you conduct in the lab and CSTR or completely mixed flow reactor any typical unit process in water or waste water treatment or most of them so you have activated sludge process, you know you have continuous mixing you typically assume that the concentration of the relevant compound in your particular reactor is the same right are typically some you know lakes let us say.

You can assume lakes to be behaving as a completely stir tank reactor obviously there will be deviations because in the actual case the concentration of the relevant compound throughout the reactor will not be the same in the case of lake and then you can model the river or lake not lake pardon me river or the stream or canal with a plug flow reactor right. So which of these 3 cases would apply to your PRB right.

I mean we are discussing material balance and mass balance yes, but obviously we need to be able to apply to the PRB here right. So if you think of it what is happening inside the PRB you have let us say mass of the, not mass pardon me, the zerovalent iron or the reactive media in this particular thickness let us say right and the compound is now reaching the relevant reactor and it comes in contact with the zerovalent iron and the relevant reaction start.

So as it goes forth you know it is still in contact what happens more reactions or rates of formation let us see or pardon me rate of loss and so you are going to observe a decrease in the relevant compound concentration as you what do you say go from the face of the reactor to the back of the reactor. Reactor being the PRB here right. So in this case as you see the concentration is changing with distance right and we are assuming that that is going to be uniform flow one of the fundamental aspects were what is it now plug flow reactor right.

So as you see here your PRB can be modeled by the plug flow reactor right. Plug flow reactor right. Now let us try to apply that here. So I have my PRB here and groundwater is coming in and going out right and what is happening inside this if this is concentration and this is thickness of the PRB and at steady state anyway that is what we are typical discussing.

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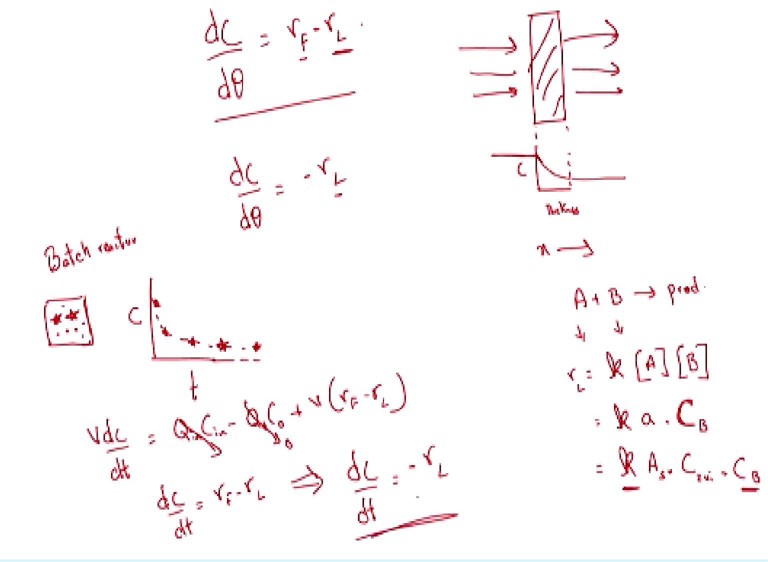

So this is the case, how is it changing the concentration is coming in at particular value C0 let us say and then decreasing right and then staying the same right. So this is obviously with distance. So now I am going to use the relevant aspect derived with respect to the plug flow reactor aspect as in the material balance equation dc/d theta = rate of formation - rate of loss right, so that is the relevant application.

So obviously how do I get to this stage as you remember I need to be able to understand the rate of loss right typically in our case where PRB, it is going to be dc/d theta = - the rate of loss right, rate of loss the compound typically is not form the compound of concern anyway. So if let us say I have A + B goes to products right and we mentioned that let us say this is zerovalent iron and this is my contaminant.

So what is rate of loss in this case though right it is going to be the rate constant times concentration of A times concentration of B right. It is a second-order reaction, but as we discussed, what do we have? We have the surface area per volume of water right because it is zerovalent iron, you have pellets right and the water comes in, water or the compound comes in contact with these pellets.

So we are concerned about surface area per volume into the concentration of the relevant compound let us say concentration of B here right and what is this depend upon again as we know the rate constant times A is depend upon the specific surface area and concentration of zerovalent iron into the concentration of the relevant contaminant or the compound right. So this is my rate of loss.

So obviously I need to be able to calculate K right. There are different compounds right and different kinds of zerovalent iron or let us say different kinds of reactive media. How do I calculate K, so initially I am going to conduct an experimental study in a batch reactor right? So batch reactor yes and what am I going to measure in this batch reactor, I am going to put in the relevant reactive media let us say and also the compound right.

And then I am going to measure the change in concentration with time right. I am going to this is my, these are my sample concentrations let us say and then I can fit a model and what model will that be again I need to apply the mass balance to this batch reactor. So what was the mass balance for the macroscopic scale it was VDC by DT right = Q in C in – Q out C out + volume * rate of formation – rate of loss right.

Obviously no flow coming in or flow going out right and let us say now I am concerned with or left with dc/dt = rate of formation - rate of loss the compound is not being formed in this case, so this transforms into dc/dt = - rate of loss right. So I have this particular case and you know that you have the values with respect to concentration in time that is what you measured right and now you can get the rates and from that you can calculate the rate constant right.

So once I calculate this rate constant I can use that in my plug flow reactor relevant system and then apply that and get that through right. So looks like I am running out of time, so I will apply this particular aspect in the next session maybe 5 or 10 minutes and then we will move on to the relevant case study that we discussed earlier right and I guess that is it from me for today and thank you.