Hydration, Porosity and Strength of Cementitious Materials

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Lecture – 15
Portland Cement Based Paste Systems

Hi, good morning one and all. I am K. V. Harish Assistant Professor, Department Of Civil Engineering IIT Kanpur. You are watching MOOCs lecture course on Hydration, Porosity and Strength of Cementitious Material.

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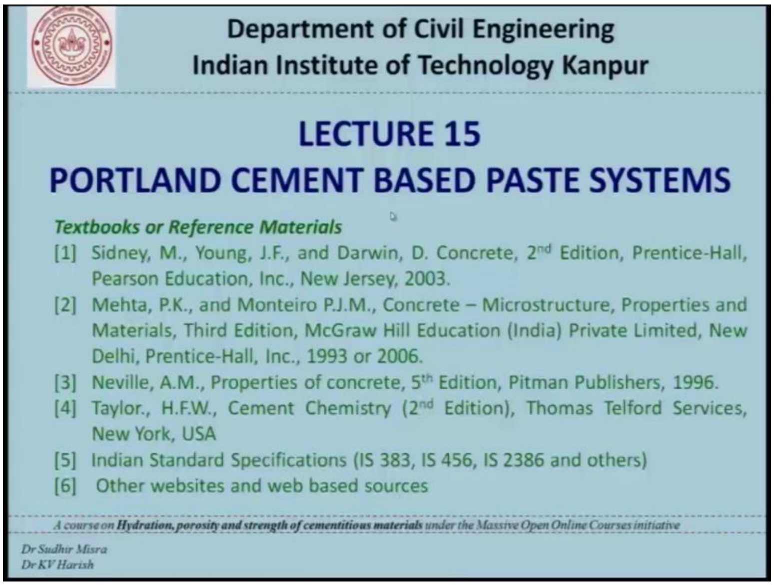

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LECTURE 15
PORTLAND CEMENT BASED PASTE SYSTEMS

Textbooks or Reference Materials

[1] Sidney, M., Young, J.F., and Darwin, D. Concrete, 2nd Edition, Prentice-Hall, Pearson Education, Inc., New Jersey, 2003.
[2] Mehta, P.K., and Monteiro P.J.M., Concrete – Microstructure, Properties and Materials, Third Edition, McGraw Hill Education (India) Private Limited, New Delhi, Prentice-Hall, Inc., 1993 or 2006.
[3] Neville, A.M., Properties of concrete, 5th Edition, Pitman Publishers, 1996.
[4] Taylor., H.F.W., Cement Chemistry (2nd Edition), Thomas Telford Services, New York, USA
[5] Indian Standard Specifications (IS 383, IS 456, IS 2386 and others)
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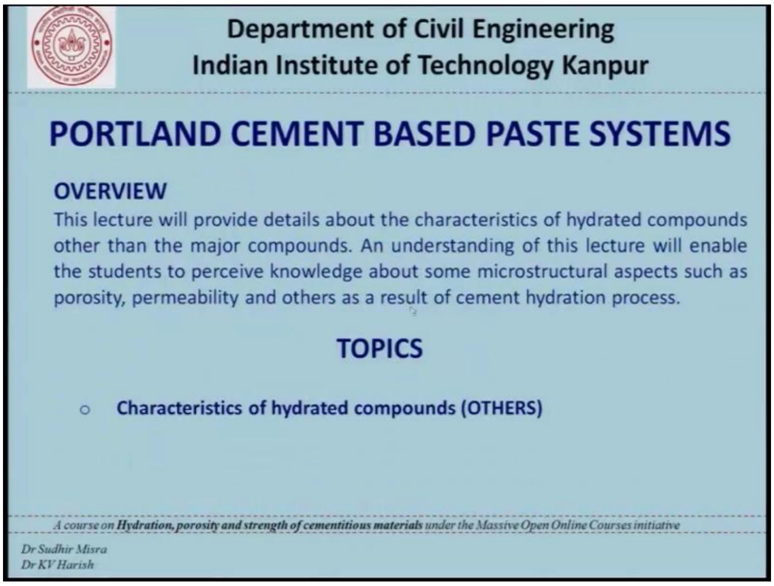

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PORTLAND CEMENT BASED PASTE SYSTEMS

OVERVIEW

This lecture will provide details about the characteristics of hydrated compounds other than the major compounds. An understanding of this lecture will enable the students to perceive knowledge about some microstructural aspects such as porosity, permeability and others as a result of cement hydration process.

TOPICS

- **Characteristics of hydrated compounds (OTHERS)**

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Today we will see lecture 15 Portland cement based paste systems and the text books and reference materials are shown. So, in today’s lecture the topic that we will be seeing is characteristics of hydration compounds. Remember that in the previous lecture we have dealt about major compounds like a calcium, silicate, hydrate, calcium hydroxide, ettringite and monosulfoaluminates. And we will see the other important things in hydrated compounds.

This lecture will provide details about the characteristics of hydrated compounds other than the major compounds. And understanding of this lecture we will enable the students to perceive knowledge about some micro structural aspects such as porosity permeability and others as a result of cement hydration process.

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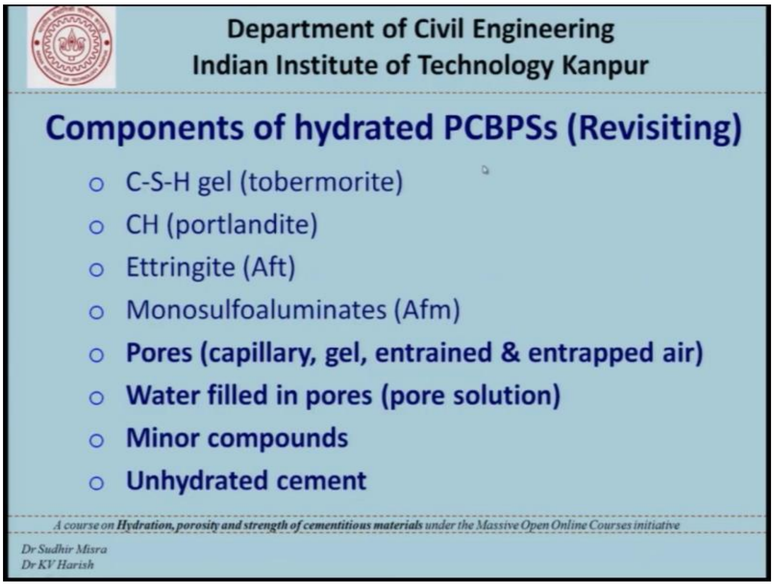

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Components of hydrated PCBPSs (Revisiting)

- C-S-H gel (tobermorite)
- CH (portlandite)
- Ettringite (Aft)
- Monosulfoaluminates (Afm)
- **Pores (capillary, gel, entrained & entrapped air)**
- **Water filled in pores (pore solution)**
- **Minor compounds**
- **Unhydrated cement**

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So, now characteristics of hydrated compounds: so what we have seen is we have seen the first 4. And in this lecture we will see about pores water filled in pores minor compounds and unhydrated cement.

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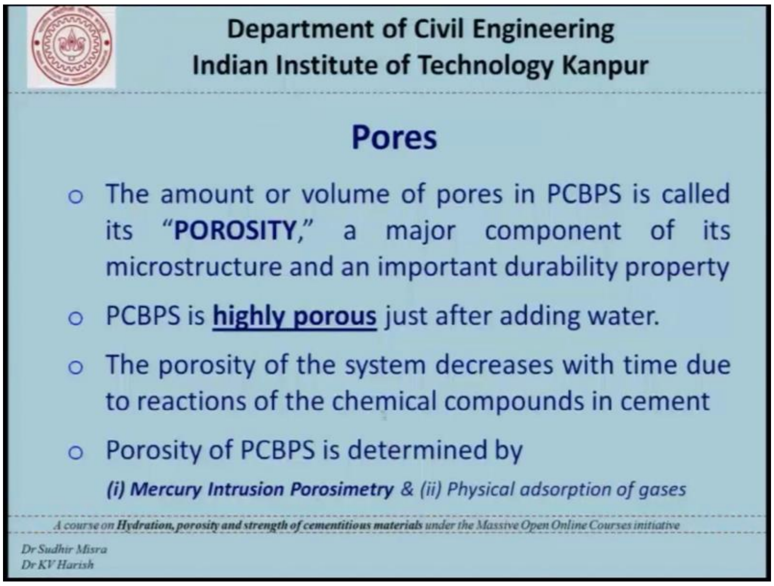

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Pores

- The amount or volume of pores in PCBPS is called its "**POROSITY**," a major component of its microstructure and an important durability property
- PCBPS is **highly porous** just after adding water.
- The porosity of the system decreases with time due to reactions of the chemical compounds in cement
- Porosity of PCBPS is determined by
  *(i) **Mercury Intrusion Porosimetry** & (ii) Physical adsorption of gases*

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First is pores the amount or volume of pores in Portland cement based paste system is called as porosity. And it is a very important component of the microstructure. And it is also an important durability property. The Portland cement based paste system is highly porous very important, highly porous just after adding water to the cement. The porosity of the system decreases with time due to the chemical reaction of the compounds and once the hydrated compounds are formed the porosities starts decreasing. The porosity is measured using 2 different methods, one is mercury intrusion porosimetry which is very famous and popular the other one is physical adsorption of gases.

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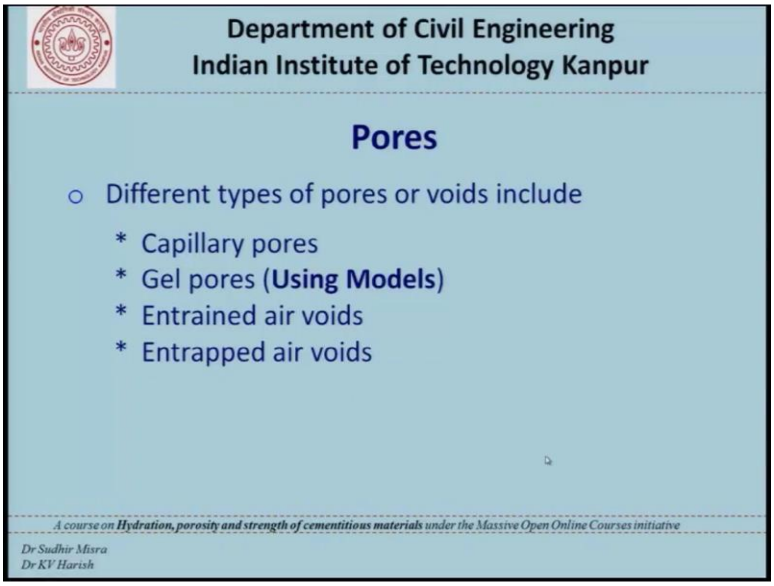

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Pores

- Different types of pores or voids include
  - Capillary pores
  - Gel pores (**Using Models**)
  - Entrained air voids
  - Entrapped air voids

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So, what are the different types of pores that are present in Portland cement based paste system. Typically, there are 4 different types of pores one is the capillary pores, the second one is the gel pores, the third one is not called as pores, but they are generally called as voids. So, entrained air voids and the fourth one is entrapped air voids we will right now see capillary pores.

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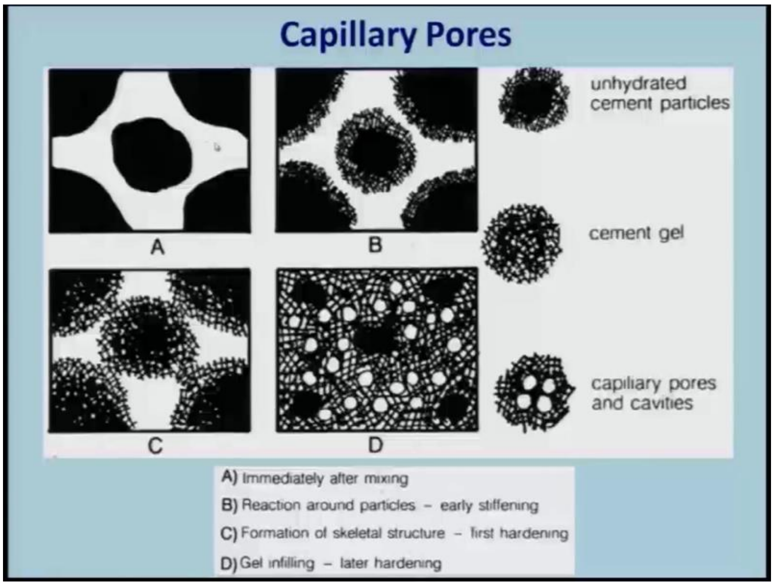

Capillary Pores

A) Immediately after mixing
B) Reaction around particles – early stiffening
C) Formation of skeletal structure – first hardening
D) Gel infilling – later hardening

So, the figure the figure that is shown here contains 4 different parts A B C D, and in the first part the whitish region is the water zone and the black region is the cement zone. And this will be the status as soon as water is added to cement. And in the second part slowly the products are getting formed and what you see is early stiffening stage, where some enttringite crystals are formed and in the third stage where slowly you have the formation of skeletal structure. And it is also referred as first hardening, and slowly with more hydrated compounds that are formed, you also see that the porosity is slowly getting reduced.

And finally, the fourth stage where you see some white colour spots they are called as capillary pores or capillary cavities. In Portland cement based paste systems the hydrated region is generally referred to as cement gel, and this cement gel primarily contains the major hydration compounds like calcium silicate hydrate gel calcium hydroxide AFT, ettringite and AFT monosulfo aluminates all club together is called as cement gel.

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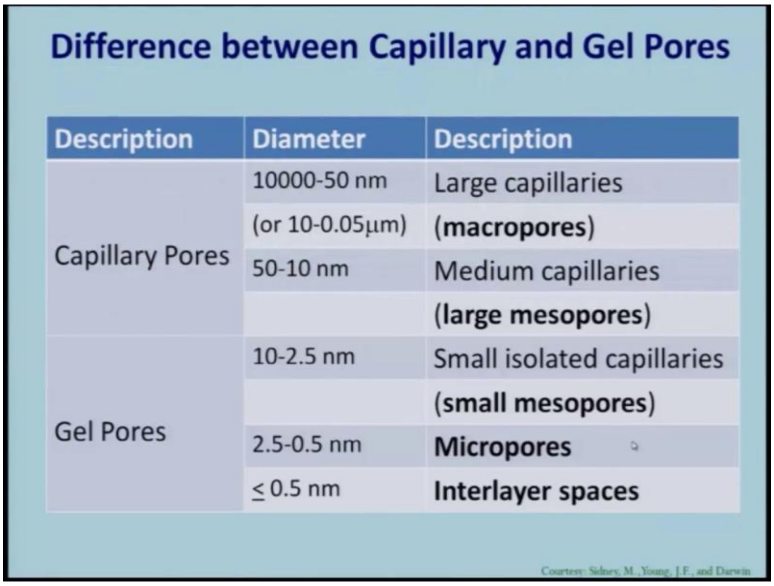

Difference between Capillary and Gel Pores

Description	Diameter	Description
Capillary Pores	10000-50 nm	Large capillaries
	(or 10-0.05μm)	(**macropores**)
	50-10 nm	Medium capillaries
		(**large mesopores**)
Gel Pores	10-2.5 nm	Small isolated capillaries
		(**small mesopores**)
	2.5-0.5 nm	**Micropores**
	≤ 0.5 nm	**Interlayer spaces**

Courtesy: Sidney, M., Young, J.F., and Darwin

Now, what is the difference between gel pores and capillary pores. Capillary pores and gel pores are primarily distinguished from their size or size ranges. Typically, capillary pores or larger in size or size ranges and the size typically varies from 10,000 to 50 nanometers. If you want to know in terms of microns it is 10 to 0.05 micron meters. And they are also classified into 2 categories, one is macropores the other one is large mesopores. And in the case of macropores the size range is 10,000 to 50 nanometer; in the case of large mesopores it is between 50 to 10 nanometers.

In the case of gel pores the size range is between 10 nanometers to about less than 0.5 nanometers. And again this gel pores are divided into 3 parts one is small mesopores micropores interlayer spaces and each of the size ranges are showed here. So, the pores are basically classified into 2 types, capillary pores. And gel pores and the gel pores are primarily the pores that we see in the cement gel and capillary pores are typically that is present as white spots in the hydrated system.

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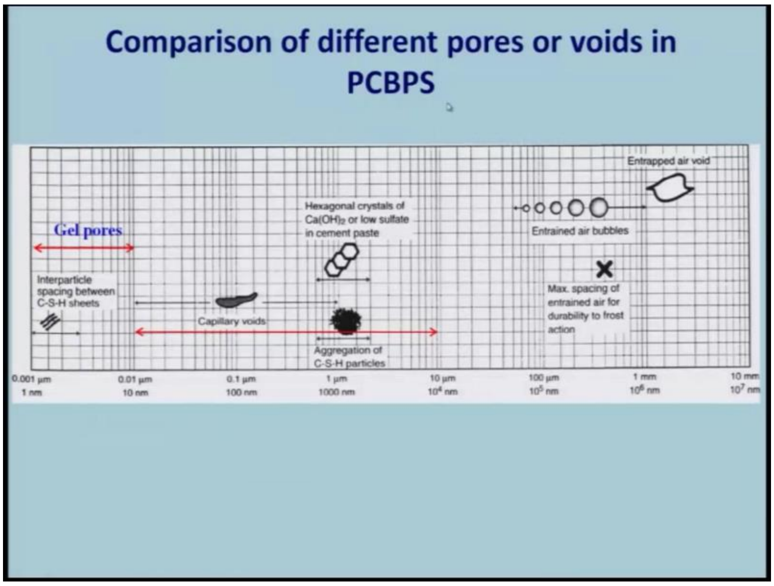

Comparison of different pores or voids in PCBPS

If we have to take the size in the x axis and comparatively see; what is the size range of gel pores with capillary pores, here the figure is shown, in which the size is varying from 1 nanometer to as high as 10 power 7 nanometers. Remember nano is nothing, but 10 power minus 9 meters. So, and you see that the gel pores typically range from 0.001 micron meter to 0.01 micron meter, and capillary pores varies from 0.01 micron meter to as high as 10 micron meter.

We will revisit this slide just to have a comparative study about the sizes of entrained air voids entrapped air voids with gel pores and capillary pores.

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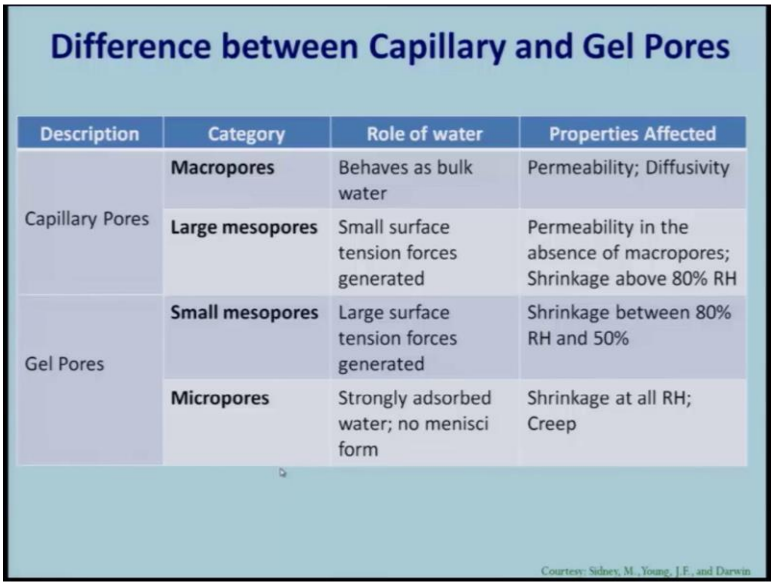

Difference between Capillary and Gel Pores

Description	Category	Role of water	Properties Affected
Capillary Pores	**Macropores**	Behaves as bulk water	Permeability; Diffusivity
	Large mesopores	Small surface tension forces generated	Permeability in the absence of macropores; Shrinkage above 80% RH
Gel Pores	**Small mesopores**	Large surface tension forces generated	Shrinkage between 80% RH and 50%
	Micropores	Strongly adsorbed water; no menisci form	Shrinkage at all RH; Creep

Courtesy: Sidney, M., Young, J.F., and Darwin

So, is size only the difference between capillary pores and gel pores, or do we have more differences? Answer is we have more differences. So, in the case of capillary pores has already mentioned the macro pores and large mesopores, they have their own rolls likewise the small mesopores and micropores which come under gel pores they have their own roles. So, the water that is present in the capillary pores will behave as bulk waster. And you have small surface tension forces that are generated in the capillary pores. In the case of gel pores you have large surface tension forces generated and you may also have some absorbed water which do not have meniscus.

We will talk about meniscus and surface tension at a later stage. And the importance of the capillary pores and gel pores to the properties of Portland cement based paste systems are also listed. In the case of capillary pores, they substantially affect the permeability properties and diffusivity of Portland cement based paste systems. They also affect the shrinkage behavior and permeability in the case of mesopores and likewise if you take gel pores they affect the shrinkage behavior and they are in the case of micropores they affect shrinkage and creep behavior.

Remember that the discussions about shrinkage will be dealt at a later stage when we are dealing with curing, and the temporary the percentage that is mentioned that is 80 percentages relative humidity and 50 percentage that is primarily from the shrinkage stand point, because the shrinkage can happen anywhere between 0 percentage relative humidity to hundred percentage relative humidity.

So, the range 80 percentage to 50 percentage has it is own relevance, which is not currently discussed, but we will discuss that when we come to curing and shrinkage in that. So, there are also some models that are provided for understanding gels.

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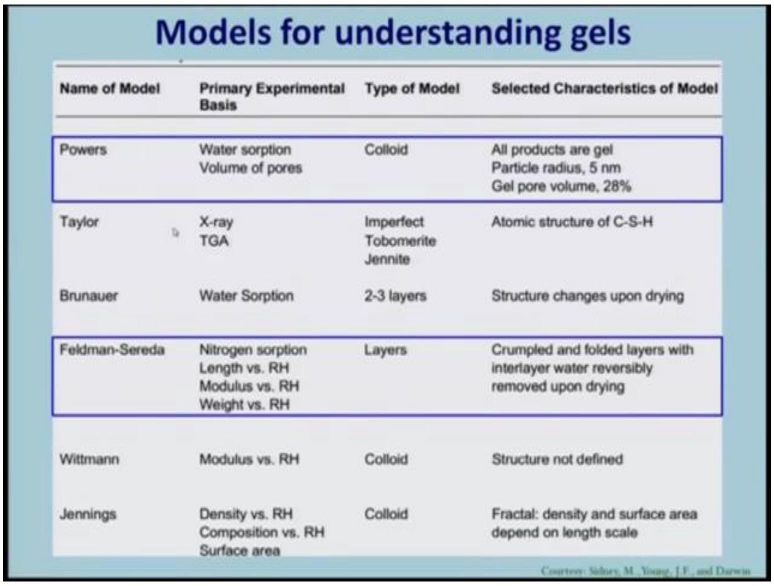

Models for understanding gels

Name of Model	Primary Experimental Basis	Type of Model	Selected Characteristics of Model
Powers	Water sorption Volume of pores	Colloid	All products are gel Particle radius, 5 nm Gel pore volume, 28%
Taylor	X-ray TGA	Imperfect Tobomerite Jennite	Atomic structure of C-S-H
Brunauer	Water Sorption	2-3 layers	Structure changes upon drying
Feldman-Sereda	Nitrogen sorption Length vs. RH Modulus vs. RH Weight vs. RH	Layers	Crumpled and folded layers with interlayer water reversibly removed upon drying
Wittmann	Modulus vs. RH	Colloid	Structure not defined
Jennings	Density vs. RH Composition vs. RH Surface area	Colloid	Fractal: density and surface area depend on length scale

Courtesy: Sidney, M., Young, J.F., and Darwin

The different models that you have or the powers models tailors model Brunauers model Feldman Sereda model Wittmanns model and Jennings model. These are generally famous models for understanding the hydration of cement. And some of the primary experimental basis type of model and a characteristics of model or listed. Most important and widely the easiest one to understand or the powers model and Feldman Sereda model; right now we will deal with the assumptions of Feldman Sereda model. Later on we will go ahead with powers model and remember that these models study or dealt only for the pure understanding of cement hydration.

Now, in the case of powers model the primary experimental basis is water absorption or water sorption and volume of pores. In the case of Feldman Sereda model the experimental basis is nitrogen sorption length versus relative humidity modulus versus relative and weight versus relative humidity. So, if you get into the details of powers or Feldman Sereda model, you will find some parameters related to this which are used in the models. Right now we will not get into each of these things because that is not important for the course. Now in the case of powers model the type of model that we use is colloid which means that the gels are basically considered as colloid. In the case of Feldman Sereda model the gels are considered basically as clay layers, and the other differences is that in the case of power the entire cement gel is considered as one unit. And the other assumptions are that the particle radius average particle radius is approximately 5 nanometers, and the gel pore volume is assumed to be 28 percentage fixed.

In the case of a Feldman Sereda model the selected characteristics or that they are crumbled and folded layers as I mentioned like a clay layers, with interlayer water reverse reversibly removed upon drying. What are interlayer water why it is should be considered as folder layers and all those things will be dealt a little later. As of now let us not get into other models, we will just take only with powers and Feldman Seredas model in the case of Feldman Seredas model the first assumption that is made is that.

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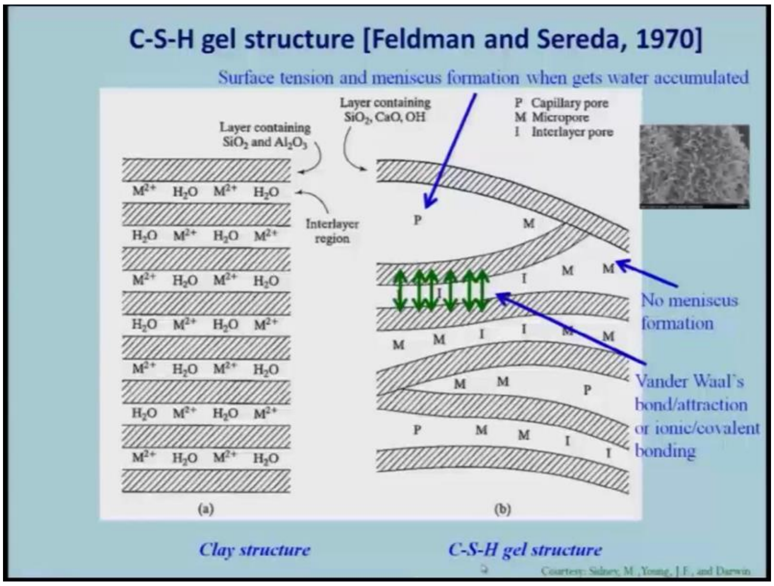

C-S-H gel structure [Feldman and Sereda, 1970]

Surface tension and meniscus formation when gets water accumulated

No meniscus formation

Vander Waal's bond/attraction or ionic/covalent bonding

Clay structure

C-S-H gel structure

Courtesy: Sidney, M., Young, J.F., and Darwin

The calcium silicate hydrate gel which is the principal strength forming phase in the Portland cement based paste systems they are considered to be equivalent to that of a clay structure. So, in the case of clay structure what we typically see is that, you have different layers of silicon dioxide and aluminium oxide. If you can recall the basics clay primarily contains silicon dioxide and aluminium oxide. And you basically have some metal ions in between the layers along with water.

So, basically water is present as a interlayer between different layers and as I said the basic assumption in this model is that ours calcium silicate hydrate gel is more or less like clay structure. So, in the calcium silicate hydrate gel the main part serves as a layer and you have some water in between. And here the pores in between are classified into 2 3 parts. One is the capillary pore which we have already seen the other one is the micropore and the other one is the inter layer. So, inter layer is the pores phase between different layers. Like you see here you have a layer you have a layer here and between 2 layers you have the interlayer. Likewise, if you have likewise micropores or the pores between 2 pores; so if you take this as one pore and the other one has another pore.

So, you have some space between 2 pores remember that there is a difference between internal layer pore and micro pore and primarily this is based on the size of the pores. So, if you get back to some previous slides that we have discussed. So, here we have discussed about micro pores and interlayers primarily distinguish based on the size of pores. And what you have the difference between to the interlayer pore. And the microphone is actually the pores in the case of interlayer what you have is a Vander wails bond or attraction or it could be ionic bond whereas, in the case of micro pore you do not have any surface tension. So, these primarily distinguish a micro pore from a interlayer in addition to the size difference that we have.

So, in Feldman Seredas model primarily calcium silicate hydrate gel structure is considered to be similar to that of clay structure.

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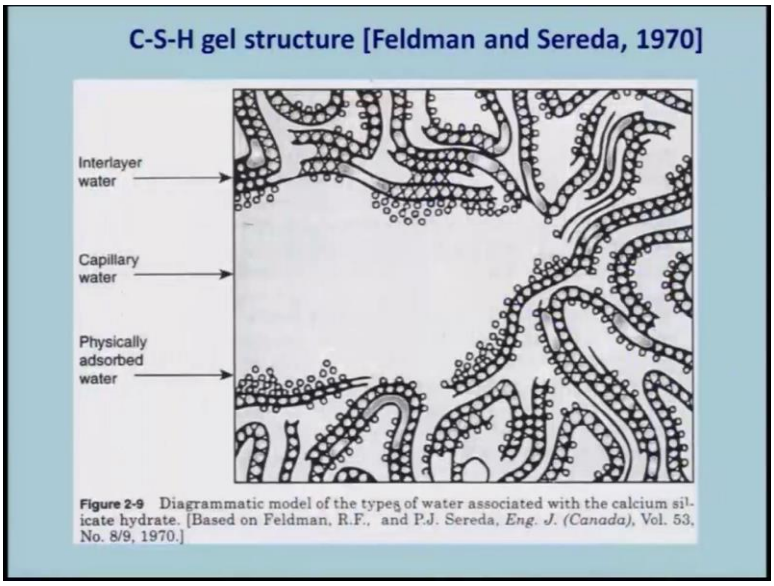

C-S-H gel structure [Feldman and Sereda, 1970]

Figure 2-9 Diagrammatic model of the types of water associated with the calcium silicate hydrate. [Based on Feldman, R.F., and P.J. Sereda, *Eng. J. (Canada)*, Vol. 53, No. 8/9, 1970.]

And an extension of that diagram is actually shown. Where you have the interlayer water that is present here in the structure and you have capillary water that is present in large amounts. And you have physically absorbed water, remember we will talk about physically absorbed water a little later as of now physically absorbed water is the amount of water that is just present outside the calcium silicate hydrate gel layer.

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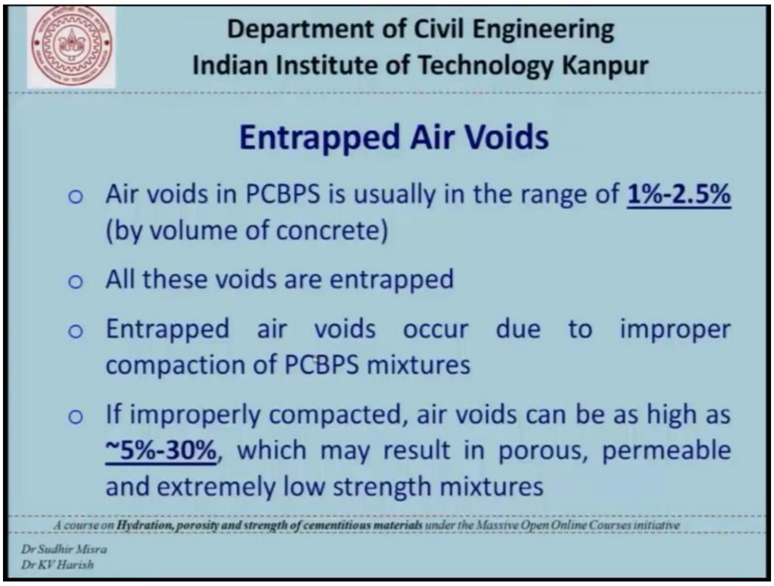

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Entrapped Air Voids

- Air voids in PCBPS is usually in the range of **1%-2.5%** (by volume of concrete)
- All these voids are entrapped
- Entrapped air voids occur due to improper compaction of PCBPS mixtures
- If improperly compacted, air voids can be as high as **~5%-30%**, which may result in porous, permeable and extremely low strength mixtures

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Now, we go to the third one which is entrapped air voids. In the case of Portland cement bases paste system the air voids the volume of air voids is usually is usually in the range of one percent to 2.5 percent, and this by volume of concrete and remember that all these voids are entrapped in nature.

Now, entrapped air voids primarily occur when you do not compact the mixture properly. So, if improperly co compacted air voids can be as high as approximately 5 percentage to 30 percentage which actually will result in porous permeable and extremely low strength mixtures. Usually this is a huge amount of air voids and we usually do not prefer such large amounts in the mixture and hence compaction is largely done in order to reduce this 5 to 30 percentage to as low as 1 percentage to 2.5 percentage. So, these substantially enhance strength of the mixture and reduce the porosity and permeability.

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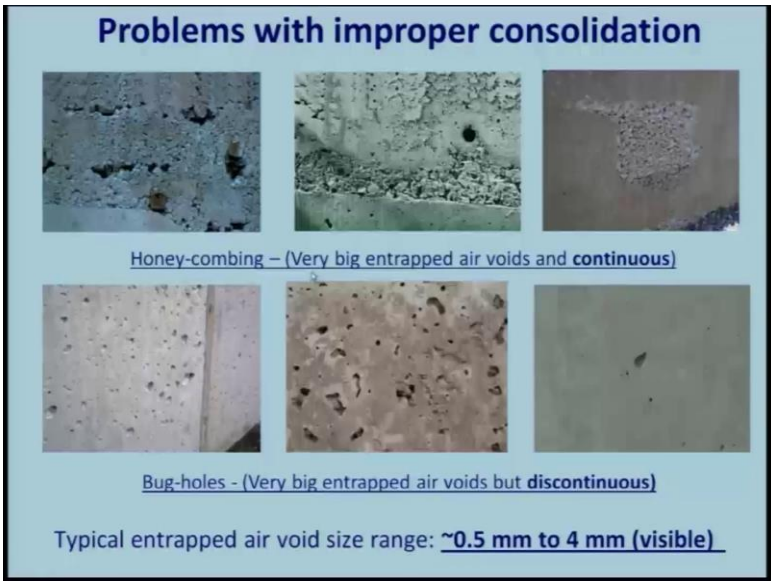

Problems with improper consolidation

Honey-combing – (Very big entrapped air voids and **continuous)**

Bug-holes - (Very big entrapped air voids but **discontinuous)**

Typical entrapped air void size range: **~0.5 mm to 4 mm (visible)**

Now, if you generally do not compact or consolidate the mixture properly typically we result in 2 types of cases. One is the honey combing case where we see that the entrapped air voids or very big in size and not only that the voids are also continuous. And in another case we can also result in bug holes which means they are also very big entrapped air voids, but the only difference between a bug hole and the honeycombing is that these voids are discontinuous. In concrete we typically do not prefer in concrete or Portland cement based paste systems we do not prefer honeycombing we also do not prefer bug holes.

Entrapped air voids; obviously, will be present, but it has to be in a certain size range. The typical size range that is acceptable is between 0.5 mm to 4 mm and at this size range typically entrapped air voids or visible to our naked eye.

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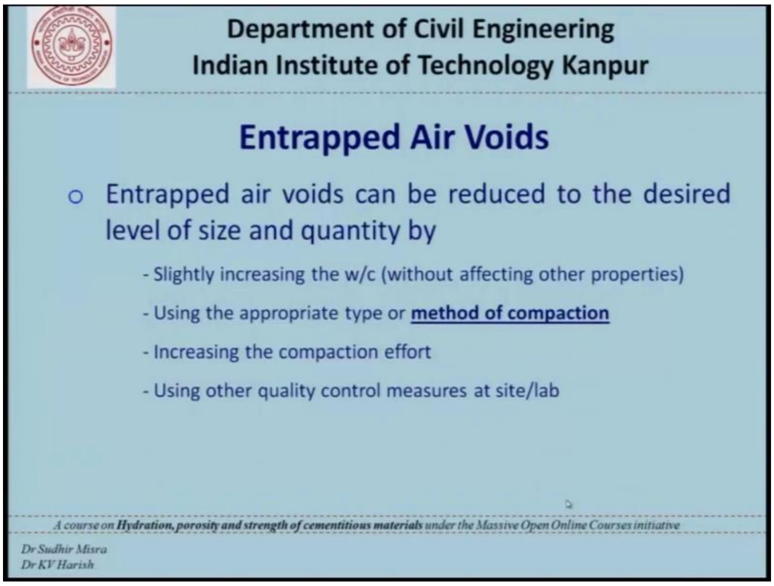

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Entrapped Air Voids

- Entrapped air voids can be reduced to the desired level of size and quantity by
  - Slightly increasing the w/c (without affecting other properties)
  - Using the appropriate type or **method of compaction**
  - Increasing the compaction effort
  - Using other quality control measures at site/lab

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Entrapped air voids can be reduced to the desired level of size and quantity by slightly increasing the water to cement ratio without affecting other properties. Remember that in the mixed design we have seen that the water to cement ratio is a very important factor which governs workability strength and durability of concrete and also sometimes economy.

So, when we adjust, when we slightly increase the water cement ratio we have to make sure that other properties are not affected. In the second case we have to we can choose the appropriate type and method of compaction. The third one we can increase the compaction effort in order to reduce entrapped air voids and we can also have other quality control measures either at the site or lab.

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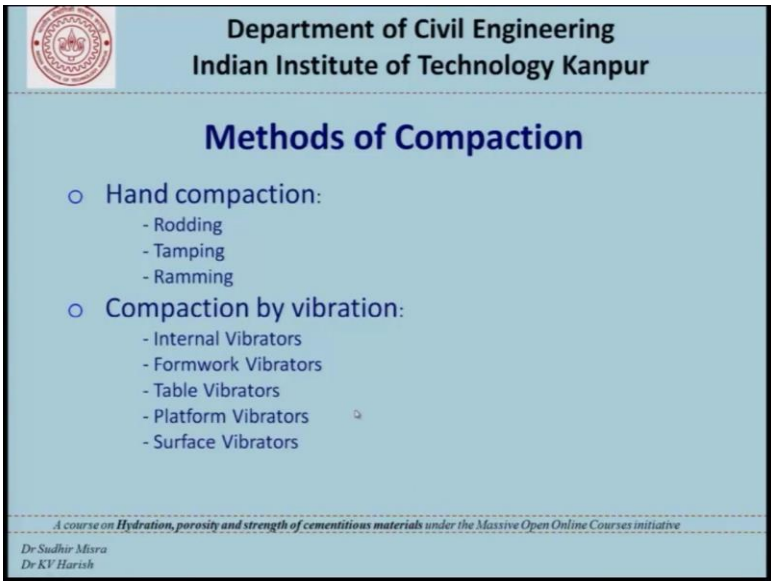

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Methods of Compaction

- Hand compaction:
  - Rodding
  - Tamping
  - Ramming
- Compaction by vibration:
  - Internal Vibrators
  - Formwork Vibrators
  - Table Vibrators
  - Platform Vibrators
  - Surface Vibrators

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So, the methods of compaction typically involves hand compaction or compaction by vibration in hand compaction, you have rodding tapping or ram ramming depending upon the site condition and in the case of vibration we have internal vibrators, formwork vibrator more like a external vibrators, table vibrators platform vibrators and surface vibrators.

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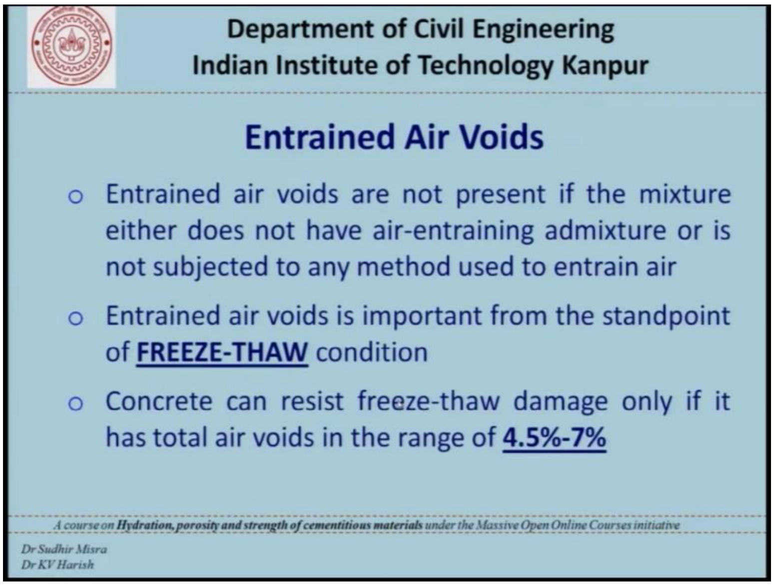

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Entrained Air Voids

- Entrained air voids are not present if the mixture either does not have air-entraining admixture or is not subjected to any method used to entrain air
- Entrained air voids is important from the standpoint of **FREEZE-THAW** condition
- Concrete can resist freeze-thaw damage only if it has total air voids in the range of **4.5%-7%**

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Now, coming onto the fourth topic which is entrained air voids. Entrained air voids are not present in the mixture very important entrained air voids are not present. If the mixture either does not have air entraining admixture remember that we have already dealt with air entraining admixture in the lecture chemical admixtures. So, if a mixture does not have air entraining admixture then typically does not have entrained air voids.

In another case if you do not use any methods by which you create air bubbles in the mixture, in that case also you do not have entrained air voids the other way of understanding is that entrained air voids can be imparted in the mixture either by using an air entraining agent or by using other methods by which you can pump air bubbles into concrete. And entrained air voids are important in the Portland cement based paste system primarily from the standpoint of freeze thaw condition. Concrete can resist freeze thaw environment only if it is total air voids is in the range of 4.5 percentage to 7 percentages. Remember that in Portland cement based paste systems what we have seen just a while before is that the entrapped air voids percentage is between one percentage and 2.5 percentage.

So, in the case of freeze thaw environment we need a higher amount of air voids primarily to resist the freeze thaw condition and the exact range is 4.5 to 7 percent and that additional air bubble that we get is primarily from air entraining admixtures.

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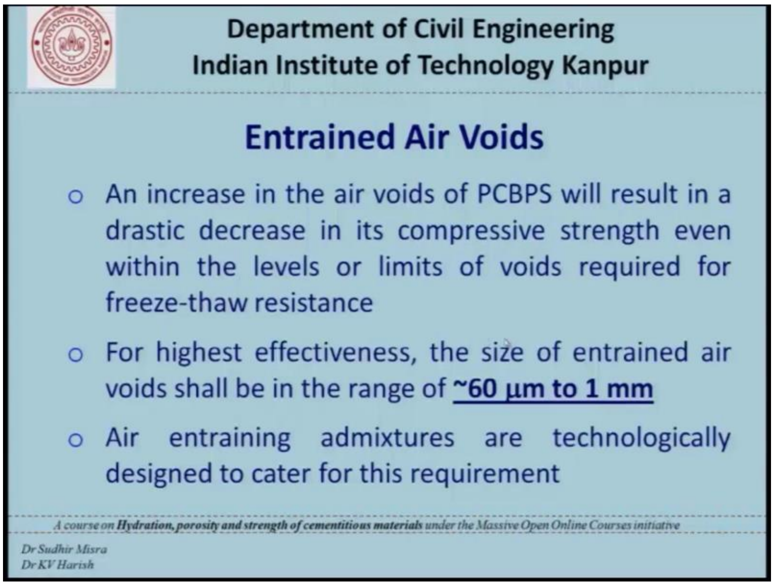

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Entrained Air Voids

- An increase in the air voids of PCBPS will result in a drastic decrease in its compressive strength even within the levels or limits of voids required for freeze-thaw resistance
- For highest effectiveness, the size of entrained air voids shall be in the range of **~60 µm to 1 mm**
- Air entraining admixtures are technologically designed to cater for this requirement

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And increase in the air voids of Portland cement based paste system will result in a drastic decrease and strength this is very important and this is one of the reasons entrained air voids are used only under freezing and thawing environments, in all other cases it is not used primarily because you have a drastic decrease in compressive strength. And remember that it is decrease and compressive strength can also be seen even within the levels or limit is of voids required for freeze thaw resistance; that means, if you have 2 mixtures one mixture containing 4 percentage air voids and another mixture containing 7 percentage air voids the one that is co containing higher air voids will have lower strength.

The next point is for highest effectiveness the size of entrained air voids shall be in the range of approximately 60 microns to one mm this is the extremely important condition to make sure that the air voids present in concrete can effectively resist freeze thaw condition. Air entraining admixtures or a technologically designed to cater for this requirement; that means, that air entraining admixtures or capable of producing entrained air voids exactly in this size range.

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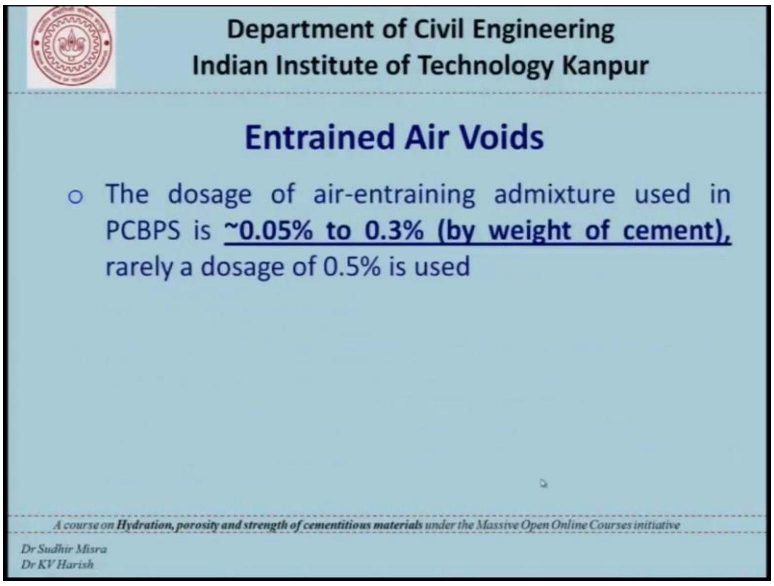

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Entrained Air Voids

- The dosage of air-entraining admixture used in PCBPS is **~0.05% to 0.3% (by weight of cement),** rarely a dosage of 0.5% is used

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The typical dosage of air entraining admixture used in the Portland cement based paste system usually ranges from 0.05 percentage to 0.3 percentage and this is with regard to the weight of cement that is used in the mixture rarely the dosage can exceed 0.5 percentage

So, revisiting the slide that we saw recently, where in the x axis what you see is the size ranges you have gel pores ranging from 1 nanometer to 10 nanometers, you have capillary voids ranging from 10 nanometer to 10 power 4 nanometers. In the case of entrained air bubbles it ranges from approximately 16 micron meter or approximately 10 power 5 nanometer to about 10 power 6 nanometer, and the entrapped air voids ranging from 10 power 6 nanometer to 10 power 7 nanometer. Or one mm to one mm in addition to the these voids we can other informations about the size is also. Given for example, if you take inter particular space between calcium silicate hydrate sheet that is again within the gel pore range and again if you take the hexagonal crystals of calcium hydroxide it is somewhere between 0.6 micron meter to about 6 micron meter likewise if you take the calcium silicate hydrate particles aggregation it is somewhere in the range of 1 micron meter and if you take the spacing of air bubbles.

So, that is somewhere between hundred micron meter to 1 mm. So, this figure primarily shows a comparison of the different voids and the some of the in hydrated and micro structural information and their size ranges. Now how do we measure pores inside Portland cement based paste system. So, the primary equipment that is used is mercury intrusion porosimetry.

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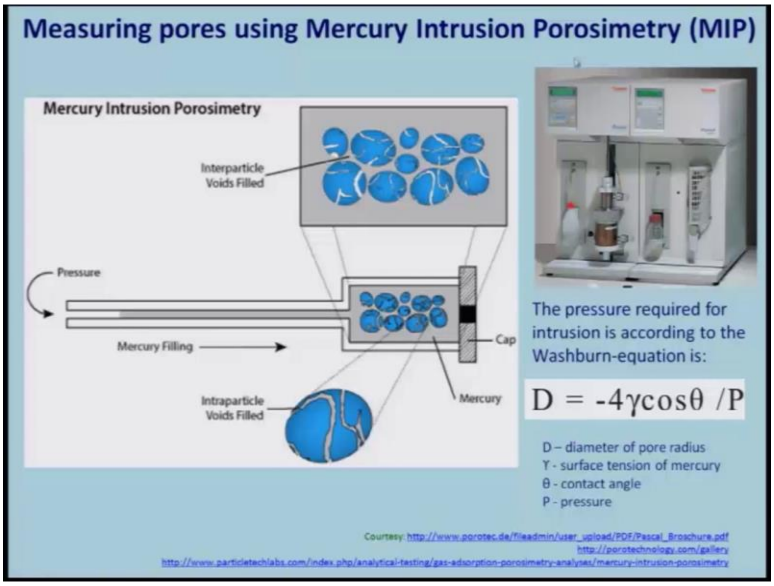

Measuring pores using Mercury Intrusion Porosimetry (MIP)

The pressure required for intrusion is according to the Washburn-equation is:

$$D = -4\gamma\cos\theta / P$$

D – diameter of pore radius
ϒ - surface tension of mercury
θ - contact angle
P - pressure

Courtesy: http://www.porotec.de/fileadmin/user_upload/PDF/Pascal_Broschure.pdf
http://porotechnology.com/gallery
http://www.particletechlabs.com/index.php/analytical-testing/gas-adsorption-porosimetry-analyses/mercury-intrusion-porosimetry

So, in this figure what you see is in the right you have the equipment and the primary principle that is used is wash burns equation which is nothing, but d is equal to minus 4 into gamma cos theta divided by p, where is where d is the diameter of pore radius and gamma is a surface tension of mercury and theta is the contact angle and p is the pressure now what this equipment basically does is actually explained in this figure.

So, what you can find in this figure is that, this vertical part is basically shown as a horizontal part for easier explanation. So, here what you find is that you have a tube through which mercury is filled in, and this basically at the bottom you have a cylinder which contains cement particles for which the porosity has to be determined. And the mercury is usually poured in this cube and that is basically occupies the space here, but remember that it can only occupy the space is space here, but it cannot get into the cement particles. Why because mercury requires more pressure to go inside cement particles because the voids in the cement paste are very small. So, we need additional pressure.

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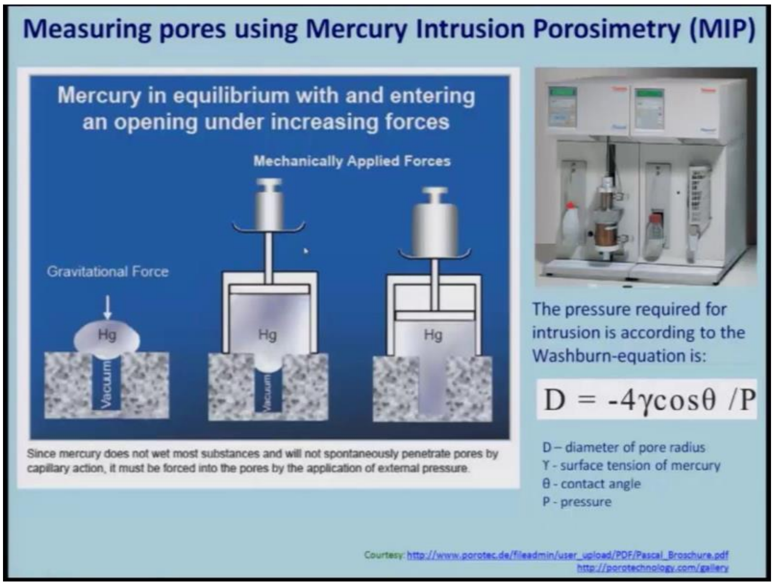

Measuring pores using Mercury Intrusion Porosimetry (MIP)

Mercury in equilibrium with and entering an opening under increasing forces

Since mercury does not wet most substances and will not spontaneously penetrate pores by capillary action, it must be forced into the pores by the application of external pressure.

The pressure required for intrusion is according to the Washburn-equation is:

$$D = -4\gamma\cos\theta\ /P$$

D – diameter of pore radius
ϒ - surface tension of mercury
θ - contact angle
P - pressure

Courtesy: http://www.porotec.de/fileadmin/user_upload/PDF/Pascal_Broschure.pdf
http://porotechnology.com/gallery

So, for this purpose huge pressure is applied to inject mercury into the air voids. So, in this figure what is shown is p setups in the first setup what it is shown is through gravitational force it is difficult to inject or penetrate mercury into the cell in the second case you need mechanical applied force to inject, and during the injection and vacuum is created and some amount of some volume of mercury actually gets into the vacuum and it gets filled and then later on at the next stage some more pressure is required in order for the mercury to penetrate into the concrete sample.

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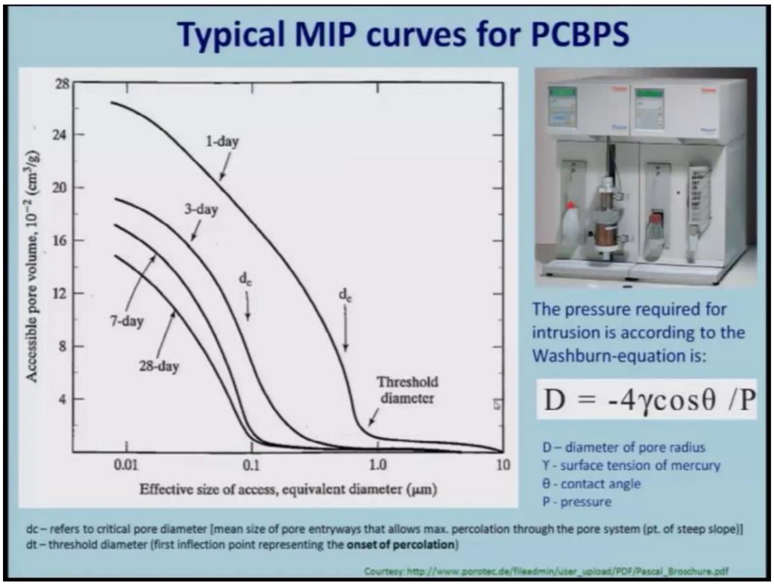

Typical MIP curves for PCBPS

The pressure required for intrusion is according to the Washburn-equation is:

$$D = -4\gamma \cos\theta \; /P$$

D – diameter of pore radius
Y - surface tension of mercury
θ - contact angle
P - pressure

dc – refers to critical pore diameter [mean size of pore entryways that allows max. percolation through the pore system (pt. of steep slope)]
dt – threshold diameter (first inflection point representing the **onset of percolation**)

Courtesy: http://www.porotec.de/fileadmin/user_upload/PDF/Pascal_Broschure.pdf

So, typical mercury intrusion porosimetry curves are showed here; what you find in this graph is that in the x axis the affective size of axis or equivalent diameter is shown. And in the y axis accessible pore volume is shown in 10 power minus 2 centimeter cube per gram.

Now, what is this acc accessible pore volume? If you revisit the formula that is used there is some pressure that we are applying to pores mercury to penetrate into the sample. And this is inversely proportional to the diameter of the pore. Initially when you apply pressure the mercury gets into the void area, and later on it needs some more volume to actually penetrate into the concrete sample. So, if you have a closer view at this figure what you will notice is that, you totally have 4 different samples one is one day cute sample the other one is 3 day cute the other one is 7 day and 28 day. And let us first take the one day cute sample and you get a typical train where the accessible pore volume decreases from the smaller size to the bottom size.

So, this curve has to be understood from a different sense. So, first of all when pressure is applied what happens is it takes approximately some amount? Say here 0 to 2 centimeter cube per gram to penetrate into the vacuum area or into the cylinder area this is considered to be a cylinder. So, to enter this area it requires some there is some quantity of mercury that is required to fill this area. So, that is actually shown by this volume from 0 to 2 approximately, because 2 refer to this flatter zone. And once the threshold volume is reached after that the mercury requires more pressure to actually penetrate into the cement paste sample.

So, the terminology here provided as threshold diameter refers to the diameter which represents the onset of percolation, which means that from this part of the curve to this part of the curve mercury does not basically enter into the cement paste sample. It is only after this part the mercury enters into the paste sample. And this region is also an indication the starting size of paste sample is somewhere between point 1 micron meter to approximately 1 micron meter.

So, once it enters it slowly penetrates into the sample and what you also see is that this keeps on increasing why because more and more mercury is getting inside. So, the accessible pore volume is actually the amount of mercury that is getting into the sample. So, the typical trend increases from this point until some value here, and this is for a 1 day specimen. And there is a terminology d c which refers to critical pore diameter, which means it is the mean size of pore entries that allows maximum percolation through the pore system. And it is the point of steepest slope in the curve. So, how it is determined and why it is required? When the mercury enters the pores of the sample you see that the pores are not just one size it is distributed. So, typically in this curve what you find is that the pores are between 0.01 micron meter to say 1 micron meter. And hence the in order to characterize this curve by just one size the value d c is used.

So, d c is actually the mean size of the different pore sizes. And how it is determined? Basically we have to draw a tangential line to the tangential line to the first derivative of this curve in order to identify the steepest slope. So, critical pore diameter refers to the mean size of the pore entry ways. Right from here to here this provides the mean pore size.

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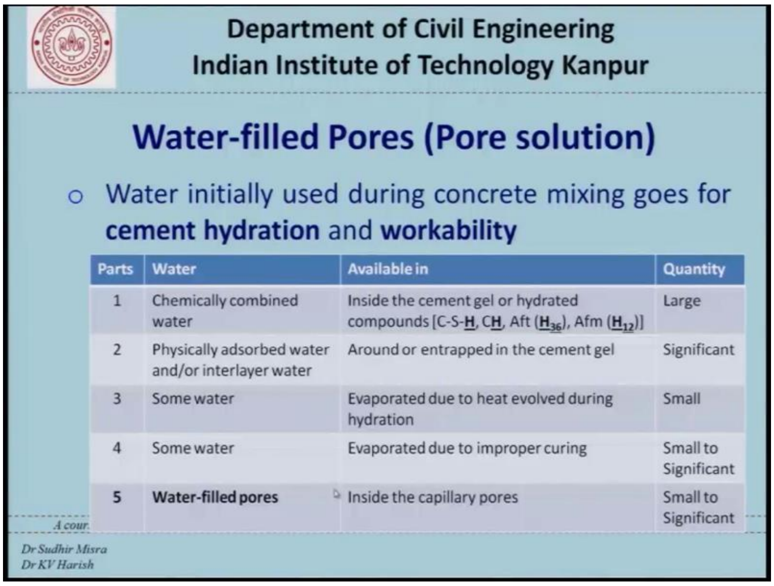

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Water-filled Pores (Pore solution)

- Water initially used during concrete mixing goes for **cement hydration** and **workability**

Parts	Water	Available in	Quantity
1	Chemically combined water	Inside the cement gel or hydrated compounds [C-S-$\underline{H}$, C$\underline{H}$, Aft ($\underline{H}_{36}$), Afm ($\underline{H}_{12}$)]	Large
2	Physically adsorbed water and/or interlayer water	Around or entrapped in the cement gel	Significant
3	Some water	Evaporated due to heat evolved during hydration	Small
4	Some water	Evaporated due to improper curing	Small to Significant
5	**Water-filled pores**	Inside the capillary pores	Small to Significant

A cour.

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Now, coming on to the next topic water field pores or pore solution. Water initially that we add in concrete goes for 2 purposes one is cement hydration the other one is workability. And; obviously, when water is added you have hydration reactions that happen and finally, the water is available in 5 different forms. One is chemically combined water the other one is physically absorbed water and or interlayer water. The third one is some water which is evaporated because of the heat evolved during hydration process, and some water which if you do not cure properly also gets evaporated to the environment and also finally, you have the fifth one which is water fill pores where some water may actually fill some capillary pores that are present.

Now, what is chemically combined water in simple terms, it is a water that is inside the cement gel or hydrated compounds. And largely this water is equal to the water that you have in the chemical structure of calcium silicate, hydrate gel chemical structure of calcium hydroxide AFT. And recall what is the formula for a for AFT or revering guide you see that there is a 36 hydrogen atoms bonded to it. So, this chemically combined water is also a part of this and also you have in AFM monosulfoaluminates you have recall the formula you have h 12. So, chemically combined water basically refers to the water associated with a hydrated compounds in the case of physically absorbed water or interlayer, water they are also water in the cement gel, but not in the cement gel, but around the cement gel or entrapped in the cement gel. And as I mentioned other water gets evaporated from the heat evolved improper curing or present in the capillary pores.

And the water filled capillary pores inside the capillary pores are called as pore solution a very important part in the cement hydration process and the quantity that you have for each one of them are large significant, small to significant depending upon whether you have done substantial curing or not in the fifth case it is small to significant depend depending upon the amount of water that is present initially.

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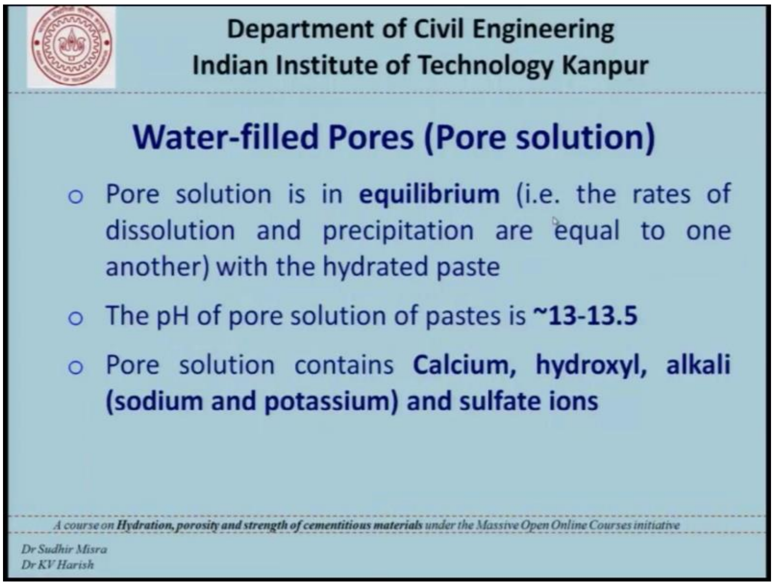

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Water-filled Pores (Pore solution)

- Pore solution is in **equilibrium** (i.e. the rates of dissolution and precipitation are equal to one another) with the hydrated paste
- The pH of pore solution of pastes is **~13-13.5**
- Pore solution contains **Calcium, hydroxyl, alkali (sodium and potassium) and sulfate ions**

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Now, more information about water filled pores. Pore solution is equilibrium with a hydrated cement paste. It is very important the pore solution or water filled pores is in equilibrium. So, what I mean by equilibrium. The dissolution rates and the precipitation rates remember; what is the dissolution if you go back to the previous lectures, we will find out what is dissolution. So, the rates of dissolution and precipitation are equal for the pore solution as well as the hydrated cement paste. And because of this the pH of the pore solution of the paste typically ranges from 13 to 13 0.5 percentage and this is also taken as the pH of the paste.

So, what does pore solution contain pore solution essentially contains calcium ions, hydroxyl ions, alkali I ions, either sodium or potassium and sulfate ions. And in the next figure what we will see is with time how does the ions or ion concentration changes with the process of hydration.

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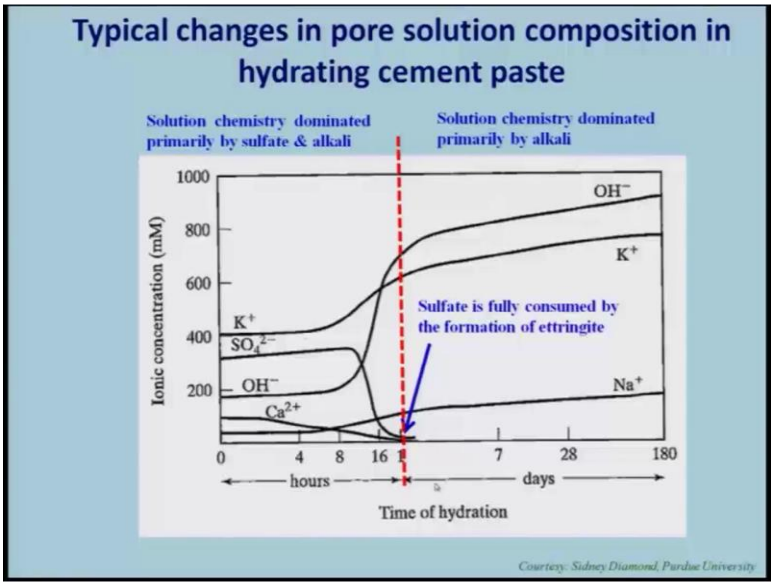

Typical changes in pore solution composition in hydrating cement paste

Solution chemistry dominated primarily by sulfate & alkali

Solution chemistry dominated primarily by alkali

Sulfate is fully consumed by the formation of ettringite

Courtesy: Sidney Diamond, Purdue University

So, in this curve what is shown is time is taken in the x axis from 0 to about one 80 days. Remember that this is a log plot and not a normal plot. So, that is why you find the hours are showed from here to here and then days shown from here to here in this this scale is not to scale, the x axis is not to scale. In the y axis what you find is the ion concentration ranging from 0 to thousand PPM or parts per million. So, in this graph you totally have about 5 curves let us see one by one.

So, during the initial hours say from 0 hours to about say 16 or 16 or 24 hours what you find is that the calcium ions are initially present and slowly they get reduced to 0, why because we have already seen in the previous lectures about hydration and hydration reactions that the calcium that is present in the unhydrated 7 compounds basically reacts together and form the hydrated compounds. So, in the pore solution even though it is present initially slowly it becomes zero; that means that this calcium is completely utilized in the formation of hydrated compounds. In the case of sulfates what you find is that since gypsum is present in Portland cement at the initial stages you find that the sulfate concentration is high, but this concentration is high only until the formation of ettringite. Once the ettringite changes from ettringite to monosulfo aluminates this reduces and finally, this also goes to 0, say approximately at 24 hours the sulfate is fully consumed by the formation of a ettringite or reconversion from ettringite to monosulfo aluminates.

In the third one what you see is that the sodium that is present as minor compounds slowly increases because they do not actively participate in the hydration process and they are present in the pore solution, and say at an age of say one 80 days the concentration of sodium is the highest compared to that at 0 days likewise if you take potassium at the initial level it is generally high and with time it increases and finally, say at about 180 days, it is extremely high and in the case of hydroxyl ions what you find is initially, you have some hydroxyl ions remember that some portion of hydroxyl ions are also consumed for the formation of hydration products and later on suddenly it is deeply increases why because water is not fully utilized in the hydration process and it is substantially available in capillary pores.

So, suddenly increases and say about 180 days or. So, where it can be expected that ninety to 95 percentage would have already happened in such case the hydroxyl ions is maximum and finally, if you take a matured sh Portland cement paste system in the pore solution, what you have is only 3 ions largely one is sodium ion potassium ion and hydroxyl ions remember that the calcium ions are already consumed, and also the sulfate ions are completely consumed and the distinction ,here is shown to indicate that in the first part the solution chemistry dominated primarily by sulfates and alkalis in the later part the solution chemistry is dominated primarily by alkalis.

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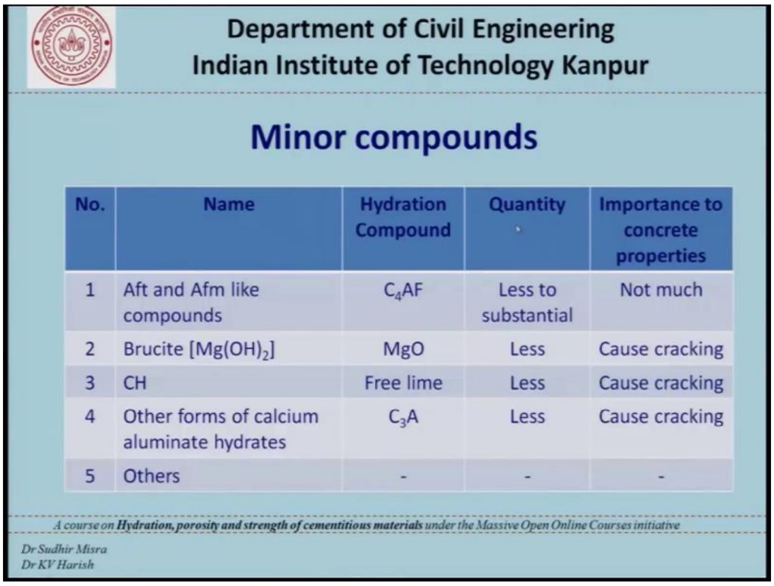

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Minor compounds

No.	Name	Hydration Compound	Quantity	Importance to concrete properties
1	Aft and Afm like compounds	C_4AF	Less to substantial	Not much
2	Brucite [$Mg(OH)_2$]	MgO	Less	Cause cracking
3	CH	Free lime	Less	Cause cracking
4	Other forms of calcium aluminate hydrates	C_3A	Less	Cause cracking
5	Others	-	-	-

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Now, coming on to the next topic minor compounds in addition to all that we have seen previously, we also have minor compounds including the ettringite and monosulfoaluminate like compounds very important like compounds primarily because they are not AFT and AFM, they are ettringite and monosulfoaluminate like compounds primarily from the hydration of C4AF, which we have already seen in the previous lectures. And their quantity is less to substantial depending upon the percentage of C4AF in the system, and the do they contribute to the properties of Portland cement based systems answer is no they do not contribute substantially their presence is still fine, but they do not negatively affect as well as positively affect the properties other compounds such as brucite.

Remember we discussed brucite probably in the fourth or fifth lecture brucite is nothing, but magnesium hydroxide formed because of the hydration of magnesium oxide present in cement. And remember that usually these cements have to be within some limit and the quantity is generally low. But with regard to concrete properties they cause cracking and not they are not usually preferred in the mixture likewise you also have calcium hydroxide remember the calcium hydroxide that we are discussing here is not the calcium hydroxide that we get from the major compounds hydration of the major compounds this is from the hydration of free line.

And this is also very vulnerable and causes cracking this sometimes also be present in less quantities. Other forms of calcium aluminate hydrates like a from C3A, we have already seen this like solid solutions of calcium aluminate hydrates or hydro carbonate or whatever those may also be present in lesser quantities, but remember that they also cause cracking and they are also not good for concrete properties, but even in a well controlled system wherein if you have the right amounts of sulfates as well as aluminates, you may still find a little portion of calcium aluminate hydrates.

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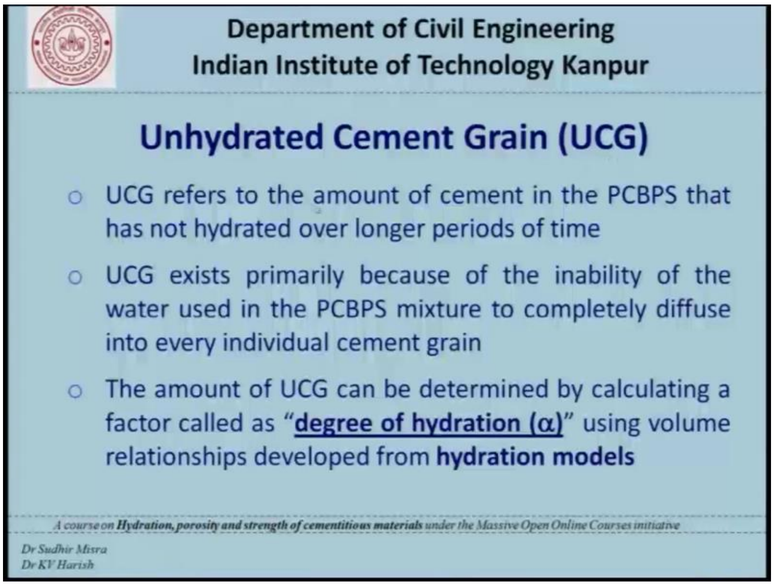

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Unhydrated Cement Grain (UCG)

- UCG refers to the amount of cement in the PCBPS that has not hydrated over longer periods of time
- UCG exists primarily because of the inability of the water used in the PCBPS mixture to completely diffuse into every individual cement grain
- The amount of UCG can be determined by calculating a factor called as "**degree of hydration (α)**" using volume relationships developed from **hydration models**

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In other things you also have other minor impurities coming onto the final one which is unhydrated cement grain in this lecture it is denoted as UCG, unhydrated cement grains refers to the amount of cement in the system that has not hydrated over longer periods of time. And this primarily happens because of the inability of water to get into the mixture after sometime. We have already seen through solution mode and solid state or topo chemical mode, where we have seen that beyond certain level water can only diffuse into concrete and cannot freely enter concrete.

So, in such cases the diffusion happens over a longer period of time. And in such a case the cement grains may not be fully hydrated. The amount of unhydrated cement grain can be determined by calculating a factor called degree of hydration very important factor which is used in cement hydration process alpha denoted by alpha, and it is obtained using volumetric relationships developed from hydration models. We will see more about a degree of hydration and other things in the subsequent lectures when we deal with hydration models now again getting back to un-hydrated cement grain.

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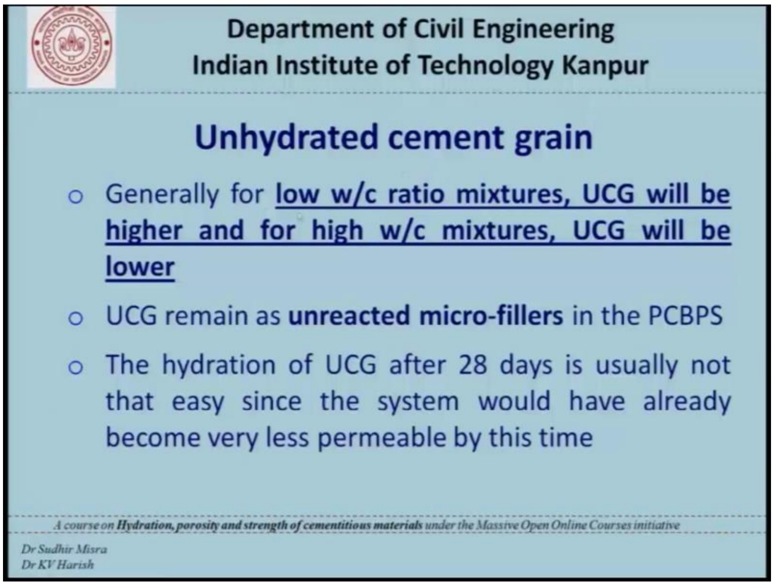

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Unhydrated cement grain

- Generally for **low w/c ratio mixtures, UCG will be higher and for high w/c mixtures, UCG will be lower**
- UCG remain as **unreacted micro-fillers** in the PCBPS
- The hydration of UCG after 28 days is usually not that easy since the system would have already become very less permeable by this time

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Generally, for very low water cement ratio mixtures un-hydrated cement grain will be higher. And for high water cement ratio mixtures un-hydrated cement grains will be lower. This is very obvious, but very important from the stand point of understanding.

Un-hydrated cement grain remain as unreacted micro fillers in the system, when unhydrated cement grains are present and even if they are present in minor quantities they are still and they act as micro fillers. The hydration of unhydrated cement grain after 28 days is usually not easy since the system would have been already become very less permeable by this time; that means, is that if you have unhydrated cement grain after 28 days and if you want to hydrate it, by adding littler more water it is very difficult primarily because the hydration products are already found in the system and hence the system has already become less permeable and water cannot enter to the cement grain so easily.

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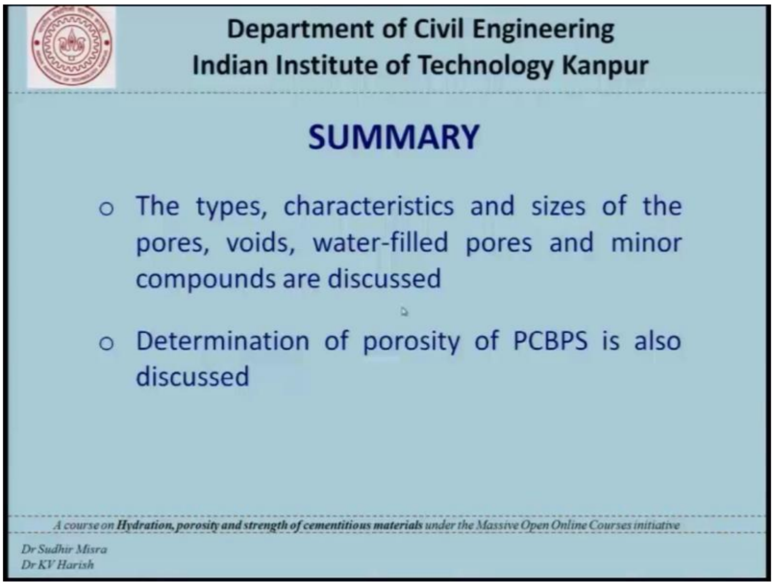

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SUMMARY

- The types, characteristics and sizes of the pores, voids, water-filled pores and minor compounds are discussed
- Determination of porosity of PCBPS is also discussed

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Now, in summary what we have seen is the different types characteristics and sizes of pores voids water filled pores and minor compounds. And we have also seen how to determine porosity using mercury intrusion porosimetry.

With this I am completing this lecture.

Thank you.