Fundamentals of Particle and Fluid Solid Processing
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Lecture - 60
Colloids and nanoparticles (Contd.)

Hello everyone and welcome back for the final time in this lecture of Fundamentals of Particle and Fluid Solid Processing. We were continuing our discussion on the Nanoparticles and the Colloids; we started our discussion on the suspension geology.

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There we have started with the assumption for the understanding of the influence of solution concentration or say the solids concentration on the suspension by initially assuming that this is the hard sphere model can be applied or say the hypothesis of hard sphere approach can be applied to understand them. And then; that means, we initially neglected there was no inter particle interactions, but then we introduced repulsive force the surface force that is repulsive in nature. And we have seen that it is behaving similarly to the case of hard sphere model, but there we have enhanced or say the elevated viscosities at every stage because of this interaction that we had or the inter particle interaction exists.

Now, in case of attractive force the fundamental difference between this hard sphere or say the repulsive particles in dilute suspension is that here we have to break a bond between the particles. Because of this attraction between the particles there is the bond between the

particles and if we try to alter it is viscosity we have to break that bond. So, this attractive bonds between the particles eventually leads to attractive particle network, also the network of particles that are attractive in nature while at rest without any shear rate.

Now here the material of the suspension behaviour are typically viscoelastic or say the yield stress or say the shear thickening. The viscoelastic nature is the combination of the solid and the fluid behaviour. That means, when some force is applied to it; that means, some shear rate is applied to deform the particle some of the energy is stored in the fluid and some is actually dissipated as a viscous dissipation, and when that force is withdrawn it behaves as an original state.

But with the yield stress rate we have seen that that we need some initial force or the initial stress to initiate the viscous movement or the viscous interaction. And the shear thinning we have just seen that its viscosity goes down as we increase the shear rate. So, this kind of behaviour are typically seen in the case of attractive forces, the particles with attractive forces or the suspension with attractive particles.

Now, in this case we have more pronounced shear thickening of the same particles and same volume fraction than the other two cases; that means, the hard sphere approach or the hard sphere behaviour or say the repulsive forces behaviour. And here the shear thinning mechanism is also different than what we have seen in the case of the repulsive particles or say the hard sphere particles, non-interacting particles.

So, one thing is clear that as the material property will be depending on that quality we will have this bond strength. As strong the bonds will be it will be difficult or that much amount of extra force or stress we have to apply in order to have its alteration in the viscosity or in order to make it a flow.
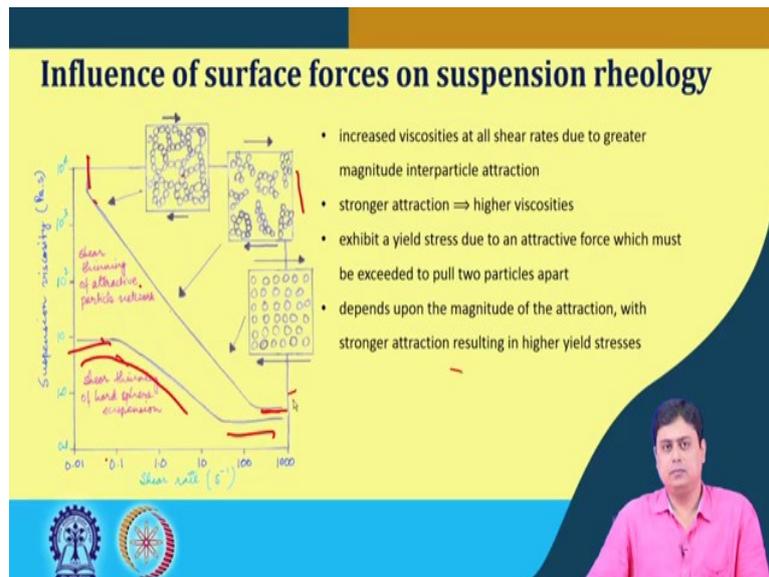
So, what happens here; so, the bottom line here the curve below this one is what we have seen in case of the hard sphere model that is the non-interacting particles. So, here we have that low shear rate Newtonian plateau high shear in Newtonian plateau and in between we have the shear thinning behaviour. In case of this attractive particles, we have the network of particles initially.

So, now this network of the particle this bond in between it has to be broken. So, at while at rest these networks basically contains or actually encircle some of the liquids. So, as this network is squeezed or say flattened or the bonding breakage is happening with a high shear rate more and more liquid will be released from those spaces or inside that network. So, at increased viscosities we can see in all cases in all the shear rate we have the increased viscosity than the repulsive or the hard sphere cases and this is due to the greater magnitude of inter particle attraction.

So, in the case of attractive particles we will have always elevated viscosities compared to the other two cases that we have discussed due to the greater magnitude of inter particle attraction; now the stronger the attraction the higher the viscosities. And sometimes it exhibit a yield stress due to this attractive force which we have to exceed in order to pull the two particles apart to break that bond.

So, this is the yield stress behaviour and then once we break the bonds, now depending on this the magnitude of the attraction this stronger attraction will result in higher yield stress.

Now, as we break the bond it starts to flow, we have steel in aggregates and at very high shear rate this again are broken into individual pieces and becomes in a preferred flow state or preferred flow structure, and then again we can have a high shear rate Newtonian plateau.

So, in order to summarize this schematic is that here we have particle network which captures the liquid inside that network as that network is broken by the shear rate more and more liquids are released it starts to flow it becomes smooth to flow. And at a very high shear rate we can have this preferred flow structure or again the rearrangement of the particles that would help for smooth flow and then we can have again a Newtonian plateau for a certain time.

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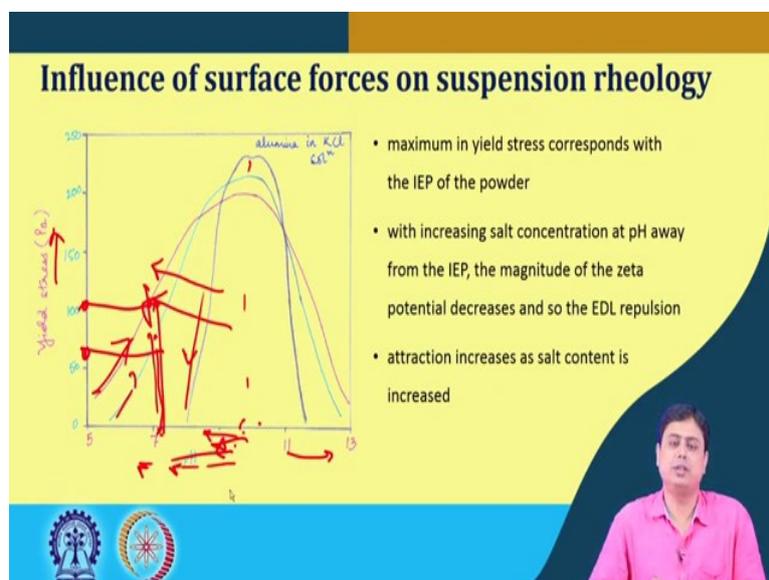
So, say this influence of surface forces on the suspension rheology containing attractive particles, it has been seen that this maximum in yield stress correspond to the IEP of the powder which is ISO Electric Point of the powder.

So, this is an example or a schematic for alumina in KCl solution as we increase the salt concentration or the morality of the salt. We can see that for a particular pH as we increase the salt concentration the, we have the higher and higher yield stress that is away from the IEP. This is the IEP, away from the IEP we see that for a particular Ph we require more and more yield stress which is shown in the y axis as the salt concentrations are increased. Because as we increase the salt concentration away from IEP the magnitude of the zeta

potential decreases and so, the EDL repulsion. So, it becomes more and more attractive in nature.

So, this attraction increases as we increase a salt content. So, once the overall interaction is attractive in nature then quite naturally we need higher yield stress to initiate the flow. And for say a certain concentration of the salt as we go away from this IEP, in this case what happens the zeta potential increases so, the repulsion increases and the yield stress goes down.

So, this is how the surface forces are influencing the rheological parameters of the suspension. The rheological parameters means the viscosity yield stress the suspension behaviour and all this stuff. So, similar behaviour not observed in other solutions and the other solid particles or the fine particles.

So, I hope this schematic is clear to you that where we have shown here that a certain concentration of fine particles of alumina in a salt solution as we increase the salt concentration this is of higher salt concentrations. At pH away from the IEP, we see that for a particular pH if we increase the salt concentration the value of yield stress increases, this is because the zeta potential decreases and so, do the EDL repulsion.

So; that means, the overall interaction between the particles becomes attractive in nature and as becomes attractive, it is then difficult to flow the yield stress increases. But for a certain salt concentration or a given salt concentration if you go away from IEP change in pH the zeta potential increases. So, do the EDL repulsion and as it increases it becomes a more free flowing in nature or more dispersive in nature yield stress decreases.

Now, in terms of say the particle size, how it is influencing the solution rheology or the suspension rheology. In the case of hard sphere approach there was no influence of solid particles on the suspension rheology. So, this is another biggest difference between this two approach or two considerations. Because here we have seen that the particle size influences the surface forces, and once we take into account the surface force; that means, the particle size will influence the surface force and consequently the suspension rheology. But, in hard sphere there was non-interacting particles. So, the size was not of any matter or consideration in that approach.

Now here the yield stress say this property how it would be influenced by the particle size and similarly such kind of analysis can be done for the other particle other parameters. So, yield stress basically is proportional to the number of bonds per unit volume and the strength of the bond.

$$\tau_Y \propto \frac{Number\ of\ bonds}{Unit\ volume} \times Strength\ of\ bonds$$

$$Strength\ of\ bonds \propto x$$

Because, this is what in attractive suspension or suspension containing attractive particles is what matter that the number of bonds we need to break and the bond strength. Now, the strength of bond is proportional to the particle size that we have seen the strength of bond

means, the surface interactions the particle-particle interaction, it varies linearly; varies proportionately with the size of the particle.

Now, if we assume that the structure of the this particle network is independent of particle size, the structure of the particle network is independent of particle size then

$$\frac{Number\ of\ bonds}{Unit\ volume} \propto \frac{1}{x^3}$$

$$\tau_Y \propto \left(\frac{1}{x^3} \times x \right) \propto \frac{1}{x^2}$$

So, by simple this relation one would expect that as the particle size is increasing the yield stress would increase. But that is not the case in case of when the surface forces are involved it is also that how many number of bonds per unit volume that it creates and it has to be broken.

Now. in case of larger particles that number of bonds varies with in this manner; that means, as the particle size grows the number of bonds per unit volume becomes lesser and lesser and that is in a rapid manner, that is in the order of x cube.

So, the overall relation between the yield stress and the particle size in case of attractive particles suspension is $\frac{1}{x^2}$. So, which means as the particle size increases yield stress goes down the viscosity would be lower as the particle size goes higher. So, that is for the fine particles of higher concentration we have higher viscosities.

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So, when we have stress less than the yield stress it would behave as an elastic like response, that the bond stretches rather than it breaks. Now, this stretching and breaking is basically a statistical phenomena so, it would not be a purely elastic behaviour as one would have expected for the case of suspension or this with fine particles. Rather, it would behave as viscoelastic behaviour that I mentioned earlier that the characteristics of both solids and fluids in the same time.

So, some energy that is applied in order to deform that body or the suspension would be stored elastically and the rest would result in the viscous dissipation when the stress is lesser than the yield stress, you have to initiate that flow.

Now, this thing let us see how it practically influences in the case of sedimentation rate as well, because from the engineers perspective what we are doing in this course is one of the basic objective is to separate the flow particles from fluid. We have done it in several cases like the sedimentation filtration and etcetera. Now; that means, we if we have a colloidal suspension and if we try to understand that how those fine particles can be settled. Now that stability of colloidal suspension against gravity depends upon the ratio of sedimentation flux to the Brownian flux.

Now, the sedimentation flux in that case what happens the denser particles than the fluid will move downward and the lighter particle than the fluid will move upward. But the Brownian flux will randomize the motion of these particles. So, it is the relative of these two in case of colloid suspension that would dictate that while it would be remaining suspended or it will settle, but at which time frame. So, this sedimentation flux and the Brownian flux this relativeness actually dictates its stability.

So, the timeframe of stability or say a critical time after which it will settle that depends on the particle and fluid properties. So, if we assume that the suspension is stable for a period of time during which the distance travelled by a particle due to this Brownian motion is greater than the distance that it takes settle over the same period of time then, we can estimate the time that is required or the time frame for its stability or the time it is required to settle us first particle from the colloidal suspension.

Now, the distance that it travels due to Brownian motion we have seen this expression that is in creeping flow design, considering the Einstein equation and Stoke's law in the creeping regime we have seen the length that it can travel.

$$L=\sqrt{\frac{2kT}{3\pi x\mu}t}=\frac{(\rho_p-\rho_f)x^2 g}{18\mu}t$$

$$t=\frac{216\,kT\mu}{\pi g^2 (\rho_p-\rho_f)^2 x^5}$$

And also rearranging the Stoke's Law in this terminal velocity in that expression; we can find now, what is the value of t, the expression of t and that has to be positive, because here it is root t and here you have t.

So, it is a bit complex relation, but if we find out the positive root of t then we find this expression. This gives us the settling time so; that means, if we provide a sufficient time all the suspension will settle, but the logical question is what the time frame? We cannot have months to work in a sedimentation tank, we cannot provide a month in a sedimentation tank or a thickener to have the particles settled.

It has to be in the order of hours, or in some cases in some suspension we do not want the settling to happen. Say for example, the fragments that we use regularly, in that case it is the very fine droplets of oil it is suspended in the liquid phase. And as I mentioned earlier that such scenario can also be considered as the particle suspended in solution. Now, we do not want that to be separated, we want fragments to be retained for years.
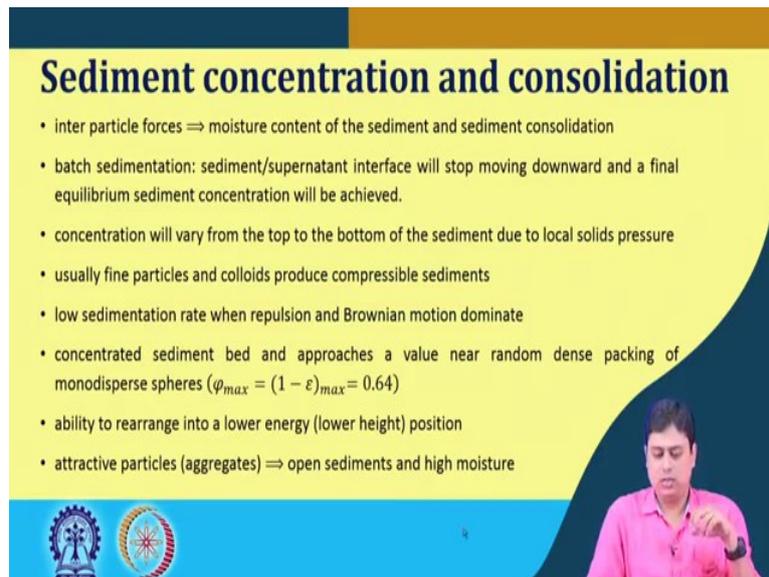
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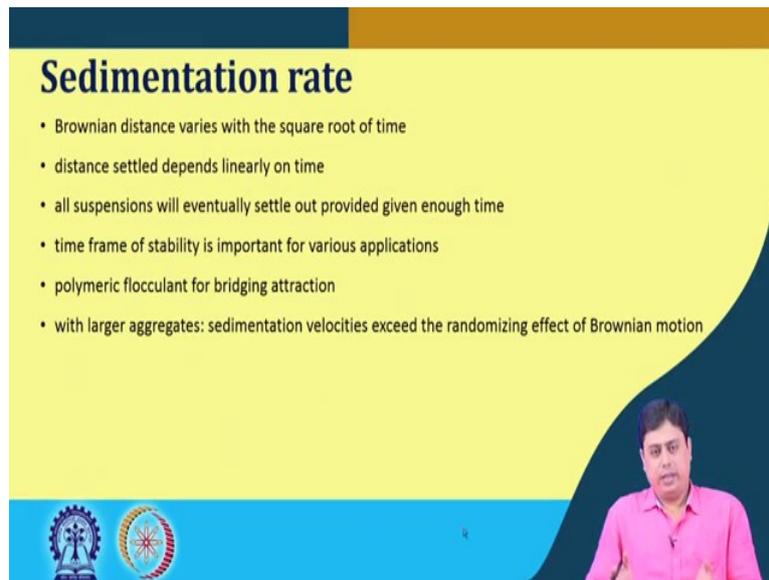
So, both the scenarios exist now; that means, this Brownian distance we have seen it varies with the square root of time, and the distance settle depends linearly on time. So, all suspension will eventually settle out provided we give enough time and it is as I said important in various applications. And in order to make it faster polymeric flocculent are provided for the bridging attractions that we have seen earlier, that we add polymeric solution a polymeric material it adsorbs on the surface and it can create aggregates. With larger aggregates the sedimentation velocity and then exceeds this randomizing effect of the Brownian motion and it helps in gravity settling.

So, if you want it to have by gravity settling it is the typical flocculent that we add which creates aggregate and again the mass or the size of the particle increases. So, size enlargement happens as it increases the sedimentation velocity increases or the body forces increases which overcomes the surface forces and then we can have the gravity settling.

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So that means, inter particle forces such as moisture content this actually dictates this moisture content of the sediment and the sediment consolidation. So, for example, in batch sedimentation the sediment and the supernatant interface will stop moving after a certain time and a final equilibrium sedimentation concentration will be achieved. The concentration in that sediment will vary from top to bottom because of the local solids pressure.

So, usually fine particles of colloids produces this compressible sediment, we have known now the definition of the compressible cake for the compressible sediment. Now, there will be no sediment rate when there is repulsive or the Brownian motion that is the dominant factor, because it would try to be remain dispersed for a longer time.

So, it would result in concentrated sediment bed and would approach a value that is near random dense packing of the mono dispersed particle. It is the maximum packing limit that it can achieve, if these particles are repulsive in nature, because it has the ability to rearrange into lower energy state. Then, the attractive particle which forms a aggregates very quickly which forms as a consequence open sediments and; that means, again the aggregates will contain more and more moisture or the liquid inside that.

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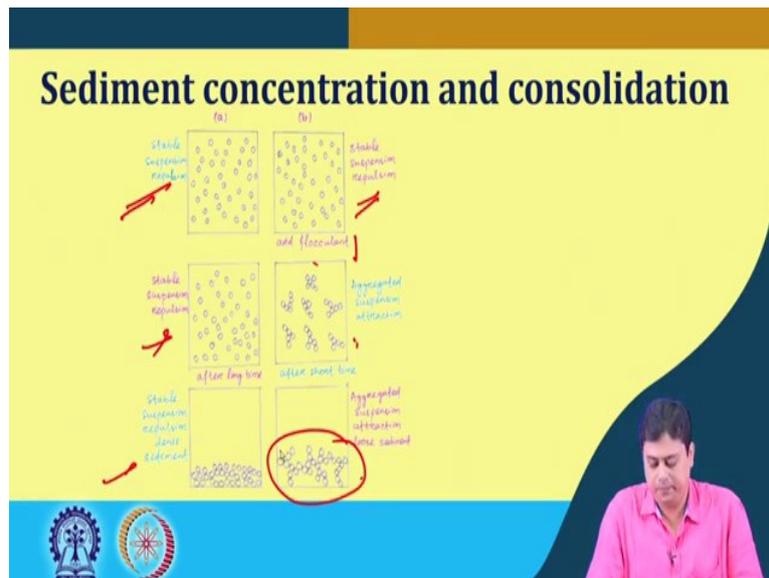
So, the scenario is something like this that this is say the stable suspension by repulsion, after a long time it would remain in the same state. Again, we put it for a further longer time we have a stable suspension which of dense sediment, in case of suspension with the repulsion if we add flocculants it would immediately create such aggregates. And after a shorter time we see the sediment with more voidage that contains that entraps the liquid phase, the moisture content is higher in this case.

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So, what can be done, the application of pressure to the particle network in order to compress that like in a filter press or a centrifuge or by putting a weight on the top of the sediment? The response for this application of pressure depends on the inter particle force, that if the

particles are repulsive in nature we have the near maximum random dense packing in all consolidation pressure. That means, we try to now consolidate the sediment for that we have now applied the pressure either by centrifuge or by filter press or by putting some weight on the top of the sediment layer.

If these are strong particles that is forming the sediment they still will have the lowest peak packing density at a particular applied pressure. When we have weakly attractive particles we have the intermediate behaviour between these two that is the maximum dense packing and the loose packing and intermediate of that.

Ideally, what should have happened the goal should be that we can have the attraction during this rapid sedimentation, but when it consolidates the sediment when it consolidates there will be repulsion. So, that it can have a dense packing or say the sediments with the low moisture.

Once again our goal should be to have rapid settling in case of solid liquid separation, rapid settling of the solid particles and for that we need attraction. So, that it create aggregates, but once it settles during consolidation of this sediment we want the particles to be of repulsive in nature. So, this kind of tuning has to be done and this is the current area of research in this case, that we need a faster settling, but with dense sedimentation. So, these are the impact of the fundamentals of fine particles when we talk about the solids handling.

We have seen in a relatively detailed manner that what are the surface forces, what its influences the suspension rheology and how a colloidal suspension or fine particle suspension and if sedimentation rates is influenced by the particle interaction. With this I would conclude this talk as well as this subject, I hope you have enjoyed this lecture and.

Thank you for your attention.