

Characterization of Construction Materials

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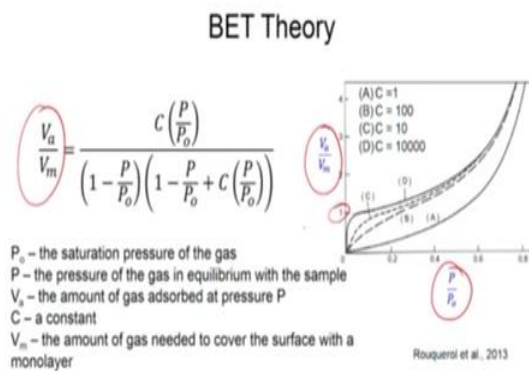
Department of Civil Engineering

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Lecture - 31

Surface Area Measurement: Calculation and Applications

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Hi, everyone, so we will continue our lecture on surface area measurement. In the last lecture we were discussing about the BET theory. So, we were wondering, there are a lot of isotherms, which cannot be explained based on Langmuir theory. So, BET (Brunauer, Emmett, Teller), they came up with this relation, where for an example, if you see in the plot, this type of isotherm Type II isotherm can be explained.

So, the relationship between V_a/V_m where V_a is the amount of gas adsorbed at pressure P and V_m is the amount of gas needed to cover the surface with a monolayer. So, when you plot V_a/V_m against P/P_0 which is the partial gas pressure, you get this kind of response. So, it kind of explains the Type II isotherm in this case. Based on the value of C you may get different shapes.

Now, we wanted to know how we can use the series to calculate the surface area. Also pay attention in this plot on this 1 (Y-axis). So, when $V_a/V_m = 1$, it means the gas adsorbed is equal to the amount of gas needed to cover the surface with a monolayer.

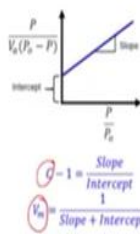
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BET Equation: Linear Form

$$\frac{P}{V_a(P_0 - P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \left(\frac{P}{P_0}\right)$$

P_0 – the saturation pressure of the gas
 P – the pressure of the gas in equilibrium with the sample
 V_a – the amount of gas adsorbed at pressure P
 C – a constant; $= \exp(E_1 - E_L)/RT$
 V_m – the amount of gas needed to cover the surface with a monolayer





So, same relationship can be written in a linear form. So here, consider $\frac{P}{V_a(P_0 - P)}$ as Y. You are changing pressure, you are measuring volume. Also here is $P/P_0 = X$, that is partial gas pressure. Also, Slope, $S = \frac{C-1}{V_m C}$ and Intercept, $I = \frac{1}{V_m C}$ this is the linear form $Y = SX + I$.


So, when you plot Y versus X, you will find a straight line and where it meets the Y-axis, that is the intercept and slope of that line will give you Slope, $S = \frac{C-1}{V_m C}$. So, if you know these, you can easily calculate the constant C, also you can calculate V_m . And you notice the constant C depends on the energy of adsorption.

$$C \approx \frac{\exp(E_1 - E_L)}{RT}$$

E_1 is energy of adsorption of i^{th} layer. So in this case, first layer. And E_L is second layer onwards, i.e., the energy of adsorption for second layer, third layer... can be written as E_L . So,

this constant C depends on the difference between the energy of adsorption for first layer and Lth layer. So, now the question comes how to calculate surface area.

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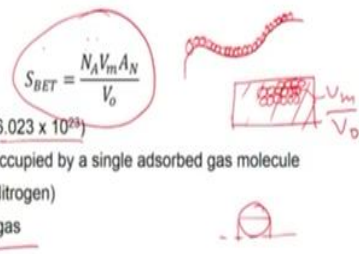



Determination of Surface Area

Surface Area:

$$S_{BET} = \frac{N_A V_m A_N}{V_0}$$

N_A – Avogadro constant (6.023×10^{23})
 A_N – the area of surface occupied by a single adsorbed gas molecule
 (16.2×10^{-20} m² for Nitrogen)
 V_0 – the molar volume of gas

So, determination of surface area lies on premise that: you have a surface and what we are assuming here, when we say the monolayer formation is complete that means, we have one layer thick monolayer. Suppose, you know that, you know the volume of gas adsorbed, when the mono layer just completes. If you look at the same thing in the plan, you may have a surface like idealized surface and you have these molecules. And you have only one layer. This we are looking from the top (Figure 1).

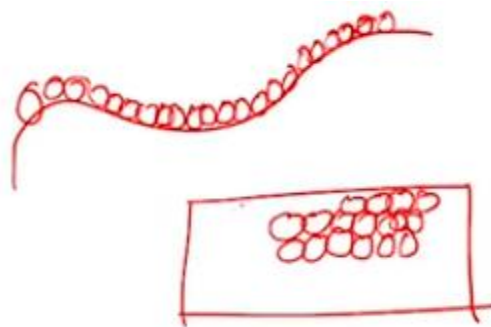


Figure 1 Adsorption of gas on surface

So how can you calculate that to find surface area and you know this layer is on the surface, it is adsorbed on the layer. So once we know the volume V_m , already we saw in the last slide, we can calculate the moles, V_m/V_0 . V_0 is the molar volume of gas. Once you know the

moles, we can calculate how many molecules will be there; one mole will have 6.023×10^{23} molecules - that is the Avogadro constant (N_A). Once you know how many molecules are there, you can calculate the area by multiplying it by area of one molecule (A_N). That is the idea. So we know the volume. We know volume of gas adsorbed (V_m) and we have to find how many moles are there, which we can do by dividing it by V_0 . Once you know that, we have to know find how many molecules are there, which you can do by multiplying it by N_A and finally, you multiply it by A_N , which is the projected area. So for example, this is the molecule (Figure 2), the area can be the projected area (you have a molecule sitting on a surface). So, the projected area on that surface will give you the value A_N .



Figure 2 Gas adsorped on surface - showing projected area

So for nitrogen (N_2), $A_N = 16.2 \times 10^{-20} \text{ m}^2$. That will change if you are changing the gas. Sometimes people use argon, krypton, so accordingly A_N will change. So here, you have a way to find surface area through BET. So you need to calculate V_m and then you can calculate number of moles, multiply it with Avogadro constant, and then multiply it with A_N . So that is what gives us the surface area.

$$S_{BET} = \frac{N_A V_m A_N}{V_0}$$

(Refer Slide Time: 06:23)



Adsorbate Selection

- Nitrogen is currently widely accepted as a standard adsorbate because of its unique properties:
 - No chemical reactivity with the surface
 - Low and well-defined cross-sectional area at its boiling point
 - No polarity
 - Wide availability
 - Current adsorption equipment can measure absolute surface area as low as 1 m^2 using N_2
- For absolute areas similar or lower than 1 m^2 , either increase the quantity of powder (if possible) or change the adsorbate to Kr or Ar with a lower saturation pressure than N_2 at 77K.

M Palacios et al., 2016




So how do we select the adsorbate? The question comes, what should the criteria be for selecting adsorbate or the gas which we use. So currently nitrogen is used, it is widely accepted as a standard adsorbate because of its unique properties, which are:

- There is no chemical reactivity the surface – it should not chemically react with the surface. That is obvious.
- Low and well-defined cross-sectional area at its boiling point. It should have low and well-defined cross-sectional area.
- No polarity - that will give you no lateral interaction, we want to make sure there is no lateral interaction between molecules.
- It should be widely available.
- Current adsorption equipment can measure absolute area as low as 1 m^2 using nitrogen. That is the limitation as far as current adsorption equipments are concerned.

But if you want to measure surface area below 1 m^2 , then either you have to increase the quantity of powder so that your net surface area increases, if possible. Otherwise, you will have to use other adsorbates like krypton (Kr), argon (Ar) with lower saturation pressure than N_2 (Nitrogen). So, there are ways you can use other adsorbates to measure lower surface areas.


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Sample Preparation

- Stopping hydration ✓
 - Preservation of microstructure is key as drying method may affect it
 - Solvent exchange using isopropanol is preferred, but may lead to dehydration of ettringite on long exposure
 - Short contact with cooled isopropanol (5°C) has been shown to preserve ettringite crystalline structure
- Degassing conditions ✓
 - Removal of gas physically adsorbed on the surface before gas adsorption measurement
 - Normally done under nitrogen flow or vacuum and high temperature to accelerate the process

M Palacios et al. 2016



So it is very important to know how to prepare the sample for this. So first of all, we have already talked about stopping hydration. There are ways and you have to follow a way which can preserve the microstructure.

- Preservation of microstructure is key as drying method may affect it. When you dry things, it will affect your microstructure, and if your microstructure changes, it will change your surface properties.
- So, solvent exchange using isopropanol is preferred, but it may lead to dehydration of ettringite on long exposure - that is the downside of it. For long exposure ettringite may get dehydrated.
- So, what is recommended is short contact with cooled isopropanol (5°C) has been shown to preserve ettringite crystalline structure.

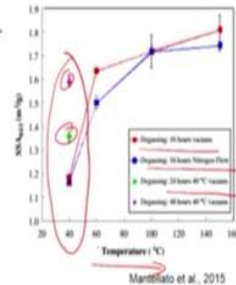
So, once you stop hydration and you have the sample, before you do this adsorption test, you have to degas the sample. Degassing sample means you have to remove any gas which is physically adsorbed on the surface before making adsorption measurements. So it is normally done under nitrogen flow, degassing means you do it under nitrogen flow or vacuum and high temperature to accelerate the process, because if you do not use high temperature it might take a long time. But you also do not want to use too high temperature as we will see in the next slide.

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Influence of Degassing Temperature

- Figure shows the impact of the degassing conditions on the SSA of anhydrous Portland cement
- Degassing at 40°C under N₂ flow for 16 hours has been shown as an optimal degassing method.



So, what is the influence of degassing temperature on surface area measured by BET. So, here we see this figure (in slide), shows the influence of degassing conditions. On X-axis, you have temperature (°C), where you see 40°C, 60°C, 100°C. What is evident is, as you are increasing the degassing temperature your surface area also is increasing. So that is affecting the surface area.

So, degassing at 40°C under nitrogen (N₂) flow for 16 hours has been shown to be an optimal degassing method. If you do it for longer, then it may affect your microstructure. And that will reflect in your measurement. See here in the graph, so this red one is degassing for 16 hours in vacuum. The blue one is degassing 16 hours in nitrogen flow, and these both are pretty much close.


But if you do degassing for 24 hours at 40°C in vacuum, that is, as you are increasing the time, you see it is affecting your surface area, that is just at 40°C only and you increase the time. But if you increase the temperature also that significantly increases your surface area. The point is it is good to maintain low temperatures and not too high temperature, because if you go for high temperature, although it will accelerate your degassing, it will affect your microstructure which you do not want.


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Specific Guidelines for N₂ Adsorption Test

- Adsorbate gas
 - Nitrogen with a purity of 99.9% must be used as adsorbate gas.
- Sample weight
 - Sample weight is always controlled before and after degassing as well as after the adsorption measurements.
 - Sample weight should provide at least absolute surface areas equal or higher than 1 m² (when nitrogen is used as adsorptive gas).
- Sample tubes
 - Tube cells should be immersed to a depth of at least 5 cm below the liquid nitrogen level.
 - Isothermal jacket should be used to maintain a constant temperature in the sample tube immersed in the Dewar while the liquid nitrogen evaporates.
- Stopping of hydration and degassing conditions
 - In the case of anhydrous cementitious materials:
 - For cementitious materials containing gypsum, mild degassing conditions must be applied to preserve gypsum microstructure and composition, specifically degassing at 40°C under N₂ flow for 16 h. Higher temperatures and/or vacuum treatment would prompt gypsum dehydration involving significant structural changes.
 - Clinker or supplementary cementitious materials such as slag can be degassed at relatively high temperatures, 200°C, for 1 hour without modifying its microstructure.

M Palacios et al., 2016





So, here are some specific guidelines if you want to use nitrogen absorption test.

First of all, about the adsorbate gas - nitrogen with purity of at least 99.9% must be used - highly pure nitrogen.

Sample weight - sample weight is always controlled before and after degassing as well as after adsorption measurements. Sample weight should provide at least absolute surface area equal or higher than 1 m² for nitrogen. If you have to go below 1 m², then you may have to use other adsorbates like krypton, argon.

Sample tubes - tube cells should be immersed to a depth of at least 5 cm below the liquid nitrogen level, because you are putting your sample in nitrogen environment, so, it should be at least 50mm below the liquid level. Isothermal jacket should be used to maintain a constant temperature in the sample tube immersed in Dewar while the liquid nitrogen evaporates.

Stopping of hydration and degassing conditions – In case of anhydrous material, if you analyse cement, fly ash, SCMs, (anhydrous cementitious materials). So, for cementitious material containing gypsum, mild degassing conditions must be applied to preserve gypsum microstructure and composition. You know that cement contains gypsum, so if you use high temperature it will lead to dehydration of gypsum. So you have to make sure that you are using mild degassing conditions. Specifically, degassing at 40°C under nitrogen flow for 16 hours is recommended. That does not affect that is what people have seen. Higher temperatures or

vacuum treatment would prompt gypsum dehydration involving significant structural changes. If you use higher temperature it will lead to dehydration of gypsum and involve significant structural changes, and that will be reflected in your surface area measurements.

Clinker or supplementary cementitious materials - clinker does not have any gypsum and supplementary cementitious material such as slag can be degassed at relatively high temperatures. So, where you think that there is no effect on constituents, you can use high temperature (say 200°C) for 1 hour, in this case without modifying its microstructure. So, it depends on what kind of material you want to analyse.

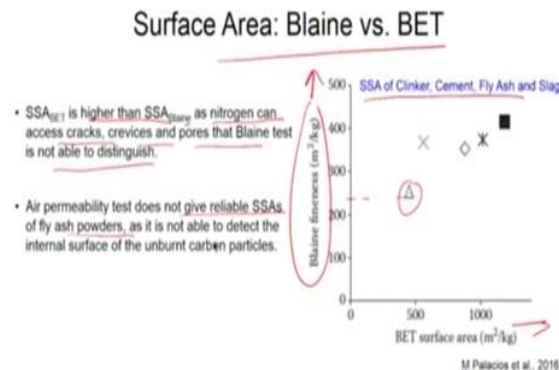
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The slide is titled "Reporting SSA" and features a list of four bullet points. The first bullet point, "Equipment used", has a red checkmark next to it. The second bullet point is "Method of stopping hydration in the case of hydrated samples". The third bullet point is "Degassing conditions (temperature, pressure – if vacuum or N₂ flow was used – and time)". The fourth bullet point is "SSA including standard deviation from repeated measurements". In the top right corner of the slide is the NPTEL logo. In the bottom right corner, there is a small video inset showing a man in a light blue shirt speaking. Below the video inset, the text "M Palacios et al., 2016" is visible.

So, typically how do we report specific surface area?

- We report the equipment used - very important, when you do the work, you have to report which instrument was used.
- Method of stopping hydration - it is very important to also mention which method was used to stop hydration because that is going to have an impact on your measurements.
- Degassing conditions, like temperature, pressure, if vacuum or N₂ flow was used and time - for how long and what the conditions of degassing were.
- Finally, it should include standard deviation from repeated measurements. These are typically things which we report when we carry out surface area measurement using BET.

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Now, you have looked at various techniques. We saw that we can determine surface area using Blaine air permeability, also we can determine using laser diffraction, and BET. Now it is good to compare, so here we have a comparison between Blaine vs. BET. So, usually specific surface area determined by BET is higher than Blaine ($SSA_{BET} > SSA_{Blaine}$), we talked about it because as nitrogen can access cracks, crevices and pores that Blaine test is not able to distinguish. So, nitrogen has that capability to go inside cracks, crevices and pores, which are not considered in Blaine test. So usually the values you get of surface area through BET will be higher than that obtained in Blaine test.

So, in the graph shown, on the Y-axis is the Blaine fineness (m^2/kg), and on X-axis is the BET surface area (m^2/kg). So, typical values suppose this one is close to 500 in this case (BET) and here about 200-250 m^2/kg (Blaine fineness). So, you can see here, this is the specific surface area of clinker, cement, fly ash, and slag from this paper (M. Palacios et al., 2016). So, if you look at the specific surface area determined for clinker, cement, fly ash, slag, you see, it is a general trend. So BET values are higher, so, that is good to know.

Also, air permeability test does not give reliable SSA values for fly ash powders, as it is not able to detect the internal surface of the unburnt carbon particles. So, a lot of times you have unburnt carbon in fly ash. So that internal surface, we cannot measure using air permeability.

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SSAs Determined Using Different Techniques

	BET (m ² /kg)	Laser Diffraction* (m ² /kg)	Blaine (m ² /kg)
Fly Ash 1	452	384, 415*	240
Fly Ash 2	560	279, 293*	387
Slag 1	1025	370, 688*	369
Slag 2	721	402, 640*	--
Silica fume	17102	6180	--

* Using two different optical models (n, k)

E Arvaniti et al., 2015



Again, here is a table which gives you an idea about the comparison, here we are comparing SSAs obtained using BET, laser diffraction, and Blaine. So, this was done, you can refer to this paper if you want to know more (E Arvaniti et al., 2015). So, the test was done on 2 types of fly ashes, 2 types of slags and silica fume. So, again you can see that BET values are higher than Blaine and laser diffraction, so that you should know. This happens because other tests do not consider the porosity, roughness of particles. So here, nitrogen molecules can access cracks, get into the pores. So, as long as they can go inside, you will be able to determine the surface area. That is the take away from this slide.

And also notice that in laser diffraction, it is very critical to the optical model you use. Lot of times we do not pay attention. So here you see 2 different values. The star denotes 2 different optical models, and what does that mean? It means different values of 'n' and 'k' have been used. 'n' is refractive index of your particle, and 'k' is adsorption coefficient. So in this case I think 'n' value was same but 'k' was changed and so it gives you different numbers. So, it is very important when you do these tests to know the limitations, assumptions, and what optical model you choose. So, here that is why you see 2 different values.

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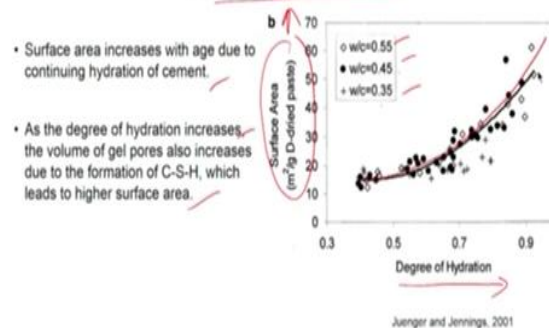
Applications of BET Surface Area to Construction Materials



Now we will look into applications of this BET surface area to construction materials. Now, we know that we can measure surface area using different techniques, but in this case, we will look into the application of BET surface area, which is commonly used and gives you very close to true surface area.

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Surface Area of Cement Paste: Influence of Degree of Hydration

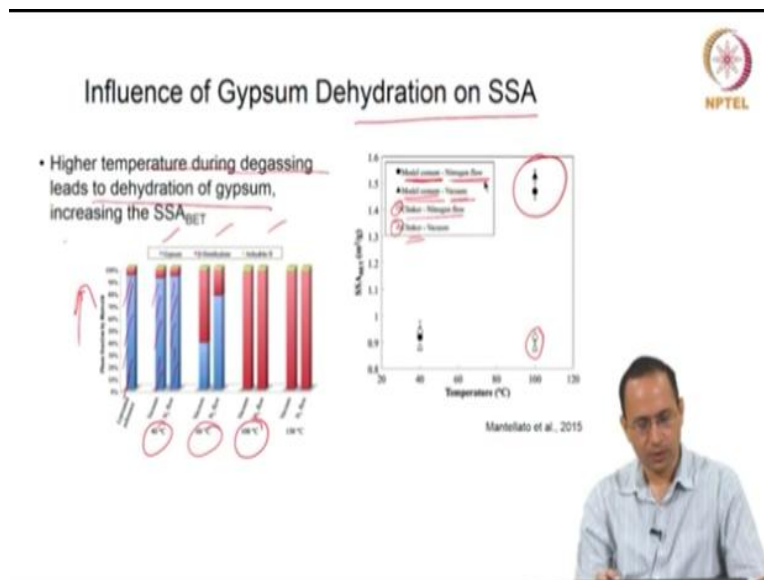


So, how does surface area of cement paste change with hydration? We know that cement hydrates you have formation of calcium silicate hydrate (C-S-H) with time. So degree of hydration increases with time. So, what is the influence of degree of hydration? So here you see on Y-axis you have surface area plotted versus degree of hydration on X-axis. So, you see an

increase as the hydration progresses, that is, as the degree of hydration increases, you see increase in surface area because, increase in the degree of hydration will lead to increase in the amount of calcium silicate hydrate (C-S-H), which is the gel and that means you form more gel pores. So, you are forming more gel pores as the degree of hydration increases and leads to increase in the surface area.

Here is the data from different water-cement ratio (In graph in slide). Here you see it is combined, w/c of 0.35, 0.45, 0.55 and when it is put together, there is a nice correlation between surface area and degree of hydration.

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So, let us look at the influence of gypsum dehydration. We talked about that, at higher temperature gypsum may dehydrate. So how does that affect the surface area measurements? So here you see. So, high temperature during degassing leads to dehydration of gypsum. So here you see 2 temperatures (in graph on the right in slide). Measurements were done at 2 different temperatures - one is 40°C, and one is 100 °C.

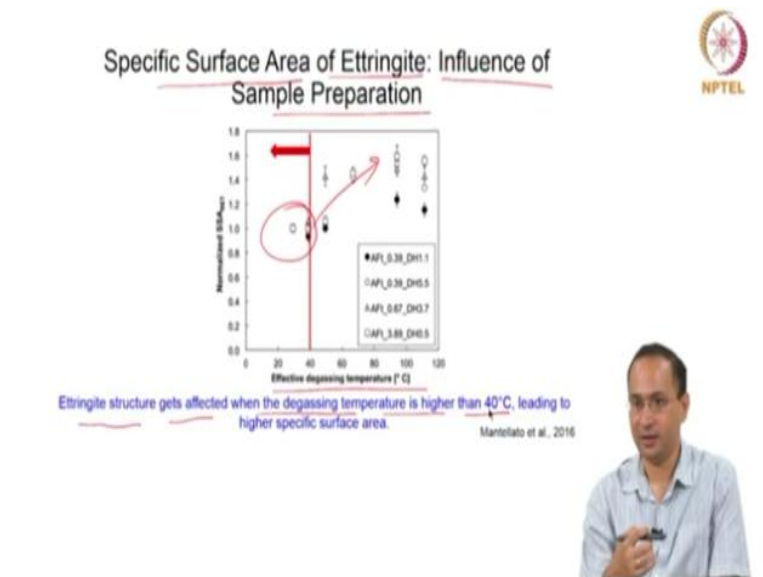
Before carrying out adsorption test, you have to degas your sample, that is, you have to make sure there is no gas adsorbed in your sample. And also you see different data points here, one is the model cement done in nitrogen flow, one is model cement degassed in vacuum. One is clinker in nitrogen flow and one is clinker in vacuum. So, you see that clinker does not get

affected (as seen in the graph). So, clinker does not get affected because there is no gypsum. But if you look at cement, which has gypsum, you see an increase. So, that clearly tells you gypsum is getting affected by your degassing temperature.

Also, if you look at the plot on the left, we have phase fraction by Rietveld, you can do quantitative X-ray diffraction, as we discussed in X-ray diffraction lecture. As these are crystalline phases, you can determine how much of it is in the cement. So, you have here gypsum, hemihydrate, and anhydrite. You have significant gypsum, in untreated reference (untreated cement). In 40°C there is not much change (shown in blue in bar graph). when you increase to 60 °C you see reduction in gypsum and increase in hemihydrate.

So you see that the dehydration of gypsum is taking place. Finally, at 100 °C, most of your gypsum is gone. You have anhydrite and hemihydrate. So it tells you that as you increase the temperature, it leads to dehydration of gypsum. And that will get reflected in the measurements. So, it depends on the kind of material. If you are analyzing clinker, it is fine maybe to go to higher temperature for degassing, but if you are working with cement then it is important to restrict the degassing temperature to 40 °C.

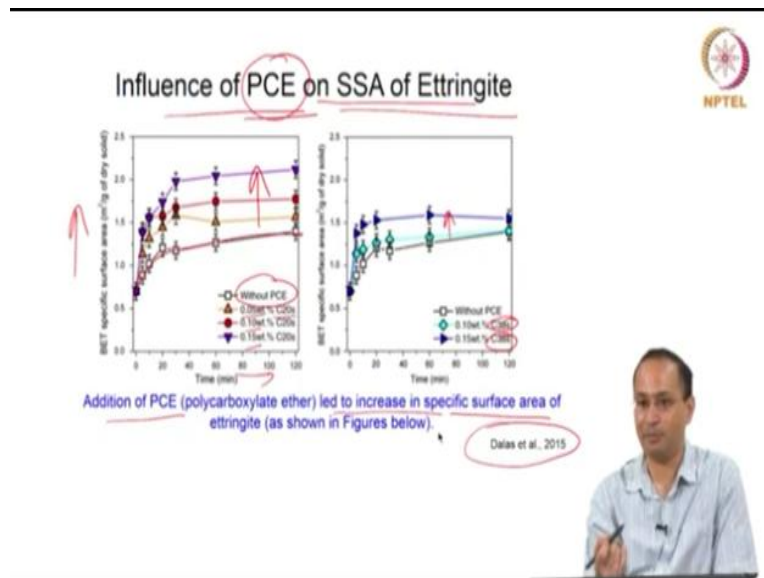
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Also we can determine specific surface area of ettringite. What happens when you use different sample preparations, because the ettringite phases are also very sensitive to temperature. So, here also you see as long as the temperature (degassing temperature) is below 40 °C, you do not see much change, but as you increase the temperature to 60 °C, 80 °C, 100 °C, you see increase in BET surfaces. So, ettringite structure gets affected when the degassing temperature is higher than 40 °C leading to higher specific surface area.

So, these are the things you have to be aware of. Suppose you have a cement where you expect ettringite. Now, if you want to determine the surface area, then you have to restrict the temperature to 40 degrees celsius. If you go higher, then it will affect your structure that will get reflected in your surface area measurements.

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Here we see the influence of PCE (polycarboxylate ether) it is kind of a superplasticiser, we know why we use a superplasticiser – to increase the workability. So here we'll see the influence of superplasticiser on the specific surface area of ettringite. What do you see here?


So on the left plot, we have Surface area plotted on Y-axis vs. Time (min) on X-axis. So, you see when you do not have any PCE in the sample, a trend is observed. Then you add PCE 0.05wt%, 0.1 wt%, 0.15wt%, you see an increase with the time. And here they used the different type of PCE - C20 and C38 - this is just a difference in the polycarboxylate ether

superplasticiser. Again you see a similar trend. So, what does it tell you? Addition of PCE in this case led to increase in specific surface area of ettringite. So, this kind of things can be monitored using nitrogen adsorption.

So, if you want to look at the interaction, what happens to surface area, it tells you definitely that something is happening. Anyway we are not going in detail. For details you can refer to the paper here (Dalas et al., 2015) to find out what is the cause or what is happening, but these are the changes, which you can capture using nitrogen adsorption test.

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Specific Surface Area of Clays



Sample	Mineralogy	Sample	SA _{N₂}	SA _{N₂}	SA _{N₂}	SA _{N₂}	SA _{N₂}
SY-1 (control)	Montmorillonite	SY-1 (control)	40.40	40.40	40.2	3.10	0.1
SY-2 (graphite)	Montmorillonite	SY-2 (graphite)	40.40	41.25	40.3	4.10	0.2
SY-3	Ca-montmorillonite	SY-3	39.70	41.20	40.8	3.00	0.0
SY-4 (graphite)	Montmorillonite	SY-4 (graphite)	41.70	42.00	41.8	4.00	0.0
SY-5 (illite)	Illite	SY-5 (illite)	40.40	40.70	40.6	4.10	0.0
SY-6 (illite)	Illite	SY-6 (illite)	40.40	40.70	40.6	4.10	0.0
SY-7 (illite)	Illite	SY-7 (illite)	40.40	40.70	40.6	4.10	0.0
SY-8 (illite)	Illite	SY-8 (illite)	40.40	40.70	40.6	4.10	0.0
SY-9 (illite)	Illite	SY-9 (illite)	40.40	40.70	40.6	4.10	0.0
SY-10 (illite)	Illite	SY-10 (illite)	40.40	40.70	40.6	4.10	0.0
SY-11 (illite)	Illite	SY-11 (illite)	40.40	40.70	40.6	4.10	0.0
SY-12 (illite)	Illite	SY-12 (illite)	40.40	40.70	40.6	4.10	0.0
SY-13 (illite)	Illite	SY-13 (illite)	40.40	40.70	40.6	4.10	0.0
SY-14 (illite)	Illite	SY-14 (illite)	40.40	40.70	40.6	4.10	0.0
SY-15 (illite)	Illite	SY-15 (illite)	40.40	40.70	40.6	4.10	0.0
SY-16 (illite)	Illite	SY-16 (illite)	40.40	40.70	40.6	4.10	0.0
SY-17 (illite)	Illite	SY-17 (illite)	40.40	40.70	40.6	4.10	0.0
SY-18 (illite)	Illite	SY-18 (illite)	40.40	40.70	40.6	4.10	0.0
SY-19 (illite)	Illite	SY-19 (illite)	40.40	40.70	40.6	4.10	0.0
SY-20 (illite)	Illite	SY-20 (illite)	40.40	40.70	40.6	4.10	0.0
SY-21 (illite)	Illite	SY-21 (illite)	40.40	40.70	40.6	4.10	0.0
SY-22 (illite)	Illite	SY-22 (illite)	40.40	40.70	40.6	4.10	0.0
SY-23 (illite)	Illite	SY-23 (illite)	40.40	40.70	40.6	4.10	0.0
SY-24 (illite)	Illite	SY-24 (illite)	40.40	40.70	40.6	4.10	0.0
SY-25 (illite)	Illite	SY-25 (illite)	40.40	40.70	40.6	4.10	0.0
SY-26 (illite)	Illite	SY-26 (illite)	40.40	40.70	40.6	4.10	0.0
SY-27 (illite)	Illite	SY-27 (illite)	40.40	40.70	40.6	4.10	0.0
SY-28 (illite)	Illite	SY-28 (illite)	40.40	40.70	40.6	4.10	0.0
SY-29 (illite)	Illite	SY-29 (illite)	40.40	40.70	40.6	4.10	0.0
SY-30 (illite)	Illite	SY-30 (illite)	40.40	40.70	40.6	4.10	0.0

Dogan et al., 2007

Also we can use nitrogen adsorption test to determine specific surface area of clays. Here in this paper (Dogan et al., 2007) a very detailed study was done on different types of clays - montmorillonite, illite, etc. Mineralogy is given and you can determine the specific surface areas and you get very good reasonable values with very low standard deviation. So, idea is this can be also used to study clays.

Here, different clays were studied, you can see the values in some cases you have high values also, like in synthetic clays (SY), you see the values are higher. So, you can use this nitrogen adsorption to determine the surface area of clays.

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Summary

- Particle size distribution determination
 - Sieving
 - Feasible for large particle sizes ($> 50 \mu\text{m}$)
 - Laser diffraction (assumption: spherical particle size)
 - Requires knowledge of refractive and absorption indices of particle
 - Overinterpretation of PSD tails should be avoided for non-spherical size particles
 - Dispersion conditions need to be optimized for SCMs
- Surface area measurement
 - Blaine air permeability (assumption: mono-sized spherical particles)
 - Empirical calibration is required
 - Lower surface area than true surface area
 - Laser diffraction (assumption: spherical shape of particles)
 - No consideration for roughness and particle porosity
 - No calibration required
 - Lower surface area than true surface area
 - Gas adsorption theory
 - No assumption regarding particle shape and size
 - Close to true surface area



So, in summary, these are the main points you should take away from this lecture.

Both particle size distribution and surface area are complimentary. If you have a particle, if you have material which has very fine particle size distribution that tells you it has higher surface area. So, these tests are complimentary. So, how do you determine particle size distribution?

- Easy way to determine is 'sieving' - commonly used but sieving has its limitation. If you have particles below $50 \mu\text{m}$, it makes it difficult and it is not feasible. So, for coarser particles, it will work.
- Another technique commonly used is laser diffraction. Again you have to remember the assumption. It assumes that the particle shapes are spherical.
 - Requires knowledge of refractive and adsorption indices of particle. You need to know these indices of your material, and then only you will be able to get reasonable values.
 - Also you need to avoid overinterpretation of PSD tails for non-spherical size particles, because if you have non-spherical size it tends to broaden the distribution. So, overinterpretation is not recommended.
 - Dispersion conditions need to be optimized - if you have a particular dispersion method (dispersion means you to make sure you are de-agglomerating your sample). If you have conditioned for cement, which may not be directly applicable to SCMs, you will have to optimize this dispersion condition, like,

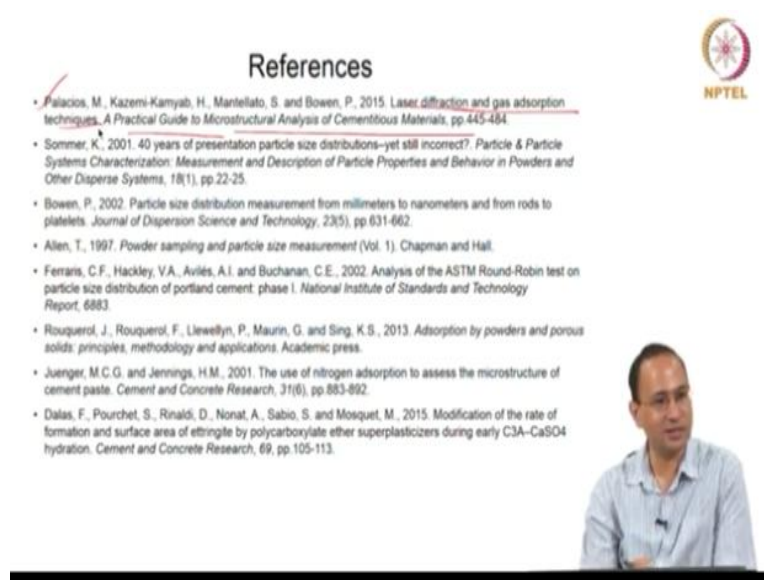
what is the frequency, if you are doing sonication. So, these dispersion conditions specifically need to be optimized for SCMs.

Then we looked into 3 ways of surface area measurements.

- Blaine air permeability - you have to remember the assumption there (Mono-sized spherical particles).
 - So for that, you have to calibrate your apparatus. So empirical calibration is needed.
 - The value you get is lower than true surface area because of its limitation.
- Next one is Laser diffraction where the assumption is spherical shape of particles.
 - There is no consideration for roughness and particle porosity.
 - No calibration required, unlike in Blaine air permeability test.
 - Again the values are lower than true surface area. It has also its limitation where you are measuring volume but do not know about the roughness of particles or the porosity of particles. Those are not taken into account.
- Finally, Gas adsorption theory
 - There is no assumption regarding particle shape and size.
 - It gives you value very close to true surface area.



So, these are the main take away points from this lecture.

(Refer Slide Time: 28:50)




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With that we'll conclude this lecture. I will just point out again most of the material was taken from: A Practical Guide To Microstructure Analysis of Cementitious Materials, from this chapter (Reference 1) on laser diffraction and gas adsorption techniques. There are a lot of other papers; you can see the books where the material has come from.

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So, that will conclude this lecture. So, in the next lectures, Professor Manu Santhanam will be talking about Microscopy, Image Analysis, Spectroscopy and pore size determination using Mercury Intrusion Porosimetry and also Impedance techniques.