Building Materials and Composites
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Lecture - 19
Cement

So we are in lecture 4 of module 4, which is on concrete. And in my previous lectures, we have seen how concrete is being cast and then after that we had started to enter into each of the ingredients. The last lectures were on the two aggregates that was the fine aggregate and then the coarse aggregate. Now today we are trying to cover the most important player which is the binder, which binds all the substances or the ingredients, that is cement.

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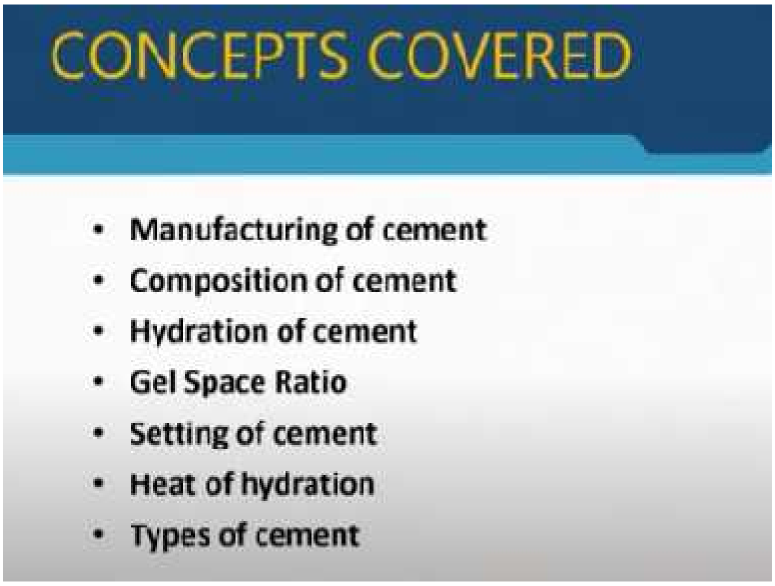

It is the costliest within the mix and which is the minimum used in a mix almost and in most of the times. And yes, we will try to cover its manufacturing, composition and then the main part which is actually giving it the strength that is the hydration of cement, the gel space ratio setting of cement, then the heat of hydration and the different types of cement which we will try to open it to you.

Mostly we use the ordinary Portland cement for our general constructions and particularly in our atmospheric condition. That means the temperature and the humidity.

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Now cement was found as long back and was named as magic powder. Why magic? Because it could set, it was an adhesive; it was helping in the binding of any kind of material. So initially, when it was found and it was grey in color and ordinary Portland cement was the name when it was started manufacturing. So we have two types of cements.

One is the hydraulic cement, which sets in presence of water, which is the ordinary Portland cement. The other one is the non-hydraulic cement, which we also had discussed that is lime and gypsum. It does not set in water. So it delays the process. Otherwise, in the case of ordinary Portland cement, if we will come to the ingredients then we will know that whenever it comes in contact with water, it sets.

Even the bags of cement which are purchased are to be kept and used within a short period of time so as to avoid setting. A bag usually contains about 50 kg of cement and if it sets, it is a loss of the money. For example a big of cement costs around 380 to 400 rupees. So we have to understand that if we expose the hydraulic cement which we use regularly it sets. So let us come to each of the phenomena one by one and first we try to know what it is made of.

Unlike the sand (fine aggregates) and gravels (coarse aggregates), those were naturally occurring. But here it is man-made and you see again it is the list of the stones. The calcareous rocks having limestone that is rich in calcium. Argillocalcareous rocks which is again clayey limestone. Argillaceous rocks which is having alumina, that clay. There are iron ore which helps in formation of the ferrites.

And sand which helps in formation of the silicates of the calcium etc., which is present in the rocks. So now again you see it is the same material from which we are making the usable material, which is the binder in the entire item of concrete. So rocks are crushed and then heated in kiln. It is a very basic line I have used but these rocks come in various proportions that is batching is required and there is a dry process, there is a wet process. I am not elaborating much into it.

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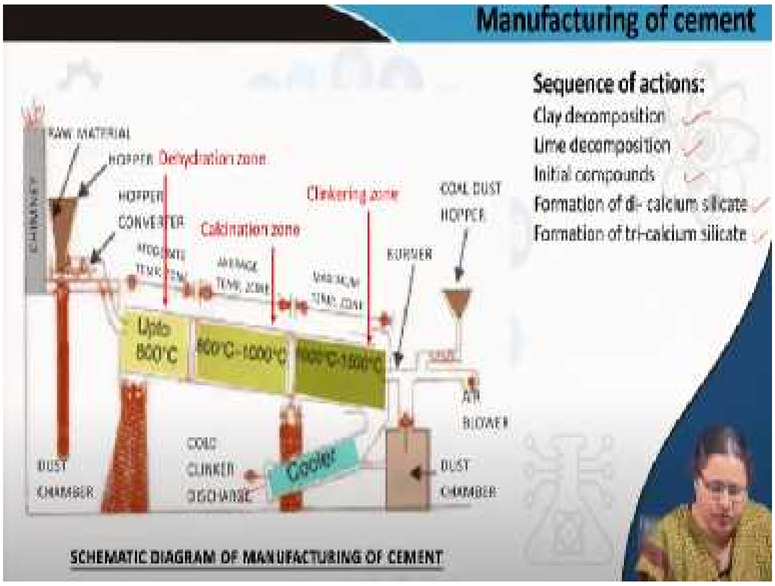

But coming to the major part, when these dusts in their proportions are mixed, they are actually put into a system where you see the first part, it is the moderate temperature zone, then it is the average temperature zone, then it is the maximum temperature zone, which shows that the heat is sent from this direction. So here is the burner and the temperature gradually moves from this end to that end, keeping this end as the hottest part.

This is the hottest part. You can see the temperature written over there. But the raw materials are being fed from this direction. So the raw materials gradually move from this side to this side. So here it receives some 800°C temperature. And here actually the dehydration of the entire stone takes place. This area is the calcination zone. And the last part is the clinkering zone.

Clinkers are small ball like substances which are the transformation of all the dust, the mixed dust which had been fed into the system as raw material. As you see the sequence of actions here, the clay decomposes, the lime decomposes, some initial compounds are formed, that is the mixing of the items are happening.

The compounds namely the calcium silicates, the di-calcium silicates, the tri-calcium silicates, the aluminum ferrites and the calcium aluminates, start forming and you see these are finally formed. So you see here is the clinkering zone and it is the cooling side. Gradually it moves into the cooler part and it is discharged. So the clinkers are now ready for grinding. So what is this clinker?

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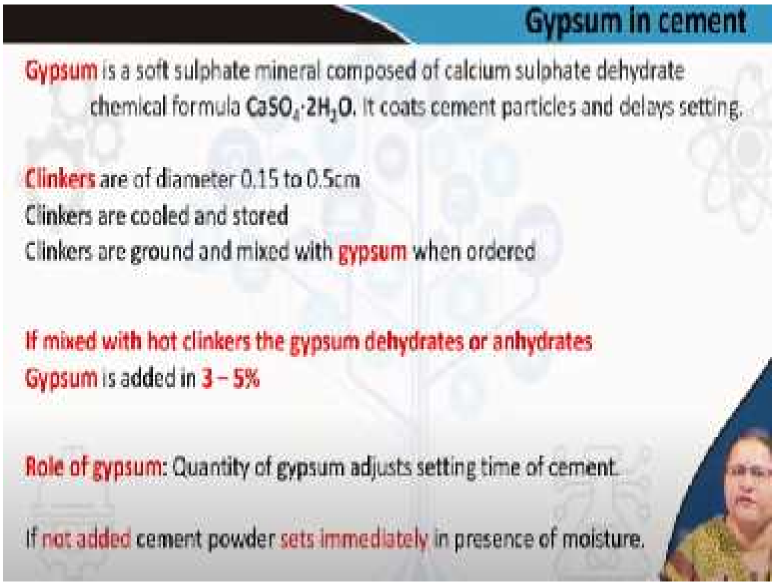

These clinkers are varying in size from say 0.5 cm to around 5 cm small balls like substances. But these are kept aside. Why? We come to the next item, which is gypsum. Gypsum is nothing but a mineral sulphate, calcium sulphate, which has two molecules of water, so this hydrated calcium sulphate is required to be added to the clinker. Now this clinker what has happened? This clinker needs grinding.

This clinker needs to be dry and cold. So those are preserved, those are cooled and now you are grinding it. Clinkers are ground and they are mixed with gypsum when ordered. Ordered means ordered from the site. Because once this powder is made, which is named as cement which reaches the site, its life starts from there.

And you cannot keep it on shelf for a longer period of time. So the person or the manufacturer will lose the cement if it is not ordered and he is manufacturing continuously. So the clinkers in cold condition are mixed with gypsum when the order is placed and it is bagged in form of cement. Now if it was mixed when clinkers were hot, what would have happened?

The hydrated gypsum, the two molecules of water in gypsum would become anhydrous. It would have evaporated because this gypsum coats the cement particles and delay the setting process. So we will come to setting later but setting in one word is the binding. Usually 2% to 5% or 3% to 5% maximum gypsum is added. If you keep on increasing the amount of gypsum, the setting will be much delayed.

So we have to also keep an eye about how much gypsum is added as because adding more and more would not help. So the role of gypsum is to adjust the setting time. So if you require a quick setting, for example you need construction to be usable or to be transported very quickly or it is an underwater item being cast or it is a foundation in a very marshy land. You need quick setting. So what will you withdraw?

The percentage of Gypsum added will be withdrawn. How? Can you take it out? No. When you are ordering you have to order for quick setting cement. So if you add more of gypsum it will delay setting. If you withdraw gypsum it will make flash setting or quick setting.

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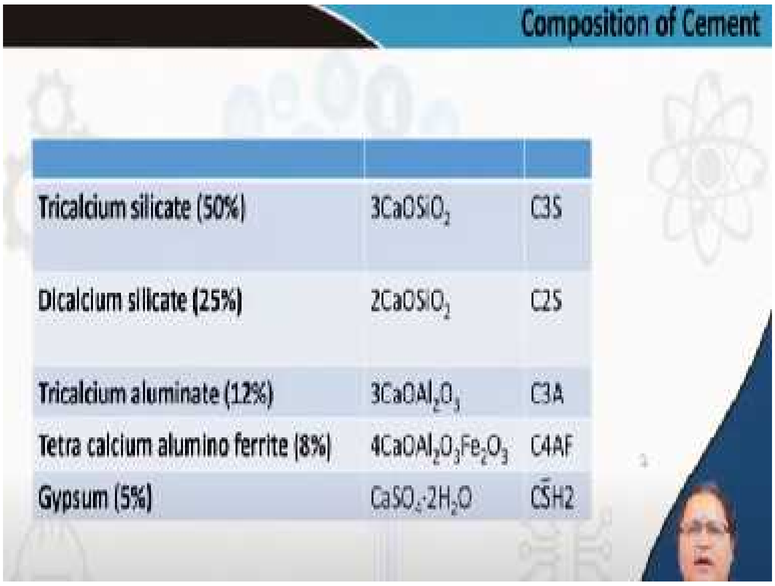

Now coming to the composition of cement of which one is Gypsum you have all known, but what are the other formations of those stones which you have added. They have formed finally tri-calcium silicate, Dicalcium silicate, Tricalcium aluminate, Tetra calcium alumino ferrite. Now here you see it is $3CaOSiO_2$ and it is abbreviated as C3S. So this indicates Tricalcium silicate.

Next is Dicalcium silicate and abbreviated as C2S. If you see Tricalcium aluminate you see C3A. And you see Tetra calcium alumino ferrite it is $3CaOAl_2O_3$ and $4CaOAl_2O_3Fe_2O_3$. So it gives C4AF. Now here you see there is a ferrite. And finally, it is Gypsum which is added at the last and its percentage varies. And Gypsum is also abbreviated as CSH2, as it is calcium sulphate. S bar and H2 implies two molecules of water.

So whenever we talk of cement, whenever we say C3S it is Tricalcium silicate, C2S is Ficalcium silicate. Tricalcium aluminate is C3A and the other two. So you do not have to remember all the formula, but it is the basic way of remembering. Why we need to remember? Because all these items react in different times to have or help in the setting process.

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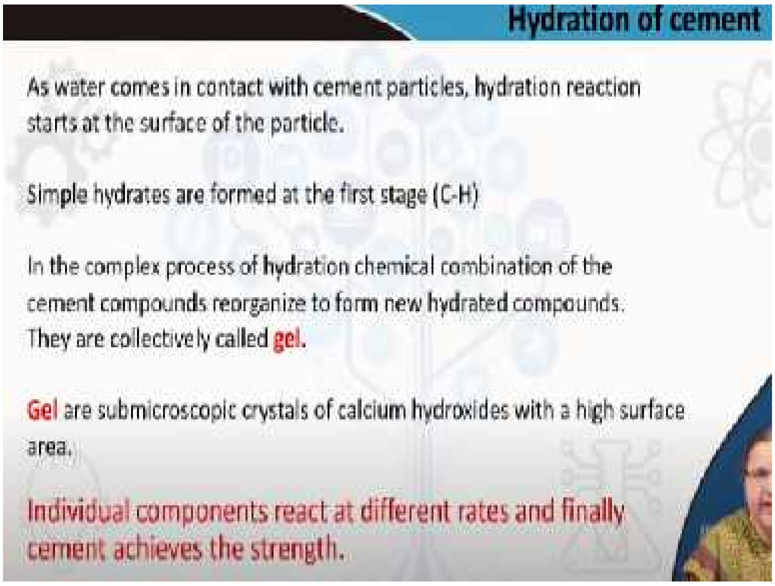

So that it brings to the hydration of cement. When water is added to the cement, actually all the ingredients which we had talked earlier, starts their reaction with water and it is a surface reaction. So you see, carbon hydrogen it is actually calcium, it is the calcium oxide and H is the water. So these hydrates are forming. And gradually, this hydration keeps on forming with time.

It is a function of time and not all are reacting always. Who is reacting first? The Tricalcium sulphate is reacting first and it also liberates heat. So we will come to the heat liberation part also. But, now presently we are looking into the hydration process. The water and the cement together form slurry, which is called the gel. This gel is nothing but submicroscopic crystals of calcium hydroxide, C-H. C was calcium oxide and H was water.

So they combined and formed calcium hydroxides. You get a lot of series of hydration reactions and collectively it is called hydration and they have high surface area. Why you need this surface area? The area is required because in case of sand particles, all of them are surrounded by this cement gel.

And if you remember during sand we discussed clay, if there was clay in the sand, then the clay would have not allowed this gel to reach the sand particle. So this high surface area, the gel actually coats the sand, which sits on the top of the coarse aggregate and finally, that binds. So individual components react at different rates and finally cement achieves the strength and all other ingredients along with it get bound.

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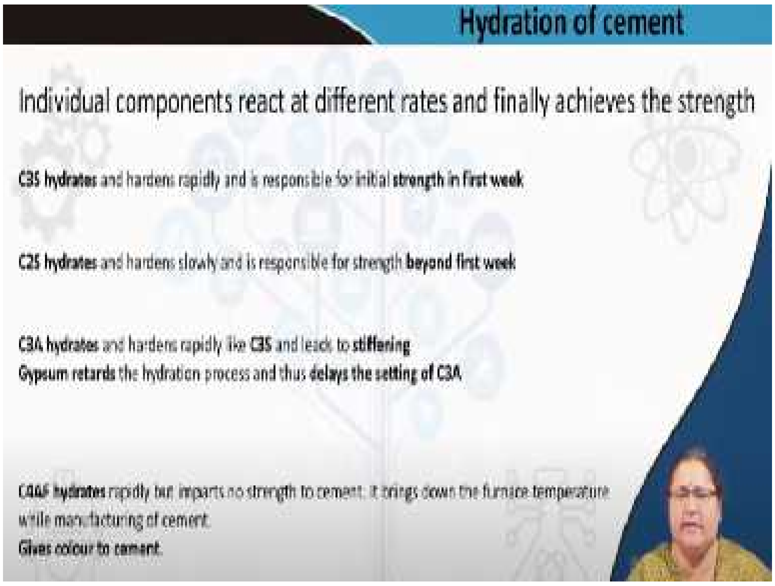

C3S or Tricalcium silicate hydrates and hardens rapidly and it is responsible for the initial strength in the first week of concrete casting. If you remember the curing of concrete, which was discussed in the first lecture, we have to cure concrete for 28 days. So this hydration process of cement of this particular C3S, it is a very initial phenomenon as well as surface phenomenon which gives the initial strength to the concrete mass.

C2S or Dicalcium silicate hydrates and hardens slowly and it is responsible for the strength beyond the first week. It is the strength of the concrete. Though the reaction of cement starts with its neighboring items that are sand or coarse aggregate, but the strength of the entire mass builds up after first week due to Dicalcium silicate.

C3A which is Tricalcium aluminate hardens rapidly similar to C3S and leads to stiffening of the item. So item become stiff, because and you cannot reshape it. Gypsum retards the hydration process and thus delays the setting of C3A and also of C3S. So that is the major role of gypsum in cement. C4AF or Tetra calcium alumino ferrite hydrates the cement rapidly but imparts no strength to the cement.

It is important to bring down the kiln temperature when the cement formation was happening. If you remember the kiln temperature as I told varies from 800^{o}C to 1000^{o}C and then up to 1500^{o}C, it would not have happened in 1500^{o}C if there was no tetra calcium alumino ferrite. So it brought down the temperature of clinkering while in the manufacturing of cement and this actually is giving or imparting color to cement. And to be precise, it is the ferrite which is giving the color.

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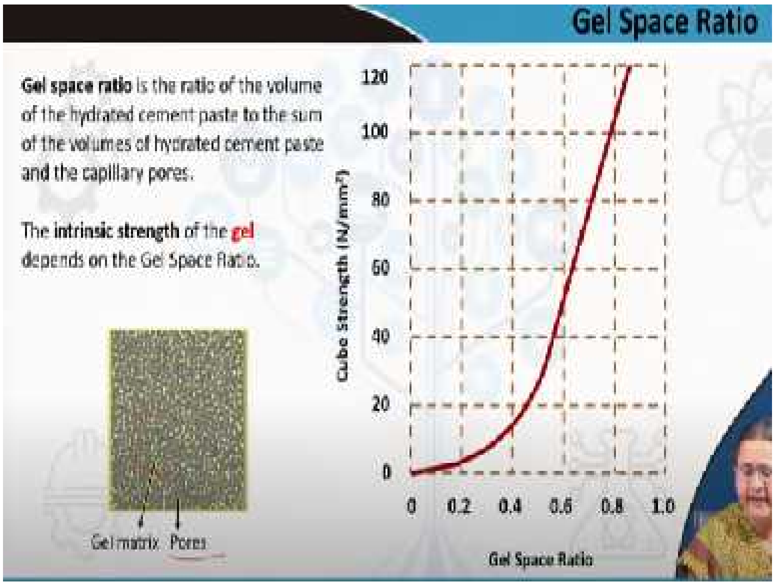

Now we come to the gel and see how it looks. When water is added to cement you can see (in the picture) that lots of gaps are there, it is the gel matrix and these gaps are called the pores. These spaces in between which are actually in cement makes it is the or in the gel it is the void or the gaps.

So gel space ratio as you can see, it is the ratio of the volume of the hydrated cement paste. It can expressed as follows

$$G \quad S \quad R = \frac{V \quad of\, hy \quad c\epsilon \quad p}{V \quad o \quad hy \quad c\epsilon \quad p + V \quad o \quad C \quad p}$$

So it is the actual volume divided by the sum of the volume of the hydrated cement paste and the capillary pores. So if you add up all these capillary pores with the volume, what you get is the denominator.

But on the top it is actually what volume you have added and that you are supposed to get. But because of this pores it has increased in volume. So the gel space ratio the spaces actually at the pores or the voids. So lesser will be the void higher will be the strength. So the intrinsic strength of the gel depends on the gel space ratio.

So this water and the cement together that forms the gel leaves pores inside and if these pores are more the strength of the cement will be less. So here you can see the graph and here is the compressive strength in N/mm^2. It starts with a decent amount from gel space ratio of 6 when it is 40 N/mm^2. And it goes higher when you end up with minimum of capillary pores.

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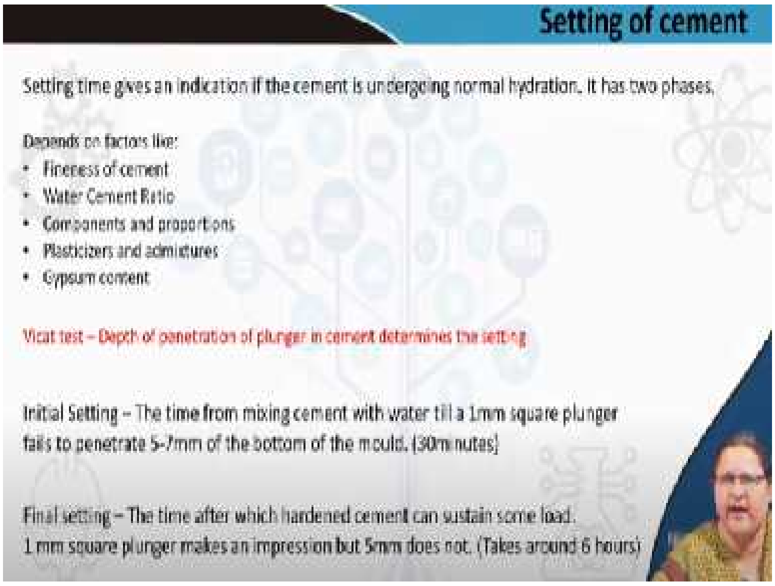

Now coming to the how to know the settling time. As we had talked about the setting of cement like how it hardens and we have talked that C3A, C3S is important for the initial setting. So setting time actually gives an indication of how much of hydration has happened, whether it is undergoing normal hydration, whether it has enough of water and usually the setting time is split into two.

As we discussed that C3S and C3A are mostly responsible for the initial setting. Their rates of reaction or hydration happen faster in the very beginning and gradually as the time increases the hydration still continues. And that is why during curing you always need to keep water. Yes the water is mixed inside it, but that gradually the strength gain happens.

So depending factors are, how fine the cement is, how is the water cement ratio, we will come to that little later in the next lecture, what are the components and their proportions? What are the kinds of plasticizers and admixtures added? We will also elaborate on that and what is the gypsum content because gypsum retards the initial setting. We have the Vicat test where actually a plunger is allowed.

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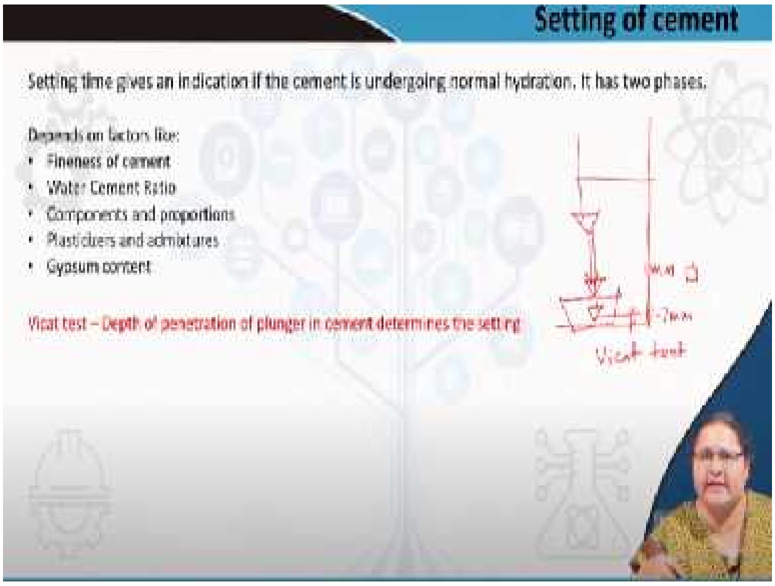

A plunger with a given tip dimension is allowed to fall on a cement mix. Here it is a mix of cement and water and this plunger drops into it. So when it is initial set it will penetrate and it will penetrate at a depth of 5 mm to 7 mm measured from the bottom of the mix. The needle penetrates because after initial setting, the mix has not hardened totally. The needle or the plunger is of 1 mm in dimension and has a square base.

And it enters into it. Now this plunger is held by a support and that is called the Vicat test. There are images but as those are not free images I did not use it here. You can always check it if you are if you can access internet. After some time if we go for testing again, this plunger would not get inside so much, it will just stick and stop here if the mix has finally set.

It will just make a mark if it is 1 mm square plunger that is the base is 1 mm square in dimension. And if it is a 5 mm square dimension, it will not even make a mark. That means the cement has undergone final setting. So here is the initial setting. It is written it takes it should be done after 15 minutes but within 30 minutes.

And here is the final setting where the hardening has happened and the cement can take the load. It is 1 millimeter square plunger making an impression and 5 millimeter does not, 5 millimeter square plunger does not. It is to be done around after 6 hours. So this is how you can understand the setting of cement.

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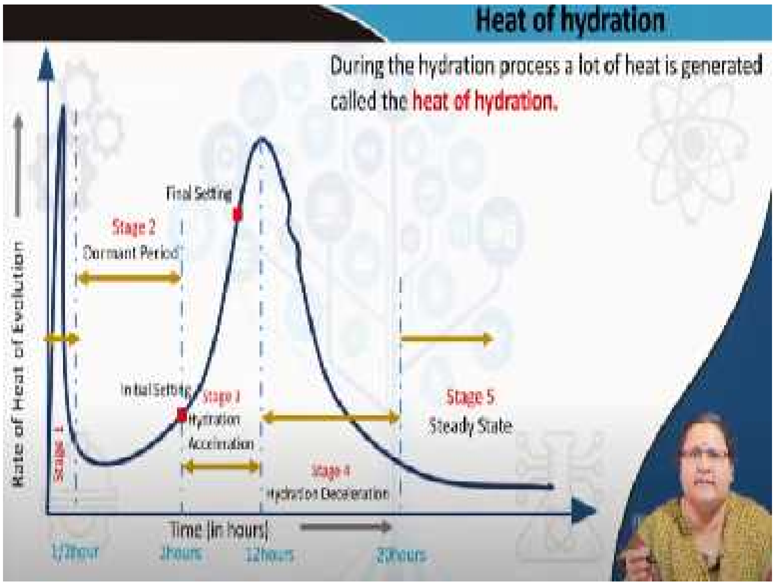

Let us come to the heat evolution process. The value of heat evolves per gram of cement is 120 calories (cal). It is not a matter of joke, 1 gram of cement liberating 120 cal of heat. And if you see the graph here in the initial setting process that is in stage 1, the heat evolved is maximum; within the first 15 minutes to half an hour because of addition of gypsum it is delayed. Otherwise that time would have been farther reduced.

You see the graph has gone high. As a comparative you can make out and in stage 2 it is dormant. This entire period is under initial setting. During this time actually the C3S and C3A are getting hydrated. Others have initiated the process of hydration and you can see again the graph rises up. But it is a gradual process, some 12 hours to 20 hours the stage 3 and gradually coming down this hydration decelerates.

So in these two time periods i.e. Stage 3 and 4, the amount of heat liberated is not taken out gradually, it may lead to finer cracks inside. So these points are to be remembered. Hence concrete whenever it is done, it is kept moist and also in contact with air and it gradually cools down. That helps this gradual process of this heat being liberated in a controlled way, so that you do not end up in cracks.

So this is the heat of hydration. What you need to know is the process of initial setting and the process of final setting and this hydration process which is happening very gradually and that actually gives you the final strength.

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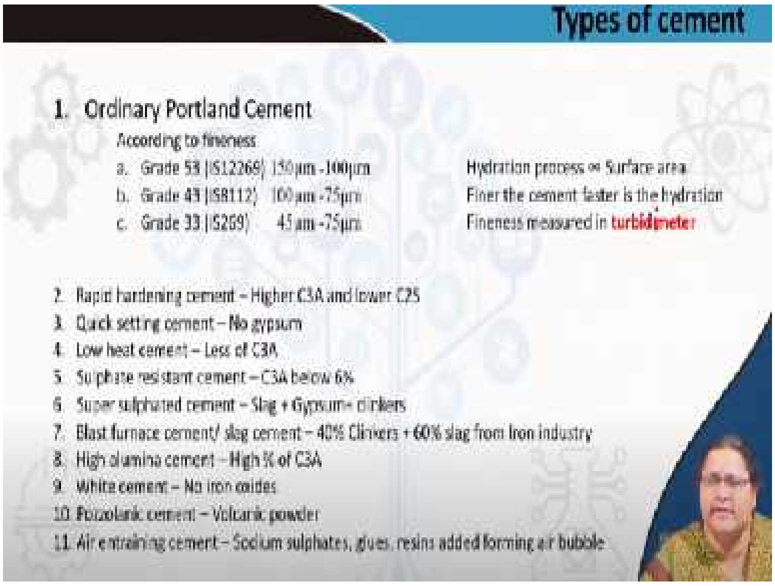

Now coming to the types of cement to close with, it is mostly we use ordinary Portland cement. We see it has three grades as we had seen fineness modulus, here also this can be done with the help of a turbidimeter and we have grade 53, grade 43 and grade 33, the dimensions are given and the IS codes are also specified. Any item that is to be incorporated is given in code.

So hydration process is proportional to the surface area. So finer the cement more the number of particles and faster is the hydration. This I had discussed when we touched sand. So the finer particles that were in contact with water bulked more. Here it is the hydration process is faster. So fineness is measured by in a turbidimeter.

Here is a list of other different types of cement. Rapid hardening cement means, it will set quickly. So higher will be the amount of C3A and lower will be the proportion of C2S. Similarly quick setting cement will have less of gypsum or maybe no gypsum. So it will set very quickly.

Low heat cement means it will have less of C3A. That means, the first part or the initial setting time where the heat liberation was maximum in a very short duration of time it will have no heat or low heat will be generated. So it is low heat cement. For Sulphate resistance cement the amount C3A should be below 6%. Super sulfated cement is the combination of slag, gypsum and clinkers all together almost equal in amount.

Blast furnace cement or slag cement is again combination of 40% clinkers and 60% slag from iron industry. High alumina cement implies it will have high percentage of C3A. Automatically the other percentages will change. White cement will have no iron oxide i.e. the alumino ferrite would be missing because iron was imparting color and you will not get any specific color of cement and you will get white cement.

And this is a very costly item. This is available in bags amounting 1 kg or 2 kg, not in bulk like 50 kg, and these are used mostly for finish purposes. Pozzolanic cement is obtained from volcanic rocks in powder form and air entraining cement forms when sodium sulphate, glues, raisins added, it forms air bubble within it and that gives it a lesser density, porous, insulating capacities.

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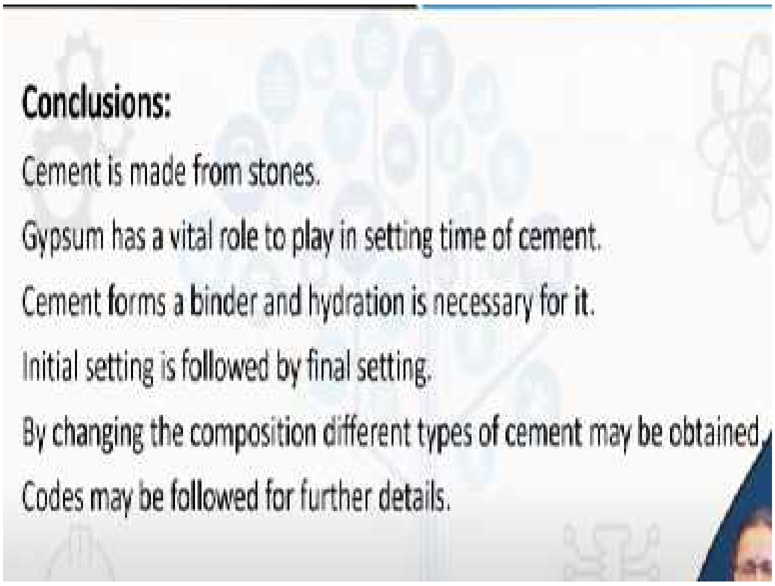

So with all these, we conclude that cement is a man-made thing from stones. Gypsum has a vital role in playing the role in playing the setting time of cement. Cement forms the binder and hydration is necessary for it. Initial setting is followed by final setting and by changing the composition of the different constituents; you may get different types of cements.

Codes are to be followed whenever we are dealing with any kind of cement or cement within a concrete mix. Cement as itself can be used, the slurry can be used as a finished material on top of floors, which we call usually as the Indian patent stone. Many floors where there is no finishing, cement slurry is given and it creates a very thin layer (5 mm to 6 mm) and it gives a very neat cement finish.

Otherwise, it can be used with sand as a mortar or in concrete as a mass or composite where cement plays a vital role as a binder. So we end today's lecture here.