Characterization of Construction Materials

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Lecture-30

Surface Area Measurement: Different Techniques – Part 2

So far we have looked into particle size distribution. Next thing we are interested in is surface area, because we saw that in the first slide of this lecture, that surface area influences your reactivity. If you are talking about dissolution for an example, that is dependent on your surface area, surface property. So, it is important to measure surface area.

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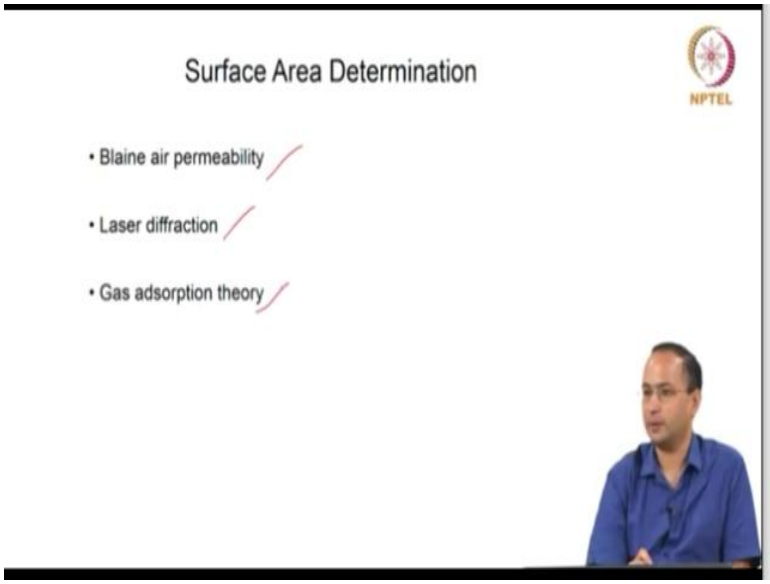

Surface Area Determination

- Blaine air permeability
- Laser diffraction
- Gas adsorption theory

In this lecture we will cover 3 commonly used techniques. So, we can use Blaine air permeability test which most of you must be familiar with and we define Blaine fineness, when we have a cement always it will have some Blaine fineness. So, Blaine air permeability test is used to determine that. Laser diffraction can also be used to determine the surface area and we will also look into Gas adsorption theory.

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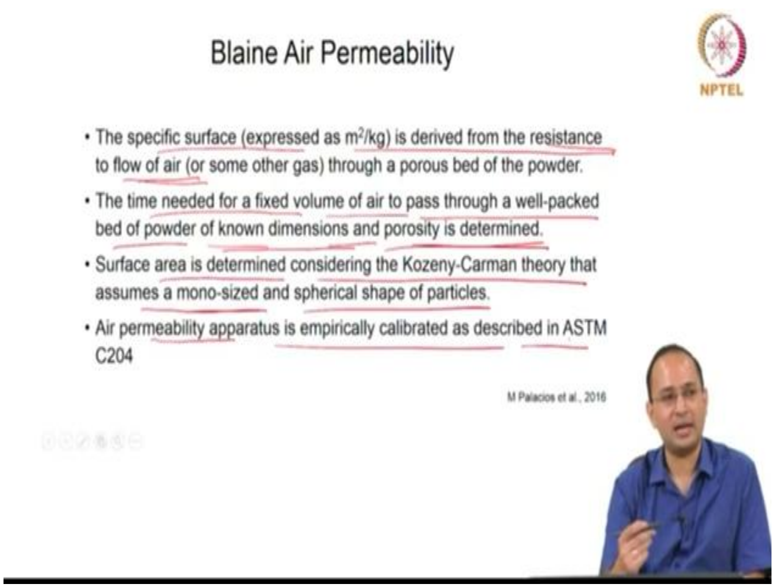

Blaine Air Permeability

- The specific surface (expressed as m^2/kg) is derived from the resistance to flow of air (or some other gas) through a porous bed of the powder.
- The time needed for a fixed volume of air to pass through a well-packed bed of powder of known dimensions and porosity is determined.
- Surface area is determined considering the Kozeny-Carman theory that assumes a mono-sized and spherical shape of particles.
- Air permeability apparatus is empirically calibrated as described in ASTM C204

M Palacios et al., 2016

So, what is Blaine air permeability test? Basically it is derived from the resistance to flow of air through a porous bed of powder. So, you have a porous bed of powder and we are basically measuring what the resistance is to flow of air through it. So, the time needed for a fixed volume of air to pass through a well-packed bed of powder of known dimensions and porosity is determined. So, we are measuring time for a fixed volume of air to pass through a well-packed bed of powder of known dimensions and porosity, and that is what we do in this.

Surface area is determined considering the Kozeny-Carman theory that assumes a mono-sized and spherical shape of particles. So, you have to pay attention to these limitations. So, this is the assumption here, mono-sized (single size), spherical shape particles.

This air permeability apparatus is empirically calibrated, we have to calibrate this apparatus, and for those details you can refer to ASTM C204 which talks about how to do calibration.

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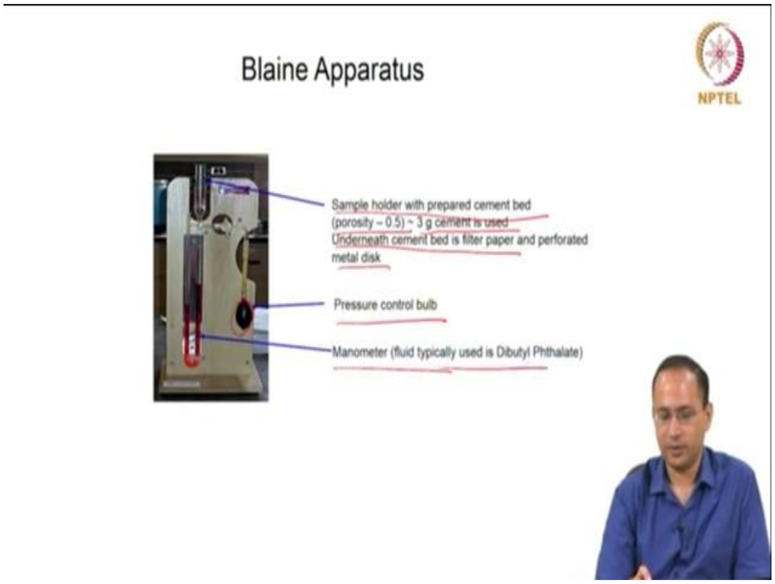

Blaine Apparatus

Sample holder with prepared cement bed (porosity ~ 0.5) ~ 3 g cement is used

Underneath cement bed is filter paper and perforated metal disk

Pressure control bulb

Manometer (fluid typically used is Dibutyl Phthalate)

This is what a Blaine apparatus looks like. So, you have a sample holder with prepared cement bed, porosity around 0.5 and you use roughly 3 grams of cement. Underneath that cement powder bed, you have filter paper and perforated metal disk. You have pressure control bulb here, and that is what you use to control the pressure and then you have a manometer.

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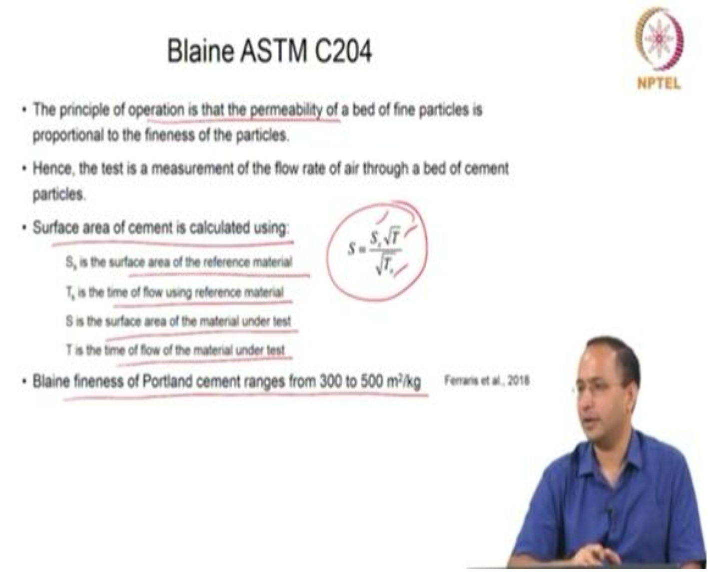

Blaine ASTM C204

- The principle of operation is that the permeability of a bed of fine particles is proportional to the fineness of the particles.
- Hence, the test is a measurement of the flow rate of air through a bed of cement particles.
- Surface area of cement is calculated using:
  - S_s is the surface area of the reference material
  - T_s is the time of flow using reference material
  - S is the surface area of the material under test
  - T is the time of flow of the material under test

$$S = \frac{S_s\sqrt{T}}{\sqrt{T_s}}$$

- Blaine fineness of Portland cement ranges from 300 to 500 m^2/kg Ferraris et al., 2018

So, the principle of operation is that the permeability of a bed of fine particles is proportional to the fineness of the particles. So, here the test is a measurement of the flow rate of air through a bed of cement powder; we are measuring the flow rate. How do we calculate? The surface area of cement can be calculated using this relation:

$$S = \frac{S_s\sqrt{T}}{\sqrt{T_s}}$$

Where S is surface area of the material under test

S_s is the surface area of the reference material.

So, you need a reference material of known surface area to calibrate it.

√T is the time of flow of the material under test. So, you are using your material, so how much time it takes; we measure that.

T_s is the time of flow using reference material. So, you have to calibrate your apparatus using reference material. Once you know S_s, T_s, T, you can calculate surface area.

The Blaine fineness value you get for Portland cement roughly ranges from 300 to 500 m^2/kg, and that is the number you will find when you purchase cement or if you ask for certificates, it will have this range. Obviously, it will vary depending on the type of cement but this is the common range.

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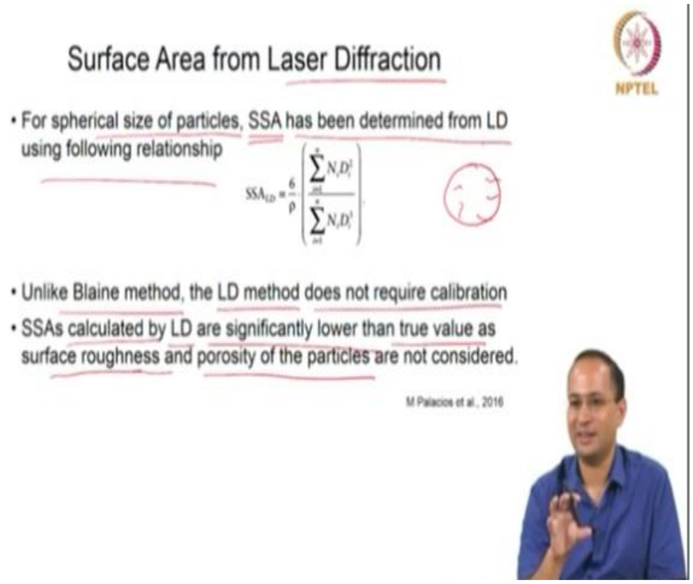

Surface Area from Laser Diffraction

- For spherical size of particles, SSA has been determined from LD using following relationship

$$SSA_{LD} = \frac{6}{\rho}\left(\frac{\sum_{i=1}^{n} N_i D_i^2}{\sum_{i=1}^{n} N_i D_i^3}\right)$$

- Unlike Blaine method, the LD method does not require calibration
- SSAs calculated by LD are significantly lower than true value as surface roughness and porosity of the particles are not considered.

M Palacios et al., 2016

So that was the Blaine air permeability test. We can also use laser diffraction to determine the surface area. So for spherical size of particles specific surface area (SSA) can be determined using this relation.

$$SSA_{LD} = \frac{6}{\rho}\left(\frac{\sum_{i=1}^{n} N_i D_i^2}{\sum_{i=1}^{n} N_i D_i^3}\right)$$

Where ρ is density

Ni, Di, these are the size intervals and the average diameter in that size intervals

n is number of particles.

So, you can use this to get the specific surface area, these all quantities, you know already when you do your laser deflection. So, unlike Blaine method, LD method does not require any calibration.

SSAs (specific surface areas) calculated by laser diffraction are significantly lower than true value because it does not take into account the surface roughness. It is measuring based on the diameter, volume. So, surface roughness and porosity, because particles may have inherent porosity and also there will be some roughness that will add to your surface area which is not captured using LD. So the values you get from laser diffraction are usually lower than true surface area.

So, using Mie theory, we are calculating the volume of particle in laser diffraction. But in real life, your particle will have surface roughness, porosity, so that will lead to your surface area. So, the values you get from laser diffraction are lower. We only know this is the size (refer to Figure drawn in slide), equivalent surface, but it might have some roughness that it does not take into account. It may have some inherent porosity; what we are seeing is only volume. So, these things will add to your surface area which is not captured using laser diffraction. But it is captured using gas adsorption theory which we will discuss.

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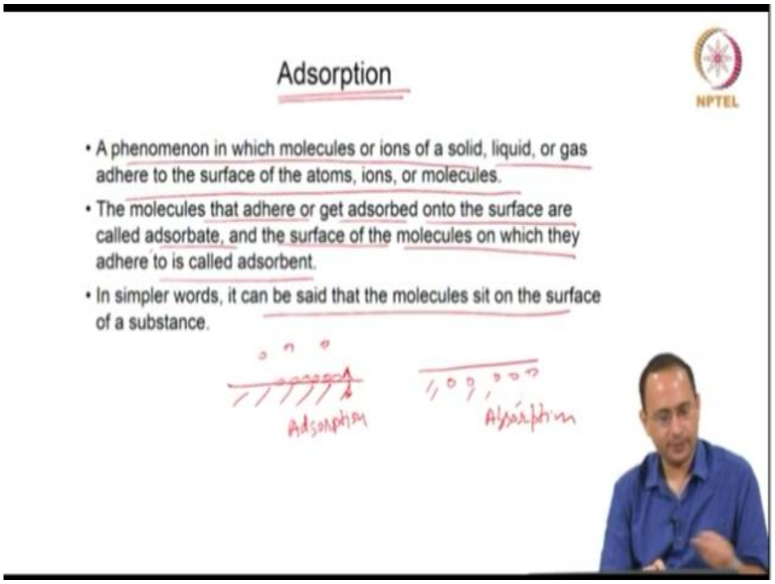

Adsorption

- A phenomenon in which molecules or ions of a solid, liquid, or gas adhere to the surface of the atoms, ions, or molecules.
- The molecules that adhere or get adsorbed onto the surface are called adsorbate, and the surface of the molecules on which they adhere to is called adsorbent.
- In simpler words, it can be said that the molecules sit on the surface of a substance.

So, these are the limitations of the earlier techniques, so if you have high roughness, also if you have porous particles, then your values from laser diffraction will be lower. Now idea is how do you capture true surface area? In reality, you have these particles which are irregular, which are porous, which are rough, so for that we use gas absorption theory. So what does it mean?

First of all, what is the meaning of adsorption, it is not absorption, it is adsorption. So, it is a phenomenon in which molecules or ions of solid, liquid, or gas, adhere to the surface of the atoms, ions, or molecules. The molecules that adhere or get adsorbed onto the surface are called adsorbate, like, if you are using a gas molecule it will be adsorbate, and the surface of the molecules on which they adhere to is called absorbent.

So, you have a surface here and these are the gas molecules. Refer to Figure 1 which shows difference between adsorption (on left) and absorption (on right).

Figure 1 On left – Adsorption; On right - Absorption

So, in adsorption, the molecules just sit on the surface of a substance, and we are talking about very weak bonds, not strong chemical bonds in case of adsorption.

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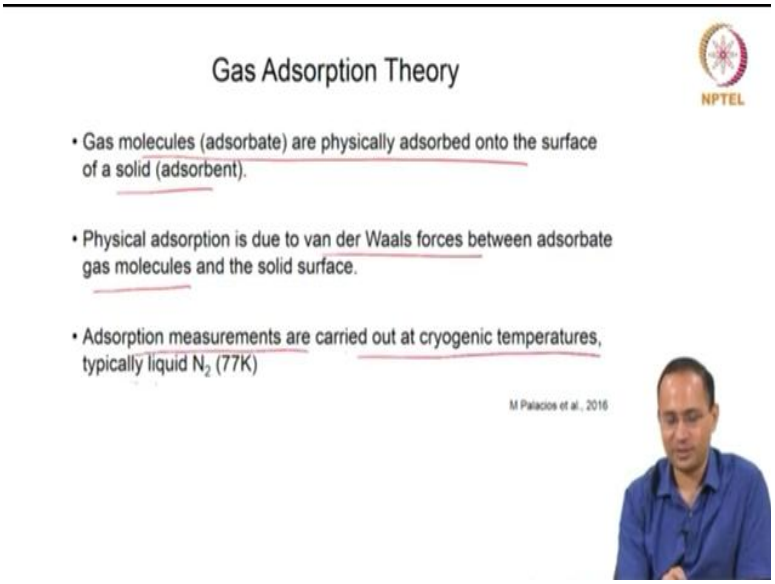

Gas Adsorption Theory

- Gas molecules (adsorbate) are physically adsorbed onto the surface of a solid (adsorbent).
- Physical adsorption is due to van der Waals forces between adsorbate gas molecules and the solid surface.
- Adsorption measurements are carried out at cryogenic temperatures, typically liquid N_2 (77K)

M Palacios et al., 2016

So, the gas molecules are physically adsorbed onto the surface of a solid. They are physically adsorbed, not chemically; there are no chemical bonds. So, we are talking about van der Waals forces between adsorbate gas molecule and solid surface.

Usually adsorption measurements are carried out at cryogenic temperatures, typically liquid nitrogen (N_2); 77 Kelvin, which corresponds to -196°C, these are the conditions.

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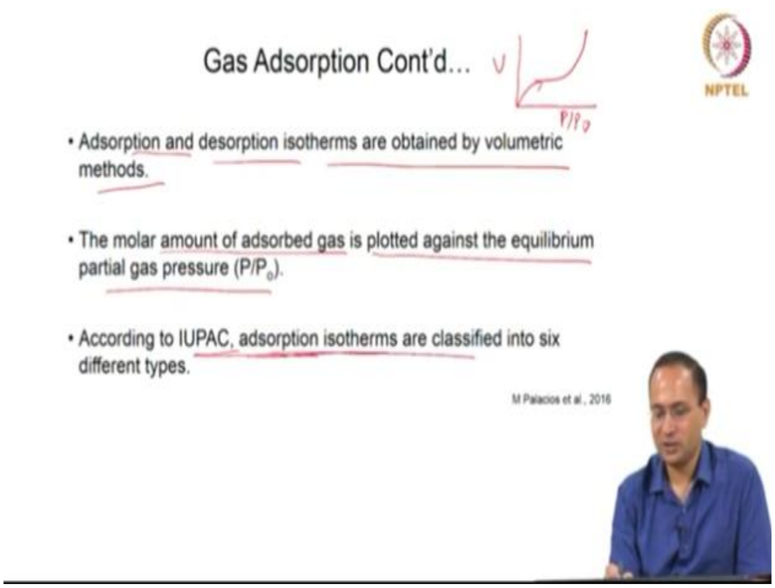

Gas Adsorption Cont'd…

- Adsorption and desorption isotherms are obtained by volumetric methods.
- The molar amount of adsorbed gas is plotted against the equilibrium partial gas pressure (P/P_0).
- According to IUPAC, adsorption isotherms are classified into six different types.

M Palacios et al., 2016

So, adsorption and desorption isotherms are obtained by volumetric methods. So, we carry out this adsorption test and also desorption, which is removing whatever is absorbed, and we can get these isotherms, isotherm is if you plot your volume of adsorbed gas versus let us say in this case, partial pressure (refer to graph drawn in slide). So obviously it will increase as you are increasing the partial pressure.

You can think of it as a relative humidity all of you must be familiar with relative humidity. If it is very dry, 20, 30% relative humidity is very dry, very less humidity, if you go to 100% relative humidity means complete saturation. Similar concept but here we are talking about the pressure and this is the adsorption, similarly you can remove the adsorbed gas you can desorption. So, these are the isotherms; we will come back to it.

These are obtained by volumetric methods, where we are calculating the volume of adsorbed gas and molar amount of adsorbed gas is plotted against the equilibrium gas pressure - you are plotting the molar amount of adsorbed gas against the equilibrium partial gas pressure (P/P_0).

So, you can relate it to relative humidity concept, in case of your concrete, like curing for an example. So, now, we are talking about these isotherms, this is kind of a characteristic, what happens, when you increase the partial pressure to saturated level where $P/P_0 = 1$, how does a material respond, this is a specific characteristic. So, according to IUPAC, adsorption isotherms are classified into 6 different types.

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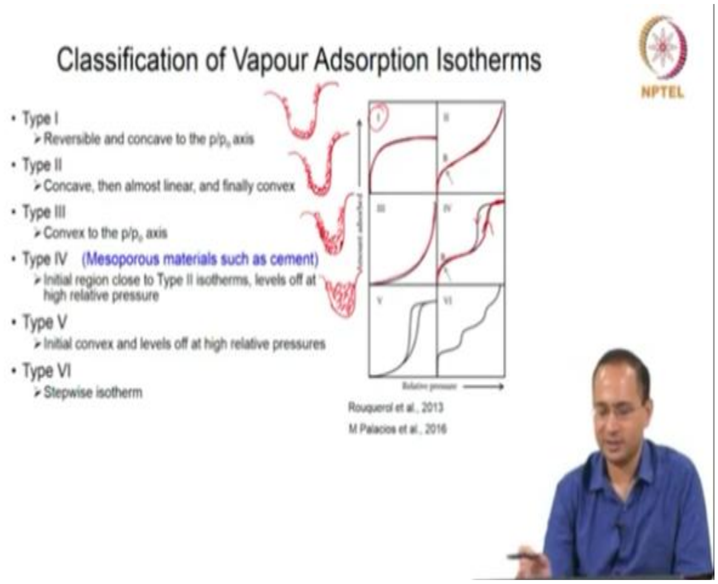


Classification of Vapour Adsorption Isotherms

- Type I
  - ➢ Reversible and concave to the p/p_0 axis
- Type II
  - ➢ Concave, then almost linear, and finally convex
- Type III
  - ➢ Convex to the p/p_0 axis
- Type IV (Mesoporous materials such as cement)
  - ➢ Initial region close to Type II isotherms, levels off at high relative pressure
- Type V
  - ➢ Initial convex and levels off at high relative pressures
- Type VI
  - ➢ Stepwise isotherm

Rouquerol et al., 2013

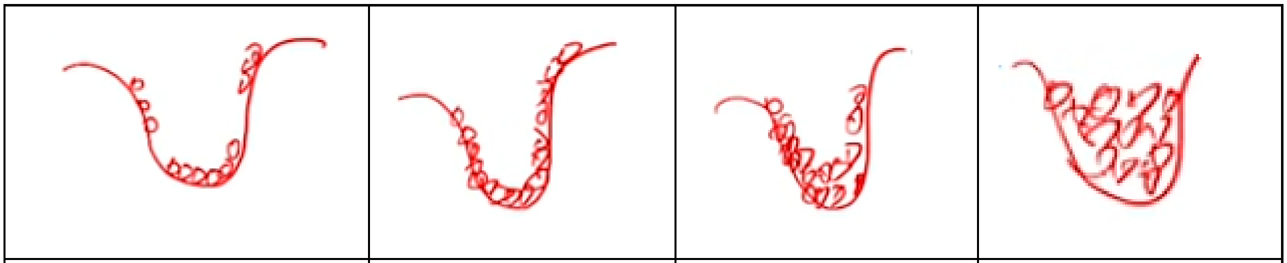
M Palacios et al., 2016

So, we have classification, there are 6 types of isotherms you can get. These are typical 6 types of isotherms we see, classified as per IUPAC. So how do they look like? See the Type I (Refer to graph in slide), looks like reversible and concave to axis, concave to the X-axis (P/P_0). In Type I, you can see that it increases, and then reaches a plateau. Type II, the difference is you have a concave first like Type I, then almost linear, then finally convex. So Type II is concave, linear and convex.

Type III is convex to (P/P_0) axis.

In Type IV, the initial region is close to Type II see this region (concave), is close to Type II. Then it levels off at high pressures. What you see here is a hysteresis now, there is an absorption curve (Refer to Type IV graph in slide) and what happens when you do desorption? So you would not come back on the same curve, that is why we call it hysteresis, this signifies that it is a mesoporous material. Mesoporous materials show this hysteresis. So, basically this kind of isotherm will be applicable to cements. Why we see this hysteresis is because of capillary condensation.

So, what you are doing is you are filling pores as you increase the partial pressure. Let us see it; you have pores like this (Refer to Figure 2 (a.)). So, these are the gas molecules as you increase the partial pressure. So we are starting from 0. So, some gas molecules will get adsorbed, what will happen in the next stage? You will have a mono-layer formation (Figure 2 (b.)). What happens next? You may have a couple of layers (Figure 2 (c.)), then it will get filled as you increase the partial pressure (Figure 2 (d.)), you can see the sequence.



(a.) (b.) (c.) (d.)

Figure 2 Gas adsorption in pores

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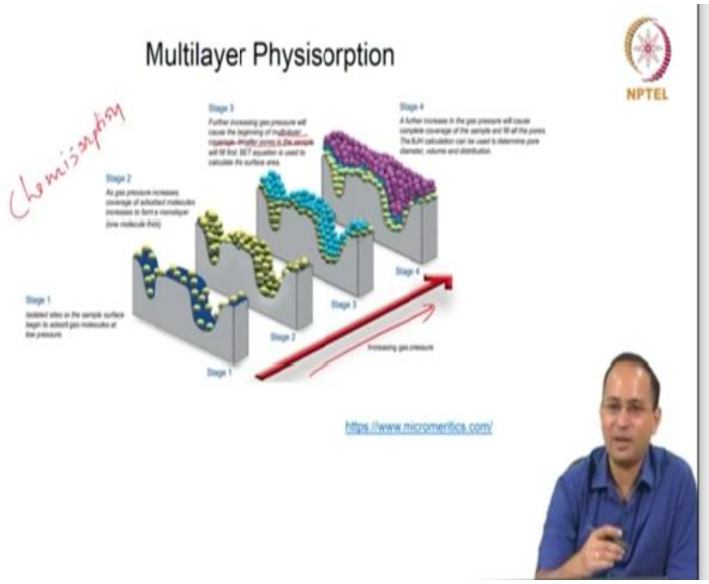

Multilayer Physisorption

Chemisorption

https://www.micromeritics.com/

Let us see here so, what happens? Stage 1 is isolated sites on the sample surface begin to adsorb gas molecules at low pressure. So, not the whole surface area is occupied. Stage 2, as gas pressure increases coverage of adsorbed molecules increases to form a monolayer. Monolayer means one molecule thick layer. This we can use to determine the surface area.

The principle here is that, suppose you have a monolayer formation and you know the volume of gas which was adsorbed, you can use that information to calculate the surface area. We are increasing the gas pressure along this direction (along the red arrow shown in figure in slide). It is similar to increasing the relative humidity; we can draw that analogy here.

So, Stage 3 is further increasing gas pressure will cause beginning of multi-layer coverage. Smaller porous in the samples will fill first. Then finally (Stage 4), further increase will cause complete coverage of samples and fill all the pores. This is the absorption. Now we can reduce the partial pressure also to get the desorption branch (as seen in graphs from previous slide). So in the hysteresis, when you come to desorption branch at the same level of partial pressure (P/P_0), it takes more effort to remove it. So, when you are on desorption branch, the volume of adsorbed gas is higher than that on adsorption branch. This signifies the capillary condensation basically and you have to remember this Type IV is for mesoporous materials and it is applicable to materials like cement.

Type V is initial convex now see the initial convex then levels off at high relative pressures. Type VI is Stepwise - you see steps, that is why it is called Stepwise.

So, these are the 6 different types of isotherms, applicable to different materials.

We discussed this multi-layer physisorption we are using the term physisorption, not chemisorption. Chemisorption will involve strong chemical bonds, whereas physisorption is weak physical bonds (van der Waals bonds).

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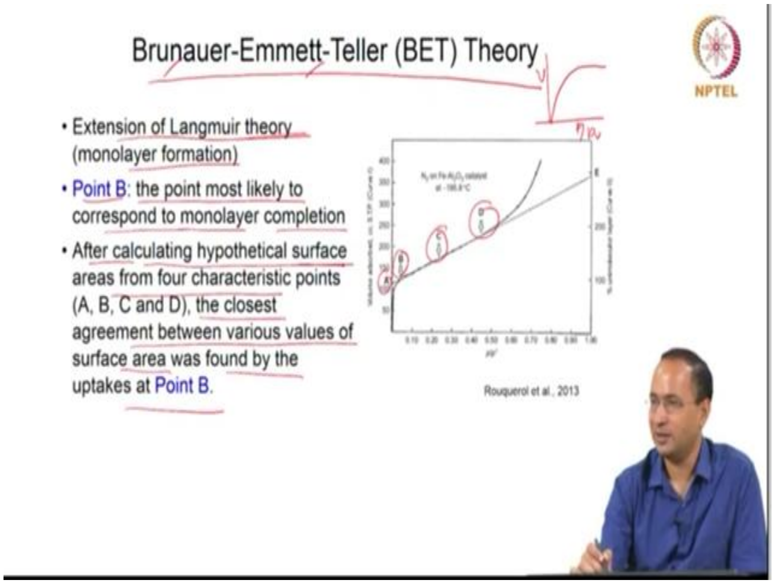

Brunauer-Emmett-Teller (BET) Theory

- Extension of Langmuir theory (monolayer formation)
- Point B: the point most likely to correspond to monolayer completion
- After calculating hypothetical surface areas from four characteristic points (A, B, C and D), the closest agreement between various values of surface area was found by the uptakes at Point B.

Rouquerol et al., 2013

So how do we calculate surface area? That is what we are interested in. So, commonly the most famous technique in gas absorption is BET theory, given by 3 scientists - Brunauer, Emmett-Teller. So what is BET theory? It is the extension of Langmuir theory. So, Langmuir theory - basically the Type I isotherm can also be called as Langmuir isotherm.

So, initially Langmuir thought if you plot V vs. (P/P_0), you'll have this kind of isotherm (Type I), but in real life, you have different types of isotherms, Type II for an example, Type I cannot explain what is happening in Type II. So, Brunauer-Emmett-Teller came up with the BET theory because Langmuir was right on only monolayer formation and then you have saturation.

But now they were trying to explain this behavior why this is happening (as shown in Graph in slide), which is not Type I. So in this, they say Point B, where you see the change in slope is the point most likely to correspond to monolayer completion. They say that here (at Point B) is the point where the monolayer completes (one molecule thick layer).

After calculating the hypothetical surface areas from four characteristic points (A,B,C, and D) and the closest agreement between various values of surface areas was found by the uptakes at Point B. So, you can calculate surface areas based on this volume, but the closest agreement they found was for B.

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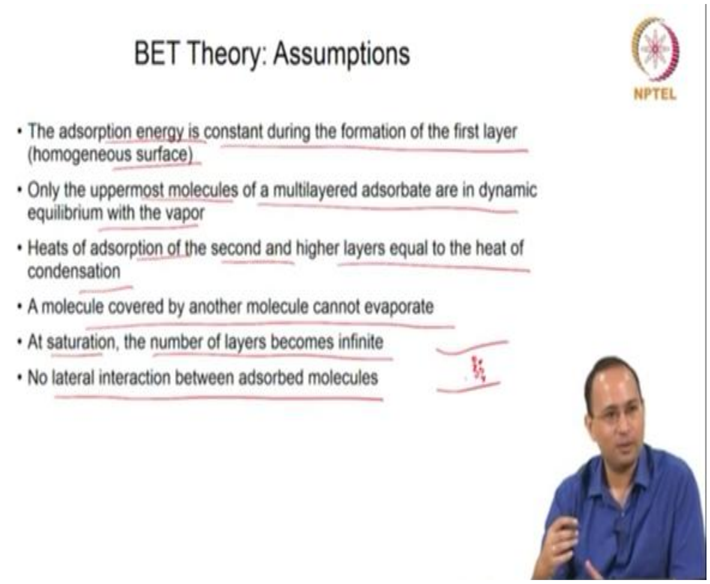

BET Theory: Assumptions

- The adsorption energy is constant during the formation of the first layer (homogeneous surface)
- Only the uppermost molecules of a multilayered adsorbate are in dynamic equilibrium with the vapor
- Heats of adsorption of the second and higher layers equal to the heat of condensation
- A molecule covered by another molecule cannot evaporate
- At saturation, the number of layers becomes infinite
- No lateral interaction between adsorbed molecules

So, these are the assumptions of this theory.

- The absorption energy is constant during the formation of the first layer. The absorption energy does not change when you are forming the first layer.
- Only the uppermost molecules of multi-layered adsorbate are in dynamic equilibrium with the vapor. So, suppose you have a multi-layer formation, the upper most molecules of a multi-layered adsorbate are in the dynamic equilibrium with the vapor.
- Heats of adsorption of the second and higher layers equal to the heat of condensation.
- Molecule covered by another molecule cannot evaporate. So, if you have another molecule covered, it cannot evaporate.
- At saturation, the number of layers becomes infinite - when you have full saturation, the number of layers will be infinite.
- No lateral interaction between adsorbed molecules - you will have your surface, if you see plan view, you will have molecules, and there is no lateral interaction.

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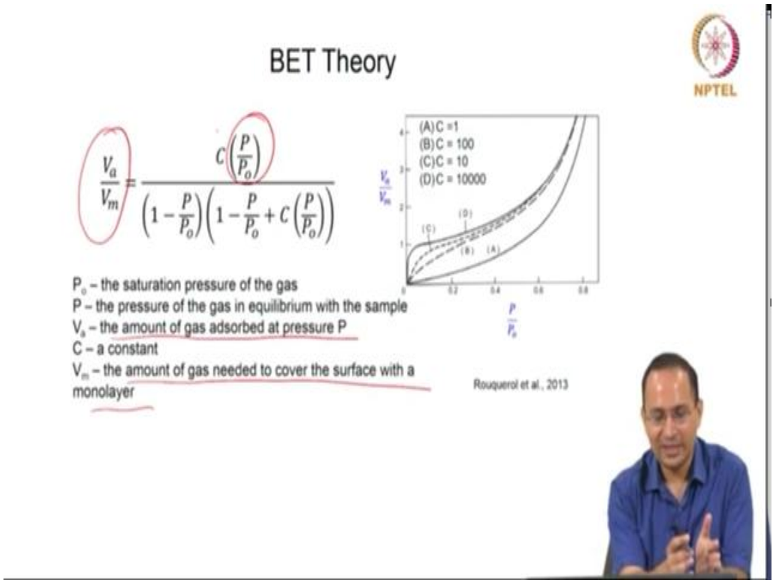

BET Theory

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

P_o – 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
V_m – the amount of gas needed to cover the surface with a monolayer

Rouquerol et al., 2013

Finally, they were able to come up, we are not going in detail, they were able to relate (V_a/V_m) to this partial pressure, (P/P_0). P/P_0 will range from 0 to 1, where 1 is fully saturated. So, this relationship could explain the trends:

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

Where V_a is the amount of gas absorbed at pressure P

V_m is amount of gas needed to cover the surface with a monolayer

So, if you plot it based on C value, where C is the constant, you get this kind of isotherms (shown in slide). So, they were able to explain isotherms like Type II. So, that is why it is called extension of Langmuir theory. Langmuir would be something like Type I, but could not explain these other isotherms which we see. So, they came up with this. Another thing is depending on the constant C, you can get different shapes.

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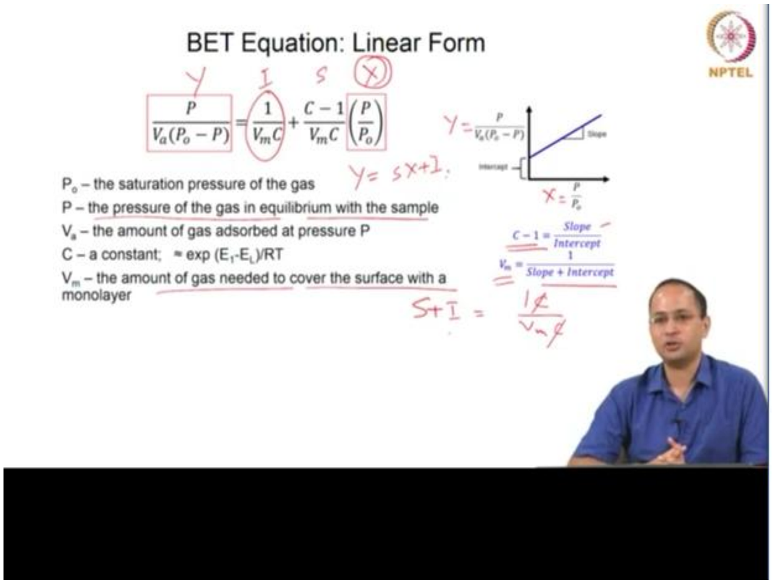

BET Equation: Linear Form

$$\underset{Y}{\boxed{\frac{P}{V_a(P_o-P)}}} = \underset{I}{\frac{1}{V_mC}} + \underset{S}{\frac{C-1}{V_mC}} \underset{X}{\boxed{\left(\frac{P}{P_o}\right)}}$$

$Y = SX + I$;

P_o – 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

$Y = \frac{P}{V_a(P_o-P)}$

$X = \frac{P}{P_o}$

$C-1 = \frac{Slope}{Intercept}$

$V_m = \frac{1}{Slope + Intercept}$

$S + I = \frac{1\cancel{C}}{V_m\cancel{C}}$

So now that equation can be written in linear form also as:

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

Where V_a is the amount of gas absorbed at pressure P

Vm is the amount of gas needed to cover the surface with a monolayer

P_o is the saturation pressure of the gas

P is the pressure of gas in equilibrium with the sample

C is a constant.

Now suppose $\frac{P}{V_a(P_o-P)}$ is Y, $\left(\frac{P}{P_o}\right)$ is X, we can write the same equation in this form.

Now, you are varying this partial pressure. If you plot Y against X, this is like a straight line (Y=SX+I). So, you will get a straight line. So, we can say:

$$\text{Intercept, I} = \frac{1}{V_mC}\text{ ; Slope, } S = \frac{C-1}{V_mC}$$

So basically, you can get constant C.

$$C - 1 = \frac{Slope}{Intercept}$$

So you got this plot, and now you measure the slope, you measure the intercept, divide it, and you will get the constant C. Also coming to V_m, we are interested in what is the amount of gas needed to cover the surface with a monolayer. So we V_m can be calculated as:

$$V_m = \frac{1}{Slope + Intercept}$$

So, $S + I = \frac{C}{V_m C}$, and so the above equation is verified. So if you know slope and intercept, you can calculate V_m and C.

In the next lecture, we will see how we can calculate the surface area and we will also look into applications of BET in cement-based materials.