Concrete Engineering and Technology
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Lecture - 5
Hydration of cement

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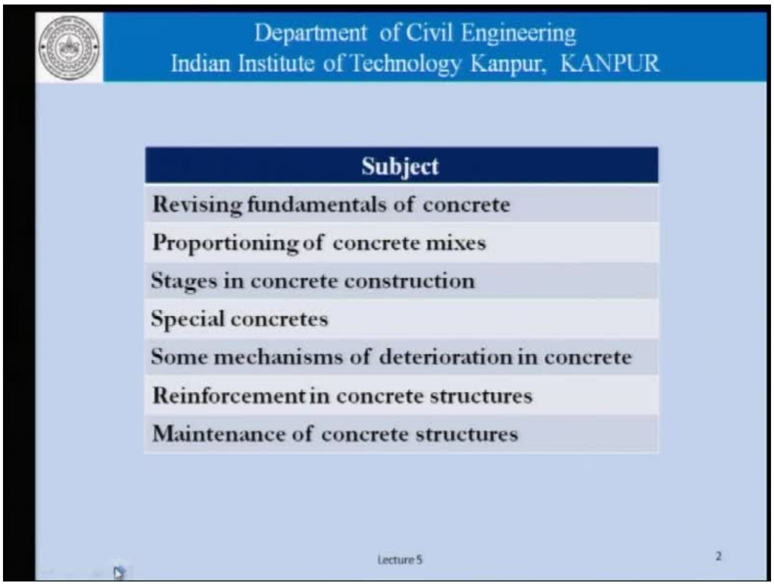

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Subject
Revising fundamentals of concrete
Proportioning of concrete mixes
Stages in concrete construction
Special concretes
Some mechanisms of deterioration in concrete
Reinforcement in concrete structures
Maintenance of concrete structures

And welcome to this lecture on concrete engineering and technology. In this series we have been talking about: fundamentals, proportioning, stages in concrete construction, special concretes, mechanism of retail ration, reinforcement and maintenance.

Now continuing with the discussion on the fundamentals which is the first part of the discussion, we have been talking about constituents of concrete and we know that concrete comprises of coarse aggregate, fine aggregate, ordinary Portland cement and water. We are not talking of mineral and chemical add mixtures which have become and inherent integral part of the concrete construction, what we will talk about that later. As far as the first round is concern, we will talk of absolutely normal concrete comprising of these four elements.

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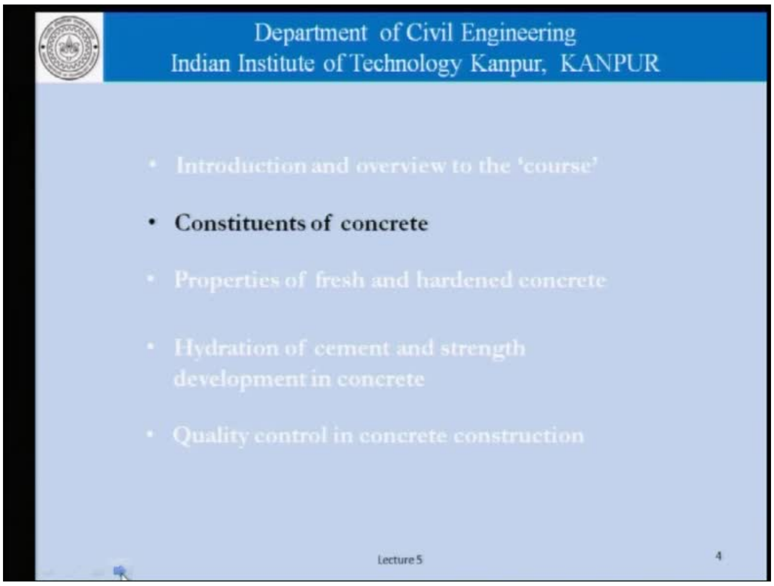

- Introduction and overview to the 'course'
- Constituents of concrete
- Properties of fresh and hardened concrete
- Hydration of cement and strength development in concrete
- Quality control in concrete construction

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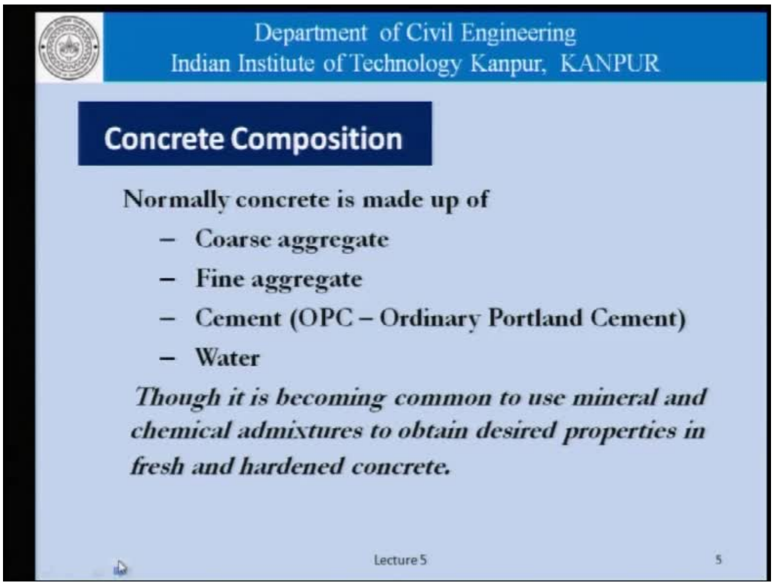

Concrete Composition

Normally concrete is made up of

- Coarse aggregate
- Fine aggregate
- Cement (OPC – Ordinary Portland Cement)
- Water

Though it is becoming common to use mineral and chemical admixtures to obtain desired properties in fresh and hardened concrete.

Now, coming to the discussion on cement which is the ordinary Portland cement, we must remember that cement is the only reactive component in concrete and the hydration products which are formed when cement reacts with water that provides the binder for the aggregates. Therefore, the properties of concrete are determined to a large extent from the properties of cement and binding hydration products. Also cement is the most expensive of the components and efforts need to be made to minimize the cement contained in the concrete mix. Codes often prescribe a minimum and a maximum content of cement in a concrete mix. The minimum is prescribed from the point of few of durability and so on, whereas the maximum is sometime prescribed from considerations of heat of hydration and so on as we shall see sometime later.

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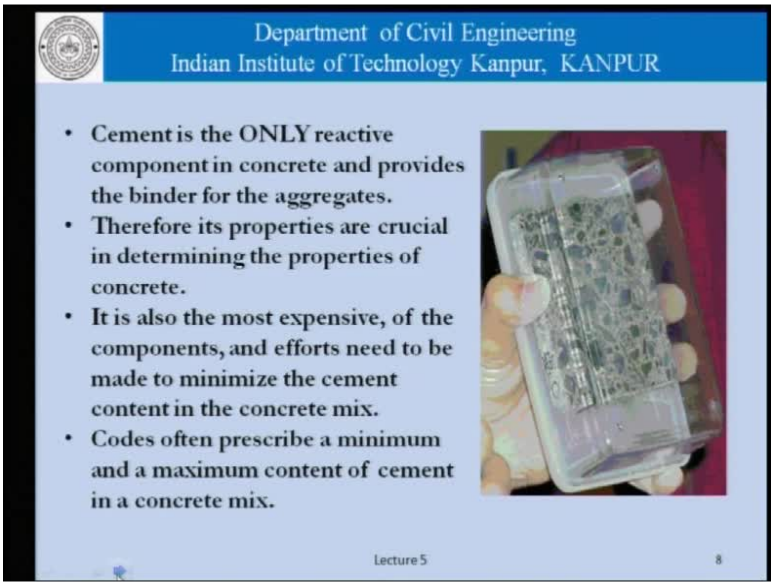

- Cement is the ONLY reactive component in concrete and provides the binder for the aggregates.
- Therefore its properties are crucial in determining the properties of concrete.
- It is also the most expensive, of the components, and efforts need to be made to minimize the cement content in the concrete mix.
- Codes often prescribe a minimum and a maximum content of cement in a concrete mix.

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Ordinary Portland Cement

- Manufacture of OPC
- Constituents
- Physical and chemical properties
- Hydration characteristics

Now coming to order Portland cement, we already talked about some of these things manufactured, constituents, physical and chemical properties and hydration. Today we largely concentrate on the properties of OPC and the hydration reaction that are important in our understanding of the properties of the cement paste as well as the properties of concrete.

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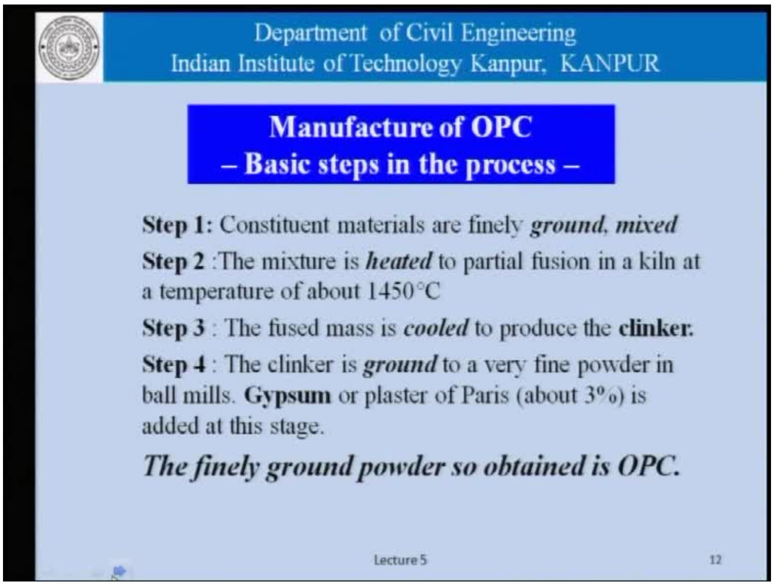

Manufacture of OPC
– Basic steps in the process –

Step 1: Constituent materials are finely ***ground, mixed***

Step 2 :The mixture is ***heated*** to partial fusion in a kiln at a temperature of about 1450°C

Step 3 : The fused mass is ***cooled*** to produce the **clinker.**

Step 4 : The clinker is ***ground*** to a very fine powder in ball mills. **Gypsum** or plaster of Paris (about 3%) is added at this stage.

The finely ground powder so obtained is OPC.

Now, as far as the these three things are concerned we already talked about that and we know that manufacture of OPC essentially involves grinding of constituent materials, mixing them, heating the mixed in a kiln to a temperature of about fourteen 1450 to 1500 degree centigrade, cooling this fused mass to produce what is called ‘clinker’ and then grinding the clinker to a very fine powder involvements and that is how we get ordinary Portland cement. During the grinding, gypsum or plaster of Paris to the extent for about 3 percent is added to control and regulate the iteration of the cement and that is the role of gypsum.

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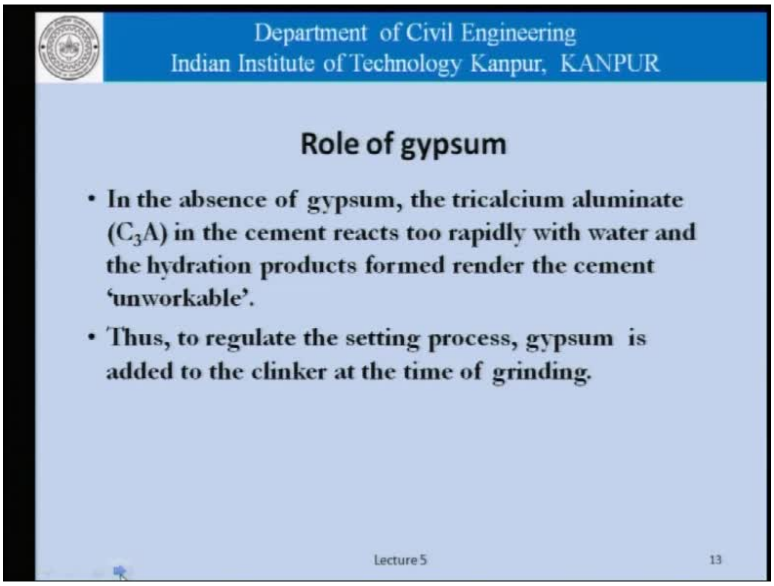

Role of gypsum

- **In the absence of gypsum, the tricalcium aluminate (C_3A) in the cement reacts too rapidly with water and the hydration products formed render the cement ‘unworkable’.**
- **Thus, to regulate the setting process, gypsum is added to the clinker at the time of grinding.**

In the absence of gypsum, the tricalcium aluminate C 3 A which is one of the principle constituents of the cement reacts too rapidly with water and the hydration products formed render the cement on workable and thus to regulate the setting process gypsum is added to the clinker at the time is grinding. We shall remember that in order to have reasonable construction using concrete, the cement should be such that it allows the concrete to remain workable for at least some time so that the concrete can be transported, placed, vibrated and transportations sometimes takes a lot of time it could be 30 minutes, 40 minutes, may be 1 hour if we are using ready mix concrete.

Even if you are using the concrete at site, even then it might take about 15 minutes or 10 minutes to transport the concrete from the actual mixing sites to the place where it has to be placed or the structure which is being cast. Therefore, concrete must remain workable during that time. Having said that after that it should hearten and the concrete cannot be allowed to remain workable for a two longer period of time and therefore, there has to be a lower bound on the initial setting time of cement and an upper bound on the final setting time of cement. And that is the window in which we play and once we have the cement which conforms to regulations we are ready to use it in concrete constructions.

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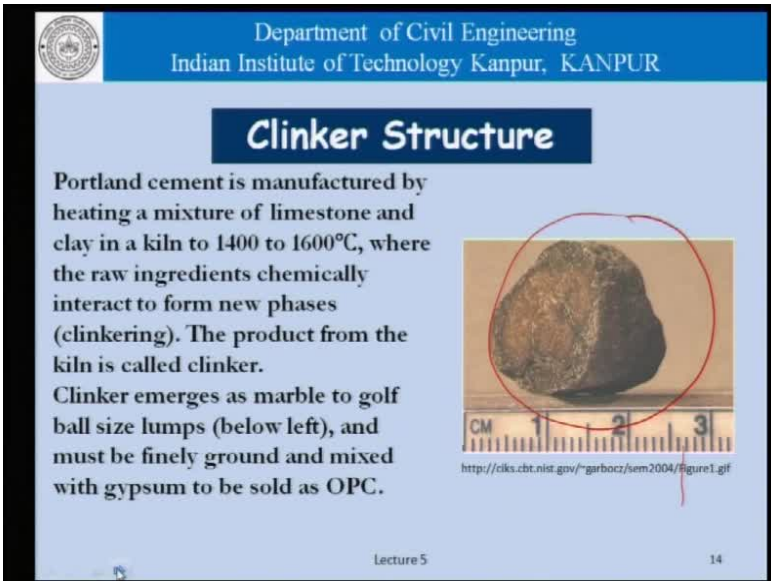

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Clinker Structure

Portland cement is manufactured by heating a mixture of limestone and clay in a kiln to 1400 to 1600°C, where the raw ingredients chemically interact to form new phases (clinkering). The product from the kiln is called clinker.

Clinker emerges as marble to golf ball size lumps (below left), and must be finely ground and mixed with gypsum to be sold as OPC.

http://ciks.cbt.nist.gov/~garbocz/sem2004/figure1.gif

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Now, coming to the clinker we have seen this photograph before. Portland cement as we said is manufactured by heating a mixture of limestone and clay in a kiln to 14 feet in a kiln to a temperature of 1400 to 1600 degree centigrade where the raw ingredients chemically interact to form new phases during clinkering and the product being called clinker. And this clinker emerges as marbles of golf sized lumps as shown here and that must be finding the ground to produce the OPC. So, this we can see here is a particle of clinker and we if we sit along this kiln which is given at the bottom we can see that this particle or this piece this about 2 and a half centimeters in diameter or having a dimension of about 2, 2 and half centimeters.

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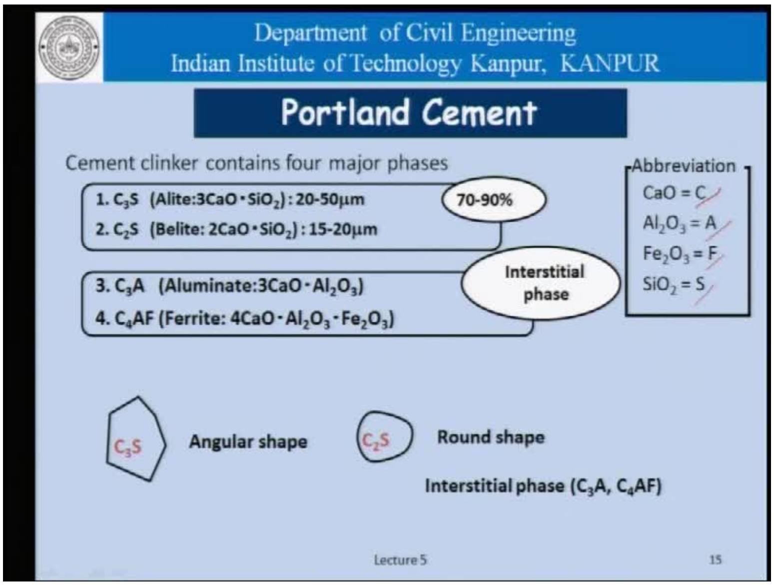

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Portland Cement

Cement clinker contains four major phases

1. C_3S (Alite:$3CaO \cdot SiO_2$): 20-50μm
2. C_2S (Belite: $2CaO \cdot SiO_2$): 15-20μm

70-90%

3. C_3A (Aluminate:$3CaO \cdot Al_2O_3$)
4. C_4AF (Ferrite: $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$)

Interstitial phase

Abbreviation
$CaO = C$
$Al_2O_3 = A$
$Fe_2O_3 = F$
$SiO_2 = S$

Interstitial phase (C_3A, C_4AF)

Now, if we look at chemical composition of the clinker it contains C 3 S that is the tri-calcium silicate also called Alite which are about 20 micro meters to 50 micro meters and Blite which is di-calcium silicate C 2 S. C 3 A and C 4 A F, which are aluminate and the ferrite phases in the clinker and they are there in the interstitial phase. Whereas, the C 3 A,C 2 A which constitutes about 70 to 90 percent of the clinker. We must also remember that C 3 S, if you look at it in a microscope is sufficient magnification you will find that it is angularly shape, whereas, C 2 S is rounded. Recall that in cement chemistry C is calcium oxide, A is aluminum oxide, F is a F e 2 O 3 and S is S i O 3. So, then we say C 2 S, C 3 S we are talking of complexes which are formed due to the fusion of calcium oxide a silicon oxide and so on.

Now, continuing with the discussion on the constituents. We have seen that since the raw material is essentially oxides that are of calcium, silicon, aluminum and iron. The product that is OPC is also made up of these oxides typically the oxide composition for the composition of OPC in terms of the oxides is shown here. These we should remember are very stable compounds and therefore, do not break when they are subjected to heat and grinding and so on. Whereas, products like calcium carbonate they get decomposed to give you S i, to give calcium oxide and carbon dioxide and so on.

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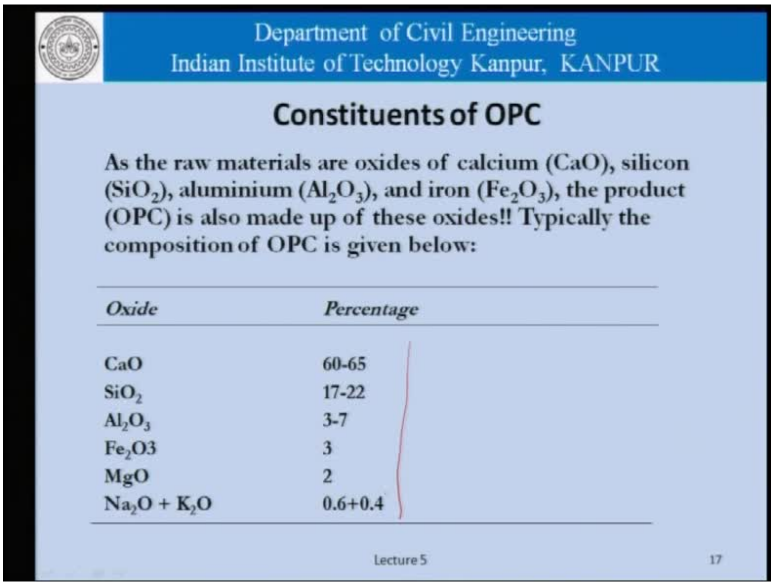

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Constituents of OPC

As the raw materials are oxides of calcium (CaO), silicon (SiO_2), aluminium (Al_2O_3), and iron (Fe_2O_3), the product (OPC) is also made up of these oxides!! Typically the composition of OPC is given below:

Oxide	*Percentage*
CaO	60-65
SiO_2	17-22
Al_2O_3	3-7
Fe_2O3	3
MgO	2
$Na_2O + K_2O$	0.6+0.4

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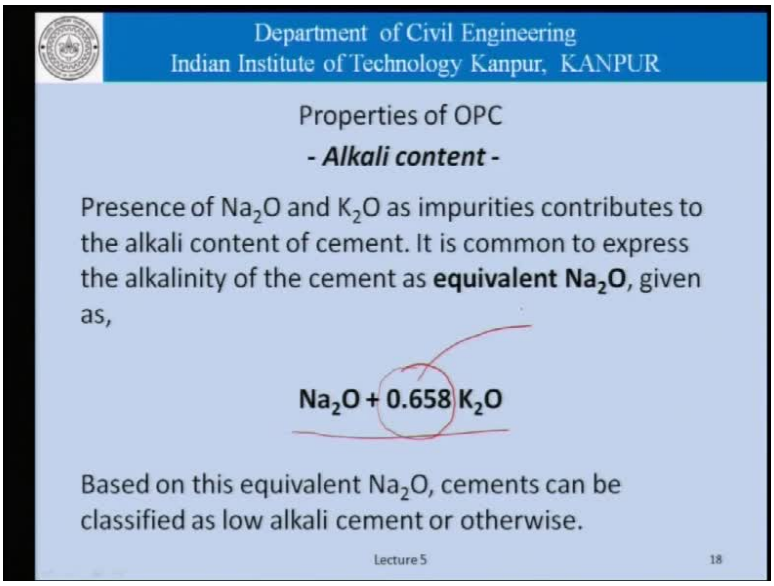

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Properties of OPC

- *Alkali content* -

Presence of Na_2O and K_2O as impurities contributes to the alkali content of cement. It is common to express the alkalinity of the cement as **equivalent Na_2O**, given as,

$$\underline{Na_2O + \boxed{0.658}\, K_2O}$$

Based on this equivalent Na_2O, cements can be classified as low alkali cement or otherwise.

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Now, if you look closely at these this composition. There is a alkali content of the cement which is basically rising out of the presence of sodium oxide and potassium oxide which are impurities that contribute to the alkali content, it is common to express the alkalinity of the cement as equivalent N a 2 O given by N a 2 O content and 0.658 the K 2 O content. I am leaving as an assignment for you to determine what is the basis of this factor of 0.658? Please try to do some simple arithmetic and I am sure you get the answer.

And based on this equivalent N a 2 O that we have in the cement, the cements can be classified as low alkali cements or otherwise as specification can always say that if the N a 2 O equivalent of cement is more than 1 percent the cement will be classified as high alkali cement. If it is less than 0.3 percent it will be low alkali cement. These numbers are arbitrary and professionally decided by engineers and their bodies which are responsible for writing the code then specifications for cement concrete and construction.

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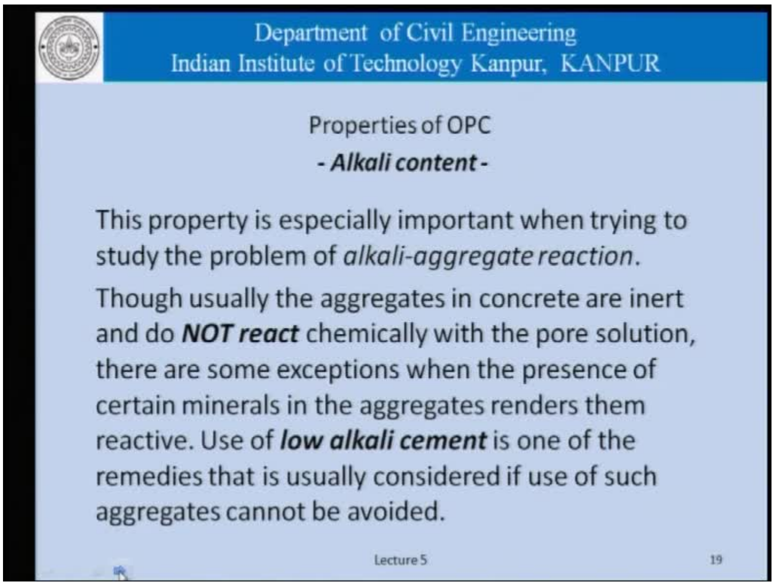

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Properties of OPC
- *Alkali content* -

This property is especially important when trying to study the problem of *alkali-aggregate reaction*.

Though usually the aggregates in concrete are inert and do ***NOT react*** chemically with the pore solution, there are some exceptions when the presence of certain minerals in the aggregates renders them reactive. Use of ***low alkali cement*** is one of the remedies that is usually considered if use of such aggregates cannot be avoided.

Now what is the importance of the alkali content, the properties especially important when we are trying to study the problem of alkali-aggregate reaction? Though usually the aggregates in concrete are inert and do not react chemically with the pore solution. There are some exceptions, when the presence of certain minerals in the aggregates renders them reactive. That is they react with the pore solution, which may have sodium and potassium ions and of course hydroxide ions and this reaction leaves to pre matured detritions of the concrete and that something which we study later when we talk of alkali aggregate reactions. And in these cases when the aggregate that we use is reactive then the use of low alkali cements is one of the remedies that can be considered when the use of such aggregates cannot be avoided. Please remember that in concrete construction or civil engineering construction in general we are often forced to use locally available material. If we are constructing a dam or a bridge at a particular location, it becomes economically unviable that material such as aggregate which is required in the quantities which are several hundreds of tons to be transported from a very faraway place.

So, we have to make to with using the aggregate which is locally available, may be available within 50 kilometers, or may be 70 kilometers or 80 kilometers and so on. But, it will be very difficult, but it is an engineering decision which is often not taken to reject all the aggregate which is locally available unless the situation is so bad that it cannot be really avoided. Under these conditions when we have to use the aggregate which is locally available, which has been classified as potentially reactive then, we have no other choice but to resort to mean such as the use of low alkali cement and so on to make sure that even though alkali aggregate reaction may occur extent of the reaction or the extent of the duration is still under control. So, it is largely engineering decision when we do this kind of things.

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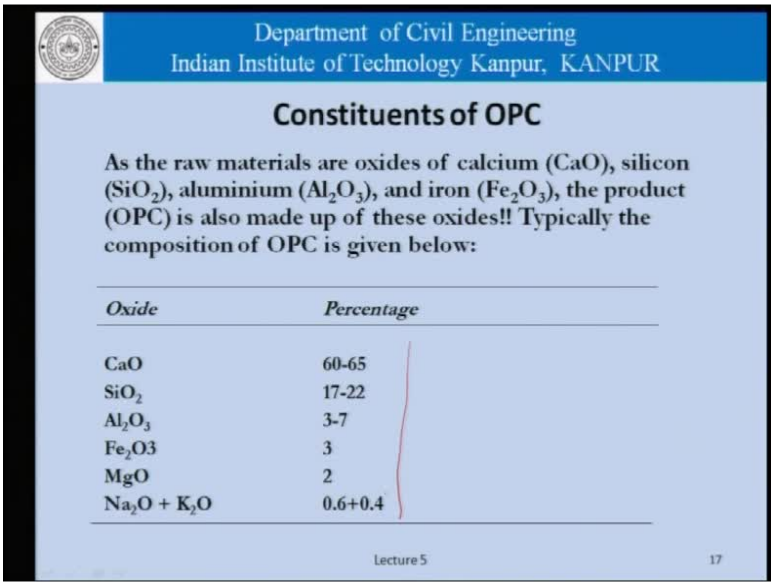

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Constituents of OPC

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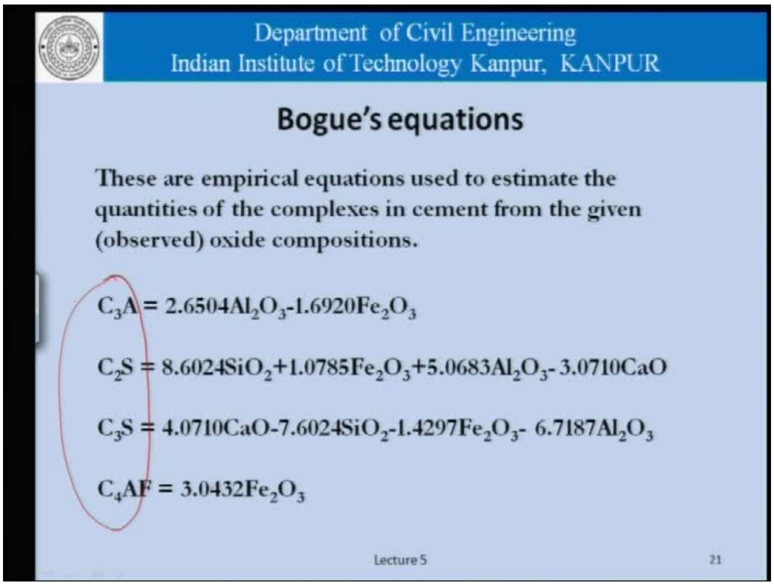

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Bogue's equations

These are empirical equations used to estimate the quantities of the complexes in cement from the given (observed) oxide compositions.

$C_3A = 2.6504Al_2O_3 - 1.6920Fe_2O_3$

$C_2S = 8.6024SiO_2 + 1.0785Fe_2O_3 + 5.0683Al_2O_3 - 3.0710CaO$

$C_3S = 4.0710CaO - 7.6024SiO_2 - 1.4297Fe_2O_3 - 6.7187Al_2O_3$

$C_4AF = 3.0432Fe_2O_3$

Now, going back to this chart if we look at the other part that is the oxide composition which is given other than the alkali metals. Then, we should remember that these oxides do not occur as oxides in the clinker they occur as these four complexes and we have seen how these complexes or the amounts of these complexes are determined using the brogue equations which are empirically equations and help us estimate the quantities of C 3 S, C 2 S, C 3 S, C 4 A F on the basis of the oxide composition of the cement.

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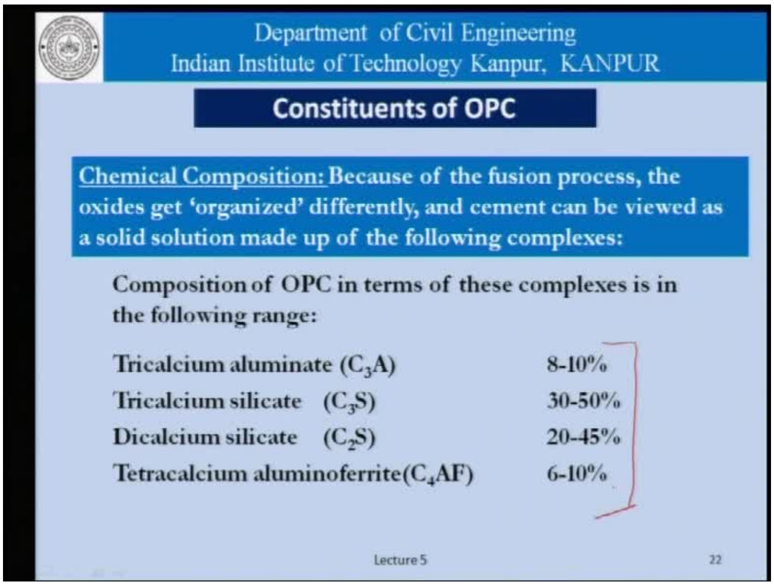

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Constituents of OPC

Chemical Composition: Because of the fusion process, the oxides get 'organized' differently, and cement can be viewed as a solid solution made up of the following complexes:

Composition of OPC in terms of these complexes is in the following range:

Tricalcium aluminate (C_3A)	8-10%
Tricalcium silicate (C_3S)	30-50%
Dicalcium silicate (C_2S)	20-45%
Tetracalcium aluminoferrite(C_4AF)	6-10%

We also know that during the fusion process the oxides get organized differently and the cement can be viewed as the solid solution made up of these complexes and this here gives us the rough breakup of the chemical constitution of cement in terms of the 4 principle complexes that we have.

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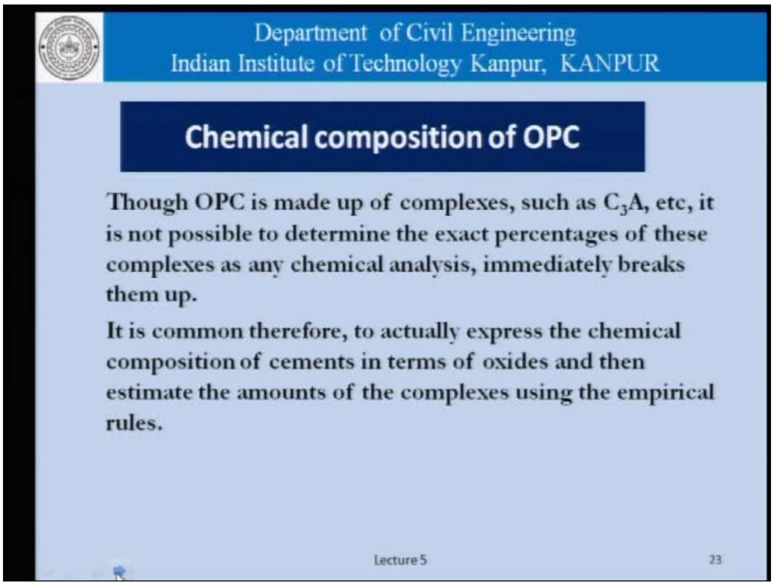

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Chemical composition of OPC

Though OPC is made up of complexes, such as C_3A, etc, it is not possible to determine the exact percentages of these complexes as any chemical analysis, immediately breaks them up.

It is common therefore, to actually express the chemical composition of cements in terms of oxides and then estimate the amounts of the complexes using the empirical rules.

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It is not easily possible to determine the exact percentage of C 3 A and so on. Because the moment we try to do any chemical analysis these complexes, disintegrate or breakup and what we can only determine is the oxide composition. And therefore, use of brogue’s equations etcetera helps us only gives an estimate of the actual amount of C 3 A and other complexes which represent in a cement and as far as most civil engineering application are concerned that is quite sufficient.

Now, continuing our discussion with the properties, these are some of the properties that we can attribute we need to study as far as physical properties which is specific gravity and fineness, consistency, setting time, initial and final, strength development, early strength, 28 days strength, ultimate strength, soundness, ignition loss and alkali contents.

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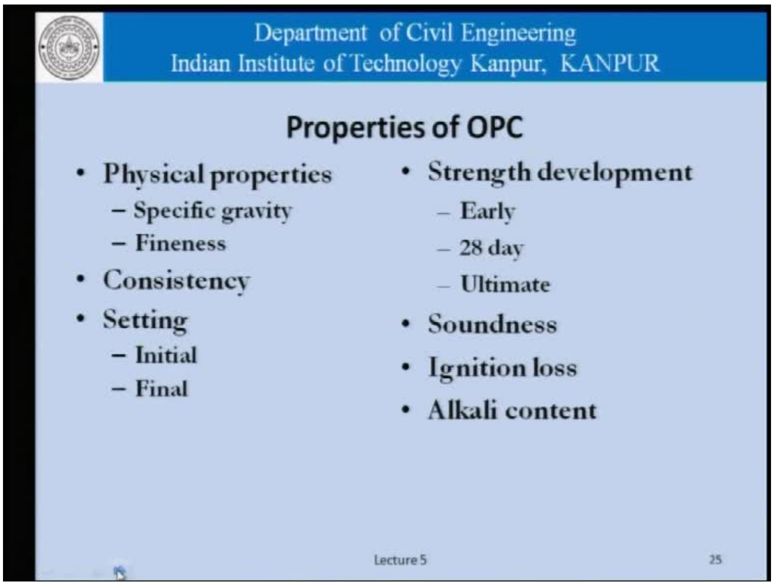

Properties of OPC

- Physical properties
  - Specific gravity
  - Fineness
- Consistency
- Setting
  - Initial
  - Final
- Strength development
  - Early
  - 28 day
  - Ultimate
- Soundness
- Ignition loss
- Alkali content

These are some of the properties that are important, what we must we remember is that these properties are often inter-related. The fineness of cement is related to the consistency, the fineness of cement is also related to the strength development and so on. So, when we are looking at the properties of cement, then we should remember to also look at a comprehensive picture, where we try to relate one property verses the other and be careful as to whatever is specification are? What are the kinds of properties that we really require in a particular case? As I said just now,

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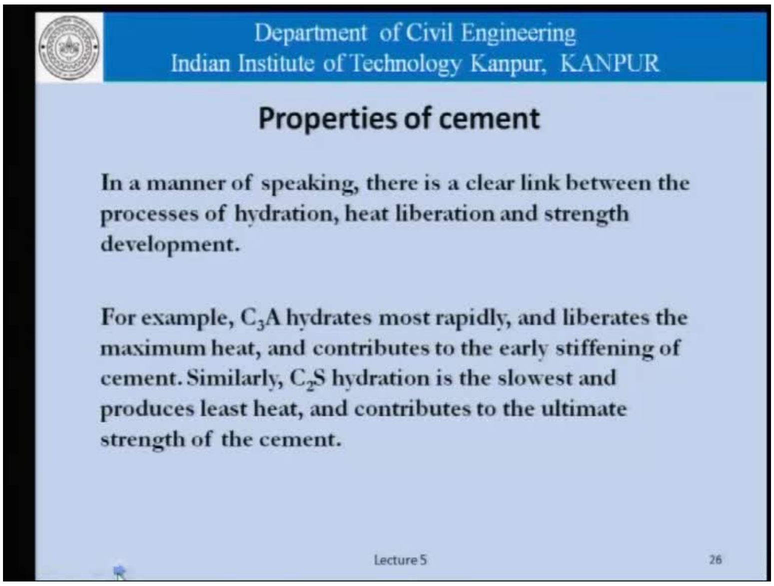

Properties of cement

In a manner of speaking, there is a clear link between the processes of hydration, heat liberation and strength development.

For example, C_3A hydrates most rapidly, and liberates the maximum heat, and contributes to the early stiffening of cement. Similarly, C_2S hydration is the slowest and produces least heat, and contributes to the ultimate strength of the cement.

There is a clear link between the processes of iteration heat liberation and strength development. For example, C 3 A tri-calcium aluminate hydrates most rapidly and liberates the maximum amount heat and it contributes to the early stiffening of the cement. Similarly, C 2 S the hydration is the lowest and produces least heat and contributes to the ultimate strength of cement. In principle what really happens is the following: When water is added to cement hydration starts in immediately and there are different words that we associate with this process setting, stiffening, strength development and so on.

These basically referred to the different amounts of work ability that the cement paste still has. Because at the end of it after the water has been added and the reaction starts and the hydration starts, gradually cement paste becomes stiffer and it is a matter of time when this stiffness translates into strength development. So, it is really that kind of test that we use to determine or estimate extent of this hydration reaction that helps us figure out the setting time, the stiffening time or the initial and the final setting time and what is the strength development and all that. Depending on a particular application we try to have a cement which has a certain characteristic. So, this is something which we must keep at the back of our mind. Cement that is stiffening very rapidly will also have early strength development.

And in order that the cement stiffen very rapidly the chemical composition should be such that hydration products are formed early and then we must try to see that those complexes which react faster than the others they are present in the right amount as far as the cement is concerned. Similarly, if we want the cement to not set very early, for example, there is a long lead time we do not want to have a construction joined and all that then we must try to control those complexes which hydrate very early which give us early stiffness. So, if we control those complexes then will have a cement, which is having a longer initial setting time.

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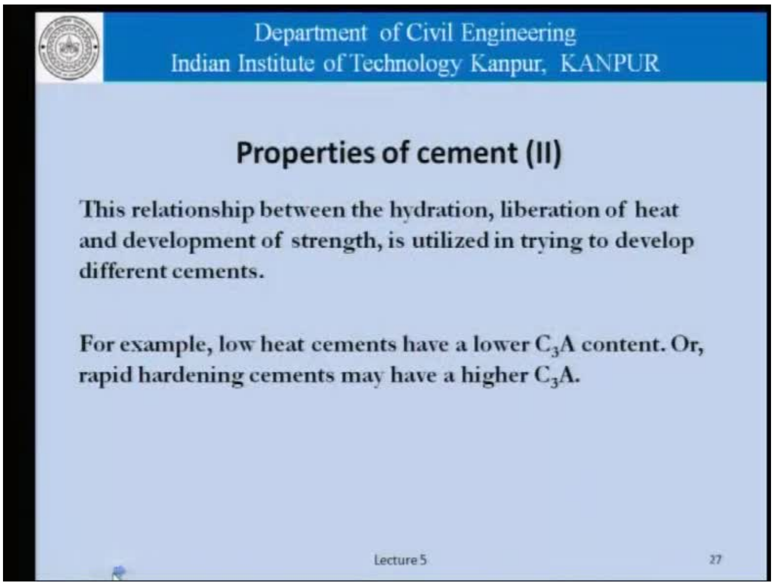

Properties of cement (II)

This relationship between the hydration, liberation of heat and development of strength, is utilized in trying to develop different cements.

For example, low heat cements have a lower C_3A content. Or, rapid hardening cements may have a higher C_3A.

So, with this back ground let us continue with our discussion and we will try to study the problem and we will try to study the relationship between hydration, liberation of heat and development of strength and we in fact use this relationships in developing the special cements or different cements. Low heat of hydration cements we will have a lower C 3 A content, rapid hardening cements may have a C 3 A content, that is how we kind of classifies cements and we need to have a different specifications on the chemical composition of this cements.

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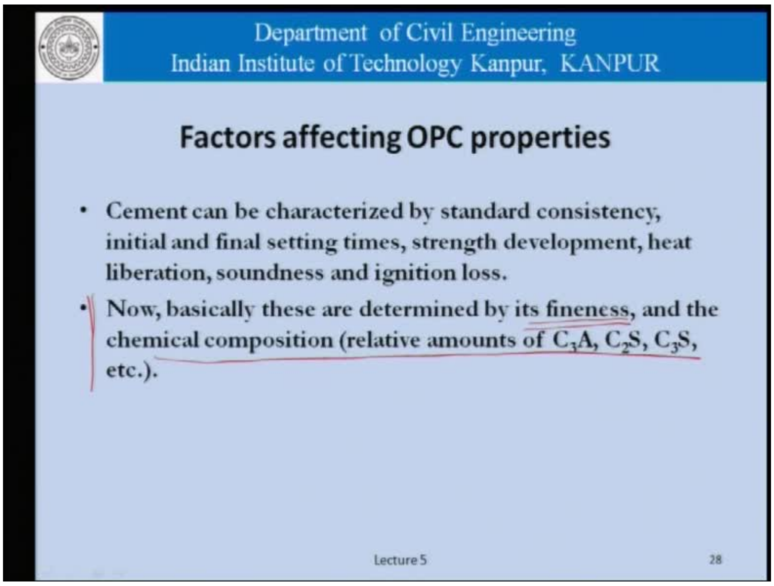

Factors affecting OPC properties

- **Cement can be characterized by standard consistency, initial and final setting times, strength development, heat liberation, soundness and ignition loss.**
- **Now, basically these are determined by its fineness, and the chemical composition (relative amounts of C_3A, C_2S, C_3S, etc.).**

And as far as the factors effecting the OPC properties is concerned, the cement can be characterized in terms of standard consistency, initially and final setting times, strength development, heat liberation, soundness and ignition loss. Some of these things will talk about today in data detail.

And these properties are all determinant some extent by the finesse which is the extent to which the cement is been ground and the chemical composition which is the relative amounts of the 4 solid complexes. I must retreat here, that the chemical composition of the clinker and the chemical composition of the cement is basically the same, there is no change in the chemical composition during the grinding process except for the addition of gypsum which is a physical process and it comes into play only as far as hydration is concerned or regulating the hydration processes is concerned. As far as the cement is concerned, chemically the clinker and the cement is more or less the same and that is why we have making a statement here that the chemical properties of cement in terms of chemical composition of these compounds and the fineness which is an independent increment, which are independent property, they really determine the properties of a cement.

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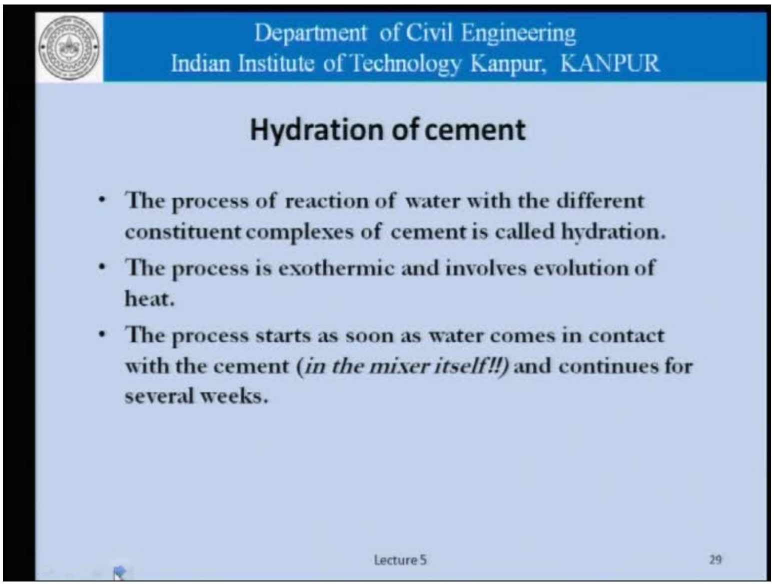

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Hydration of cement

- The process of reaction of water with the different constituent complexes of cement is called hydration.
- The process is exothermic and involves evolution of heat.
- The process starts as soon as water comes in contact with the cement (*in the mixer itself!!*) and continues for several weeks.

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For the same clinker, it can be ground to different levels of fineness and it will have different properties but, that is because it has different fineness. For the same fineness of course, you can have different clinkers and they will have different chemical compositions and therefore, the properties of the cement can be different. So, we must remember that the properties that of cement in terms standard consistency, initial and final setting time and so on, they are all determine by two basic parameters. One is the fineness and the second is the chemical composition.

Now, let us try to look at the process of hydration of cement a little more closely. The process of reaction of water with different constituent complexes of cement is what is called hydration. The process is exothermic in nature and involves evaluation and liberation of heat. The process starts as soon as water comes in contact with the cement and that is in the mixer itself and continues for several weeks. This is the basis of all our understanding and the discussion that we will have as far as the properties of cement and to that extent even the concrete as we see later on in this series of lectures.

Cement comprises of the different complexes and once water is added to the cement all these complexes more or less simultaneously start the reaction process. Depending on how fast or how slow the reaction of individual complexes is, the cement per say has different rates of reaction. The cement chemists who work with different solid complexes, they artificial manufactured the different complexes and study there hydration characteristics, in terms of the rate of hydration, amount of heat liberated and the kind of hydration product that are formed and so on. And the performance or the reaction of a cement is essentially the sum total of the reactions of all this complexes. So, this picture we must keep at the back of our mind when we study the hydration of cement and the effect of that hydration on the properties or the changing properties of the cement placed or concrete on a count of that hydration process.

Now, as far as hydration of the Portland cement is concerned this is a simplified view of the actual reactions which are taking place. C 2 S and C 3 S they react with water to form C S H which is calcium silicate hydrate gel and a lot of calcium hydroxide. So, these are basically the hydration products formed on a counter the hydration of tri-calcium di-calcium silicates. As far as C 3 A and C 4 A F are concerned they react with the water and the gypsum regulates that reaction and again we get ettringite monosulfate and so on which again become a feeder here the calcium the tri-calcium aluminate reacts with the ettringite to give us hydration products.

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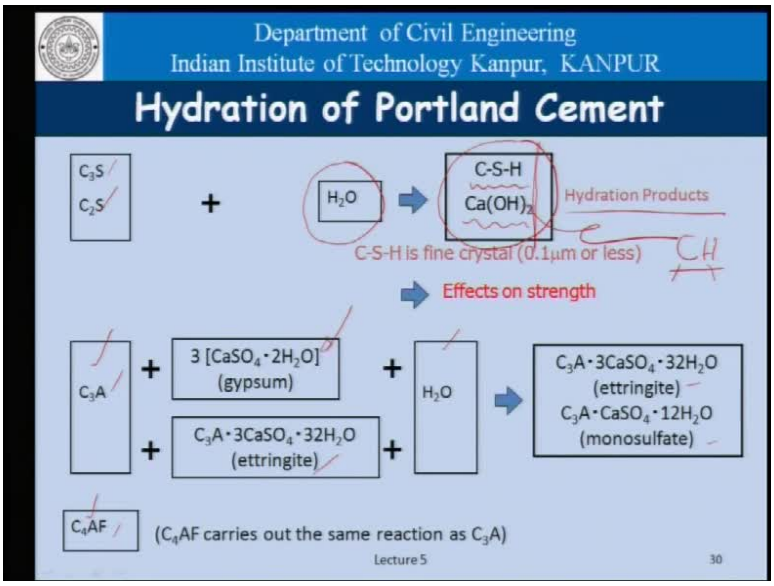

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Hydration of Portland Cement

C_3S
C_2S
+
H_2O
$\rightarrow$
C-S-H
$Ca(OH)_2$
Hydration Products
CH
C-S-H is fine crystal (0.1μm or less)
$\rightarrow$ Effects on strength

C_3A + $3[CaSO_4 \cdot 2H_2O]$ (gypsum) + H_2O $\rightarrow$ $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ (ettringite)
+ $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ (ettringite) + $\rightarrow$ $C_3A \cdot CaSO_4 \cdot 12H_2O$ (monosulfate)

C_4AF (C_4AF carries out the same reaction as C_3A)

Lecture 5

Now, once we understand these reaction is we know that as far as the hydration process is concerned C 3 S, C 2 S, C 3 A and C 4 A F they all react with water to give lots of hydration products and chemists have studied this process in lot more detail then civil engineers need to really know about to give us ettringite monosulfate, lot of calcium silicate hydrate gel and calcium hydroxide. As far as civil engineers are concerned most of the time at least as far as the discussion in this set of this lectures is concerned we are concerned only with the formation of calcium silicate hydrate and calcium hydroxide in large amounts.

We should remember that the C 2 S and C 3 S actually constitute the bulk of the cement as far as the chemical constitution concerned and therefore, C S H and C H calcium hydroxide is cement chemistry is also called C H. Because C is the calcium oxide and H is H 2 O and that is water. So, calcium hydroxide is often called C H when we trying to write reactions in the language that cement chemists use. So, we are really interested or we are concerned about the formation of C S H and calcium hydroxide in the hydration process. The formations of ettringite monosulfate and so on these are intermediate products which also a formed but, to a lesser extent even though there importance cannot be minimized or cannot be undermined simply because the volumes of this product is very small.

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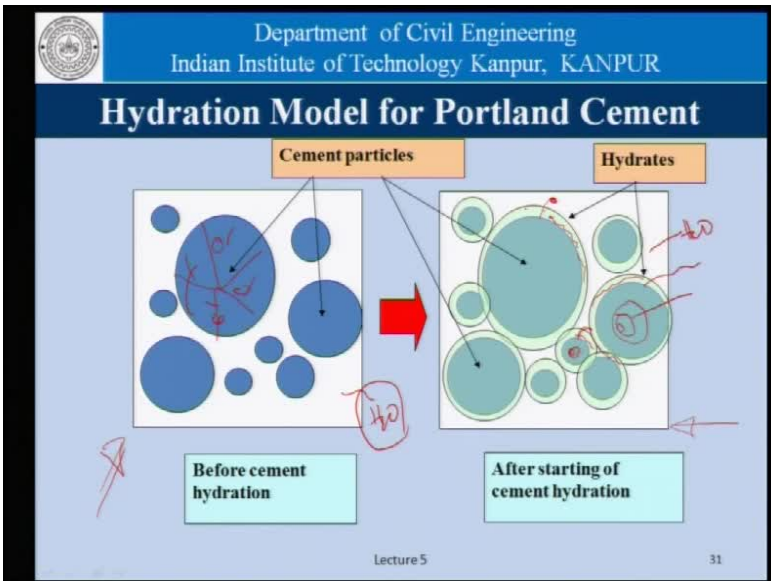

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Hydration Model for Portland Cement

Cement particles

Hydrates

Before cement hydration

After starting of cement hydration

Lecture 5

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This is a microscopic model of the hydration of cement, if we look at cement particles here which is before the hydration we can assume that the cement particles as spherical and are having different particles sizes. We should remember that the cement particles are actually not is spherical at all there actually highly angular but, from the point of view of analysis simulation of modeling there is no harm in assuming that cement is made up of spherical particles of different sizes. Now, once this cement particles are coming in contact with what is they come in contact with water what we have is hydration process starting.

Now, one way of looking at this hydration process is the formation of these hydrates here around all the cement particles and the hydration products are getting inter point between different particles of cement and there is a lot of un-hydrated cement which is still waiting to be hydrated as more and more hydration takes place and this is precisely why cement hydration takes long time because, only over a period of time does water which is sitting here and the cement which is sitting here they gradually interact, react and more and more of these hydration products are formed and the un-hydrated part of the cement strinks giving more and more hydration products. And this process once we understand we have a perfect understanding or good enough understanding to go forward and study more about the properties of the cement paste and concrete and how it changes as more and more hydration takes place. In this picture, we are talking of hydration of the cement of the cement particle we must keep at the back of our mind that each of these cement particles actually consists of different complexes C 2 S, C 3 S, C 4 A F and so on and once this cement particles comes in contact with the water each of this phases they start the own reactions and when we are talking of the un-hydrated cement particle that means that part of C 3 S is un-hydrated part of C 2 S un-hydrated part of C 3 S is un-hydrated and so on.

The extent of the availability of these un-hydrated solid complexes depends on how these individual solid complexes react, what is there individual reads of reaction as far as water is concerned. We must also keep at the back of a mind that as more and more hydration takes place the water molecule have to go through this hydration products to reach the un-hydrated layer of cement. Sooner or later therefore, we may have a situation that the hydration actually stops.

Now, what are the conditions under which the hydration actually stops? There are 3 conditions one is that all the water we have around cement is exhausted whether or not there is un-hydrated cement the there is exhaustion of water is finished. The second situation arises when all the cement has been hydrated that is there is no un-hydrated cement even if there is some water around there is no un-hydrated cement and therefore, hydration has stopped.

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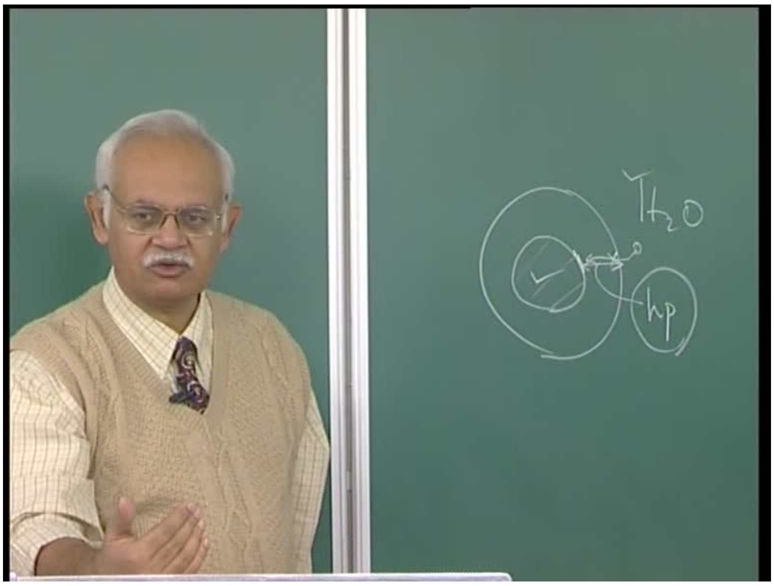

There is a third situation where the products of hydration which have been formed and deposited around the cement particles they becomes so dense that they do not allow the passage of water from the outside to reach the pore cement which is un-hydrated. If we look at this original cement particle with water sitting outside and after certain degree of hydration this is the un-hydrated cement pore. If the density and the amount of these hydration products become such that water molecules find it impossible to penetrate these hydration products and reach the surface here then the hydration is essentially stops. Even though un-hydrated cement is available, water is available but, no further hydration can takes place simply because the hydration products become a barrier to the movement of water through the hydration products and they are prevented from reaching the cement surface.

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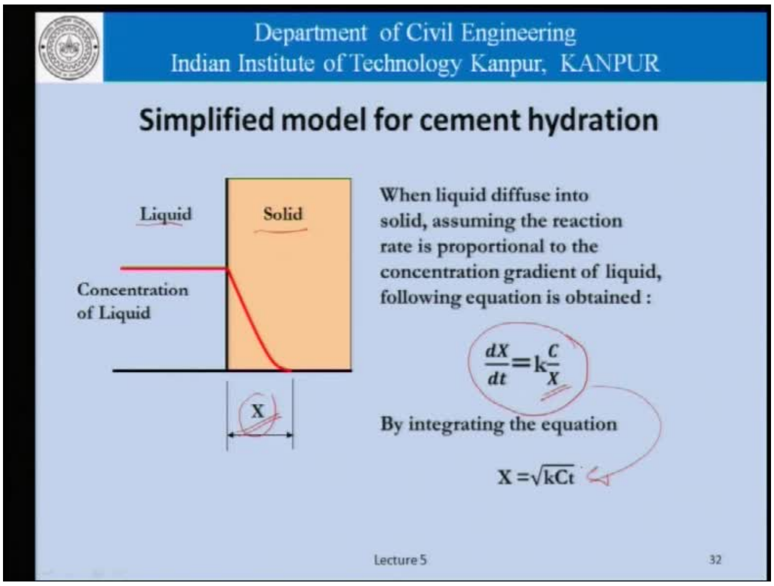

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Simplified model for cement hydration

When liquid diffuse into solid, assuming the reaction rate is proportional to the concentration gradient of liquid, following equation is obtained :

$$\frac{dX}{dt} = k\frac{C}{X}$$

By integrating the equation

$$X = \sqrt{kCt}$$

This here is simplified model for hydration of cement for those of few who are mathematically inclined. If there is a liquid outside and solid and that is what is the cement water interface looking like. If this x was very small and that indeed is very small we can assume that the liquid is actually diffusing into the solid and we can assume in that case the reaction rate is proportional to the concentration gradient of the liquid and therefore, inversely proportional to the thickness of this layer through which the liquid has to diffuse. And if you are able to write this equation which is the rate of change of this layer the d x of upon d t being equal to k times C upon x if we solve this we get in equation up to which is very simple which is something like this.

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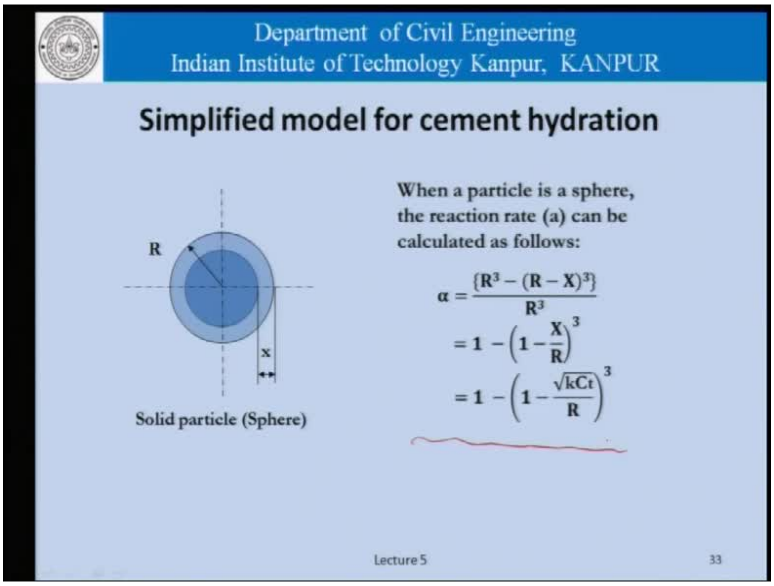

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Simplified model for cement hydration

When a particle is a sphere, the reaction rate (a) can be calculated as follows:

$$\alpha = \frac{\{R^3 - (R - X)^3\}}{R^3} = 1 - \left(1 - \frac{X}{R}\right)^3 = 1 - \left(1 - \frac{\sqrt{kCt}}{R}\right)^3$$

Now, if we are able do some more mathematics of that then we will get these kind of reactions where we can if from which we can study the rate of reaction that is the rate which the spherical particle is dissolving under the process of hydration its starts with initial radius of R and then as time goes on more and more of this X is formed and the R actually reduces. So, this is something which we can do if we doing a mathematical analysis or a simulation or modeling of the hydration process.

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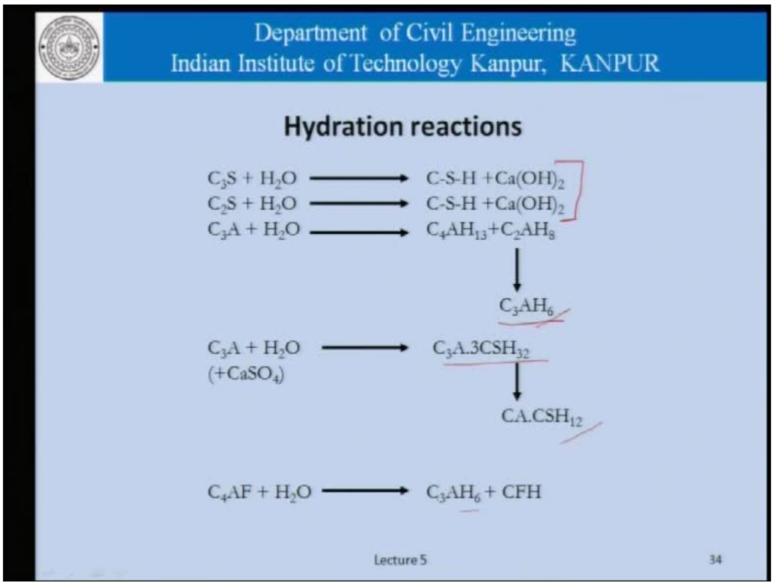

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Hydration reactions

$C_3S + H_2O \longrightarrow$ C-S-H $+ Ca(OH)_2$
$C_2S + H_2O \longrightarrow$ C-S-H $+ Ca(OH)_2$
$C_3A + H_2O \longrightarrow C_4AH_{13} + C_2AH_8 \longrightarrow C_3AH_6$

$C_3A + H_2O\ (+CaSO_4) \longrightarrow C_3A.3CSH_{32} \longrightarrow CA.CSH_{12}$

$C_4AF + H_2O \longrightarrow C_3AH_6 + CFH$

These again are reactions which we have already studies we will skip that except that I should just point out extends of C-S-H and C H which are formed in all this reactions. There other hydration products like those which are formed when calcium aluminates the tri-calcium aluminate and the tetra calcium aluminoferrites when they react they give this tri-calcium aluminate hydration products.

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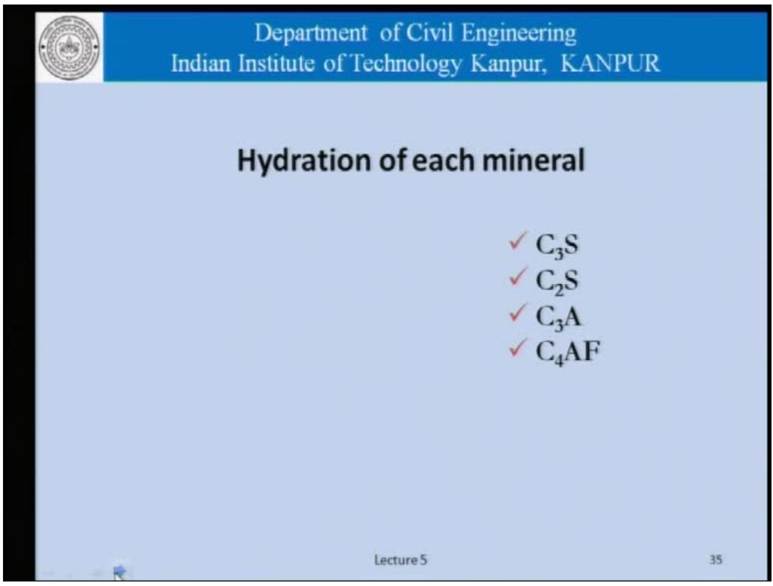

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Hydration of each mineral

✓ C_3S
✓ C_2S
✓ C_3A
✓ C_4AF

Lecture 5

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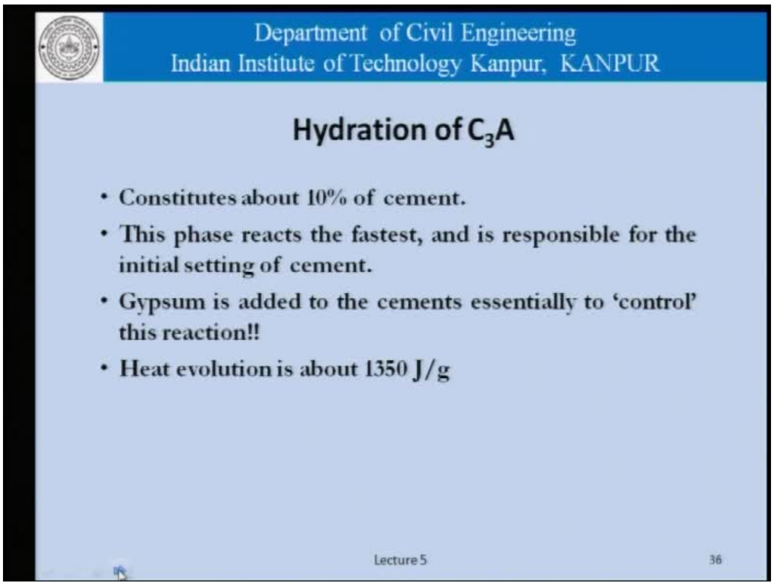

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Hydration of C_3A

- Constitutes about 10% of cement.
- This phase reacts the fastest, and is responsible for the initial setting of cement.
- Gypsum is added to the cements essentially to 'control' this reaction!!
- Heat evolution is about 1350 J/g

Lecture 5

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And now we will take a closer look at the hydration of each of these constituent minerals. As we said cement comprises of these 4 principles solid complexes and now we will take a closer look at the hydration of each of these solids. As far as 3 S concerned we should remember that it constitute about 10 percent of cement, it is the phase the reacts the fastest and is responsible for the initial setting of cement, gypsum is added in fact to the cement essentially control this reaction. And evolution involved as far as C 3 A hydration is concerned is to the extent about 1350 joules per gram.

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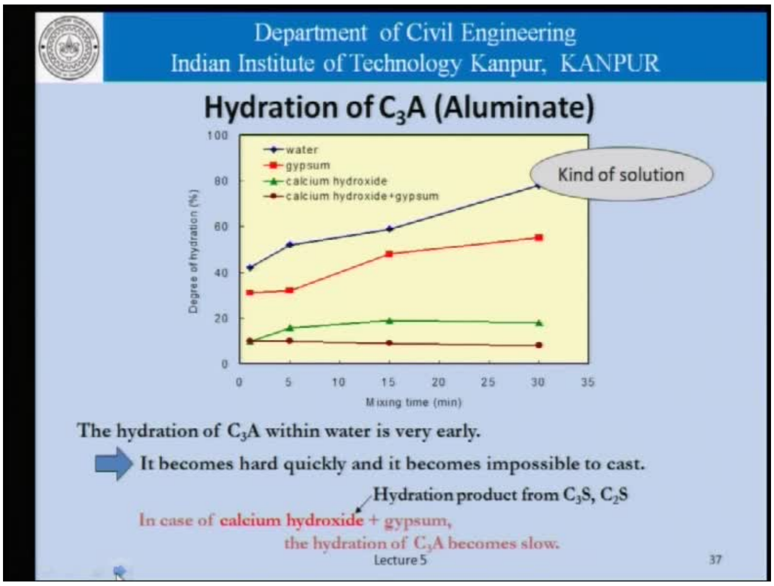

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Hydration of C_3A (Aluminate)

Kind of solution

The hydration of C_3A within water is very early.

It becomes hard quickly and it becomes impossible to cast.

Hydration product from C_3S, C_2S

In case of calcium hydroxide + gypsum,
the hydration of C_3A becomes slow.

Lecture 5

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And this is how tri-calcium aluminates they react that is after the time of mixing, what is the degree of hydration? How it moves? There is something which you will see here which is water, gypsum, calcium hydroxide which are formed the calcium hydroxide gypsum which is formed and what is written here at the bottom if you read it carefully it says the hydration of the tri-calcium aluminates is very rapid and it becomes hard quickly, becomes impossible to cast and that is what we need to control if we want to take the concrete some distance which may take some time. And the case of calcium hydroxide which is the hydration products form C 3 S and C 2 S which are also reacting at the same time, the reaction of C 3 A becomes slower. So, we are actually talking of a situation where the hydration of C 3 A is tempered by the presence of gypsum which throws in lot of sulphates into the solution.

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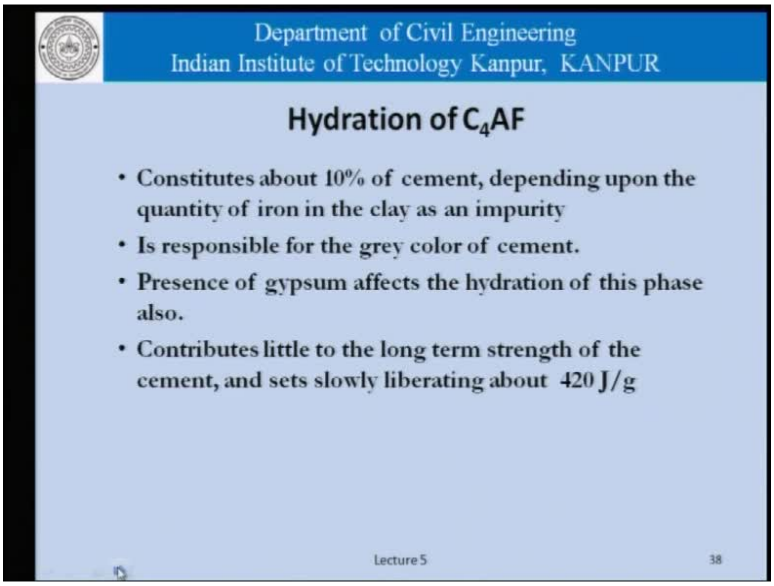

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Hydration of C_4AF

- Constitutes about 10% of cement, depending upon the quantity of iron in the clay as an impurity
- Is responsible for the grey color of cement.
- Presence of gypsum affects the hydration of this phase also.
- Contributes little to the long term strength of the cement, and sets slowly liberating about 420 J/g

Coming to C 4 A F that also constituents about 10 percent of the cement depending upon the quantity of iron in the clay as an impurity its responsible for the gray colour cement the presence of gypsum also effects the hydration of this phase and this contributes little to the long term strength and set slowly liberating about 420 joules per gram.

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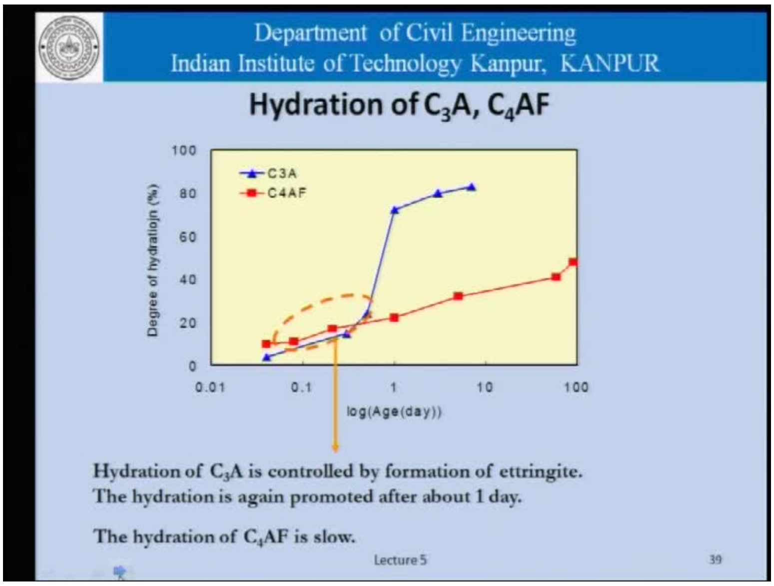

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Hydration of C_3A, C_4AF

Hydration of C_3A is controlled by formation of ettringite.
The hydration is again promoted after about 1 day.

The hydration of C_4AF is slow.

And this is the picture here which is the hydration of C 3 A and C 4 A F together. And the hydration of C 3 A is control by the formation of ettringite and that is again promoted after about the day of hydration. The hydration of C 4 A F is essentially a relatively slow reaction.

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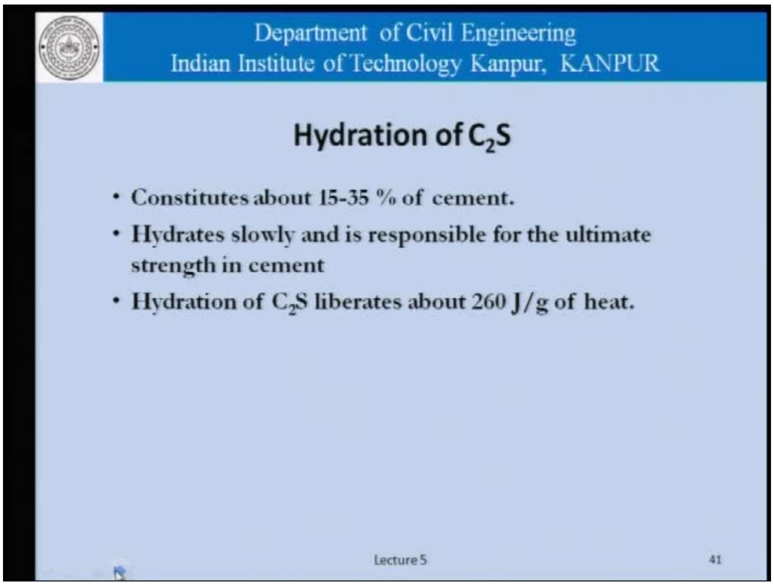

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Hydration of C_2S

- Constitutes about 15-35 % of cement.
- Hydrates slowly and is responsible for the ultimate strength in cement
- Hydration of C_2S liberates about 260 J/g of heat.

Lecture 5

As far as the hydration of C 2 S is concerned it is an important thing that we must understand because it constitutes about 15 to 35 percent of the cement, it hydrates slowly and is responsible for the ultimate strength in cement. The hydration of C 2 S liberates only about 2 hundred 60 joules per gram of heat. C 2 S we must remember contributes to the ultimate strength of the cement.

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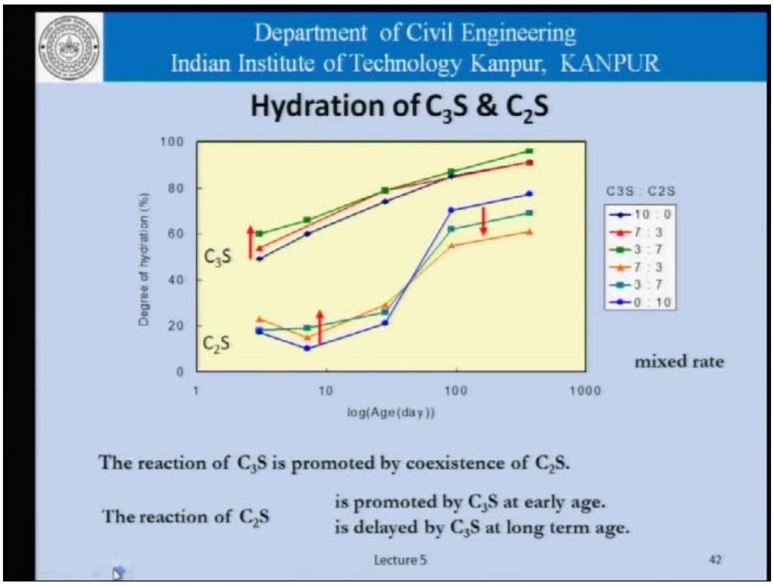

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Hydration of C_3S & C_2S

The reaction of C_3S is promoted by coexistence of C_2S.

The reaction of C_2S is promoted by C_3S at early age.
is delayed by C_3S at long term age.

Lecture 5

And this is the hydration of C 3 S and C 2 S together and the ratio of this C 2 S and C 3 S that can be vary depending on a manufacturing process the kind of raw materials that we use. The hydration of C 3 S in fact is promoted by the coexistence of C 2 S and the reaction of C 2 S is promoted by C 3 S and the earlier stages and is delayed by C 3 S in the long term. So, it is a very complex process and civil engineers are increasingly being called upon to understand the hydration process as we try to engineer the cements, we try to develop new cements where, we want ultimate strengths which may be not necessarily achieved at 28 days. That something which we will discuss some other lecture when we are probably talking of high strength concrete and so on. A lot of civil engineering structures are not subjected to high levels of float in the initial stages, may be in the first 6 months may be 1 year. And therefore, the quality control as far as these structures concerned can easily be done at 91 day strength or a 6 month strength, for that we need to have or cements that continue to hydrate much longer than normal cements where the hydration could be mostly over with the lets say about 2 months or 3 months. Of course, what also it goes with it is that the final acceptance of such concrete is delayed to the extent of 6 months may be 3 months and that is the risk that professionals take when we are talking of special concrete special cements and so on.

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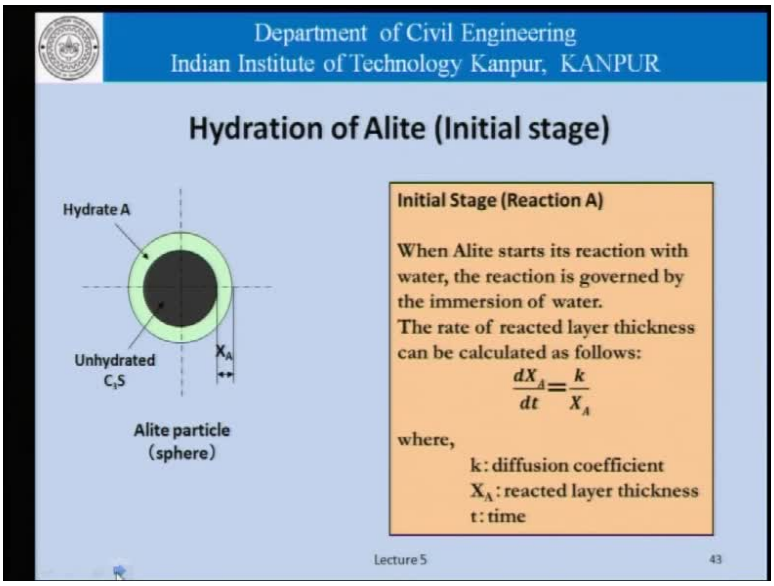

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Hydration of Alite (Initial stage)

Initial Stage (Reaction A)

When Alite starts its reaction with water, the reaction is governed by the immersion of water.
The rate of reacted layer thickness can be calculated as follows:

$$\frac{dX_A}{dt} = \frac{k}{X_A}$$

where,
k: diffusion coefficient
X_A: reacted layer thickness
t: time

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So, now as far as the reaction of Alite is concerned we are talking of C 3 S its exactly the same model that we are talked about earlier where we are taking alite be as spherical particle un-hydrated C 3 S and that is reacting initially through the formation of hydration products and water.

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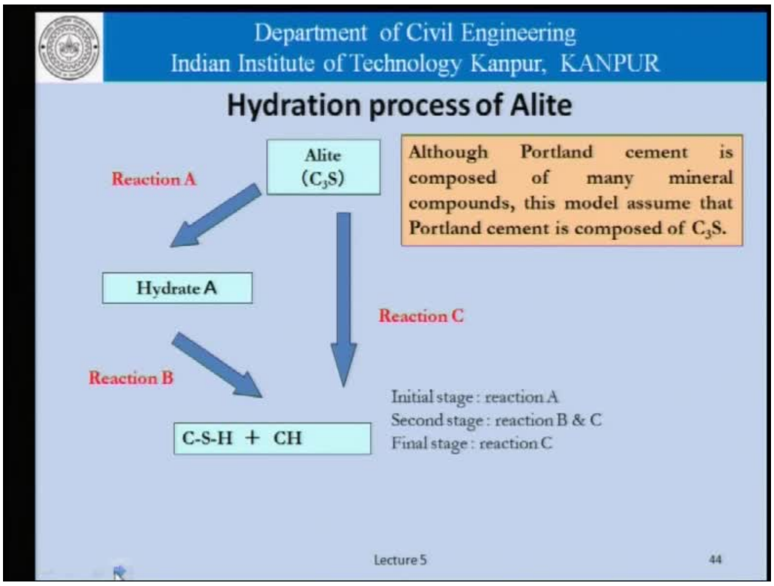

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Hydration process of Alite

Alite (C_3S)

Reaction A

Hydrate A

Reaction B

C-S-H + CH

Reaction C

Although Portland cement is composed of many mineral compounds, this model assume that Portland cement is composed of C_3S.

Initial stage : reaction A
Second stage : reaction B & C
Final stage : reaction C

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And Alite gives us hydrate A, which gives us the second reaction which is C-S-H and calcium hydroxide, the reaction C is the final stage reaction where C 3 S also at the end of it gives us C-S-H and calcium hydroxide. And all though Portland cement is composed of many minerals compounds this module assumes that the Portland cement comprises only of C 3 S. Those are simplifications which we make when we carry out simulations and model studies where instead of saying that the same cement particle has different extents or his made up of different amounts of C 2 S, C 3 S and so on. We can make an assumption and say that 12 cement comprises of different particles made up of C 3 S, C 2 S and so on. And each of them is starts to hydrate or react with water once they come in contact with water.

So, this is what we have in the final stage where we have some C-S-H outside here and some C-S-H somewhere here and there is the un-hydrated C 3 S sitting here in the inside. And depending upon the age at which we were looking at the picture. The type of C-S-H or the density of the C-S-H in this layer and this layer is different and that is what is making it impossible for the water present here to go and take the surface of cement particle which will give us further hydration.

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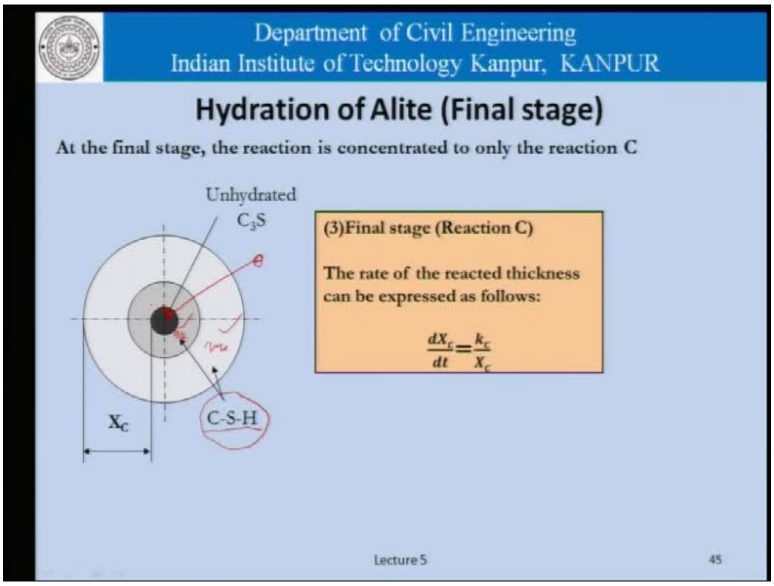

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Hydration of Alite (Final stage)

At the final stage, the reaction is concentrated to only the reaction C

(3)Final stage (Reaction C)

The rate of the reacted thickness can be expressed as follows:

$$\frac{dX_C}{dt}=\frac{k_C}{X_C}$$

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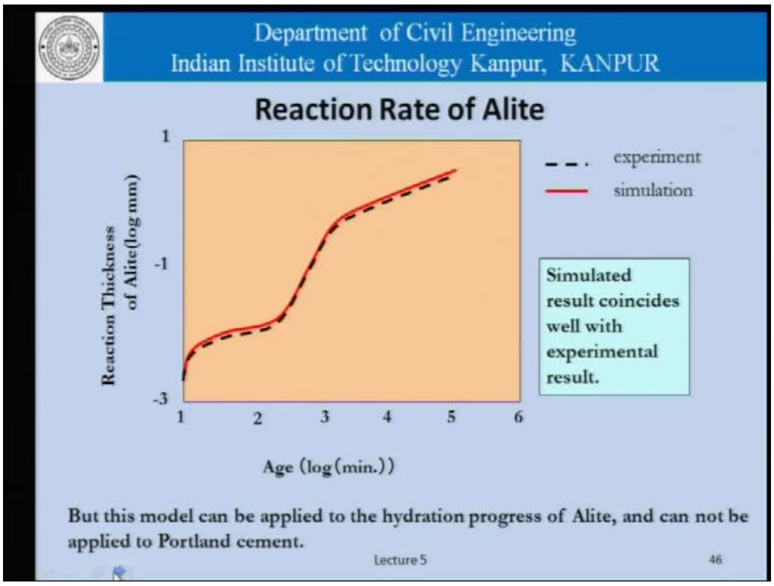

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Reaction Rate of Alite

Simulated result coincides well with experimental result.

But this model can be applied to the hydration progress of Alite, and can not be applied to Portland cement.

If we try to find out the reaction thickness of Alite which is in terms of log of millimeter, that is how it is plotted, that is how it goes. There are experiments which support the simulation process and it should can be applied only if but, we should remember that this model can be applied only to the hydration of Alite and not really to that of Portland cement.

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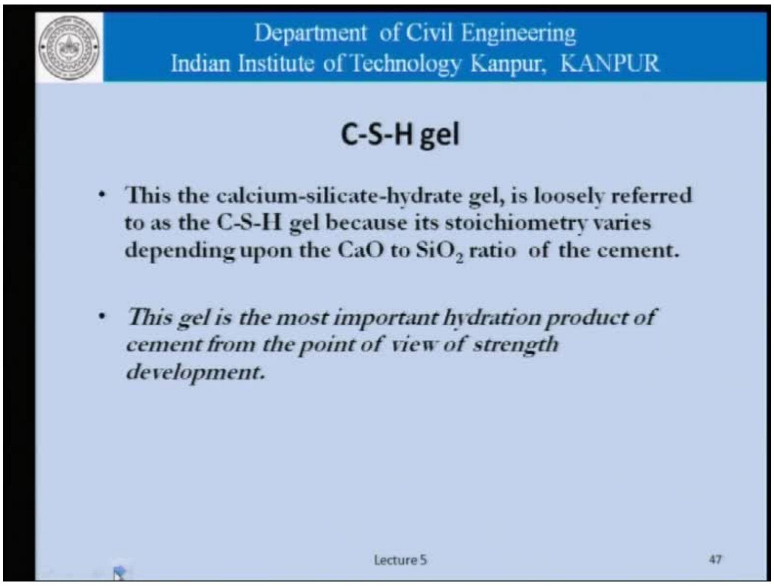

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C-S-H gel

- This the calcium-silicate-hydrate gel, is loosely referred to as the C-S-H gel because its stoichiometry varies depending upon the CaO to SiO_2 ratio of the cement.
- *This gel is the most important hydration product of cement from the point of view of strength development.*

Now, coming to C-S-H gel, which is the most important hydration product. As we talked about earlier in the discussion today because calcium-silicate-hydrate gel, which is referred to loosely as the C-S-H gel because its stoichiometry varies depending on the amounts of calcium oxide and silicon oxide in the cement. And this important gel is a most important hydration product from cement form the point of view of strength development. So, denser and the better quality C-S-H gel that we get the better is the strength as far as cement is concerned.

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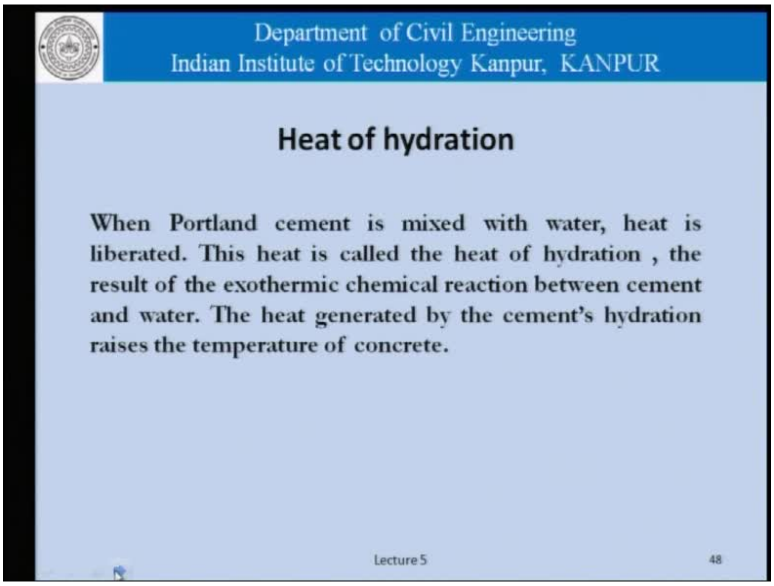

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Heat of hydration

When Portland cement is mixed with water, heat is liberated. This heat is called the heat of hydration , the result of the exothermic chemical reaction between cement and water. The heat generated by the cement's hydration raises the temperature of concrete.

Now, let us take a closer look one again at the heat of hydration. When portal cement is mixed with water heat is liberator and this is what is called of hydration and the result of which is the result of the exothermic chemical reaction between cement and water. The heat generated by the cement hydration rises the temperature of concrete. We will continue this line of discussion then we are talking of mass concrete. Today we are trying to understand that yes when cement hydrates it reacts with water a lot of heat is liberator. And this heat liberated raises the temperature of the concrete. We need to take this heat away from the concrete somehow and dissipated it in the atmosphere, that is something which the dissipation part, something which we will talk about when we talk of mass concrete.

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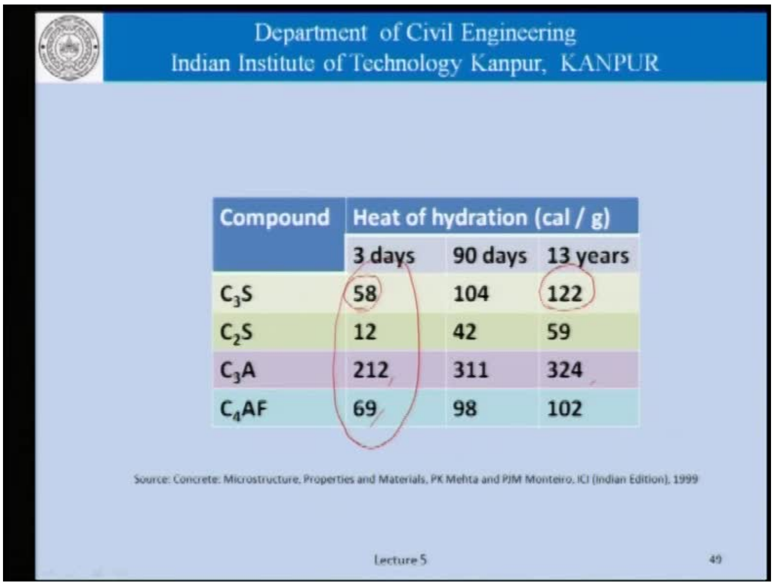

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Compound	Heat of hydration (cal / g)		
	3 days	90 days	13 years
C_3S	58	104	122
C_2S	12	42	59
C_3A	212	311	324
C_4AF	69	98	102

Source: Concrete: Microstructure, Properties and Materials, PK Mehta and PJM Monteiro, ICI (Indian Edition), 1999

This slide here taken from the text concrete microstructure properties and materials gives us the 3 day, 90 day and the 13 year heats of hydration in terms of the calories per gram for the 4 principle components and we can see that depending on the compound. The amount of heat that is liberated early is different and not only these numbers are different but, also the percentage of this particular number with respect to the ultimate heat of hydration that is quite different. For example, if we looking at C 3 S we are looking at 58 calories per gram liberated in 3 days as against 122 which may taken as the ultimate heat of hydration of C 3 S. Compared to that we have 69 in case of C 4 A F has against 102 and 212 against 324 and so on.

So, there are different ways of looking at the data here and I will leave it as an assignment or a thought for you that please look at this data and understand the properties of the cement in light of the rates of heat liberated from the different compounds.

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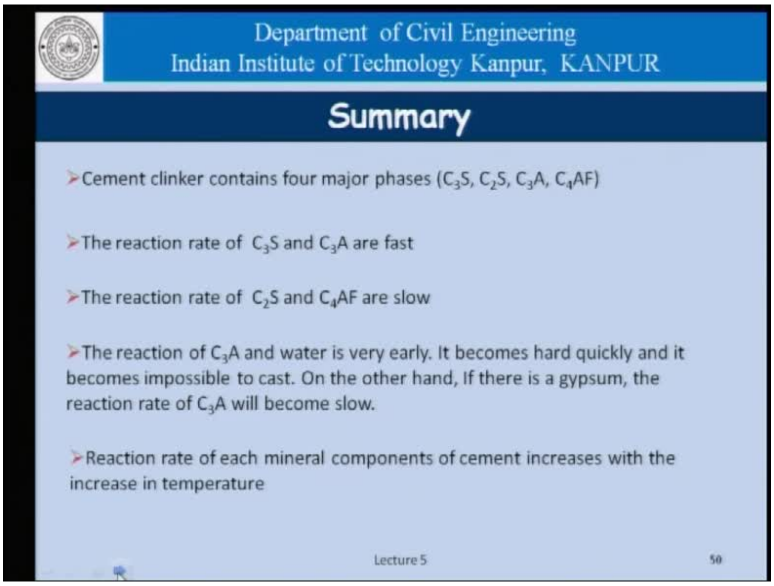

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Summary

- Cement clinker contains four major phases (C_3S, C_2S, C_3A, C_4AF)
- The reaction rate of C_3S and C_3A are fast
- The reaction rate of C_2S and C_4AF are slow
- The reaction of C_3A and water is very early. It becomes hard quickly and it becomes impossible to cast. On the other hand, If there is a gypsum, the reaction rate of C_3A will become slow.
- Reaction rate of each mineral components of cement increases with the increase in temperature

Lecture 5

Now, if you look at the summary of the properties of cement and the hydration process. Cement clinker contains 4 major compounds: C 3 S, C 2 S, C 3 A and C 4 A F. The reaction rates of C 3 S and C 3 A are the fastest, the reaction rate of C 2 S and C 4 A F are slow, the reactions of C 3 A and water is very early it becomes hard quickly. And it is impossible to cast the concrete after that process started or has been initiated. The reaction of tri calcium aluminate and water is very quick and leads to hardening of the paste rendering the concrete, difficult to cast. And on the other hand in the presence of gypsum the rate of reaction of C 3 A is controlled at becomes slow, the reaction rate of each other mineral components of cementing increases with the increasing temperature.

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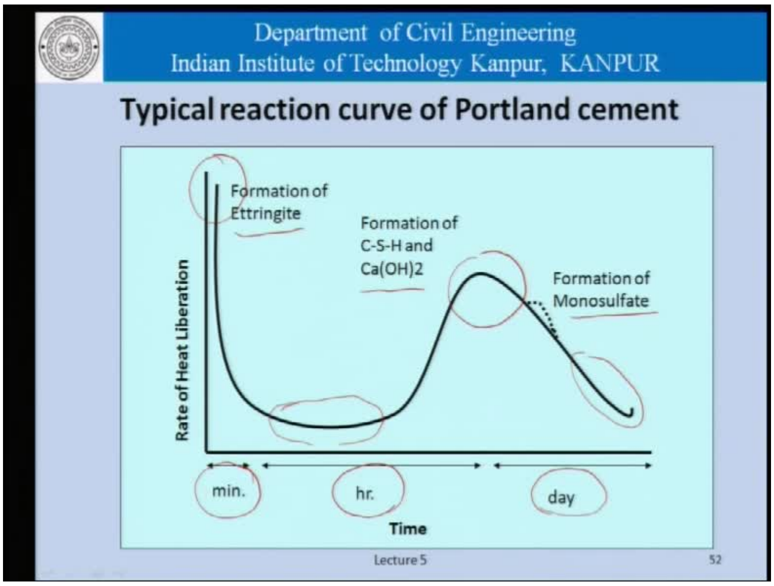

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Typical reaction curve of Portland cement

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This picture here shows the typical reaction curve of Portland cement in terms of the rate of heat liberated. Initially, we have a lot of heat liberated which goes down and there is a stable period here and again we have a peak where lot of heat is liberated and we have the gradual die out of the hydration reactions. This process here is matter of minutes, this process here is a matter of ours and this continues over several days and that is something which we must keep and the back of our mind when we study the properties of cement hydration. That the hydration reaction continues over a very long period of time and at different points in time, different products are formed as we can see here. And these products they have different roles to play as far as the properties such as settings, stiffening and strength development of concrete is concerned.

Now, as far as the interaction between the sulphates solution which is coming from gypsum and the reactivity of the tri calcium aluminate in the clinker is concerned if we have both as low what we get is normal settings, if they are both very high we get rapid setting, if there is a high low and a low high combination we get quick setting and false setting and if this is completely absent we get a flash set where, the cement is rendered hard very quickly and is impossible to cast. So, this is something, which is a summary of how the reaction of cement takes place in the presence of the gypsum.

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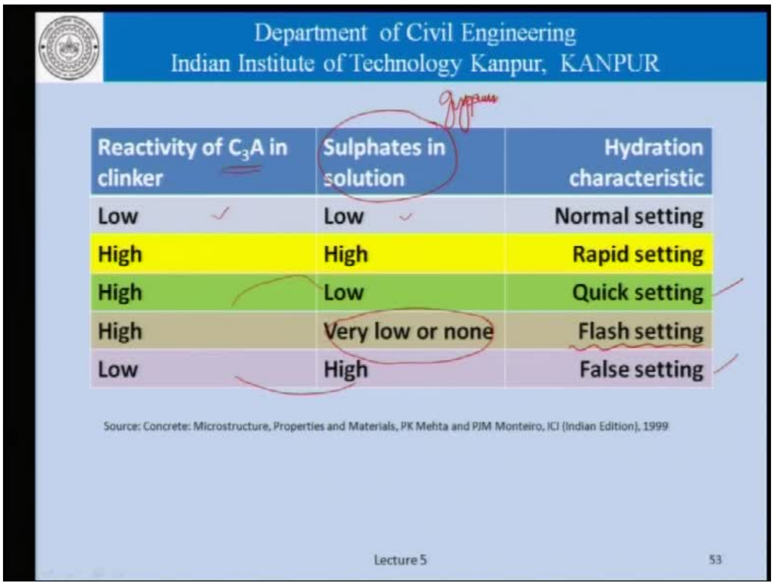

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gypsum

Reactivity of C_3A in clinker	Sulphates in solution	Hydration characteristic
Low	Low	Normal setting
High	High	Rapid setting
High	Low	Quick setting
High	Very low or none	Flash setting
Low	High	False setting

Source: Concrete: Microstructure, Properties and Materials, PK Mehta and PJM Monteiro, ICI (Indian Edition), 1999

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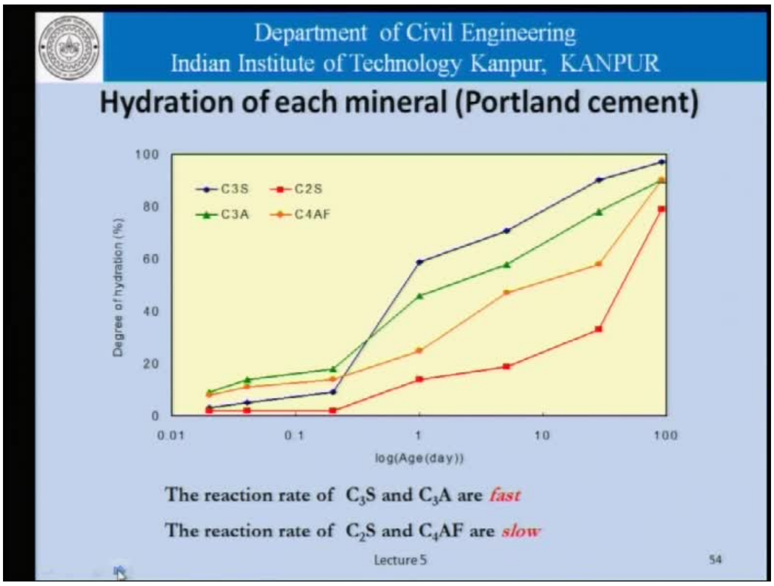

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Hydration of each mineral (Portland cement)

The reaction rate of C_3S and C_3A are *fast*

The reaction rate of C_2S and C_4AF are *slow*

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And this here is the summary of the hydration of the degree of hydration what is it’s time for the different phases of the cement that is C 2 S, C 3 S, C 4 A F and C 3 A. Now, before we close the discussion we should spend some time and try to understand the pore structure of the hardened cement composites. These are the chemical reactions of C 3 S and C 2 S and their reaction with water. There is mass involve and there is a volume involved.

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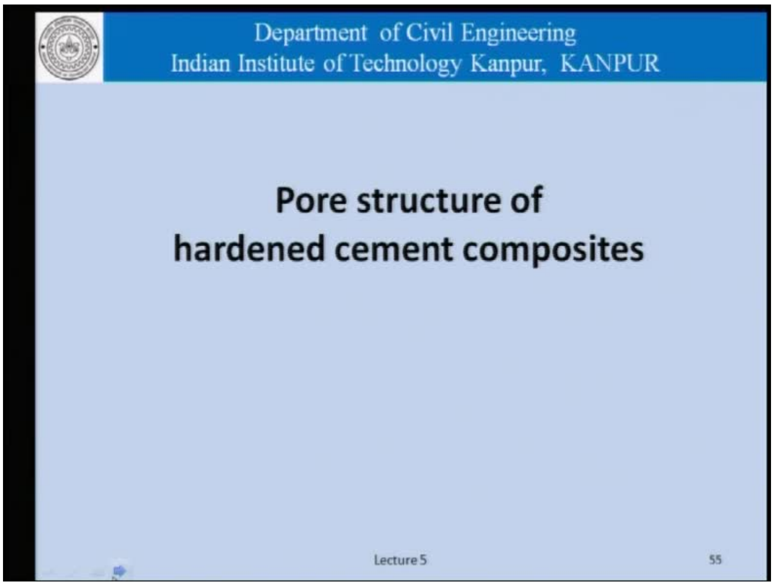

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Pore structure of hardened cement composites

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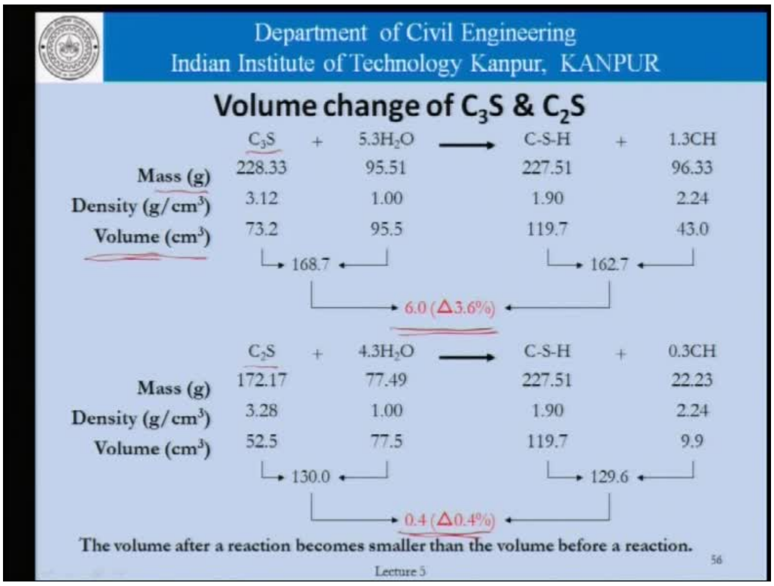

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Volume change of C_3S & C_2S

	C_3S	+	$5.3H_2O$	→	C-S-H	+	1.3CH
Mass (g)	228.33		95.51		227.51		96.33
Density (g/cm^3)	3.12		1.00		1.90		2.24
Volume (cm^3)	73.2		95.5		119.7		43.0
	168.7				162.7		

6.0 (Δ3.6%)

	C_2S	+	$4.3H_2O$	→	C-S-H	+	0.3CH
Mass (g)	172.17		77.49		227.51		22.23
Density (g/cm^3)	3.28		1.00		1.90		2.24
Volume (cm^3)	52.5		77.5		119.7		9.9
	130.0				129.6		

0.4 (Δ0.4%)

The volume after a reaction becomes smaller than the volume before a reaction.

So, the there is a mass of C 3 S and C 2 S and so on which is reactive with the water. And like all chemical reactions there is very definite stoichiometry of these chemical reactions. A certain amount of C 3 A requires a certain amount of C 3 A requires a certain amount of water for complete reaction and if we extend that principle we will have a statement pick to the effect that, in order that cement completely hydrate a certain amount of water is chemically required whether or not from engineering concentration the hydration proceeds to logical conclusion is a different story. It does not stop us from saying that from chemical point of view cement require certain amount of water to hydrate completely.

Hydration process which involves the formation of hydration product and consumption of water can also lead to changes in volume and that is what is shown here, the volume after a reaction is slightly smaller than the volume before the reaction that is, the volume of the reaction products the hydration products is slightly small. What effectively it means is that, there is a tendency for the concrete to shrink. Please remember that cement and water are only a very small constitute or a contribute only a certain extent of the total volume of concrete and therefore, the shrinkages which we see here do not reflect or do not appear in the same magnitudes when we are talking of concrete. Because of the relative volume of cement is this quite small in the concrete mix.

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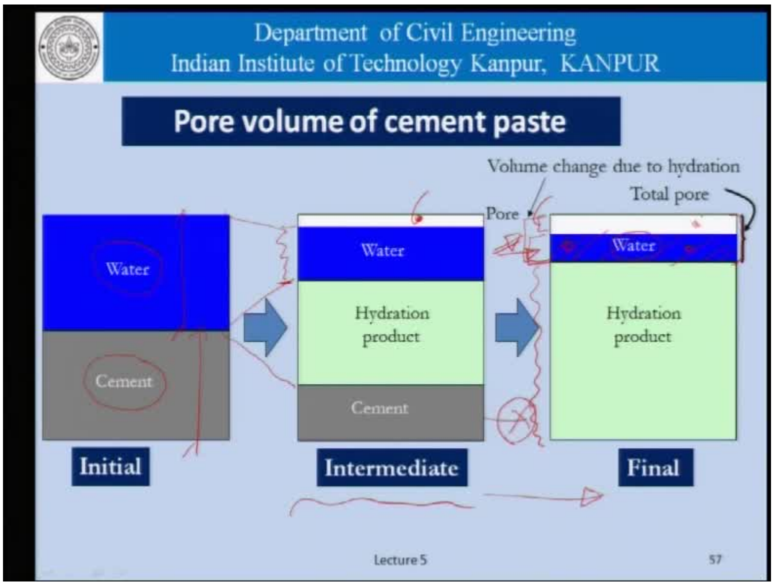
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Pore volume of cement paste

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Having said that lets look at what is happening in a schematic and qualitative sense. Initially we have cement and water which is present in the intermediate phase what has happened is that the cement has become lesser, some amount of hydration products have been found and some amount of water has been consumed. So, only this amount of water is now left and this is the amount of pore space which is been generated on a count of shrinkage. Continuing from here when we come to the final stage we have the cement is completely consumed and therefore, we do not have any cement left, all the cement has been converted into hydration products here. Some amount of water is left, because the amount of water which is added to the cement is in general is usually higher than the amount of water required from the chemical point of view for ensuing complete iteration of cement. And this water remains as water within the hydration products.

And this is the pore space on account of shrinkage. We should now try to see what happens to this water at the end of the day. This water actually escapes in the atmosphere and therefore, what we have is the total pore space available after this amount of water and cement has reacted is this, because this water once it leaves the hydration products that also leaves behind wide spaces. So, this void here and this amount of shrinkage here is in manner of speaking the total change in the volume or the total change in the solids and liquids which are there in the system.

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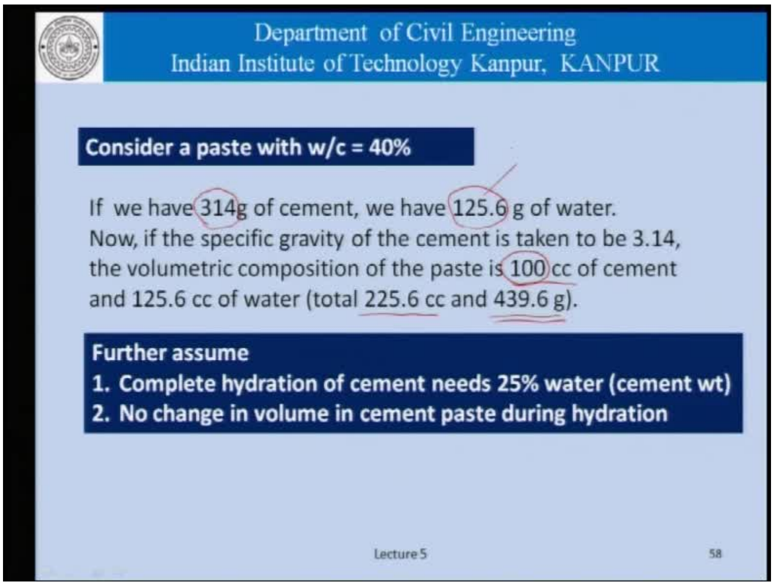

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Consider a paste with w/c = 40%

If we have 314g of cement, we have 125.6 g of water.
Now, if the specific gravity of the cement is taken to be 3.14, the volumetric composition of the paste is 100 cc of cement and 125.6 cc of water (total 225.6 cc and 439.6 g).

Further assume
1. **Complete hydration of cement needs 25% water (cement wt)**
2. **No change in volume in cement paste during hydration**

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So, let us look at the small example and numerical example which says that, let us consider a paste of water cement ratio of 40 percent. Now if you have 314g of cement we will have 125.6 grams of water. Assuming that this specific gravity of cement is 3.14, the volumetric composition of the paste is 100 cc of cement because 100 cc into 3.14 is 314. And 25.6 cc of water will be 1 and therefore, we have the total paste volume of 225.6 which is a 100 plus 125.6 and the total mass of the paste is 439.6 which are coming from 314 grams of cement and 125.6 grams of water. Now, if we assume that complete hydration also element needs 25 percent of water by rate of the cement and we assume for that time being that this no change in the volume of the cement paste during hydration. So, we are basically saying that we are ignoring any shrinkage that occurs.

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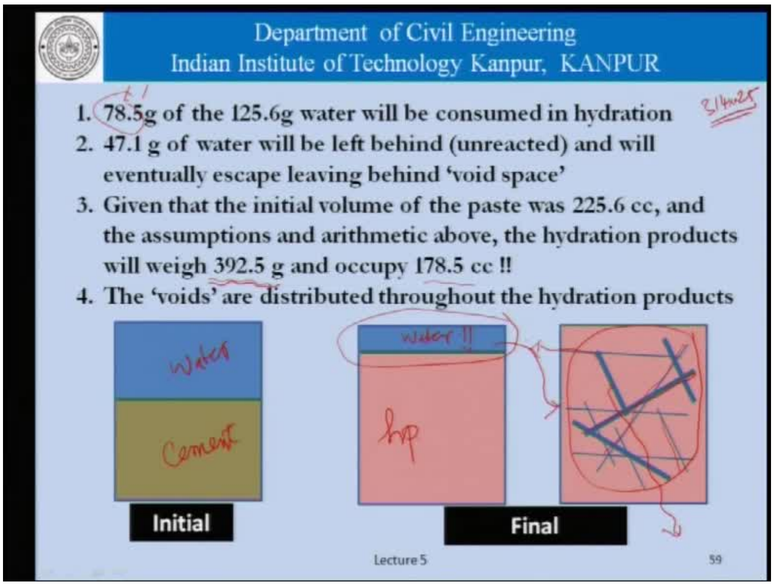

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1. 78.5g of the 125.6g water will be consumed in hydration
2. 47.1 g of water will be left behind (unreacted) and will eventually escape leaving behind 'void space'
3. Given that the initial volume of the paste was 225.6 cc, and the assumptions and arithmetic above, the hydration products will weigh 392.5 g and occupy 178.5 cc !!
4. The 'voids' are distributed throughout the hydration products

314×.25

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Then, what we are having is situation something like this 78.5 grams of the 125.6 grams of water will be consumed in the hydration, the 78.5 is nothing but 314 grams of cement multiplied by 0.25 because that is what we have assumed is the amount of water which is required for ensuring complete hydration. Now, if this 78.5 grams of water is consumed then 47.1 grams of water will be left behind which is un-reacted and will eventually escape leaving behind white spaces. Now, given that the initial volume of the cement paste was 225.6 as we saw in the last slide, and the assumption that we made that the no shrinkage and so on, and there is arithmetic what we do here, the hydration products will way 392.5 grams, which is the sum of 78.5 grams of water and 314 grams of cement, and they will occupy 178.5 cc of space.

Now, diagrammatically speaking this is the cement that we had, this is the water that we had, these are the hydration products that are formed and this is the un-reacted water that we left with at the end of the whole reaction process. Now, please remember this water does not separate and just appeared at the top of the hydration products. This water is actually distributed throughout the hydration product as you shown here, there can be large channels having larger diameter, smaller channels like this they can be connected they may not be connected and so on and so forth. These channels of water here are finally, the pores which will be left behind when this water finds its way out into the atmosphere.

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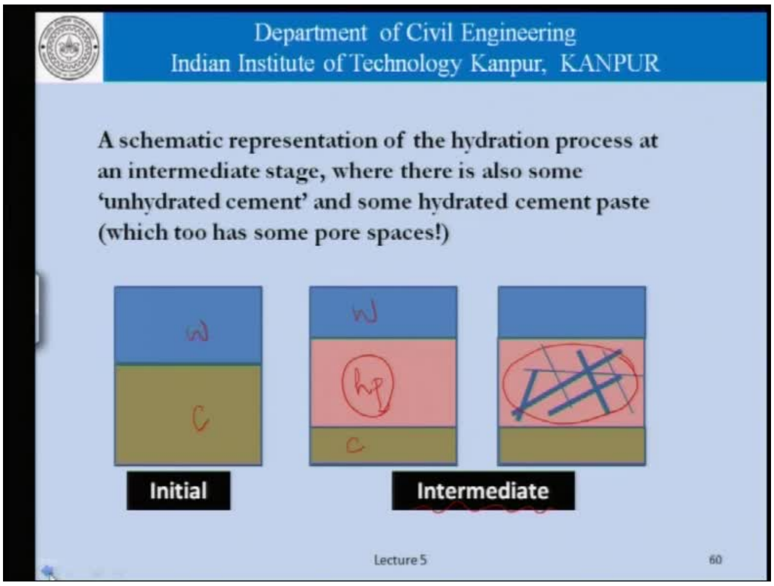

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A schematic representation of the hydration process at an intermediate stage, where there is also some 'unhydrated cement' and some hydrated cement paste (which too has some pore spaces!)

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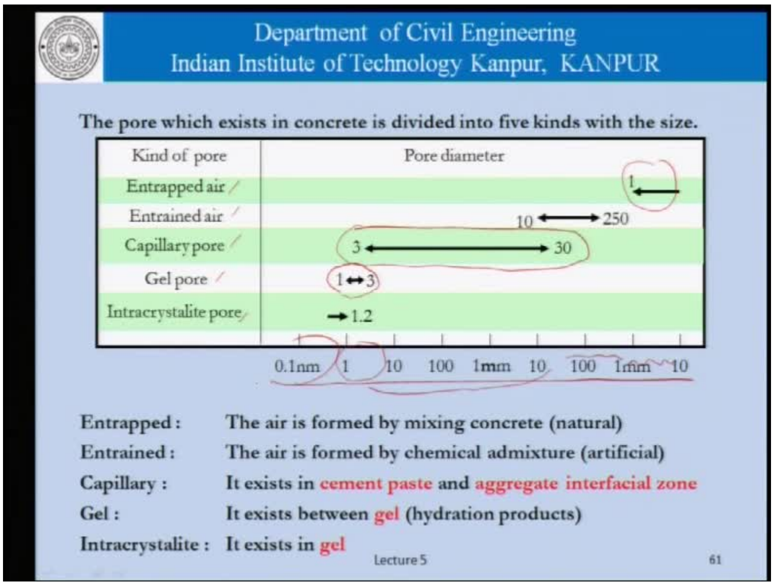

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The pore which exists in concrete is divided into five kinds with the size.

Kind of pore	Pore diameter
Entrapped air	1 ←
Entrained air	10 ↔ 250
Capillary pore	3 ↔ 30
Gel pore	1 ↔ 3
Intracrystalite pore	→ 1.2

Entrapped : The air is formed by mixing concrete (natural)
Entrained : The air is formed by chemical admixture (artificial)
Capillary : It exists in cement paste and aggregate interfacial zone
Gel : It exists between gel (hydration products)
Intracrystalite : It exists in gel

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Now, if you look at an intermediate situation we can have cement water, un-hydrated cement in the intermediate stage, un-reacted water and whatever hydration products of formed. And these hydration products themselves also have a certain amount of water which is trapped within, which at the end of it will escape. And depending on whether or not the final product or the final reaction reaches this state whether is no hydrated cement we can have situation that they will be some un-hydrated cement also sitting in the final system of concrete.

Now, once we have this understanding that yes water is present in the hydration products and it will eventually escape. This picture here shows us different kinds of pores that are found or that have been identified as far as we understanding of cement hydration products and concrete in gendering is concerned. There is entrapped air, there is entrained air, there is capillary pore, gel pore, intracrystalite pores, they have different size ranges.

For example, entrapped air is the largest it is there in the millimeter order, entrained air is lightly smaller and then we have a large range here of capillary force, a very small range here for gel pores and then there are some other pores the intracrystalite pores which there within the different C-S-H layers and so on. So, this picture here gives us an idea that concrete or cement hydration products they have different pores the genesis of those pores comes from largely the un-hydrated water that is left behind and which finally escapes.

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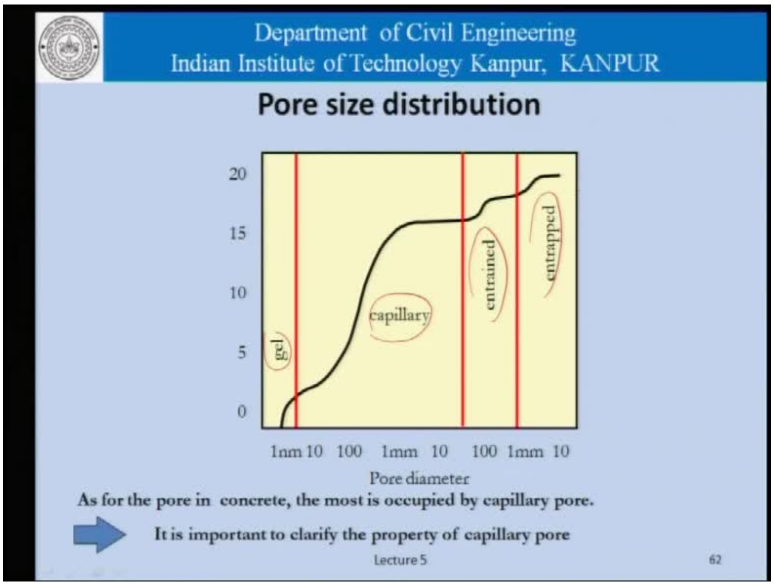

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Pore size distribution

As for the pore in concrete, the most is occupied by capillary pore.

It is important to clarify the property of capillary pore

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So, once we understand this part we can talking terms of a pore size distribution, the gel pores, the capillary pores, thus entrained air and entrapped air and we can talking terms of what is the percentage contribution of each of these pores of different sizes to the total porosity. And that is something which we will try to talk about at some other point in time. Remember that this porosity leads to the permeability of the concrete making the concrete susceptible to attack from deleterious material from the atmosphere from this line water or whatever depending on the environment to which the concrete structure is exposed.

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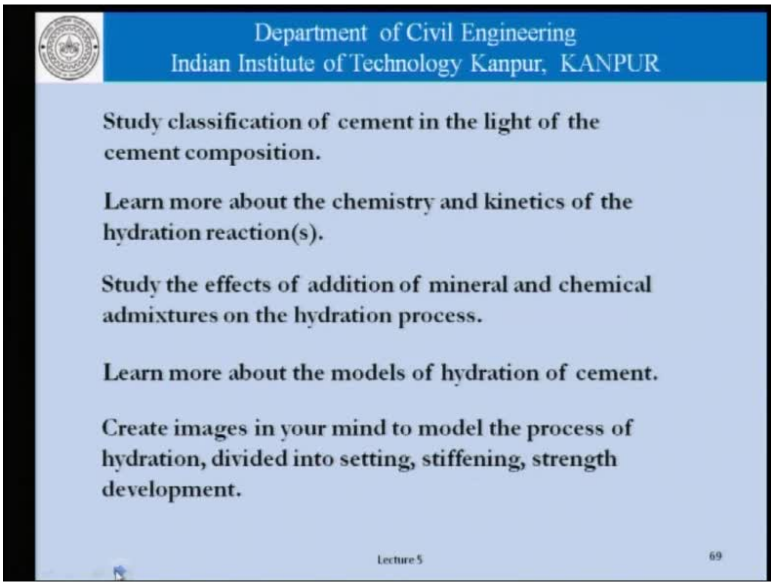

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Study classification of cement in the light of the cement composition.

Learn more about the chemistry and kinetics of the hydration reaction(s).

Study the effects of addition of mineral and chemical admixtures on the hydration process.

Learn more about the models of hydration of cement.

Create images in your mind to model the process of hydration, divided into setting, stiffening, strength development.

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Now, before we conclude a discussion today. Let us try to go back and see what we need to do further. Study the classification of cement in light of cement composition, the higher strength cement, high the low heat of hydration cements, low alkali cements and so on and so forth. Learn more about the chemistry and kinetics of hydration reactions, today we did not talk about them much. Study the effect of addition of mineral and chemical admixtures on the hydration process.

Learn more about the models of hydration of cement. There are models like that Nist model go through model literature is available about that, which explains how cement hydrates, what are the different a properties which are studied in the hydration process and how they affect the properties of the concrete. And I would like you to create images in your mind to model the process of hydration divided into settings, stiffening, instant development, because once you have that in the mind very clearly, it facilitates understanding of other processes and the concrete engineering in general.

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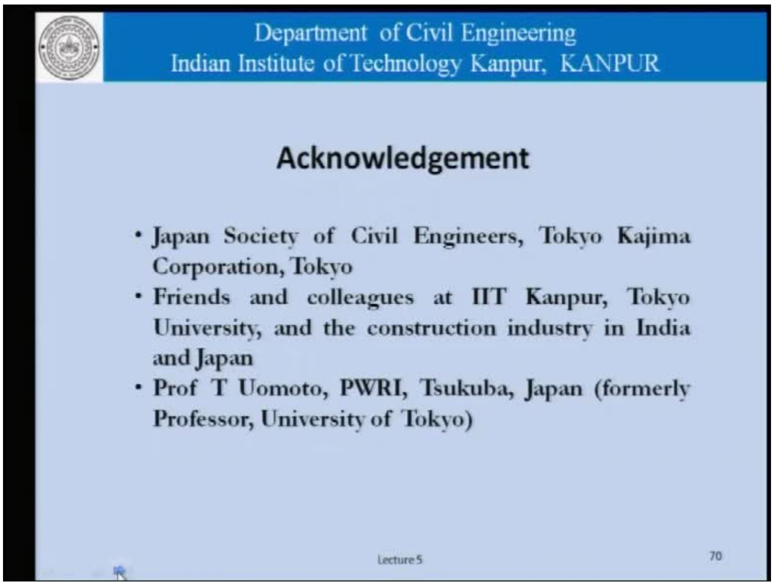

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- Prof T Uomoto, PWRI, Tsukuba, Japan (formerly Professor, University of Tokyo)

Lecture 5

I would like to acknowledge the help from the JSCE, the Tokyo and the Kajima Corporation in Japan. The Friends and colleagues at IIT Kanpur, Tokyo University and the construction industry in India and Japan. Professor Uomoto in the public work resource institute Tsukuba, formally professor of the University of Tokyo, who help tremendously to improve or to develop my own understanding of cement hydration.

Thank you.