Characterization of Construction Materials
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Lecture-28
Surface Area Measurement: Sampling and particle size distribution- Part 2

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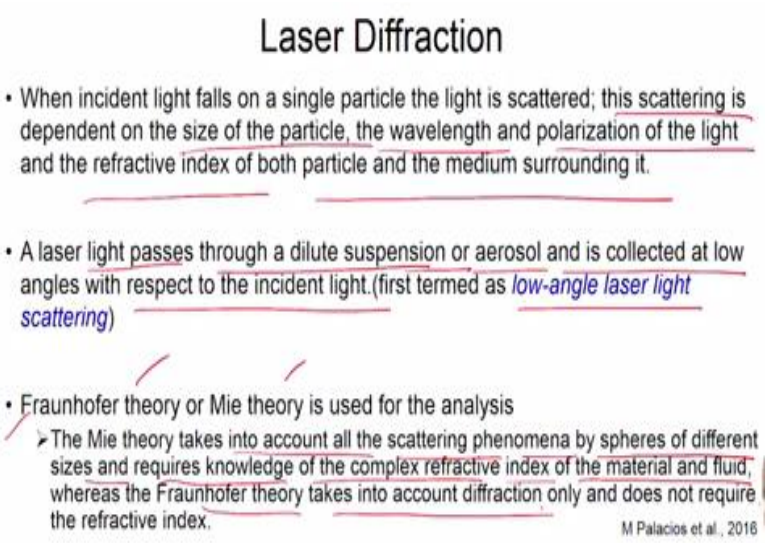

So, we know now the limitation of sieving, there is a limitation on size. If you have particles smaller than, for example 35 to like 50 µm, it becomes really difficult to use sieving, so we need a different technique. So, we will talk about laser diffraction which is which is a commonly used technique to determine the particle size distribution of powders, like any powder like cement, or SCMs. So, what is the principle, we will talk about few salient features, like what is it about then we will look at the limitations also.

So, basically, when incident light falls on a single particle, the light is scattered; and this scattering is dependent on the size of particles. So, we are talking about the laser, which is a focused beam and then scattering depends on the size of particle, the wavelength polarization of the light and refractive index of both particle and medium surrounding it.

The particle has to be dispersed; you have to make sure there is no agglomeration. Otherwise, the particle size distribution would not be correct so, usually your powders are dispersed in a

medium; we will come back to it. So, a laser light passes through a dilute suspension or aerosol and it is collected at low angles with respect to incident light, that is why it initially used to be called as '*low-angle laser light scattering*'.

How do we then determine the particle size? So we use two theories: Fraunhofer theory or Mie theory for the analysis. So Mie theory takes into account all the scattering phenomena by spheres of different sizes and requires knowledge of the complex refractive index, we will come back to it in the next slide. Whereas Fraunhofer theory takes into account diffraction only it does not require the refractive index.

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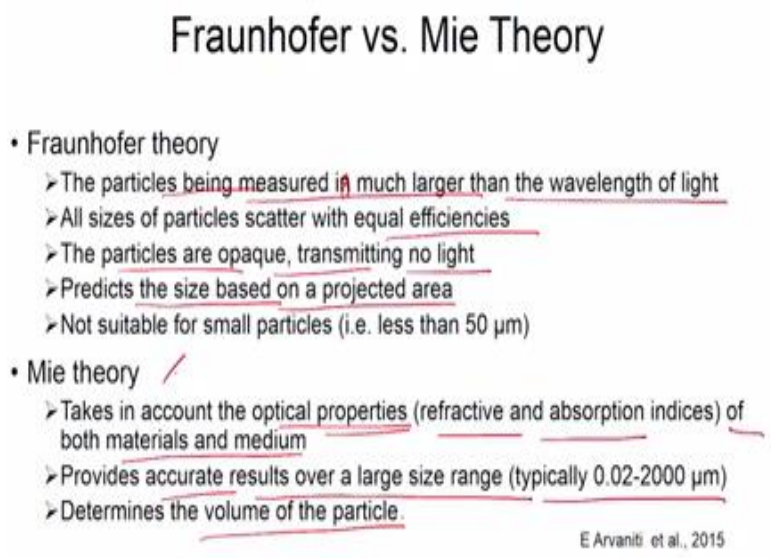

So what is Fraunhofer theory? Fraunhofer theory assumes the particle being measured is much larger than the wavelength of light. So it is applicable to large sized particles only – that is the first thing - the particles being measured are much larger than the wavelength of light.

All sizes of particles scatter with equal efficiency, these are some assumptions.

The particles are opaque, transmitting no light - there is no transmission through the particles.

How does it predict? It predicts the size based on a projected area so, you have a particle and there is a projected area, based on that it predicts the size.

It is not suitable for small particles – if you particles of size less than 50 μm, then this theory is not suitable. So, for that we use Mie theory as it is applicable for whole range.

Mie theory takes into account the optical properties. So, what happens when you have small particles? There will always be refraction, absorption. So, it takes into account these optical properties. So, what is the refractive index what is the absorption index of your particle or both materials and media. So, it takes into account this absorption, refraction which is not taken account in Fraunhofer theory and provides accurate results over a large size range.

So, it can cover 0.02 to 2000 µm and it works by determining the volume of the particle. So, there are limitations with the Fraunhofer theory, and so most particle sizes analyzers use Mie theory, because it is first of all applicable to all and also it takes into account the refraction and absorption which happens especially in smaller particles.

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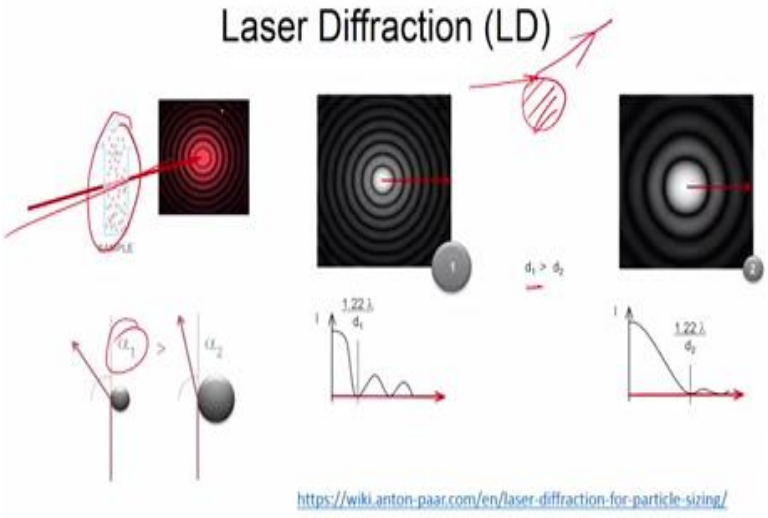

This is a schematic you can see here, you have a sample and you have a laser. So, you see this diffraction patterns, it is the principle is same, when you have a constructive interference you have diffraction (Refer to figure in slide). You can see the difference, when you have 2 different sizes, small versus big, α_1 in the case of smaller diameter particle, scattering is greater than that in bigger diameter particle ($\alpha_1 > \alpha_2$).

So, there is a difference in the diffraction angle and that can be used to get an idea about the size. Also coming to intensity, now you see these rings (Figure in slide – diffraction rings), when size $d_1 > d_2$, you have a difference in the intensity when you compare both sizes. So, there is a difference in the angle and also a difference in the intensity. So that can be used to determine the

sizes. So, you have a sample and laser passes through the sample and these rings are seen (using the detector).

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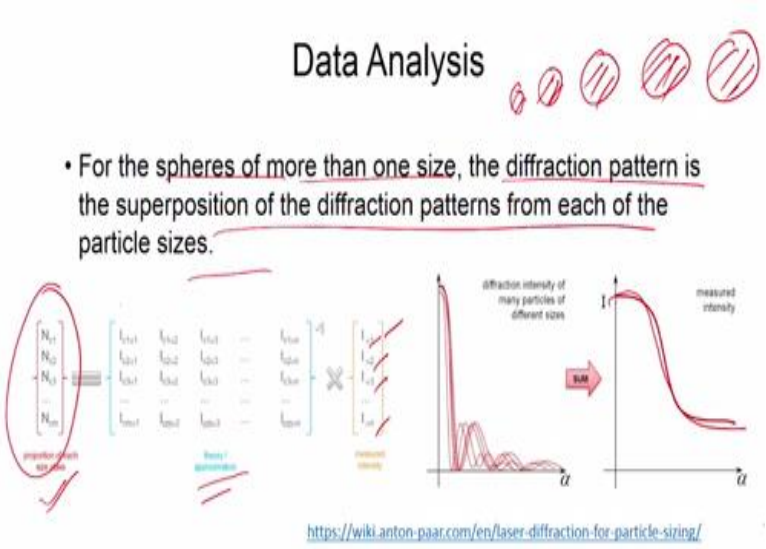

But in real life you have spheres of different sizes; those are the idealized diffraction patterns. But particles may not be exactly circular because in real life you have irregular sizes. So, for spheres of more than one size, the diffraction pattern is a superposition of the diffraction patterns from each of the particle sizes. Suppose you have a range, assume that you have spherical particles but the sizes are different. So, they will all diffract differently, the angles will be different, and intensity will be different.

So, the net pattern (Graph on right – in slide) is the combination of the diffraction pattern for each size of particles. So, same minimization you have to do, how do we calculate the number of particles? So, you see here in the matrix - proportion of each size class. Now we know that for one particular size you have one particular diffraction intensity, and so you are summing it up and then minimizing the difference. So you are assuming something, and then minimizing the difference, because you have a diffraction pattern, it is nothing but measured versus calculated. So, these are the measured intensity for α_1, α_2, which are the sizes. So, that way we can calculate. So idea is, you will get intensity like this (graph on right – in slide) which is the net intensity, and that is the combination of the intensities of many particles of different sizes. So you have different patterns and this is the net effect. So, now you have to deconvolute it and tell what the size is. That is what it is doing.

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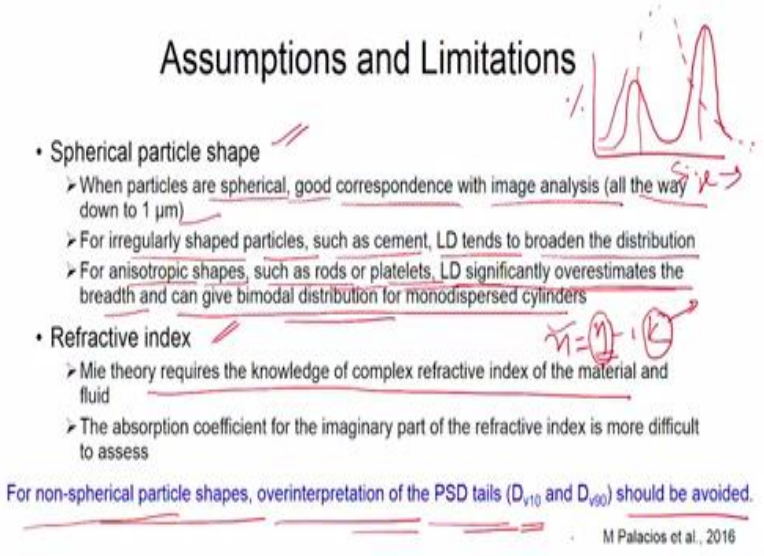

So, what are the assumptions and limitations? First assumption is we assume the particle is spherical in shape. So, that tells you, if you have a regular size you may not get the real picture, because the basic assumption here is the spherical particle shape. So, when particles are spherical, good correspondence with the image analysis, that is, when the particles are spherical then you have a good correspondence with image analysis, because using image analysis you can see what the size is, you can verify all the way down to 1 μm.

For irregularly shaped particles such as cement, LD tends to broaden the distribution - compared to real distribution, it will tend to broaden the distribution.

For anisotropic shapes such as rods and platelets, LD significantly overestimates the breadth and can give bimodal distribution for monodispersed cylinders. So, these are some limitations you have to keep in mind.

Refractive Index: Mie theory requires the knowledge of complex refractive index of the material and fluid, because it considers the refractive index. Complex refractive index can be written as:

$$\tilde{\eta} = n - i\,k$$

Where 'n' is the refractive index and 'k' is the absorption index. This is the complex refractive index, and for that you have to know 'n' and 'k' that is the idea. So, Mie theory requires the knowledge of complex refractive index of the material and fluid. So, if you do not know that will affect your results.

Bimodal - when you plot distribution, you will see 2 peaks (Refer frequency (%) vs. size graph drawn in slide). So, that is because of the anisotropic shapes. Dotted line (single peak in graph) is normal case. So, what is the bottom line, why are we talking about this is, for non-spherical particle shapes, overinterpretation of the PSD tails, D_{v10} was and D_{v90} should be avoided. We should not go too much into it, because we are talking about tails, so D_{v50} is still. But too much interpretation of $D_{v10,}$ D_{v90} should be avoided, specifically if you have a non-spherical particles shape, that is the bottom line.

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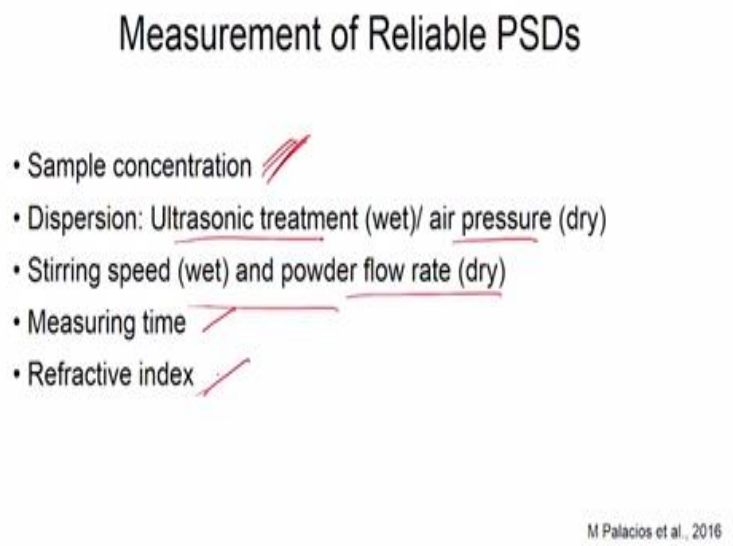

So, how do you get a reliable particle size distribution? There are so many things which affect your particle size distribution, when we talk about the laser diffraction.

Sample concentration -What is the sample concentration, because you have to disperse in a solution, normally we use isopropyl alcohol, for cement, because we do not want to use water because it will react. But what is the concentration? If you have too small amount of cement, what will happen your signal to noise ratio will be very low. If you have too much, then you have a lot of scattering that will affect your results. So it is important to pay attention to sample concentration.

Dispersion - how are you dispersing? You do not want agglomeration in powder, because if you have agglomeration that will again affect your particle size distribution. So, usually we use ultrasonic treatment to de-agglomerate the powder.

Stirring speed and powder flow rate, these are also things that can influence your PSD.
Measuring time - for how long you are keeping your sample, what is your measuring time, is it 1 second, 2 seconds, 10 seconds 30 seconds for an example, usually laser diffraction is very quick, you get results in seconds.

So you need to know what the refractive index is and also you need to know what the absorption coefficient 'k' is, because that will affect your particle size distribution.

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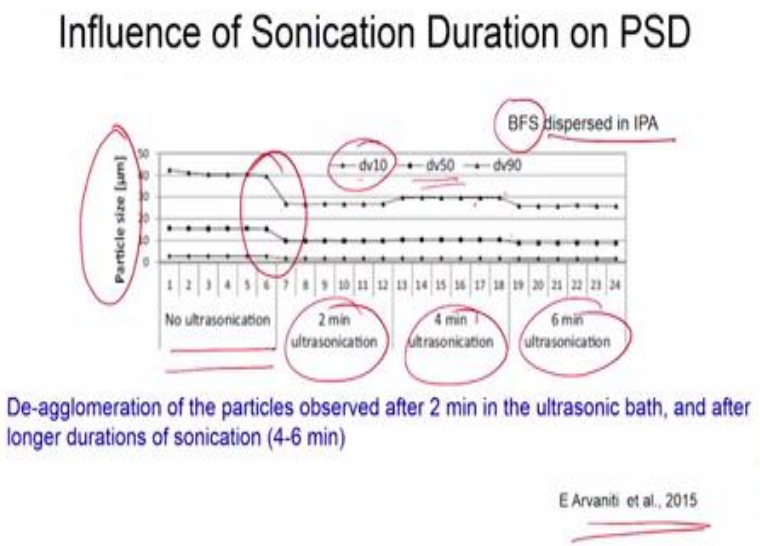

Let us see how the sonication affects your particle size distribution. So in this case, the sample is blast furnace slag (BFS) dispersed in IPA, which is isopropyl alcohol, those are the conditions and you are determining your particle size (µm). In all cases, they have 6 different samples no ultrasonication where no sonication was done. Then 2-minute ultrasonication, 4-minute ultrasonication, 6-minute ultrasonication was done and you can see the effect.

Clearly you see that after doing sonication, your determined size has reduced, because obviously if you do not do sonication there will be agglomeration. So, the particle size you will get will be at higher end. So a few minutes of ultrasonication can help you de-agglomerate the particles, but beyond that you do not see much difference, so it is good enough, 2 minutes of ultra sonication seems to work.

If you have too much sonication also it may affect your results, but you need some sonication just to make sure that you de-agglomerate your powder particles. So in this case, you can see that 2 minutes ultrasonication is good enough. So, obviously, this limit will change, frequency, all these things you will have to try on the material you work with. But the idea is we want to make sure that there is no agglomeration, that is why we want to de-agglomerate the particles because that will affect your particle size distribution.

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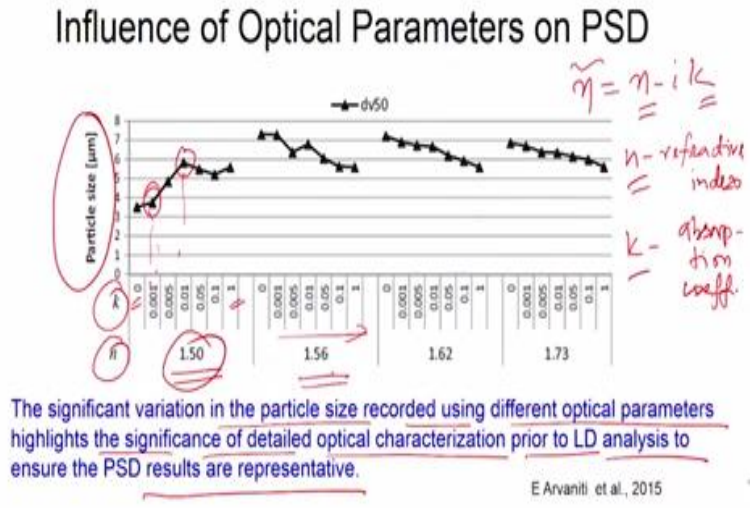

Influence of optical parameters - in most particle size apparatus, we use Mie theory, Mie theory covers whole range of particles from less than micron to 100s of microns, for that you have to assume the optical parameters, which means you have to know the optical parameters, that is very important. So, here it shows simply how the values affect your result.

So, we are plotting particle size (µm) on Y-axis and 'n' is the refractive index, and 'k' is the absorption coefficient. We are talking about the complex refractive index, $\tilde{\eta} = n - i\,k$, where, 'n' is real part 'k' is the imaginary part. So 'n' is refractive index usually you have that information and 'k' is absorption coefficient, because now we are taking into account both refraction and absorption.

So, it is important to know 'n' and 'k', here it shows how it affects your value. So in this case when you keep 'n' constant = 1.5, now if you change k from 0 which means no absorption. As you increase 'k', it means you are increasing the absorption. See the effect of that on the particle

size. So, you can clearly see that there is an effect on particle size based on the value you choose, so for n=1.56, and what happens when you change 'k' from 0 to 1.

So, the point is, it is important to pay attention to these model parameters (optical parameters). When you do particle size distribution experiment, you have to pay attention to this and you have to choose appropriate values. 'n' is normally easy to find because refractive index, you can use the database, but it is not that easy to find 'k'. So for k=0, you will have different value, like even for a smaller k=0.001, it will give you a different value than that for a larger 'k' value.

So that is why it is very important to pay attention to these optical parameters, because that affects your particle size distribution. So the significant variation in the particle size recorded using different optical parameters highlights the significance of detailed optical characterization prior to LD, so it is good to know these optical properties before you do laser diffraction. Suppose you are working with a material and you do not know any optical properties then your results will not be accurate. You will get results but would not be very accurate.

If you want to ensure the PSD results are representative then you must know these properties, as you see here, because these will affect the particle size distribution.

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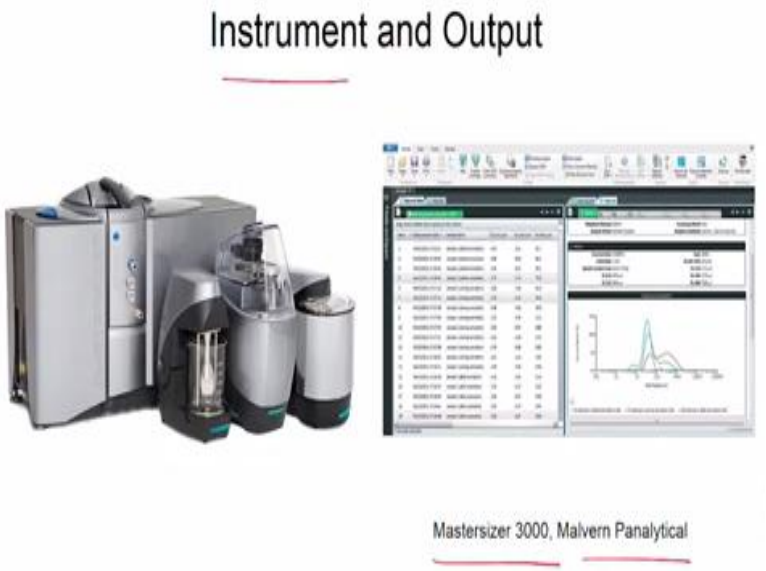

Finally, this is Mastersizer 3000 by Malvern Panalytical, typical apparatus instrument which we use for particle size analysis and this is a typical output. What you get as output is, you have a distribution from the software.

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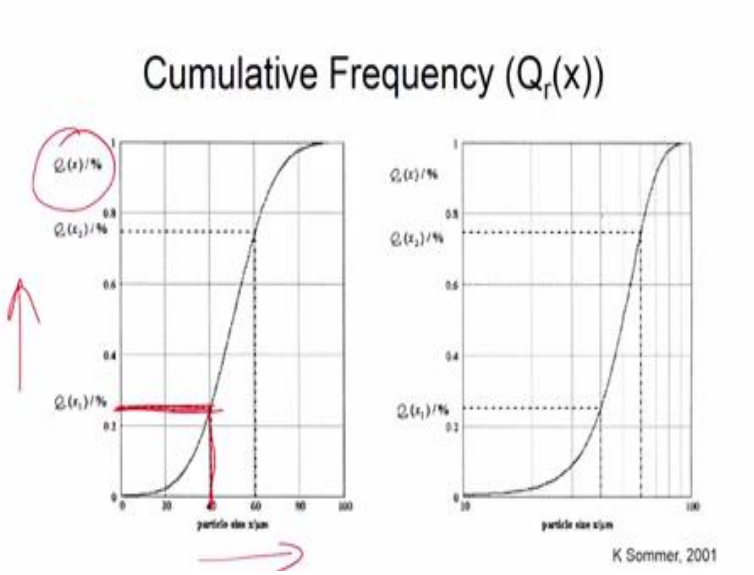

Basically what we do is we plot the cumulative percentages against the size. So, on X-axis you have particle size on Y-axis you have cumulative percentage. So, basically that means, for this percentage, say 25% particles are below 40 µm.

So, on the left plot here you have a normal axis, and on the right graph, you have a logarithmic axis for particle size. What happens when your size changes drastically, we are not talking about 10, 20, 30, 40 µm, we are talking about 0.1 to 100 or 200 µm, so, usually X-axis you plot on logarithmic scale, and when you plot your cumulative, it looks very same, only thing is you have changed your X-axis from normal to logarithmic, that is the only difference.