Fundamentals Of Particle And Fluid Solid Processing

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Lecture - 49
Particle size enlargement (Contd.)

Hello everyone and welcome back to the another class of Fundamentals Of Particle And Fluid Solid Processing and we were discussing about Particle size enlargement. Over the last three lectures we have seen it is necessity, it is mechanism; particularly we are focusing on the granulation. Granulation as we have mentioned is the aggregation of smaller particles by agitation.

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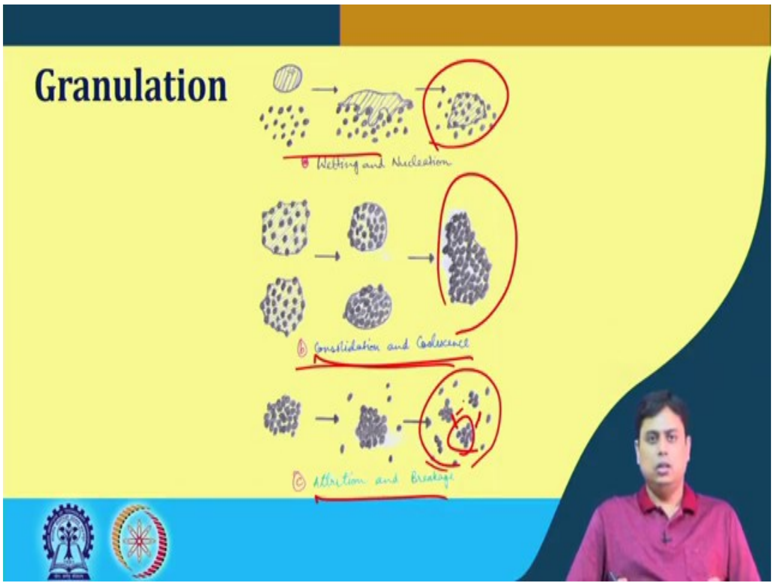

Granulation

Now, we have seen different stages in granulation or the different rate processes that actually dictates this granulation rate. So, this we covered in the last class. Now, just to give an overview what we have covered here, the schematic shows that the three rate processes that we discussed in the last class and we are actually now focusing on the details of each and every step.

So, the first step was the wetting and nucleation so; that means, when we have a bed of fine particles, the liquid binder when it is spread or spilled over this bed of smaller particles, it should form the bridges. Now in order to do that, it should penetrate through that bed and while doing so it has to wet the surfaces of the particles. Now that happens at this wetting stage. So, this schematic the first stage shows that; that the liquid drops are falling or say in a single liquid drop here is falling on the surface of very small particles and then it wets, it forms the bridges in between particle and one granule is prepared or generated.

Now, this one granule in the next state in the consolidation and coalescence step, this granule consolidates itself and that happens either by coalescing with the other granule or the coating with the smaller particle or the origin particles. So, that leads to its consolidation and coalescence. And at the end this consolidated granule undergoes attrition and consequential breakage, if the bonding by the bridges it is not sufficient to withstand that external force.

So, it creates small structures, stable structures or stable clusters. So, that stage is the attrition and breakage. And this happens due to the movement of the particles in the granulator, due to the granulation or granulator movement which induces the movement in the particle. So, this particles are colliding against each other, granules are colliding against each other, it hits the solid surface of the equipment that is the granulator.

And by doing so, this attrition and the breakage happens and once after this say critical stage the size remains more or less unaltered. So, which means we can have a size distribution of the end granules or the end product.

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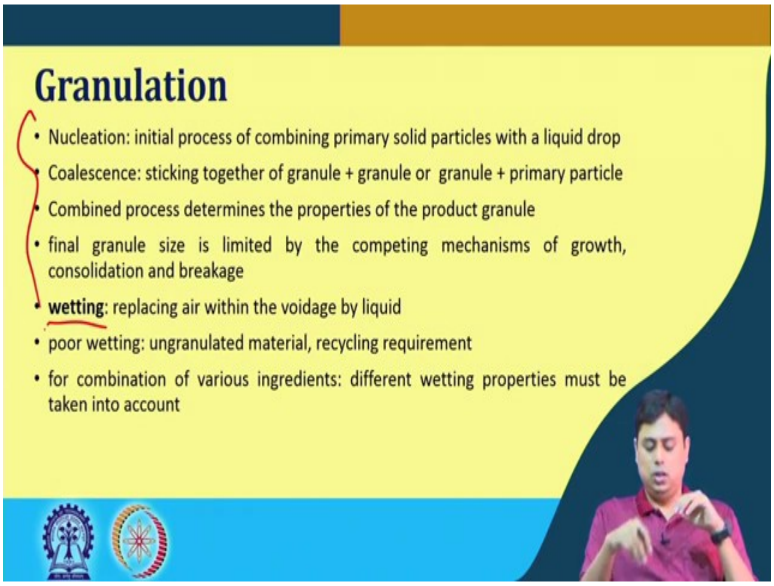

Granulation

- Nucleation: initial process of combining primary solid particles with a liquid drop
- Coalescence: sticking together of granule + granule or granule + primary particle
- Combined process determines the properties of the product granule
- final granule size is limited by the competing mechanisms of growth, consolidation and breakage
- wetting: replacing air within the voidage by liquid
- poor wetting: ungranulated material, recycling requirement
- for combination of various ingredients: different wetting properties must be taken into account

So, now we are going into the details of the particular process or the rate stage that is the wetting. So, we have mentioned this terminology; one is the nucleation which is the initial process of combining several smaller particles or the primary solid particles with a liquid drop. This is the point which say the nucleation has happened and the nucleus or the single granule has been formed.

It coalesces the sticking together of this granule with another granule or the granule and the primary particles, this happens. And basically combination of these processes determines the property of the end granules or the final product. Now, the granule size is basically limited by this competing mechanism of all these three rate steps that we have seen; that is the wetting and the nucleation, then we have coalitions, before that we had consolidation and it is followed by attrition and breakage.

So, competing mechanism of all these or the interplay of all these three phenomena dictates the final granule size. Now wetting, if we now dig into the details this wetting phenomena; it is nothing but the replacement of the air which actually fills the voidage in between particles by the liquid binder of the solvent containing liquid binder.

Now, poor wetting means, there is, the chances are there will be ungranulated material; because the liquid bridges are not formed due to the absence of liquid in those pores or say the surface wetting of the particles, if the liquid binder is not present on the surface it is not binding the particles together. So, which means this ungranulated particles have to be recycled again for the efficient operation.

Now the cases where we have multiple particles or multiple materials we are combining into a mixture, there all these materials will have their own eye wetting properties. So, those properties has to be considered when we do this kind of combining several materials into a compact form.

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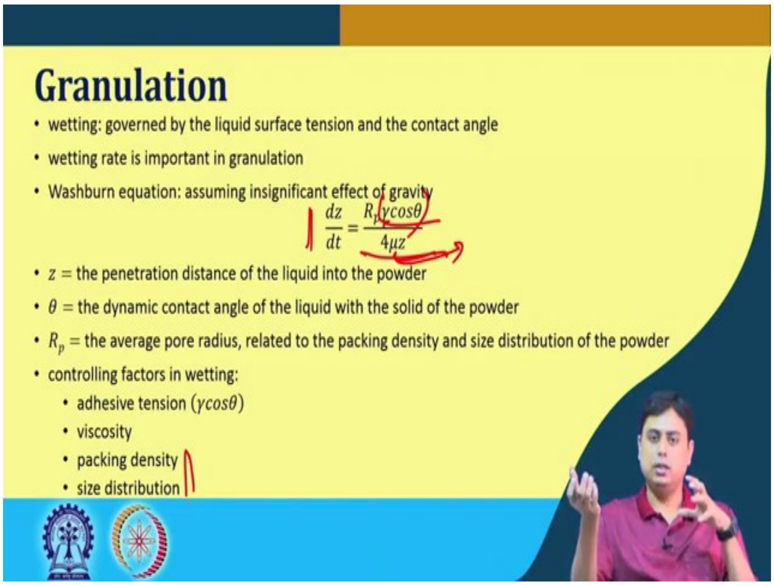

Granulation

- wetting: governed by the liquid surface tension and the contact angle
- wetting rate is important in granulation
- Washburn equation: assuming insignificant effect of gravity

$$\frac{dz}{dt} = \frac{R_p \gamma cos\theta}{4\mu z}$$

- z = the penetration distance of the liquid into the powder
- θ = the dynamic contact angle of the liquid with the solid of the powder
- R_p = the average pore radius, related to the packing density and size distribution of the powder
- controlling factors in wetting:
  - adhesive tension ($\gamma cos\theta$)
  - viscosity
  - packing density
  - size distribution

So, this wetting is governed by the liquid surface tension and the contact angle of the liquid with the solid surface of the particle surface. And this is a very important step in granulation; because this the rate at which this wetting happens, it dictates how the granulation procedure will be followed. And a measure of such assessment has been done by Washburn.

And Washburn equation says that assuming insignificant effect of gravity in that bed of small particles, this penetration rate, the droplet it drops on the surface, as I mentioned earlier it has to penetrate that depth of the small particles in order to fill in the pores of the inter particle gap. Now, this penetration rate that is

$$\frac{dz}{dt} = \frac{R_p \gamma cos\theta}{4\,\mu z}$$

where z is the penetration distance of the liquid into the powder; you can think of that is the bed depth which the droplet travels, the liquid binder droplet travels is basically this expression.

So, where this all the parameters, some of the known parameters or easily identified parameters are the viscosity, mu and theta is the dynamic contact angle. We have surface tension as well, R p stands for the average pore radius and that is related to the packing orientation, packing structure, packing density or the size distribution of the powder. So, it is depends on the size of the small particles or the finer particles; that dictates this average pore size in between particles.

So, this expression shows that this wetting rate or the penetration rate here is actually controlled by three major parameter; one is the adhesive tension, this parameter, then we have viscosity. And the other thing is depending on the particle size which basically dictates the packing orientation, size distribution, or the packing density all these things basically depends on the finer particle size or the origin particle sizes, that is making the cluster of particles or the size enlargement. So, these are the controlling factors in understanding the wetting behavior of the materials.

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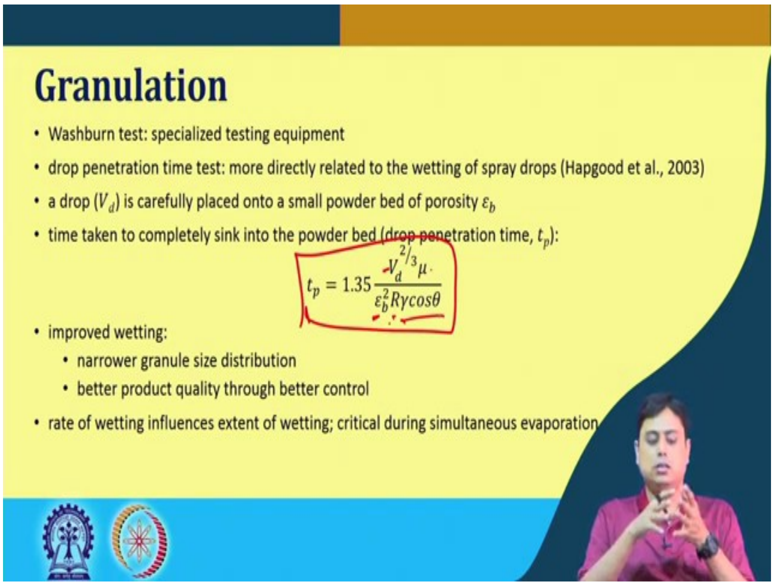

Granulation

- Washburn test: specialized testing equipment
- drop penetration time test: more directly related to the wetting of spray drops (Hapgood et al., 2003)
- a drop (V_d) is carefully placed onto a small powder bed of porosity ε_b
- time taken to completely sink into the powder bed (drop penetration time, t_p):

$$\boxed{t_p = 1.35 \frac{V_d^{2/3} \mu}{\varepsilon_b^2 R \gamma \cos\theta}}$$

- improved wetting:
  - narrower granule size distribution
  - better product quality through better control
- rate of wetting influences extent of wetting; critical during simultaneous evaporation

So, this Washburn test require some specialized equipment, specific instrument to measure this rate or the depth that it penetrates; because it is difficult in usual circumstances. As an alternative to this test or this quantitative measurement, there is a test called the drop penetration time test; where a very small droplets of known volume is gently placed onto a small powder bit of known porosity and this method directly relates the wetting of the spray drops.

So, here what happens, a drop of small volume, of known volume is placed onto the surface of small particles or the origin particles of a bed of that particles of known porosity or voidage. And then the time taken to completely sink or absorb this droplet into this bed of origin particles is measured and that has been shown has a relation of

$$t_p = 1.35 \frac{V_d^{\frac{2}{3}} \mu}{\varepsilon_b^2 R \gamma cos\theta}$$

where t_p is the drop penetration time.

All other parameters I have mentioned that, this is the volume of the droplet, viscosity of the liquid, the bed voidage, this R we have seen as the pore radius, average pore radius and this is the adhesive tension. So, this apparently is more easier to conduct in with the usual lab equipment's. Now in general improved wetting is beneficial in granulation, because improved wetting provides us narrower granule size distribution in the product.

And it also gives us better product quality control throughout the whole process. If we have a better wetting; which means, it is beneficial for the granulation and the rate of wetting influences the extent of wetting as well, which is very critical when there is simultaneous evaporation during the granulation step.

So, at the rate we at which the liquid binder or the solvent is spreading over the small particles and it is extent of wetting these are two related. And this is more of a critical in nature when we have simultaneous evaporation of the solvent in order to make the bonds more stronger by replacing the liquids; in that case this rate of wetting is a dominant factor in the granulation.

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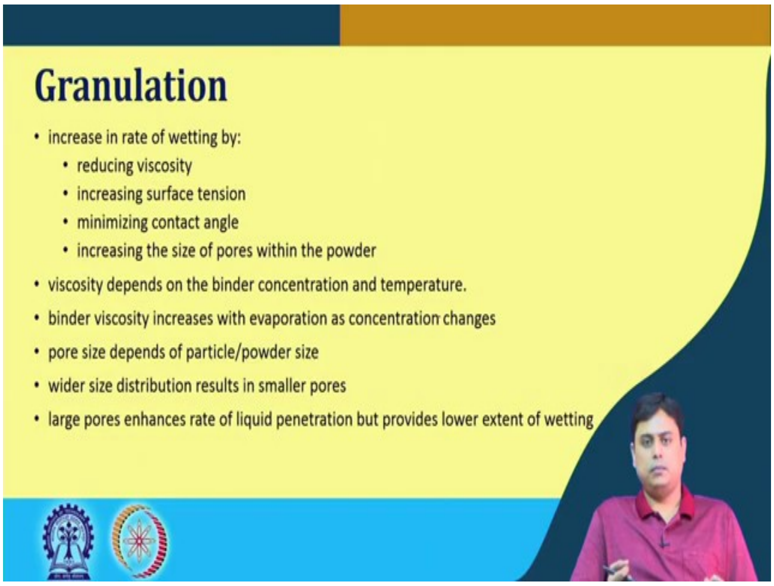

Granulation

- increase in rate of wetting by:
  - reducing viscosity
  - increasing surface tension
  - minimizing contact angle
  - increasing the size of pores within the powder
- viscosity depends on the binder concentration and temperature.
- binder viscosity increases with evaporation as concentration changes
- pore size depends of particle/powder size
- wider size distribution results in smaller pores
- large pores enhances rate of liquid penetration but provides lower extent of wetting

Now, we would like to have the increased wetting, because we have mentioned that the improved wetting is beneficial. So, increase in the rate of wetting can be achieved by several ways; one is by reducing the viscosity of the droplet or say the liquid phase, because the highly viscous liquids are difficult to flow or spread over the particle surfaces. So, it has been seen that if you reduce the viscosity, the rate of wetting increases.

Quite naturally, if we increase the surface tension, we can have the increased rate of wetting. Minimizing the contact angle, it can spread over the particle surfaces very efficiently. And increasing the size of pores within the powder, so that it can quickly penetrate, because as larger the pores will be, the liquid can penetrate easily into those gaps. Now viscosity of this solvent depends on the binder concentration and that operating temperature.

Now it has been seen that with evaporation, binder viscosity increases; because the concentration is changing, it is becoming more and more concentrated. So, the viscosity changes or increases during the evaporation step. The pore size which is the particle related or depends on the different material of the particles that is made of. So, it depends on the particle and powder size and wider distribution results in small pores. If we have wider size distribution of the particles, we can find smaller pores.

Now bigger particle will provide us bigger pores, smaller particles will be more compact during the packing. So, it will provide us smaller pores. Now this larger pores, definitely enhances the rate of liquid penetration; but it provides lower extent of wetting.

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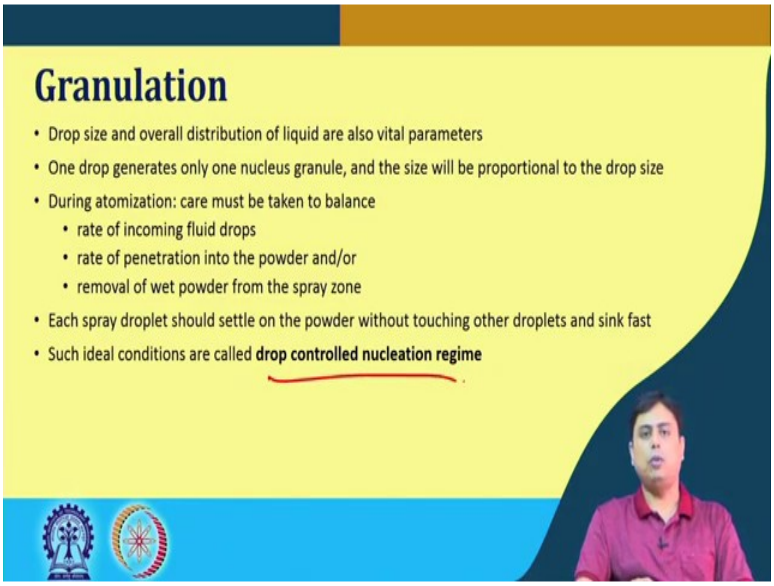

Granulation

- Drop size and overall distribution of liquid are also vital parameters
- One drop generates only one nucleus granule, and the size will be proportional to the drop size
- During atomization: care must be taken to balance
  - rate of incoming fluid drops
  - rate of penetration into the powder and/or
  - removal of wet powder from the spray zone
- Each spray droplet should settle on the powder without touching other droplets and sink fast
- Such ideal conditions are called **drop controlled nucleation regime**

Along with this criteria, we have droplet size and the overall distribution of liquid, these are the other two vital parameter that dictates the granulation process when particularly the wetting step; because say one droplet usually generates one granule and it is size is proportional to that of the drop size. So, this droplet and it is distribution, so the size of the droplet and it is size distribution during its spraying or pouring over the bit of particles, that is one of the critical factor.

So, during atomization; which means, when we flow this binders, the solvent including binders we spray over the bed of particles with a very fine droplets. We have to specifically, we have to mask take a balance between the rate of this incoming fluid drops and the rate at which it is penetrating the powder, it is ability to penetrate the powder and the removal of wet read section from the spray zone or near the spray zone.

So, we are basically spraying or atomizing say the liquid solvent including the binder over this small particle bed. Now the rate at which we are pouring in this liquid droplets over the surfaces of this smaller particles, though there should be a balance between this rate and the rate at which the droplet can penetrate. Because it should not form a pool of liquid at the top, that before it penetrates again another droplet comes on the surface of the small particles.

Because ideally each droplet should settle on the powder without touching each other and it should sink very fast, then the number of granules or the number of nucleus formations becomes larger in number or higher in higher. Such ideal condition are called the drop controlled nucleation regime; that means, each droplet is creating one granule and each droplet when it sinks, it is not touching the other droplet. Or it is effect in creating one granule is not destroyed by the presence of other one. Such ideal case or ideal regime is mentioned or identified as drop controlled nucleation regime.

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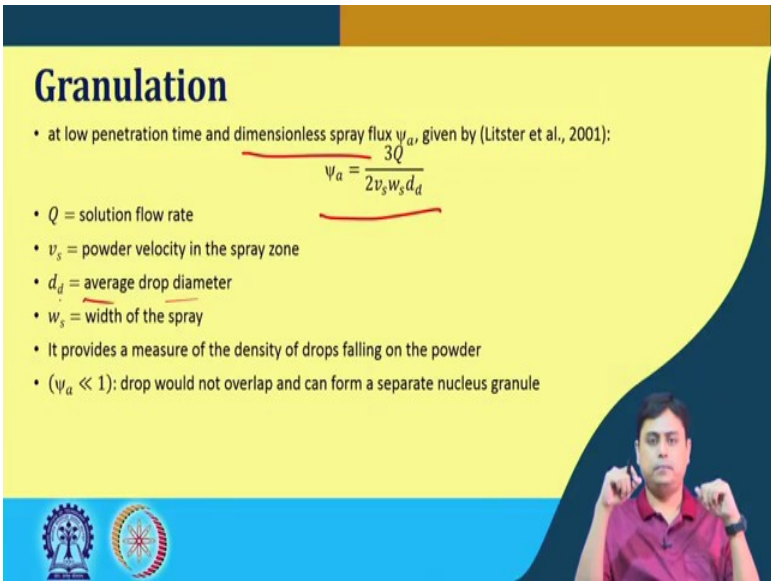

Granulation

- at low penetration time and dimensionless spray flux ψ_a, given by (Litster et al., 2001):

$$\psi_a = \frac{3Q}{2v_s w_s d_d}$$

- Q = solution flow rate
- v_s = powder velocity in the spray zone
- d_d = average drop diameter
- w_s = width of the spray
- It provides a measure of the density of drops falling on the powder
- ($\psi_a \ll 1$): drop would not overlap and can form a separate nucleus granule

Now, this happens at low penetration time; that means, it should sink fast and at a very low flux. Now that flux rate is basically proposed in a dimensionless value or number which is expressed

$$\psi_a = \frac{3Q}{2v_s w_s d_d}$$

where Q is the solution flow rate, v_s is the powder velocity in the spray zone, droplet diameter or the average droplet diameter is d_d, w_s is the width of the spray.

So, this dimensionless spray flux basically provides a measure of density of graphs that is falling onto the powder surface. If it is value is much lesser than 1, then one drop would not overlap with another one and can form a separate nucleus granule. So, means the process efficiency becomes higher; that each and every droplet and it is effect is not destroyed or hampered by the presence of other liquid, other liquid droplet.

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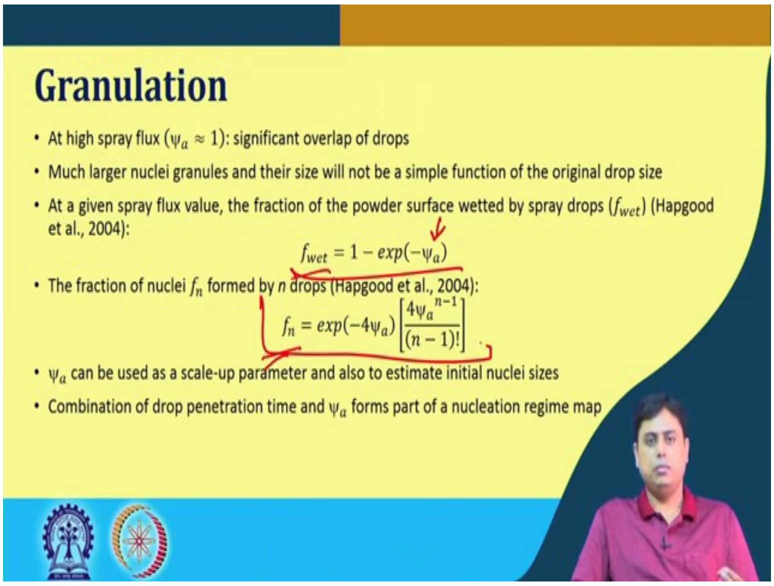

Granulation

- At high spray flux ($\psi_a \approx 1$): significant overlap of drops
- Much larger nuclei granules and their size will not be a simple function of the original drop size
- At a given spray flux value, the fraction of the powder surface wetted by spray drops (f_{wet}) (Hapgood et al., 2004):

$$f_{wet} = 1 - exp(-\psi_a)$$

- The fraction of nuclei f_n formed by n drops (Hapgood et al., 2004):

$$f_n = exp(-4\psi_a)\left[\frac{4\psi_a^{\,n-1}}{(n-1)!}\right]$$

- ψ_a can be used as a scale-up parameter and also to estimate initial nuclei sizes
- Combination of drop penetration time and ψ_a forms part of a nucleation regime map

At high flux rate there is significant overlap of drops, that results in much larger nuclei granules and their size and then would not be a simple function of the droplet diameter or the droplet size. Because was earlier, we have I have mentioned that this in this droplet control design, where one droplet should ideally form one granule and the granule size is dependent on the droplet size. So, for in case of high flux scenario, this simple function would not be there.

So, at a given flux value, the fraction of the powder surface wetted by spray drops has been proposed to be of this expression.

$$f_{wet} = 1 - \exp(-\psi_a)$$

So, if this is known, the flux rate is known, we can estimate the fraction of power this powder surface that would be wetted and the fraction of nuclei, the number formed by n number of drops can be estimated by this expression.

$$f_n = \exp(-4\psi_a)\left[\frac{4\psi_a^{\,n-1}}{(n-1)!}\right]$$

So, one hand we can estimate the powder surface area that is being wetted and the number of nucleus, the granules that has been formed that also can be estimated by a certain number of drops.

So, basically this spray flux is helpful in scale up operation or scale up design of a certain granulator, which helps us to provide an initial estimate or initial guess on the nuclei sites on the sizes. So, when one combines this drop penetration time and high flux, it forms a regime map, nucleation regime map; that means, in which scenario what kind of nucleation would take place, which factor will be dominant that kind of scenario we say the regime map. Like we had one regime as the droplet controlled nucleation and that happens we have seen at a very low penetration time and of a very low flux.

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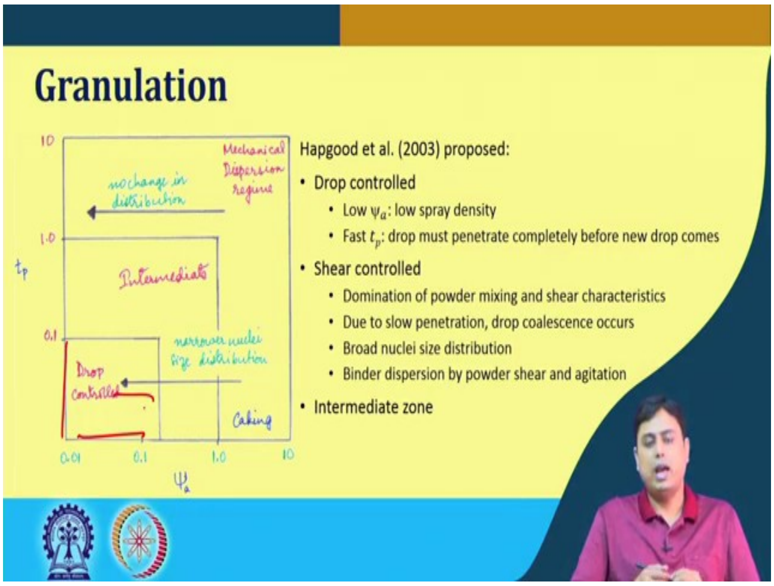

Granulation

Hapgood et al. (2003) proposed:

- Drop controlled
  - Low ψ_a: low spray density
  - Fast t_p: drop must penetrate completely before new drop comes
- Shear controlled
  - Domination of powder mixing and shear characteristics
  - Due to slow penetration, drop coalescence occurs
  - Broad nuclei size distribution
  - Binder dispersion by powder shear and agitation
- Intermediate zone

So, such flow regime can be derived from the knowledge that we have seen, where we can see there are three regimes or three zones of nucleation; one is the droplet control, which we have discussed, we have seen what should be ideally in that scenario, that it appears in the low value of the flux and a very fast penetration time. So, the drop can penetrate completely before the new drop comes, this is the ideal case in that is called the drop controlled nucleation site or the nucleation regime.

The other one is called the shear controlled mechanism, where there is a domination of powder mixing and shear characteristics. And due to slow penetration, droplet coalescence increases; before it sinks another drop comes. So, the drop coalitions occur and we have a broad nuclei size distribution, because that now bigger drop; in generic, if we consider now that is also a isolated scenario that bigger drop would create a bigger granule.

And wherever that droplet coalescence is not happening there a single droplet would create a nucleus as per it is size so; that means, we have a variation in size distribution and that is a broader size distribution.

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Granulation

Granule Consolidation:

- increase in granule density resulting from closer packing of primary particles due to removal of liquid through collisions
- can occur only during the liquid state of the binder
- determines the porosity and density of the final granules
- controlling parameters for the rate and degree of consolidation
  - particle size
  - size distribution
  - binder viscosity

Now, the binder dispersion happens here by shear and agitation, and in between these we have the intermediate zone. So, here we have a narrower size distribution; in the mechanical case, in the mechanical dispersion regime or say the sheared control design we have the broader size distribution. And then comes the granule consolidation state. So, wetting is done.

Now if we look at the granule consolidation, this granules that has been created by this wetting, this increase in the granule density resulting from the closer packing of primary particles due to removal of liquid through coalitions is what the granule consolidation. And this can occur only during the state when the binder is a still in the liquid state, because that liquid can escape and it can be compacted or consolidated.

This consolidation step basically determines the porosity and density of the final granule. But this consolidation rate and it is degree is controlled by particle size, size distribution, and the binder viscosity. So, the involved granule, its size, its distribution and the binder viscosity dictates the rate of consolidation and the degree of consolidation.

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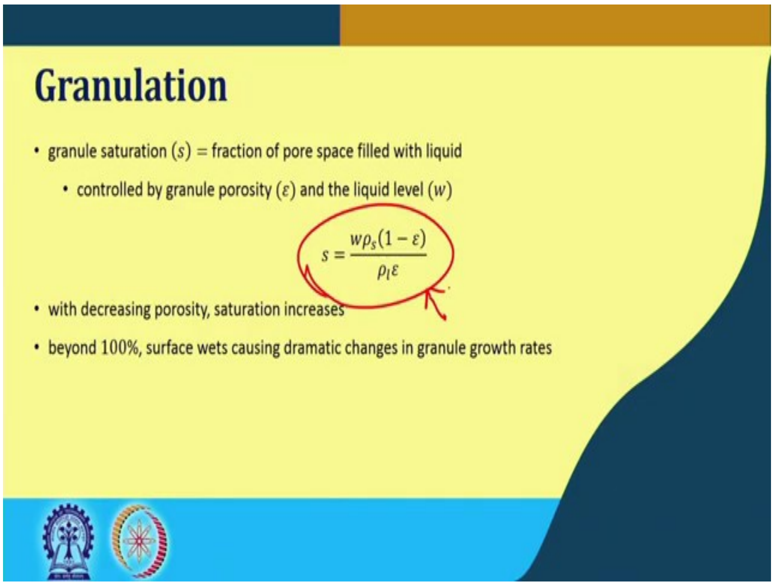

Granulation

- granule saturation (s) = fraction of pore space filled with liquid
  - controlled by granule porosity (ε) and the liquid level (w)

$$s = \frac{w\rho_s(1-\varepsilon)}{\rho_l\varepsilon}$$

- with decreasing porosity, saturation increases
- beyond 100%, surface wets causing dramatic changes in granule growth rates

So, granule saturation if that is defined as the fraction of pore space filled with the liquid is controlled by two factor; one is the granule porosity and the liquid level and this is the relation.

$$s = \frac{w\rho_s(1-\varepsilon)}{\rho_l\varepsilon}$$

From which we can see that with increasing a porosity, saturation decreases or with decreasing porosity, saturation increases. So, which means by changing one of these parameters or these parameters, we can control the granule saturation; which in turns helps us in having the compact size or the compactness or the consolidation of the granules.

But beyond 100% saturation, this liquid comes up to the surface; it causes wetting of the surfaces. And that dramatically changes the granule growth rate, which we will see in the growth mechanism in the next class. So, in the next class, we will see these growth mechanisms; how it is influenced by it is controlling factors and what are the controlling factors. And we will see a couple of industrial granulator and it is schematic and it is overview. Until then, I thank you for your attention and we will see you in the next class.