Characterization of Construction Materials
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Lecture-29
Surface Area Measurement: Different Techniques - Part 1

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Instrument and Output

Mastersizer 3000 Malvern Panalytical

Hello, everyone. So today we will continue our lecture on surface area measurement. We will try to recap what we studied in the last lecture. So, we looked into different techniques which we can use to determine particle size distribution. There are two key aspects we need to look into when we talk about surface properties. One is obviously, particle size distribution and one is surface area measurement.

So, earlier we talked about the particle size distribution, what are the various aspects we need to focus on. So, sieving is one of the most basic techniques, which we use to determine particle size distribution, obviously for coarser materials. The problem with the sieving is that you can't use it for finer materials, below 37 μm, for an example. For that we use laser diffraction which relies on the principle of diffraction. And the principle is that depending on the size, you will get the diffraction angles, or difference in the intensity. And the variation in diffraction angles and intensity depends on your size, we looked into that, so that can be used to determine the size of particles.

Also, there are two theories, which are applied to determine that. One is Fraunhofer theory, second is Mie theory and we know that Fraunhofer theory has its limitation because you cannot apply it for finer particles, right. It relies on only diffraction. On the other hand, Mie theory covers whole range. So, most softwares, most instruments will use Mie theory, which captures diffraction, reflection, refraction. We are talking about refraction happening within the particle, also absorption happening within the particle. So that is the significance of Mie theory.

Also we looked into Equivalent Spherical Diameter. In real life, you have different shapes and you are not going to have spherical shapes. So, how do you convert that? So, one way is to determine Equivalent Spherical Diameter. So, you equate the volume of your irregular shape particle to volume of a sphere. So, you know the diameter of that sphere, because sphere can be defined by its diameter. Only one unique number you need. So, that conversion is done and we say it is Equivalent Spherical Diameter. That conversion can be based on surface area also. If you are doing that for surface area, then you have to equate surface area of your irregular particle to equivalent surface area of sphere. But basic assumption of this laser diffraction and the Mie theory is all particles are spherical in nature. So, that is the basic assumption you should know. Equivalent volume is most commonly used.

So, this is an instrument you see from Malvern, Mastersizer 3000, which can be used to determine the particle size distribution of powders, commonly used instrument, from Malvern. So, what does a typical output look like? So, when you run your samples, you need to know what the various things are. I will just point out key aspects which you need to be careful about.

So, one is Particle is refractive index (RI). See often we do not pay attention to these things, but these values will change your distribution, because we talked about Mie theory which relies on optical properties. By optical properties what we mean is what the refractive index of your particle is, what is the refractive index of your medium? What is the absorption coefficient of your particle? So, based on these values we saw that it can affect your particle size distribution. So, Particle RI means Particle Refractive Index.

See in this case absorption is zero, so they assumed k = 0. So, there are two things ‘n’ and ‘k’. When you talk about the complex refractive index, it contains two parameters ‘n’ and ‘k’. ‘n’ is refractive index, ‘k’ is absorption coefficient. So, in the last class we saw the effect of these two parameters on particle size distribution. So, if you change it to 0.01, that is going to affect your results, that is the point. Zero absorption means there is no absorption, everything is getting transmitted. But in real life, you will have some absorption of particles.

Dispersant RI - so you are dispersing your powder into some dispersant, so what is the refractive index of that? So that you already know, most of the time we use isopropyl alcohol, for an example, for cement because we don't want to use water, if you use water it will react. So, these things are known. So, these are important things to keep in mind. So, based on these, your distribution will change.

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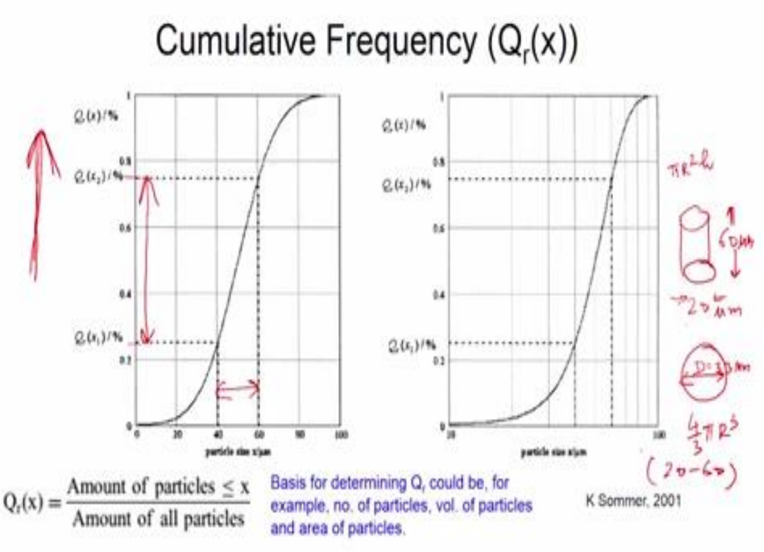

Cumulative Frequency ($Q_r(x)$)

$$Q_r(x) = \frac{\text{Amount of particles} \le x}{\text{Amount of all particles}}$$

Basis for determining Q_r could be, for example, no. of particles, vol. of particles and area of particles.

K Sommer, 2001

We will talk about one more aspect. From laser diffraction you are going to get the volume. Now what you can do is, you can also get numbers, and we saw that if you plot frequency distribution curve based on numbers versus based on volume you get different results. So, that is very important to keep in mind, when you do experiment also, when you refer to some literature, what the basis was as they may not look same.

For an example let us do one exercise. Suppose you have a sample, which consists of two sizes of particles, let us assume you have only two sizes. One is 1 µm, and one is 10 µm, and you have 50% of number of particles, having a diameter of 1 µm size and you have a 50% number of particles having 10 µm size. Now, you have to look at the volume.

So, when we are talking about the volume, 10 µm size volume will be thousand times of 1 µm size, as it is a cubic relation. So, now you have to calculate volume of your 10 µm size. Suppose you have 100 particles in total - 50 number of 1 µm size, 50 number of 10 µm size, that is the distribution based on numbers. Now, if you convert it to volume, what will be the corresponding volume for 10 µm size particles? 50 times 1000. And what will be the volume of 1 µm size particle? 50 times 1.

Now, if I asked you what is the contribution of your 10 µm size in terms of volume, you will calculate (50*1000) /((50*1000) + (50*1)). If you calculate that, the number will be close to 99.9%. So, what does it tell you? Although in numbers it seems like you have only 50% numbers of 10 µm size, but they occupy 99.9% volume. So, this simple example illustrates the importance of normalization or what is the basis? Is it number basis or is it volume basis, that is one aspect. It is very important to pay attention.

We also talked about the equivalent spherical diameter, which you understand, we have a volume, irregular shape then you can convert into corresponding sphere. So let's see, let's look at one aspect. In real life you never have all spherical shape particles. You will have irregular shape. For example, you have a cylindrical shape particle, which has, let's say diameter 20 µm and height is 60 µm. Now, if I asked you to give me the equivalent spherical diameter, can you calculate? So you know this is the cylinder of this size. You have to give me the diameter 'D' of the sphere.

Volume of cylinder = $\pi r^2 h$; Volume of sphere = $(4/3)*\pi R^3$

So now you have to just equate these. So, the sphere of equivalent volume would have a diameter of 33 µm. So, D = 33 µm. So this is the equivalent volume diameter. So, basically what you will get is the spread from 20 µm to 60 µm. So, basically how is it modeling is, you have these spheres of different sizes ranging from 20 µm to 60 µm, because that is the range here for cylindrical particle. So, it will have a spread.

But if you do just sieving, what would sieving give you? It might just tell you the size is 20 µm, because if it passes through the 20 µm size, it will give you that size. But from laser diffraction you are getting these values. So, now you understand the importance of, firstly when we talk about the basis, whether it is number of particles, or volume of particles or area of particles.

So, finally what do you get? You get sizes and you also get % volume, because in Mie theory you are calculating volume. Yes, it is up to you, and then you can convert that to number also, because it is based on assumption that all are spheres. So, once you know the total volume, you can calculate numbers.

So, this is the cumulative plot. So, on Y-axis you have %, let us say Qr(x), so how do we define it?

$$Q_r(x) = \frac{Amount\ of\ particles\ \leq x}{Amount\ of\ all\ particles}$$

Where the amount could be volume of particles, could be number of particles, could be surface area of particles. These are the different bases. So, you get this cumulative frequency. So, basically, what does it tell you? If I ask you, what is the percentage of particles between 40 µm and 60 µm, you can get the value by calculating from the corresponding Y-axis % of these sizes.

So, on X-axis you see that you have 0, 20, 40, 60, 80, 100 µm. But often you have sizes going beyond 100 µm or even below 1 µm. So, you have a wide range. So, another way of representing the same thing is through logarithmic X-axis (as shown in graph on the right). So, here you see values are in log scale. You can also extend it, right. But we are getting similar distribution, so, it’s fine. So, I will also tell you what are sometimes the issues you’ll have, but just to highlight, that is how we usually plot.

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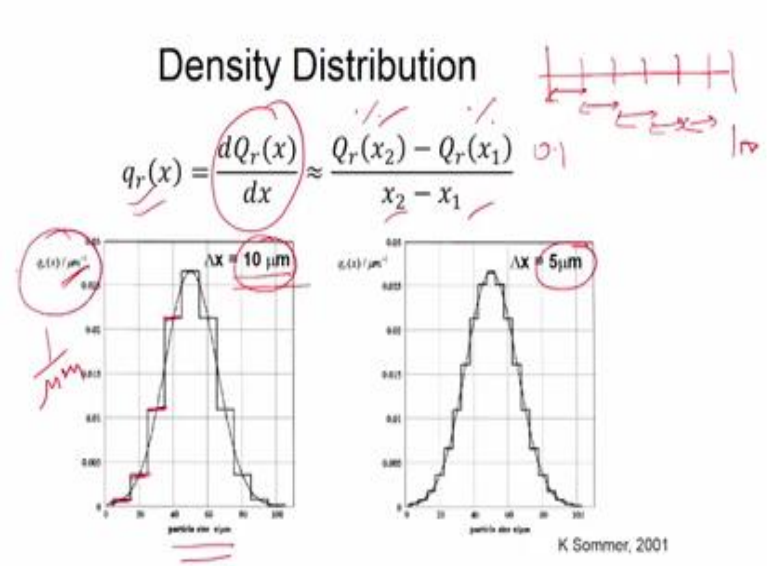

Density Distribution

$$q_r(x) = \frac{dQ_r(x)}{dx} \approx \frac{Q_r(x_2) - Q_r(x_1)}{x_2 - x_1}$$

K Sommer, 2001

So now, how do you get density distribution? Earlier we saw the cumulative. Density distribution is nothing but derivative of that plot. When you differentiate the cumulative, you will get the density, frequency distribution.

$$q_r(x) = \frac{dQ_r(x)}{dx} \approx \frac{Q_r(x_2) - Q_r(x_1)}{x_2 - x_1}$$

Let's say you have a range, which you have divided into different size intervals, we are talking about suppose 0.1 to 100 µm. So, you have divided this whole range into small size intervals. So, those size intervals are here, x_2, x_1. So, if your step size is suppose 10 µm, you know for 10 µm interval, what is the volume, so that you can calculate q_r which is the derivative. So, you will get a plot like this, which is the derivative plot.

So, on the Y-axis, you have (1/µm) unit, because Q_r is a percentage and x_2 - x_1 is your size in µm. So, your Y-axis will have (1/µm) unit. X-axis you have particle size in µm. So, when you do this, irrespective of step size, if instead of 10 µm size, if you use 5 µm as the step size, you get similar plot. Makes sense, basically you have a same plot but it is advisable to normalize it.

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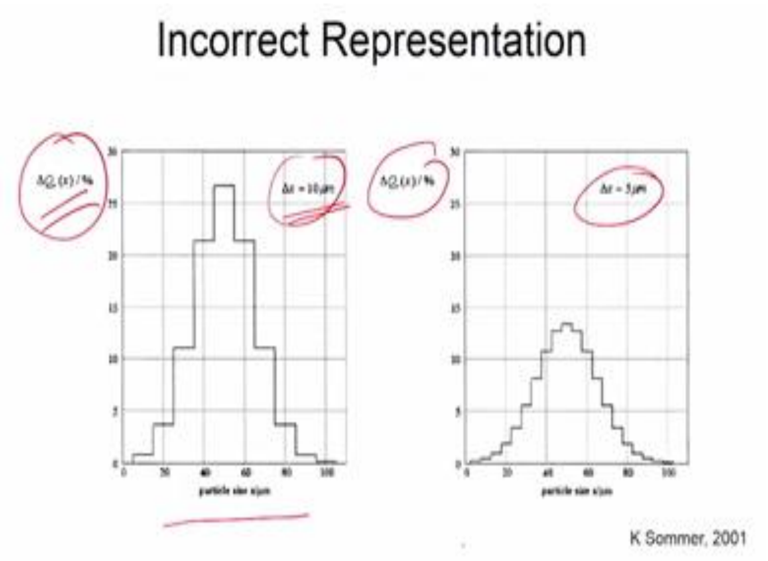

Incorrect Representation

K Sommer, 2001

Why I am saying this is because, this is incorrect representation, representation when you do it based on just percentage. Now here also same thing, on Y-axis you have percentage, and on X-axis you have particle size. First, the left plot is for 10 µm step size, right-hand side is 5 µm step size. See the difference, they look very different. So this is incorrect representation.

Why I am saying? Suppose you are getting something from a manufacturer, what will they do? Manufacturers often justify this depiction of data by claiming that it satisfies the customers' demands. So, they can adjust this step size and show you, that it meets your demands. So, you should question how they got this. This is not correct representation, you should always have normalization. In the previous slide graph, whether you pick 5 µm or 2 µm step size, you will get the similar distribution. So that is an important aspect.

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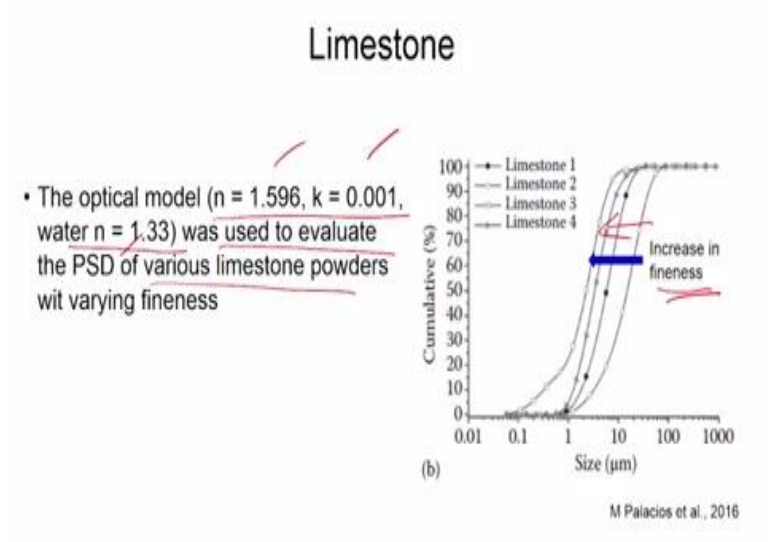

Limestone

- The optical model (n = 1.596, k = 0.001, water n = 1.33) was used to evaluate the PSD of various limestone powders wit varying fineness

M Palacios et al., 2016

So, let us look at few particle size distributions, so in this case, it is Portland cement. So, we are plotting % volume versus size. These are different tests, so this figure shows four samples taken from the same dispersion by using isopropanol and external ultrasonic treatment over 30-minute period. So you get very reliable data, so good reproducibility of laser diffraction method for a stable suspension, it works really well. So if you have a stable suspension, irrespective of time whenever you take your sample, it will give you very reasonable values. From this you can also calculate what the 50% by volume is. So, your d_{50} by volume is 10 µm, so that is a good number to remember also, if someone asks you what is the d_{50} value for cement, it's around 10 to 15 µm.

Here is the limestone. Again these are very important things and whenever you do experiment you have to pay attention, what are the values? So, this is the optical model used in this case, 'n' value was 1.596 for limestone, 'k' absorption was 0.001, and not 0, water 'n=1.33' was used as dispersant, was used to evaluate the PSD, and here you see the effect. So point is, through this you can capture, and you can clearly see the fineness is increasing. As you go in this direction (towards left), the fineness is increasing. So there is a difference in various samples.

So, you can compare, if suppose you want to understand the influence of grinding, you can do this test after grinding and see how the particle size distribution is changing. Also it is important to pay attention to these optical properties whenever you do experiments, because that will affect your results.

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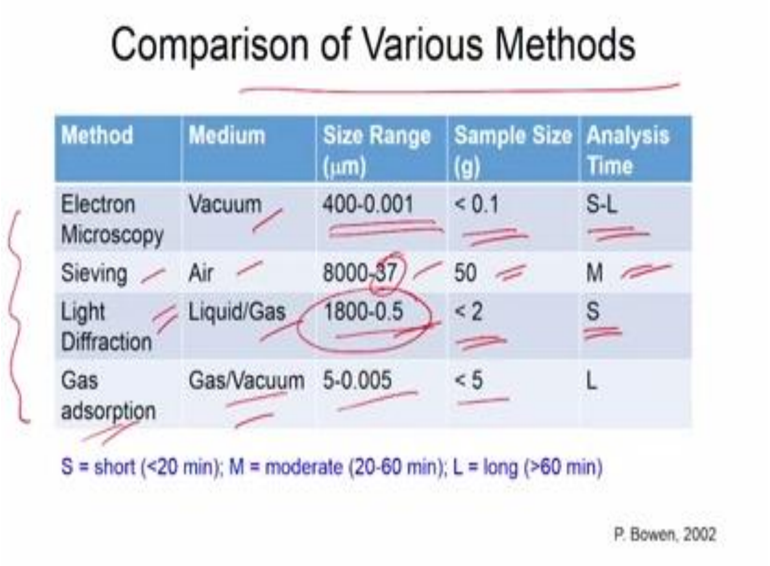

Comparison of Various Methods

Method	Medium	Size Range (µm)	Sample Size (g)	Analysis Time
Electron Microscopy	Vacuum	400-0.001	< 0.1	S-L
Sieving	Air	8000-37	50	M
Light Diffraction	Liquid/Gas	1800-0.5	< 2	S
Gas adsorption	Gas/Vacuum	5-0.005	< 5	L

S = short (<20 min); M = moderate (20-60 min); L = long (>60 min)

P. Bowen, 2002

So, coming to the commonly used techniques for particle size distribution, here we have listed at least 4. Electron microscopy is usually done in vacuum, you can cover this range (400-0.001 µm), sample size is small (<0.1g), time taken is short to moderate, it takes some time.

Sieving is done in air, size range is 8000-37 µm, you can see the limitation on this, so you cannot go below 37 µm. So for larger size, it is fine. You need a bigger sample size (50g). Also it takes moderate time, because you have to sieve it, either manually or mechanically.

Light diffraction. You can do either in liquid, gas, liquid means dispersant or you can also use gas for that. It covers whole range 0.5 to 1800 µm. Small sample size (< 2g) and it is very quick. That is the advantage of this technique.

Another technique is gas adsorption, it also can be used. This just gives you a comparison between different techniques which are used, what the advantages are.