Pavement Materials
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Lecture 49
Cementitious Materials (Part 1)

Hello everyone. Today, we are going to start a new module and this module is related to the materials that are used in the construction of concrete pavements. As we have discussed previously if you remember that the typical materials that are used and are related to concrete pavement other than the granular materials and subgrade, it includes dryline concrete mixes and it also includes pavement quality concrete.

Both in DLC and pavement quality concrete, we use cementitious materials in different forms, in different proportions and this is what we are going to discuss. Today we will discuss about the cementitious material which act as the binding agent when we talk about concrete mixes.

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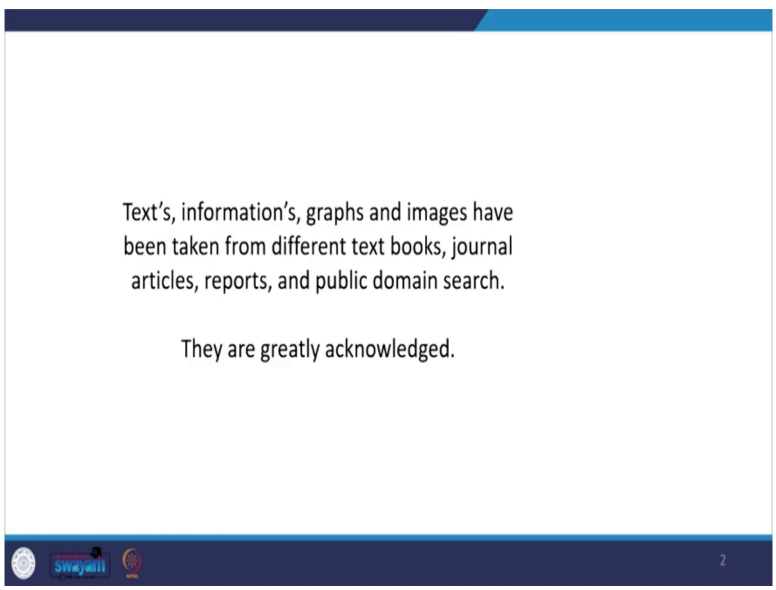

Just like the previous modules, in this module also various sources were referred in different lectures and these references have been mentioned in this particular slide and I greatly acknowledge them.

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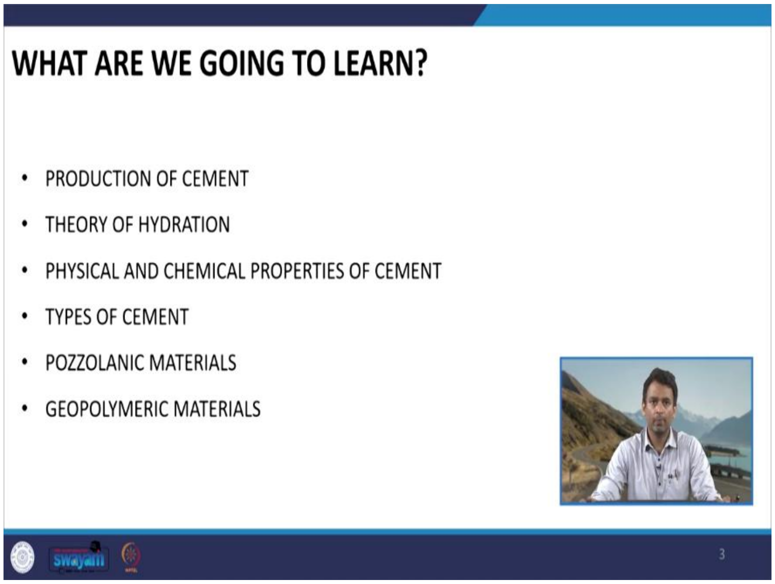

So, what are we going to talk today? We are going to talk about cement in general where we will cover topics related to production of cement, we will talk about the theory of hydration, we will talk about the basic physical and chemical properties of cement. We will also talk about the different types of cement that are typically permissible to be used for the construction of concrete pavements.

We will talk about pozzolanic materials which are used to form cementitious material, we will discuss about them. And we will also discuss about the current trend on the use of geo-polymeric material which is basically a replacement of semen. So, we will discuss about the theory related to the production of geo-polymeric cementitious materials as well.

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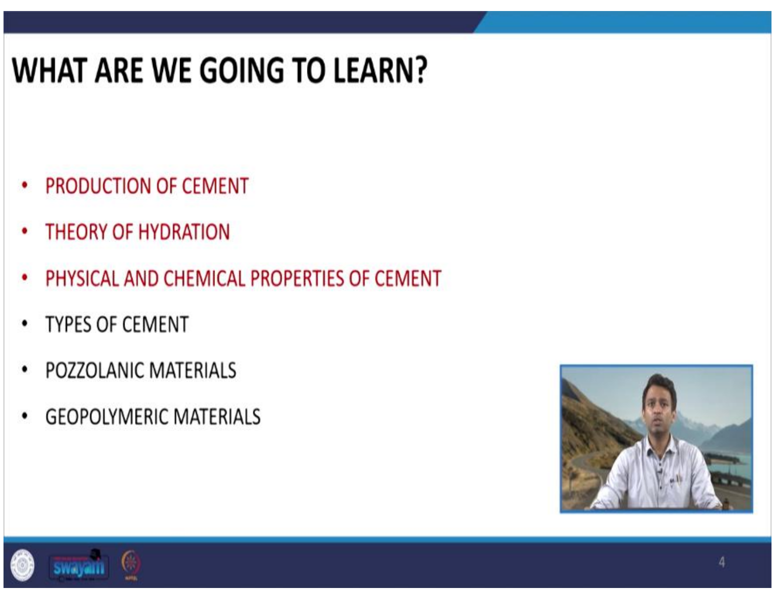

Let us start discussing about these topics. This particular module is a short module in comparison to the previous modules. So, we will try to complete this module in two lectures and today is the first lecture where we are going to talk about the production of cement, we will discuss about the theory of hydration and we will also talk about the physical and chemical properties of cement.

So, to start with let us see how the development of cement started in the history. If we see the literatures that are available, the sources that are available that tell us about the various structure that were built long back.

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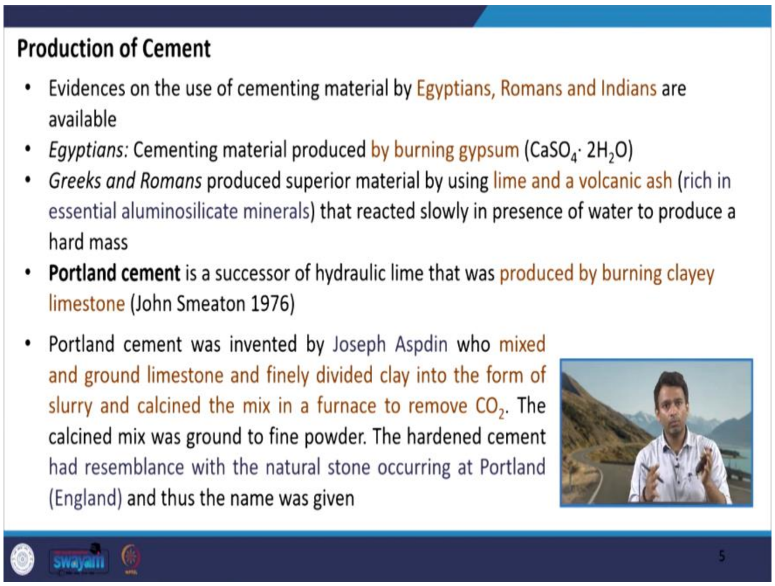

We see that cementing material where initially adopted by Egyptians, Romans and also Indians in various different forms. Of course, these were not the typical cementitious material we use today but the theory of cementitious material is ideally developed from our understanding about these structures about the materials that were used as a binding agent in these structures.

Egyptians, they basically used cementing material that were produced by burning gypsum and just for further reference also, you can try to remember that gypsum is nothing but calcium sulphate hydrate. So, it is $CaSO_4$ to H_2O, so they used gypsum as the cementing material but of course gypsum is not the only material which we use today for the production of cement.

Greeks and Romans on the other hand they produced superior material in comparison to what the Egyptians produced and they used a mixture of lime and some form of volcanic ash. Now the volcanic ash is basically rich in aluminosilicate minerals.

So, here again is a very basic concept that cementitious materials are in general developed by a combination of calcium oxides for example through lime and aluminosilicate materials, now the source can be different for the aluminosilicate materials but ideally when these materials are mixed together in some form and they undergo through some specific processes, finally we will get our semantic product. So, Greeks and Romans they used to mix lime and volcanic ash which reacted slowly in presence of water to produce a hard mass or a cementing material.

The term Portland cement or the initial manufactured cement that was used in the modern age was basically a successor of hydraulic line that was produced by burning clay limestone and this was investigated and it was developed by John Smeaton in 1976. So, he found that you know, burning some specific types of clay limestone through a specific process again, you can get a cementing product.

Portland cement which we understand today was actually invented by Joseph Aspdin, who mixed and grounded limestone and finely divided clay into the form of a slurry. So, what he did, he took limestone, he took clay material grounded them mixed them together formed a fine slurry out of it and this slurry was further placed inside a burning chamber which we also call as a kiln and it was heated to a very high temperature.

And during this process, the calcination of this combination of material will take place and because of this calcination process the carbon dioxide is liberated and he continued the process of heating until the complete removal of carbon dioxide. Further, after calcination whatever was the material which he got, what he did he grounded it to fine powder. Now this fine powder is nothing but the cement which is termed as or denoted as Portland cement because of its resemblance with the natural stone which was found in Portland which is in England and this is how the name came in.

But the Portland cement we manufacture today is not exactly the material which was proposed by Joseph Aspdin because the procedure has evolved over time. Because it was understood that when Joseph Aspdin mixed limestone and clay in finely divided form and heated it, the temperature was not very high so as to convert it into a clinker. So, clinker again is a product which we get during the manufacturing process of cement.

But his temperature was not so high. Later on other researchers they used higher level of temperatures so that this mixture of limestone and clay gets converted into clinker and finally this clinker is grounded and it is further mixed with some additional materials for example gypsum in some proportion and we finally get our product which is cement.

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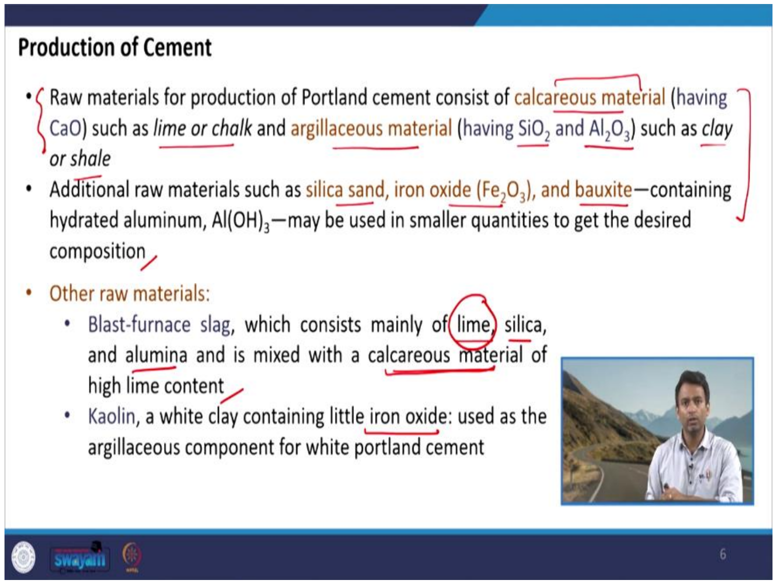

So, talking about the raw materials that are used in the manufacture ring of the modern cement which we understand, it includes calcareous material. Now this is the basic principle of manufacturing the cement and this principle was in fact taken from the experimentations that were done many-many years back and we are just evolving with time, refining things in the manufacturing process and producing various types of cementing materials.

But the principle as I mentioned will remain the same. So, we will have a calcareous material, the common calculus material or the source is basically lime or chalk through which we get abundant amount of calcium oxide and the argillaceous material which comprises of silica and alumina.

So, these three things you have to remember that cement is composed of a mixture which undergoes a process that is a different thing but the raw materials include calcareous material so we need a source of calcium oxide and argillaceous material which means we need a source for silica and alumina, a mixture of silica and aluminum. And for example, the commonly used source is clay or shale for the argillaceous material.

Now to modify the properties of cement other raw materials can be used as well for example, we can use silica sand, we can use some proportion of iron oxide, we can use some proportion of bauxite which is basically which contains hydrated aluminum to get some desired composition. But the first point tells us the basic ingredient that is required. Some of the additional raw materials now when I say that these are raw materials which means it is basically used most is a replacement of other materials which are already listed here. So, because ultimately what we need is the basic ingredients that is calcium oxide and silica and alumina.

So, there are of course other sources other than lime or other than clay or shale that can give us this product and so they can also be used. For example, we can use blast furnace slag. So, blast furnace slag which comes as a by-product from the industry. It consists mainly of lime silica and alumina, again the ingredients which are required for the manufacturing of cement and it is mixed with calcareous material because the quantity of lime here is not significantly high to initiate the process or the reactions which finally converts this raw material into cement. So, we need to add blast furnace slag with additional calcareous material of high lime content.

We can also use kaolin, kaolin is another form of clay. We also call it as a white clay and it contains some iron oxide and it can also be used as a replacement of argillaceous component for the production of white Portland cement. We can also use industrial wastes for example flyash is one of the very common industrial waste, we no longer even call it as industrial waste these days, we have to purchase fly ash but typically it is a by-product from thermal power plant and this can also be used as a replacement of cement.

So, this is a type of pozzolanic material about which we are going to discuss in detail anyway in this particular module.

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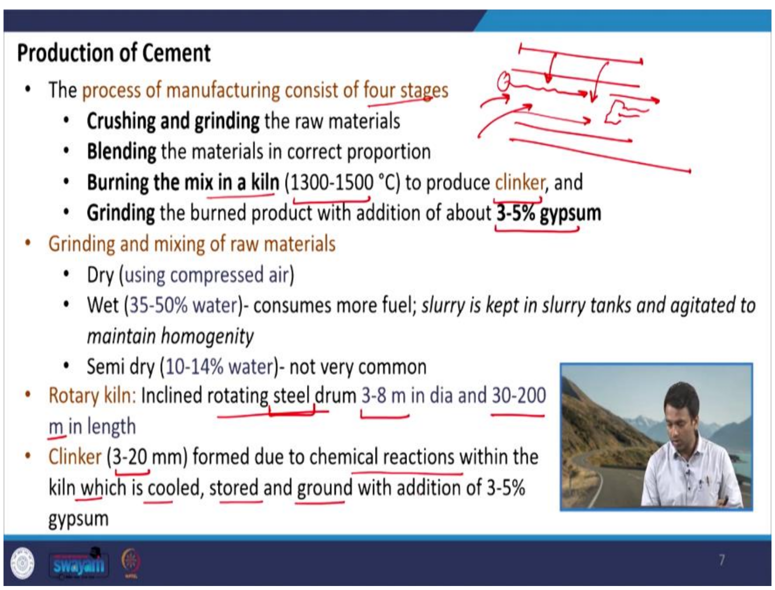

Now let us see the manufacturing process of cement. So, the manufacturing process of cement it consists mainly of four stages. So, These stages includes crushing and grinding of the raw materials. So, we have the raw materials we have silica, alumina and we have calcium oxide. We will mix them, we will crush them and will grind them together, so this is the first step.

Now we will also control the proportion of this materials. We are going to blend this material in some certain proportions, so as we get the final desired property that we want. Then what we do, we burn this particular mix which we have created that is the mixture of lime, alumina and silica and any other materials if it has been added.

So, we will mix them and finally this mixture will be burned in a kiln and in the kiln which is basically a chamber and we add the material here, the mixed material here and then we have flames. So, there is a differential temperature in this particular kiln, so we heat the mixture from it, to a level of temperature ranging from 1300 to 1500 degree Celsius and during this process when this material comes here under the action of heat and it comes out of this particular chamber, it will convert into clinker.

So, clinker are basically small nodules of the products which are formed through the chemical reaction or the calcination process and additional and other processes which takes place inside this particular chamber. Finally, the clinker which we get which comes out of the kiln, we cool it actually and then we ground it. Then this grounded mixture is basically added with about 3 to 5 percent gypsum and we get our final product as the cement.

Now let us talk few important points related to these steps or these stages. For example, if you talk about grinding and mixing of raw materials, so there are two different processes or three different processes that can be used. So, we have a dry process of manufacturing of cement, in the dry process when we are grinding and mixing the raw material, they are in dry state and they are mixed through compressed here. So, it will be a moist condition but still we call the process is dry.

In the wet process, we actually add additional water. So, what we do, we grind individual materials and when we mix them, we mix them with water to form a slurry and this slurry can be actually stored in tanks and they are continuously agitated to maintain the homogeneity. The amount of water can vary on the final product we desire usually it is 35 to 50 percent.

Now again try to imagine here, more is the quantity of water more amount of fuel will be required in this skill and in fact the dimension of the kiln will also increase because you have to dry the product. So, this is an advantage of dry process even the size of the kiln will be smaller in comparison to the size of the kiln we use in the wet process and the amount of heat that will be required will be lower in comparison to the wet process. So, I think that is very clear when we talk about drying this mixture when it has to pass through the process.

We also have semi dry process which is not very commonly used but in this process what we do, we typically add 10 to 14 percent water to mix these materials. As I mentioned its slurry or in the drive from if it has been compressed through air, finally the product has to come to the top of the rotary kiln and this is an inclined steel drum as I have already discussed. So, it is made up of steel. The dia of this drum can range from 3 to 8 meters whereas the length can vary from 30 to 200 meters again depending on the process we are adopting.

And inside the rotary kiln, finally the clinker will be formed when the mixture is subjected to high temperature. They will break down into certain particles will be discussing about those particles. So, this clinker is typically small nodules whose size varies from 3 to 20 mm and it is formed due to the chemical reactions within the kiln which is finally cooled, stored, they are grounded with addition of 3 to 5 percent gypsum before we get our final product. So, these are the steps and some important points in the process of manufacturing of cement.

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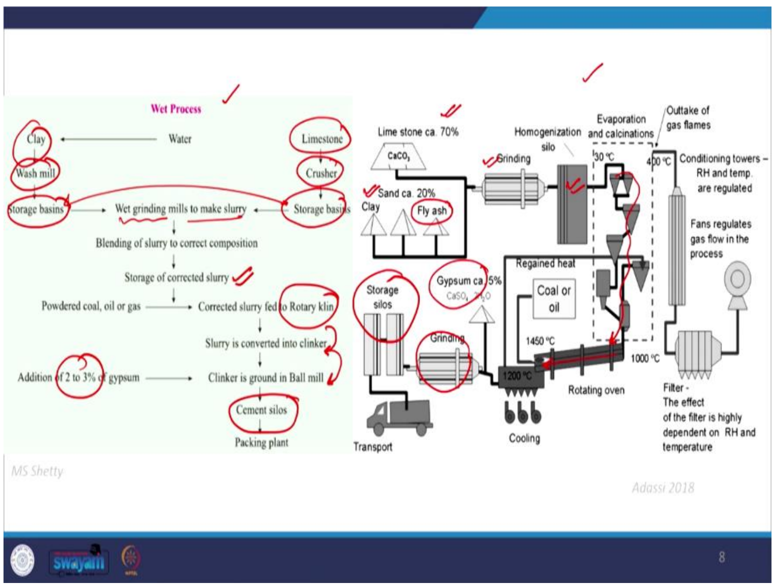

These two pictures it shows the process in different form for example, this is a flow chart for the wet process. As I mentioned, we have limestone, we have clay. It goes through wash mill, we wash and then we will store the clay in storage bins. Limestone are of larger sizes so we have to crush it and then we store it in the storage bin. We mix them together, so we have wet grinding mills to make slurry.

So, we will add as I mentioned a certain percentage of water, this is finally stored in again storage tanks and then we have to insert it into the rotary kiln where it forms clinker and then we use a ball mill to grind the clinker and mix it with 2 to 3 percent gypsum and finally we have the cement silos or the storage tank for the final product.

This gives again from a study I have taken, this particular flowchart which shows the dry process. Here again you see we have limestone, we have clay, fly ash can also be added. So, finally they go through the grinding process, they are stored then finally we are allowing them to move and reach the kiln.

And here again it will pass through the process where it will get converted into clinker and there we will finally grind, it mix it with gypsum and we will store our final product here. So, I think this flow charts are self-explanatory and we have discussed the process of manufacturing of cement.

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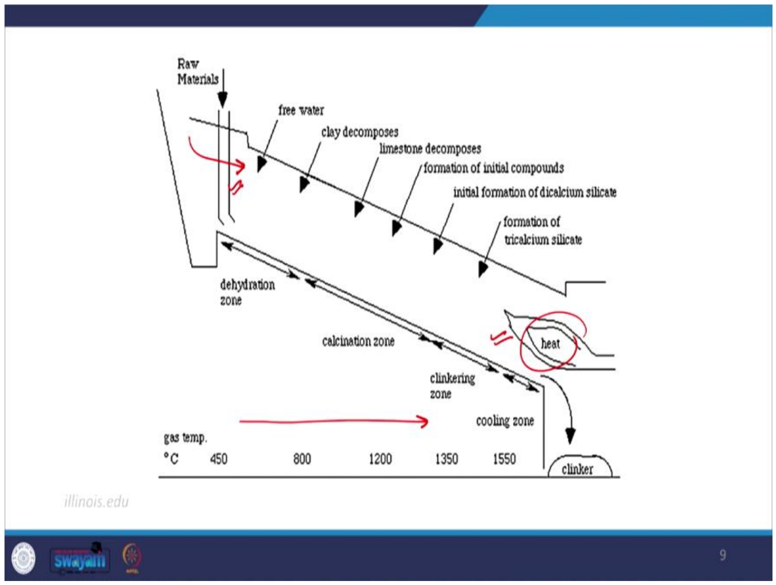

So, this is what happens in the kiln, as I mentioned the temperature is differential here. So, because we are heating, so this part will be of lower temperature in comparison to this part and material will enter here. So, when material will enter here it will have certain percentage of moisture so the free water will go then depending on the temperature the clay will decompose, the limestone will decompose, they will get fused together and they will form several products.

So, for example they will form dicalcium silicate, they will form tricalcium silicate, they will form tricalcium aluminate, they will form tetra calcium aluminum ferrite and so on. So, we are going to discuss about these products now.

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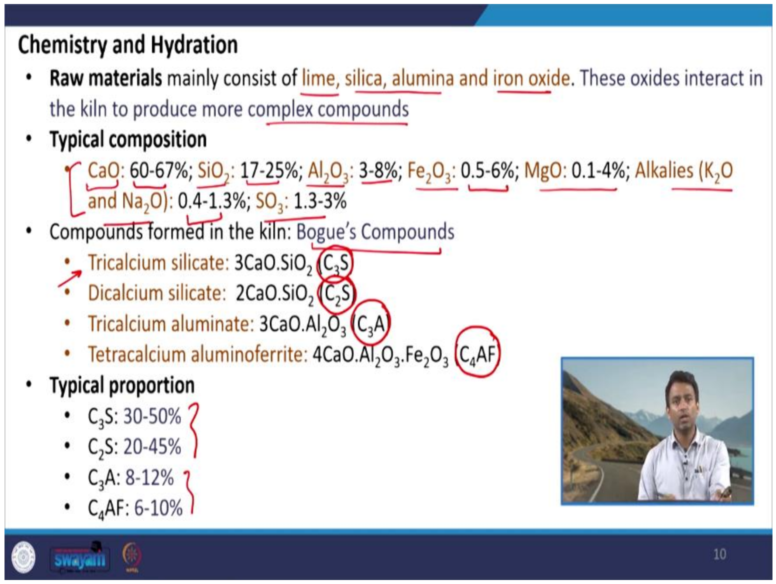

As we have discussed that the raw material basically consists of lime silica, alumina and iron oxide and these oxides finally interact in the kiln to produce complex compounds. Let us discuss about the typical proportion of these oxides.

So, calcium oxide which is basically limestone has the highest quantity which is about 60 to 67 percent for example in the last flowchart which you saw there it was used as 70 percent. Then we have SiO_2, Al2O_3 which will basically come from argillaceous material. SiO_2 ranges from 17 to 25 percent whereas Al_2O_3 ranges from 3 to 8 percent.

We have Fe_2O_3 which ranges from 0.5 to 6 percent. We have magnesium oxide point 1 to 4 percent and then we have also again depending on the raw material source, we can have certain proportion of alkalies is in form of potassium and sodium oxides and the quantity is though very less point 4 to 1.3 percent and we can also have sulphates 1.3 to 3 percent.

Now these are the raw materials, now let us talk about the materials that are formed in the kiln, that is when these materials are mixed heated together and then are allowed to stay in the kiln for certain period of time. Then again these are approximate compounds because the exact composition or chemistry is a more complicated to explain so therefore to explain the terms in a more a simpler way, we refer these compounds as Bogue's compounds, who basically categorized these materials which are formed inside the kiln.

So, they can be understood as tricalcium silicate, so it is denoted as C_3S. We have dicalcium silicate that will be formed C2S, we have tricalcium aluminate which is denoted as C_3A, we have tetra calcium aluminoferrite which is denoted as C_4AF and depending on the again the percentage of raw material, depending on the property of the raw material, the proportion in the process and it also depends on the process we are adopting.

So, the proportion of these individual components in which will be formed inside the kiln will change. And in fact, this proportion is very critical to the final properties of the cement which will be used as an engineering product to make structures.

So, therefore controlling this proportion is again very-very important to get the desirable properties from the final product because all these individual products as we will discussed very soon in this presentation that these products have to finally come in contact with water to form the final binding agent and when they come in contact with water, the reaction becomes more complicated with the individual components and different further compounds will be formed, amount of heat will be released and all these attributes, all these parameters will finally affect the strength of the structure where we will be using this cement as the binding material.

So, talking about the typical proportion of these ingredients, so tricalcium silicate is mostly of the highest proportion about 30 to 50 percent. Then is dicalcium silicate around 20 to 45 percent, we have tricalcium aluminate and tetra calcium aluminoferrite, relatively the percentage is less, it is like C_3A about 8 to 12 percent and C_4AF is about 6 to 10 percent.

So, these two materials or ingredients that is C_3S and C_2S are basically controls the strength of the final hydration product of the final structure. On the other hand, the other products that is C_3A and C_4AF, though they do not contribute significantly to the strength of the final concrete but they tends to dictate the other properties of the hydration. For example… final properties of the cemented product which we get. For example, the setting time, it will control the presence of ah other reactions involving the production of artinite and so on.

So, let us talk about the hydration. So, as I mentioned, the final binding agent will be formed or the final product that will impart strength to the structure will be formed when the cement comes in contact with the water.

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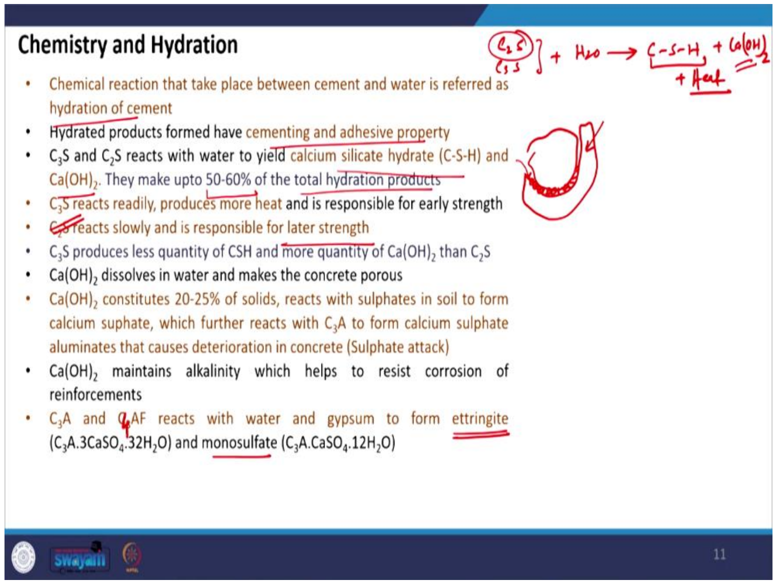

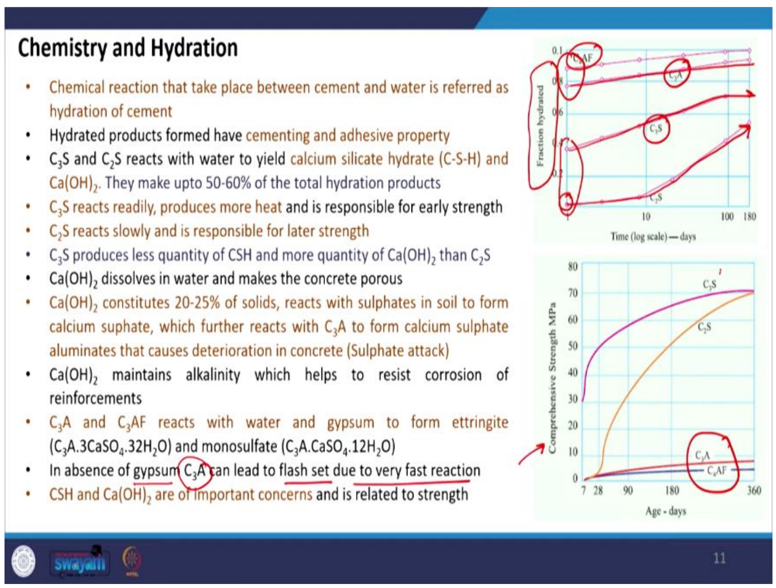

So, the chemical reaction that take place between cement and water it is referred as the hydration of cement. Now in the hydration process, hydrated products will be formed and these products will impart the cementing and these products have basically cementing and adhesive properties. Talking about, now we know that there are four main products which will be formed in the kiln is not it.

So, among those four products C_3S and C_2S, they will react with water to form calcium silicate hydrate and calcium hydroxide. So, C_2S or C_3S plus water will give us something which is called as calcium silicate hydrate. So, this is a cementing gel plus calcium hydroxide and it is it will also liberate heat which means that this reaction is an exothermic process.

And they make up to 50 to 60 percent of the total hydration products that are formed during the reaction of cement and water. If we now compare C_2S and C_3S, so C_3S reacts very fast with the water. So, it dictates the early strength of the cement so the early strength of the cement with or the hydrated product is basically due to the presence of C_3S but again we have to remember that C_3 higher amount of heat in comparison to C_2S.

So, those C two s reacts slowly. It is responsible for the later strength but the amount of heat production is less in C_2S. So, it is more desirable to have larger amount of C_2S in the cement in comparison to C_3S, if we talk in terms of strength and desirable properties because again amount of calcium hydroxide which is produced by C_3S is much higher than the amount of calcium hydroxide that is produced by C_2S.

And why we are talking about calcium hydroxide and comparing S_3S and C_2S because larger amount of calcium hydroxide is not desirable in the cement or in the hydrated product. Why it is not desirable? Because calcium hydroxide has a tendency to dissolve in water and once it dissolves in water, it will make the concrete porous which is not desirable. Calcium hydroxide it constitutes almost 20 to 25 percent of the total solids.

Now other problems related to calcium hydroxides includes its reaction with sulphates. So, it reacts with sulphates in the soil during the process, it will form calcium sulphate. Now this calcium sulphate when it comes in contact with C_3A, that is tricalcium aluminate, it will form calcium sulphate aluminate. And this basically product will affect significantly the strength of the concrete for which we are basically using cement and this process is also called as sulphate attack.

So, there will be change in volume of the concrete, there will be loss in strength of the concrete because of the production of calcium sulphate aluminate and from where it is coming? It is actually coming from calcium hydroxide, from where is calcium hydroxide coming? It is coming from the reaction of C_3S and C_2S with water and who produces the highest amount of calcium hydroxide? C_3S produces that is why when we compare C_2S and C_3S, it is desirable to have higher amount of C_2S in comparison to C_3S.

But a benefit of calcium hydroxide though it is not very significant here to discuss, is that it maintains alkalinity in the concrete and this alkalinity will help in offering resistance to the corrosion against reinforcement when we talk about reinforced concrete.

However, even a smaller quantity of calcium hydroxide is sufficient to give resistance against corrosion to the reinforcements and therefore higher amounts are not desirable. Now talking about the other two products that is C_3A and C_4A, it should be C_4AF which are formed inside the kiln, so they react with water and gypsum. So, gypsum also we added in the process of manufacturing of cement. So, they react with water and gypsum to form something which is called an ettringite.

Now this ettringite can further initiate the process or further reaction to produce monosulfate also. So, this ettringite and the presence of monosulfate, they do not contribute to the development of strength in the concrete rather they can affect something which we call as the interfacial transit zone.

So, when we have like coarse segregate and we have cement paste over it, so this location becomes very important at, how well the coarse segregates are bonded with the cement paste. Now if the amount of pores here are more than the concrete can show early failure and less is the amount of pores here which means we have a good bonding, very close bonding between the coarse segregates and the cement paste, the strength of the concrete will be higher.

And these products which we are talking about the presence of ettringite, higher amount of calcium hydroxides, the reaction which goes on they produce crystals and this crystals can occupy this space between the cement paste and the aggregate particle, thus affecting the final strength of the concrete.

If you remember we talked that when, after the materials come the clinker when it comes out from the kiln it is grounded and it is mixed with gypsum. So, the question is what is the importance of gypsum? So, the importance of gypsum is that it delays or it will reduce the occurrence of flash set in the cement. This flash set is a very fast reaction because in absence of gypsum C_3A will produce products which will quickly set the cement and it will make the cement hard.

So, in order to prevent the flash set due to the very fast reaction gypsum is added which retards the reaction of C_3A. Among all these products which we have discussed so far, our interest is basically in understanding the calcium silicate hydrate and calcium hydroxide because they are directly related to the mechanical strength of the concrete.

Though other products are equally important but with the manufacturing, with the modern manufacturing process we are well able to control the negative effects of these products and by controlling these proportions we are also able to manufacture various types of cements for specific construction purposes.

Well, these graphs just show that how the different fractions vary with time because hydration is a process which goes on for many-many days. So, initially the reaction is fast and then the reaction becomes slow which means the strength gain in the final hard end cement is basically time dependent and with time the strength increases. So, let us see that how with time the hydration of different products go on and then how different products help us to gain a higher compressive strength.

So, if you talk about the product like C_4AF and C_3A, so you see the fraction hydrated are very-very high here, in the initial period and they are they have a constant slope and it will then seize after certain number of days. On the other hand, if you see C_3S, initially it is very high then after some time it will stabilize. C_2S on the other hand, it reacts very slowly so the fraction hydrated are very less initially and then it increases over a period of time. So, that is why we say that it helps in the later strength of the concrete.

If you talk about the contribution of different products, different components on the compressive strength so you see the contribution of C_3A and C_4AF are relatively lower in comparison to C_3S and C_2S and you see that initially C_2S has a lower contribution but after some time it almost matches with C_3S which is responsible for the high early strength.

So, let us stop here today. Though I was expecting that I will be able to complete the discussing about different tests on cement but I think we have to wait for the next lecture and in the next lecture, we will complete our discussion on various common tests that are done to characterize cement. Thank you.