Hydration, Porosity and Strength of Cementitious Materials
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Lecture – 12
Portland Cement Paste System

Hi, good morning to one and all I am K V Harish, assistant professor, Department of Civil Engineering, IIT Kanpur; you are watching MOOC lecture course on hydration porosity and strength of cementitious material.

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Today we will see lecture 12; Portland cement based paste systems we have already seen in the previous lecture about an introduction about Portland cement based paste system what is the definition of that and how we define Portland cement based paste systems as and in this lecture we will see some of the selected topics in Portland cement based paste systems the textbook and reference materials are shown.

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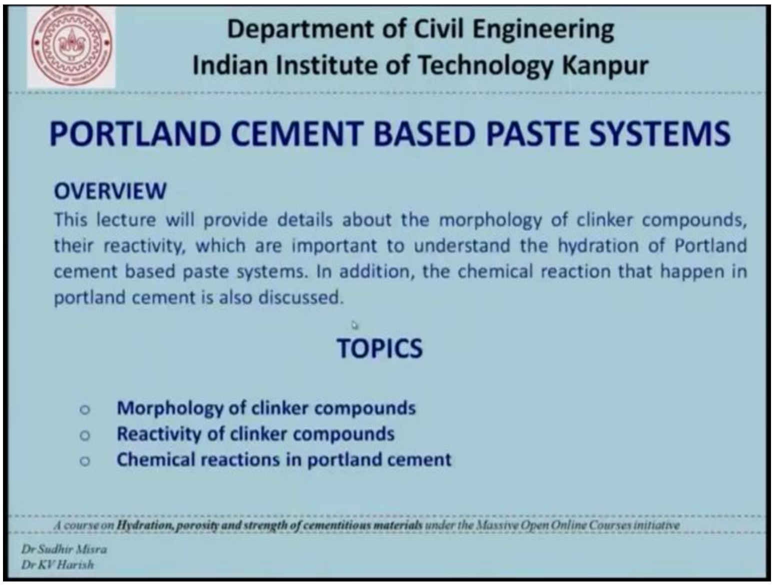

So, in this lecture the different topics that will be handled or morphology of clinker compounds reactivity of clinker compounds and chemical reactions in Portland cement the importance of this topic is primarily from the fact that these topics helps to understand the evolution of properties from Portland cement based paste systems to concrete level. So, and overview is as follows this lecture will provide details about the morphology of clinker compounds their reactivity both are important to understand the hydration of Portland cement based paste systems in addition the chemical reactions are also covered. So, in this lecture Portland cement base paste systems will be denoted as PCPBS will be using that notation very much in most of the slides. So, the audience please watch very carefully.

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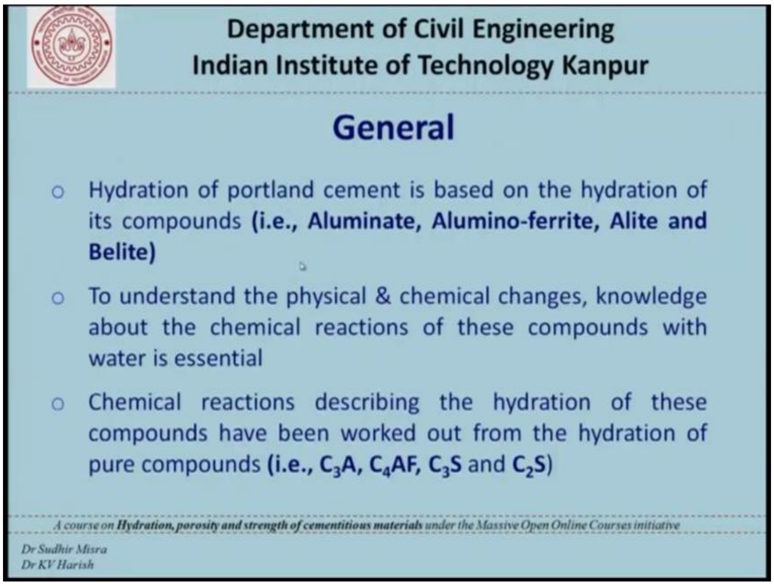

Some general information before we head on to the specific topics hydration of Portland cement is based on the hydration of its compounds, we have already seen in the lectures on Portland cement that we have aluminates alumino-ferrite, alite and belite as a primary compounds and what you may have to understand is that there are some impurities in these compounds, essentially the pure compounds or C3A, C4AF, C3S and C2S. Now the second point is to understand the physical and chemical changes knowledge about the chemical reactions are important and the chemical reactions describing the hydration of these compounds have been worked out from the hydration of pure compounds and pure compounds.

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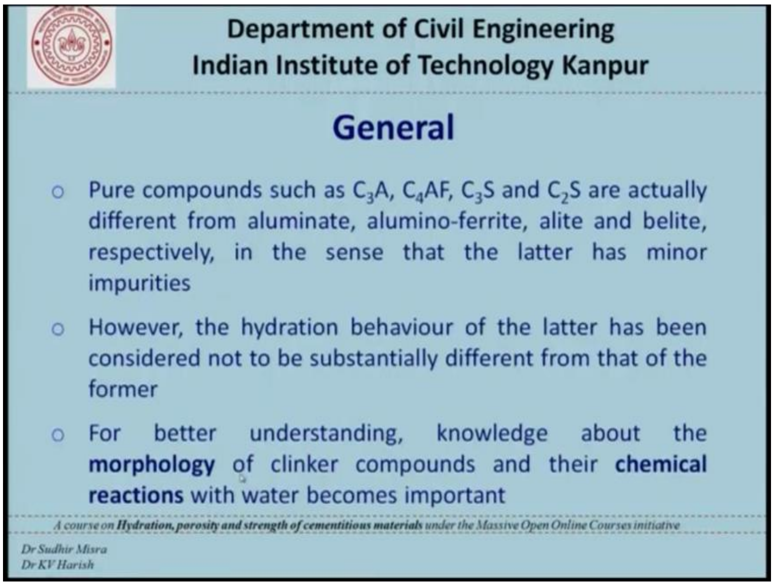

Such as C3A, C4AF, C3S and C2S are actually different from the aluminate, alumino-ferrite, alite and belite respectively in the sense that the latter has minor impurities. So, it does not substantially change the hydration behaviour, but there has been reports that the hydration of you pure compounds is slightly different from the hydration of impure compounds like aluminate, alumino-ferrite, alite and belite respectively.

So, the; however, the hydration behaviour of the latter has been considered not to be substantially different from that of the former for better understanding the knowledge about the morphology of clinker compounds and their chemical reactions are essential now let us go to the first topic which is morphology of clinker compounds.

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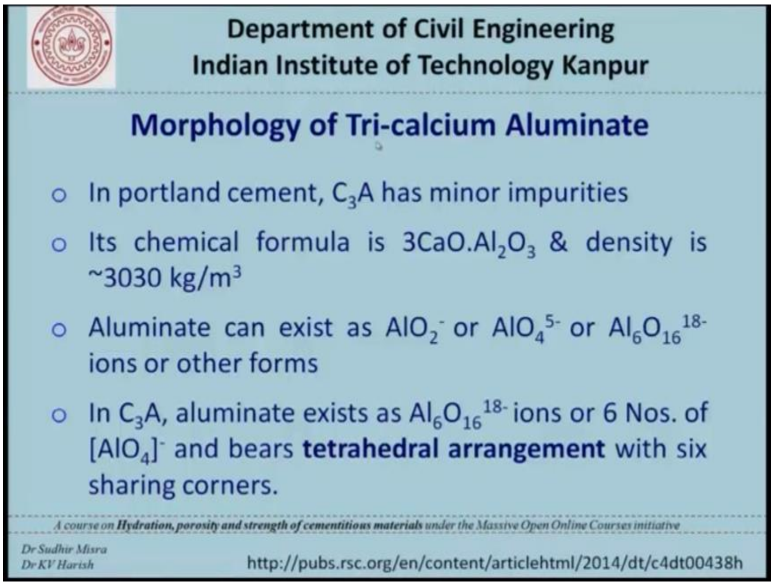

And in the first one we are discussing about tri-calcium aluminate, tri-calcium aluminate referred as C3A has minor impurities and the chemical formula which we have already discussed 3 CaO dot Al2O3 density of tri-calcium aluminate is approximately 30 k g per metre cube aluminate can exist as AlO2 minus or AlO4 5 minus or Al6O16 18 minus ions in most of the cases and in other cases there could be other forms.

However in C3A aluminate exist primarily as Al6O16 18 minus ions this is very important and Al6O16 18 minus ions can also be put up as 6 numbers of AlO4 minus ions and they are basically arranged in a tetrahedral manner which with 6 sharing corners.

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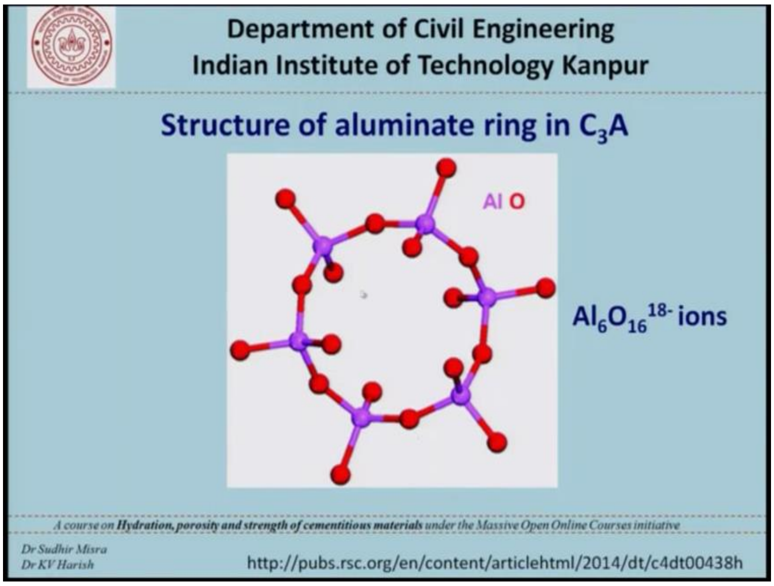

So, the structure of aluminate ring in C3A is shown where you can see that the violet colour one refers to the aluminium ions and o refers to the oxygen ions. So, if you take one single arrangement you see that 4 oxygen ions are connected or bonded to one aluminium ions and what you also see is that there are totally 6 such arrangement and the number of oxygen atoms here is totally 16, but you will have totally 18 ions which means there are 2 balance ions. So, 6 will be in the outer. So, 1, 2, 3, 4, 5, 6 and 6 will be in the inner 7, 8, 9, 10, 11, 12 and another 6 will be bonded to the aluminium ions 13, 14, 15, 16, 17 and 18.

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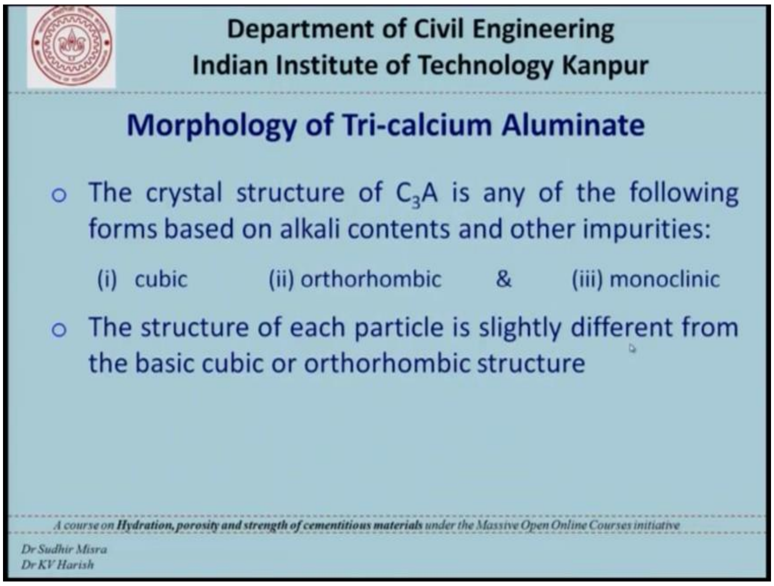

The crystal structure of C3A; it can be any one of the following and it primary depends on the alkali contents and other impurities normally it could exist as cubic structure orthorhombic structure or monoclinic structure, but are in our case it will primarily exist as cubic or orthorhombic.

The structure of each particle is slightly different from the basic cubic or orthorhombic primarily because of impurities.

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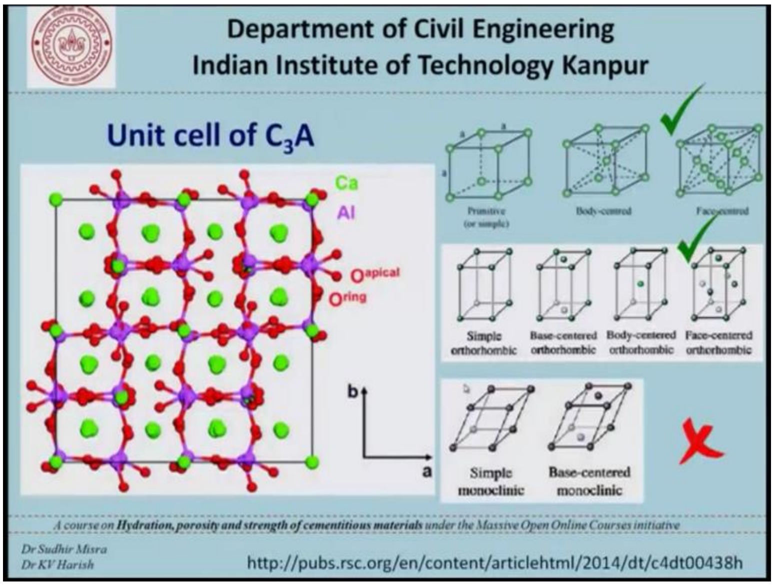

So, the figure shows a unit cell of C3A and at right you see different arrangements cell arrangements the first set of figures give the cubic arrangement the second set of figures give the orthorhombic arrangement and the third set of figures give the monoclinic arrangement and what you have to understand is the arrangement is primarily cubic or orthorhombic usually monoclinic does not exist and what you see in the left side is the arrangement of ions within one unit cell and where the green colour represents the calcium ions. So, you basically have 3 calcium atoms club together and surrounding that you have the aluminium and the oxygen atoms.

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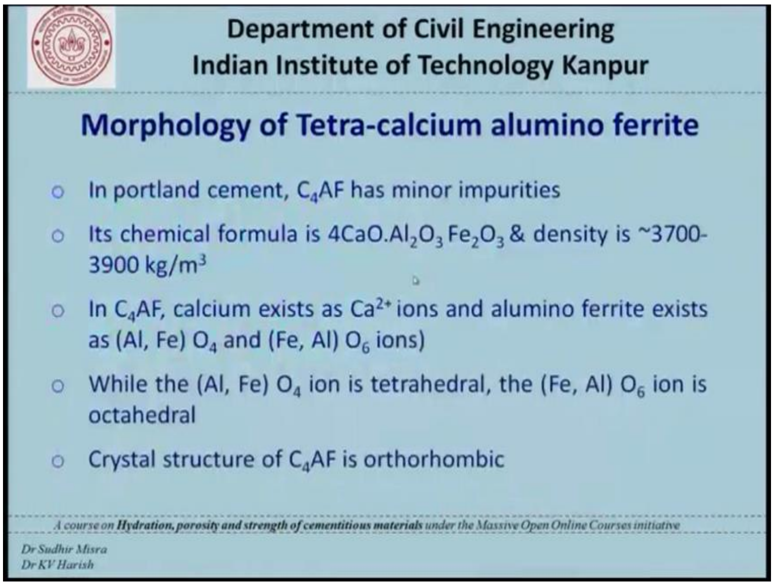

now we go to the second one which is tetra-calcium, alumino-ferrite and like C3A, C4AF also has minor impurities and the chemical formula is given and the density of a tetra calcium alumino-ferrite is approximately 3,700 to 3,900 k g per metre cube in C4A f calcium exist as calcium 2 plus ions and alumino-ferrite exist either as Al or FeO4 ions or FeAlO6 ions this is very important and AlFeO4 ion is tetrahedral in nature and FeAlO6 ion is octahedral in nature we will not discuss more about the crystal structure because it is still under research all that you have to know is that the crystal structure of C4A f is orthorhombic.

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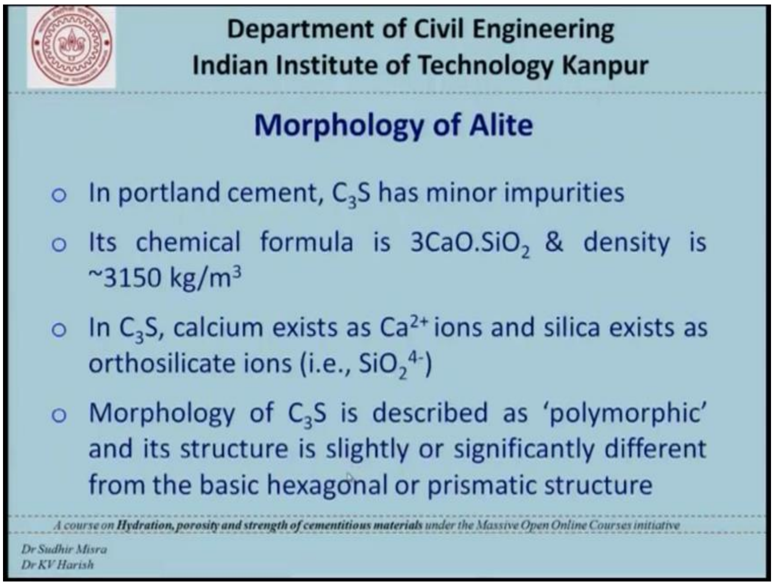

The third one is morphology of alite again in alite also has minor impurities and the chemical formula is 3CaO dot SiO2 and the density approximately is 3150 k g per metre cube in C3S calcium exist as CA2 plus ions and the silica exist as orthosilicate ions and formula is SiO2 4 minus. So, SiO2 4 minus is called orthosilicate ions very important morphology OFC3S is described as polymorphic which means you have different morphologies and its structure is slightly or significantly different from the basic hexagonal or prismatic structure.

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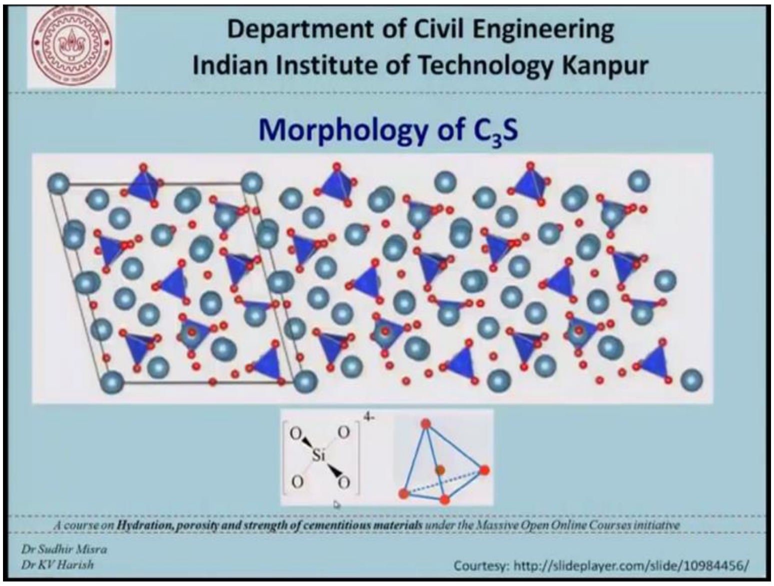

So, morphology details oFC3S is provided where the ortho silicate ions is shown here and you have the silicon atoms bonded to 4 oxygen atoms in a tetrahedral manner and in the main structure you will also you will not just see this you will also see the tetrahedral arrangement along with the calcium ions bonded to each other.

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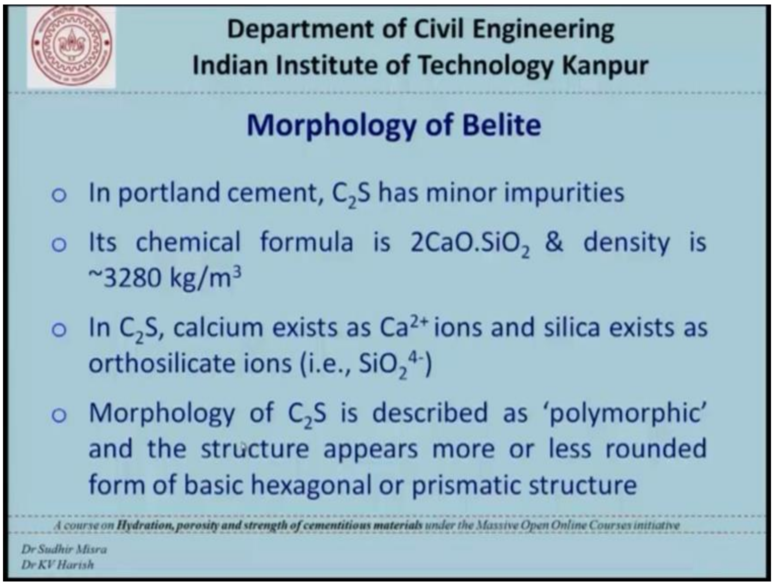

Now, the fourth one is belite, belite also has minor impurities and chemical formula is 2CaO dot SiO2 and the density is approximately 3280 k g per metre cube and similar to C3S here also calcium exist as CA2 plus ions and the silica exist as orthosilicate ions. So, SiO2 4 minus and here also the morphology is described as polymorphic which means you have different morphologies and the structure appears more or less around it from the basic hexagonal or prismatic structure.

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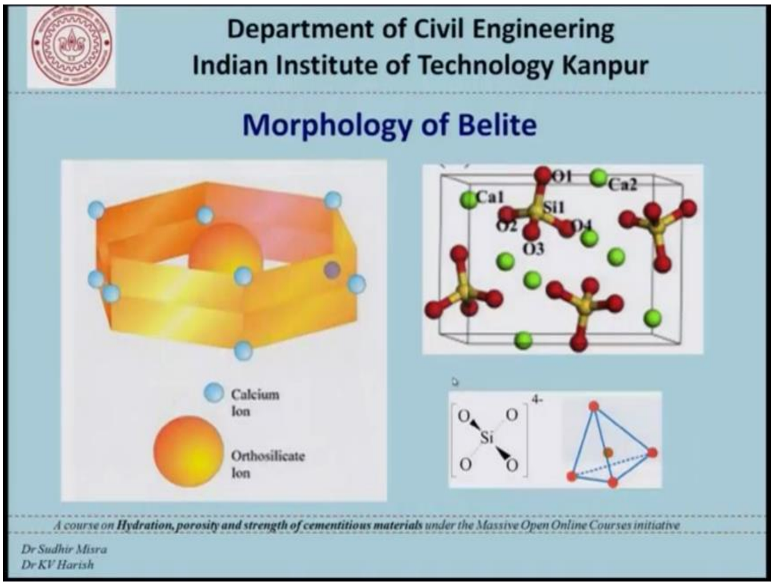

So, some morphological details of belite is given at the left side the structural arrangement is given in the right side you have the unit cell arrangement and what you can see is that one silicon atom is attached to 4 oxygen atom and you also have calcium surrounding each of the orthosilicate arrangements.

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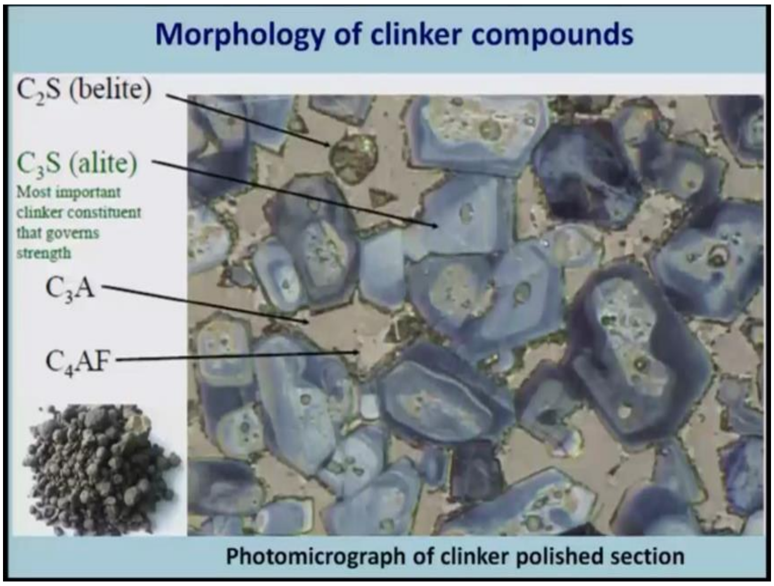

Now, if you see a photo micrograph of the clinker compound essentially it will look like this where the entire figure is having some shades of grey. So, if you have a closer look at it you have the C3S or alite; C2S or belite and C3S is seen as hexagonal prisms more or less and C2S which would also beat hexagonal, but the surface is likely rounded and the colour there is substantial difference in the sense that C3S are largely dark grey to black in colour and C2S is largely dark grey little more darker than C3S.

In a case of C3A and C4AF, they are lightish grey, but compared to C3A C4A f is lighter in this figure largely you will see hexagonal prisms mostly primary because C3S content is much higher compared to others now the next topic is reactivity of clinker compounds.

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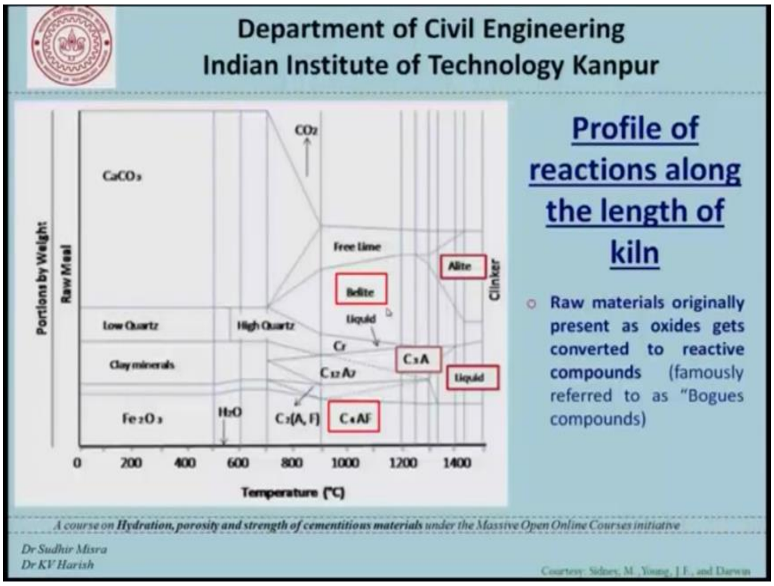

Now, when we talk about reactivity we will have to revisit one of the slide which we have already seen in the previous lecture under Portland cement where the profile of reactions along the length of the kiln is provided and what we have seen is that the raw materials originally present as oxides gets converted to reactive compounds primary active compounds are called as Bogues compounds. So, what you see in this figure is primarily the formation of C4AF belite, C3A alite and the liquid portion of the entire meant.

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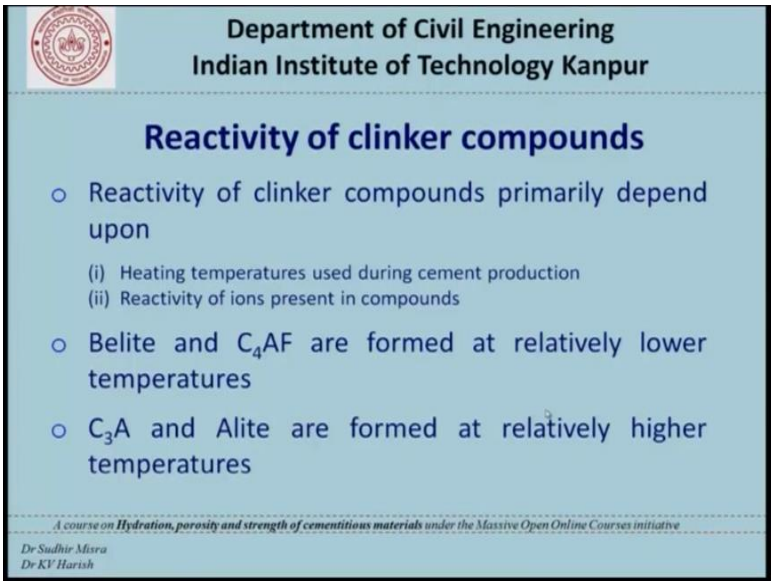

So, reactivity of clinker compounds reactivity of clinker compounds primarily depend upon heating temperatures used during cement production reactivity of ions present in the compounds.

So, belite and C4A f are formed at relatively lower temperatures if you have a closer look at the previous image what you find is that aluminium ferrite which C4AF and belite are generally formed at lower temperatures compared to C3A and alite.

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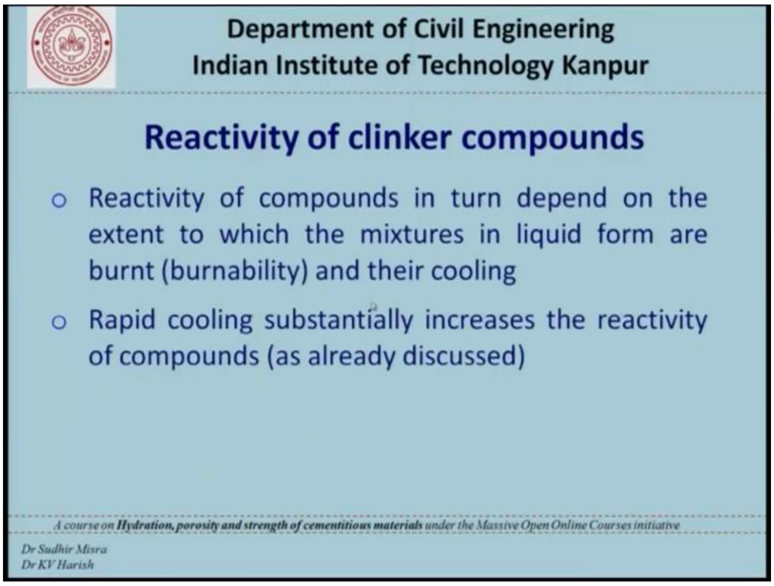

The reactivity of compounds intern depends upon the extent to which the mixtures in liquid form are burnt and how they are cooled. So, the burn ability and cooling part is extremely important when were discussing about reactivity of clinker compounds as we have already seen in the previous lecture under Portland cement rapid cooling substantially is used instead of slow cooling because it increases the reactivity of compounds.

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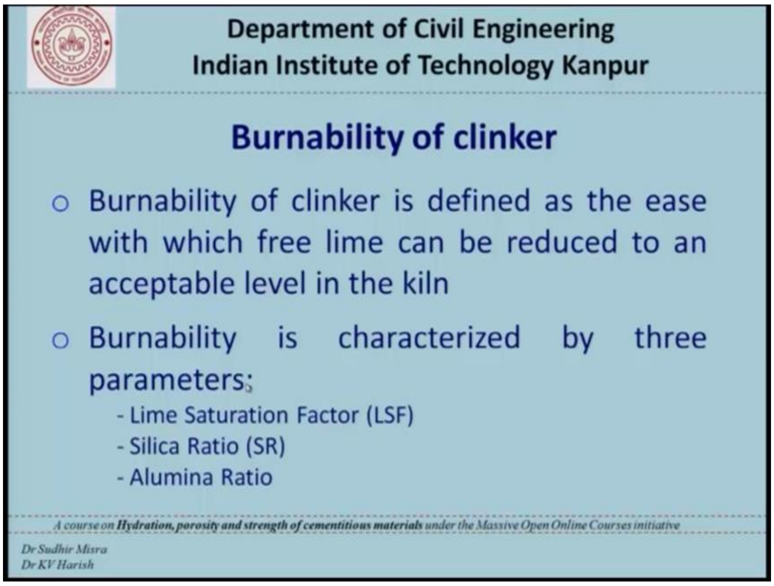

Now, the second part is burn ability and burn ability of clinker is defined as the ease with which free lime can be reduced to an acceptable level in the kiln. So, again free lime just to remind you that the free lime in Portland cement is limited to 0.8 percent primarily because we want lime to be properly burnt in the kiln. So, burn ability is characterized by 3 parameters very important parameters from the cement production standpoint number one lime saturation factor and it is referred as LSF silica ratio referred as SR and you also have the third one alumina ratio and let us see the significance of these 3 factors.

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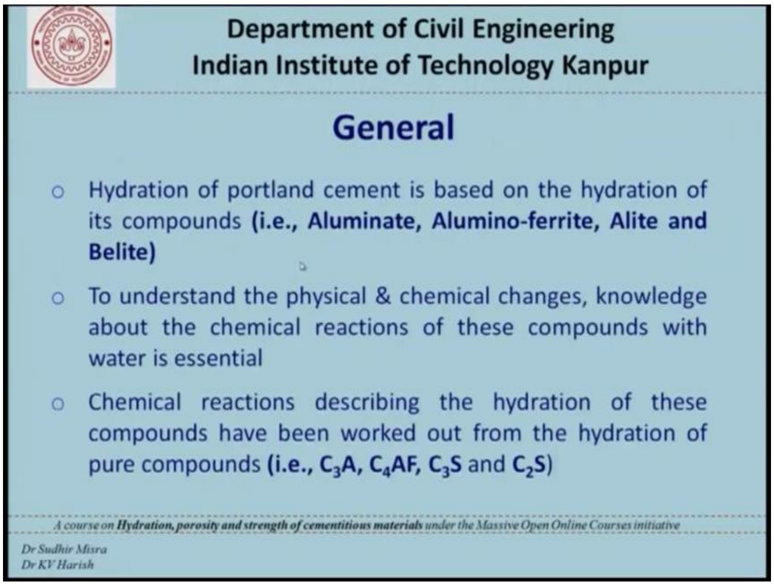

Now, first of all how do you calculate these factors lime saturation factor is calculated by using these 2 formulas depending upon the percentage of a divided by f or aluminate to ferrite ratio and silica ratio is determined by using this formula and alumina to ferrite ratio determine directly from this formula what you see in the first set of formulas is that if A by F ratio is greater than or equal to 0.64 then LFS is given by CaO divided by 2.8 into silicon dioxide plus 1.65 into aluminium oxide plus 0.35 into iron oxide.

Likewise if A by F is lower than or equal to 0.64 then LSF is given by this formula CaO divided by 2.8 times SiO2 plus 1.1 times Al2O3 plus 0.7 times Fe2O3. So, this formulas basically give direct conversion of oxides to these factors LSF, SR and A by F. So, silica ratio given by SiO2 divided by Al2O3 plus Fe2O3 and alumina to iron ratio is given by Al2O3 divided by Fe2O3. So, if you know the values of the lime saturation factor silica ratio and alumina to iron ratio we will get some idea about the burn ability of clinker.

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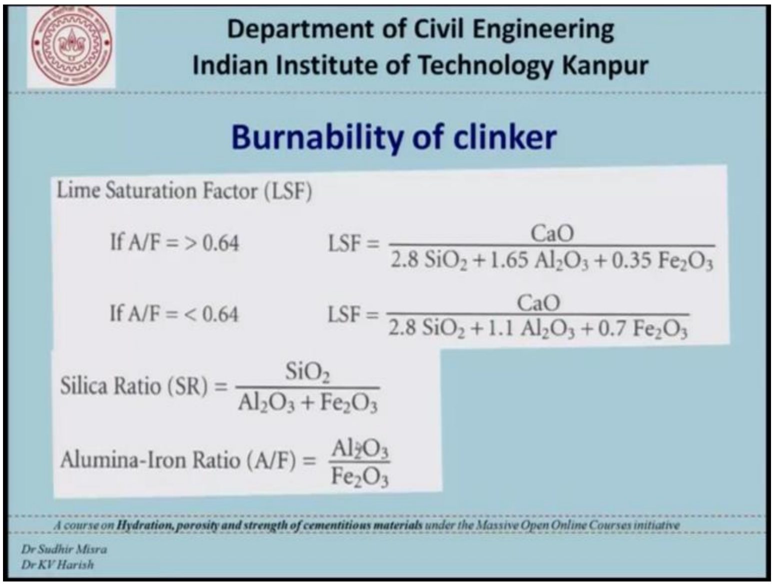

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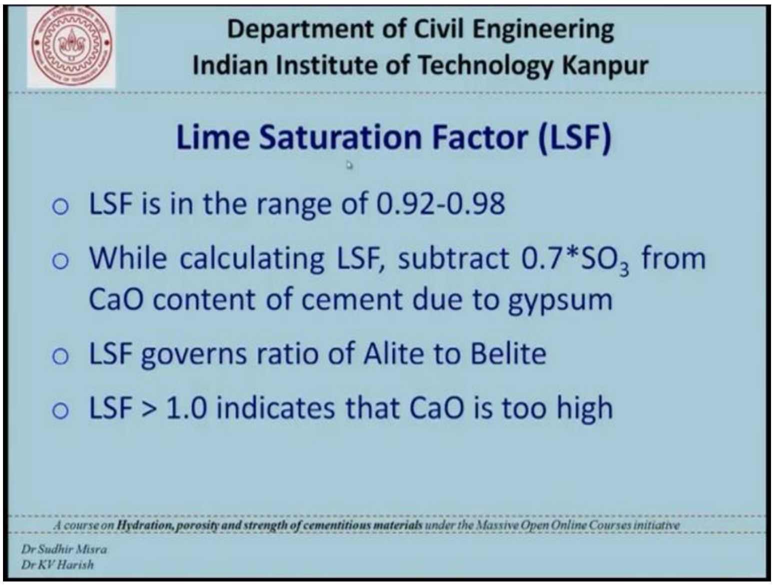

So, what is burn ability as we already seen it is defined as the ease with which free lime can be reduced to an acceptable level in the kiln. Now the significance of lime saturation factor and some information about LSF is shown lime saturation factor at the at the plant level is fixed to be in the range of 0.92 to 0.98 while calculating lime saturation factor we need to subtract 0.7 into SO3 from the calcium content of cement and this is arising primary from gypsum what does it mean.

If you see the formula here we are using calcium oxide as one of the parameters to find out lime saturation factor remember that this calcium oxide should not be from gypsum and for this purpose we have to subtract 0.7 into SO3 which is the molar equivalent for the calcium oxide that is present in gypsum. So, if you subtract that from the original calcium oxide then we can find out the LSF; LSF governs ratio of alite to belite, this is very important primarily because if at the plant level we find that a particular cement or type of cement or a particular batch of cement is not giving desired properties and if we have to adjust the chemical composition then this alite to belite ratio becomes very important now if LSF is greater than one that indicates that the calcium oxide is too high remember that it is not that we generally prefer higher calcium oxide all the compounds should be present at optimal amounts.

So, if you have higher amounts of calcium oxide we have to adjust something else to bring this factor within the range of 0.92 to 0.98.

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Now, the second one is silica ratio and this has to be in the range of 2 to 3 and the importance of silica ratio is that it governs the proportion of silicate faces a little different from what we have seen here where LSF indicates just the calcium oxide whether it is too high or low whereas, here it indicates the proportion of silicate faces and s r increase indicates that the liquid proportions are generally lower which in turn signifies that the clinker is very difficult to get burnt.

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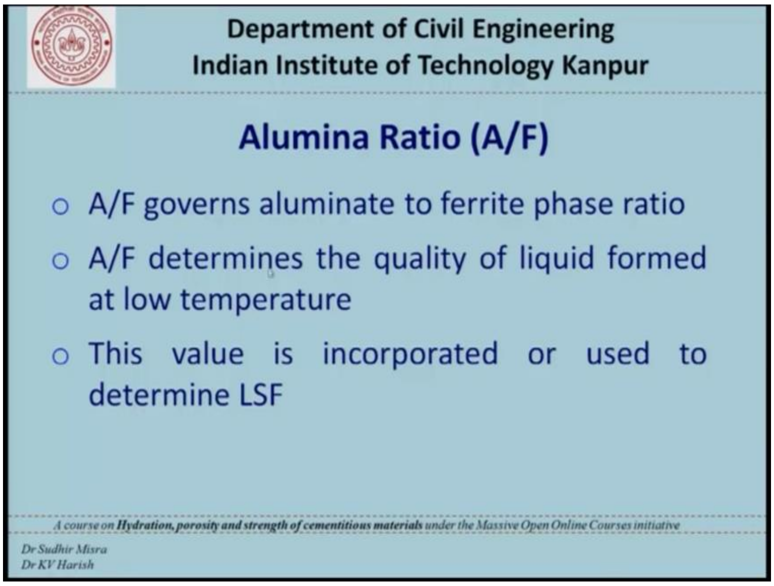

The third important factor is alumina ratio A by F and this governs primarily the aluminate to ferrite phase ratio and this determines the quality of liquid formed at low temperature this value is incorporated or used to determine LSF also.

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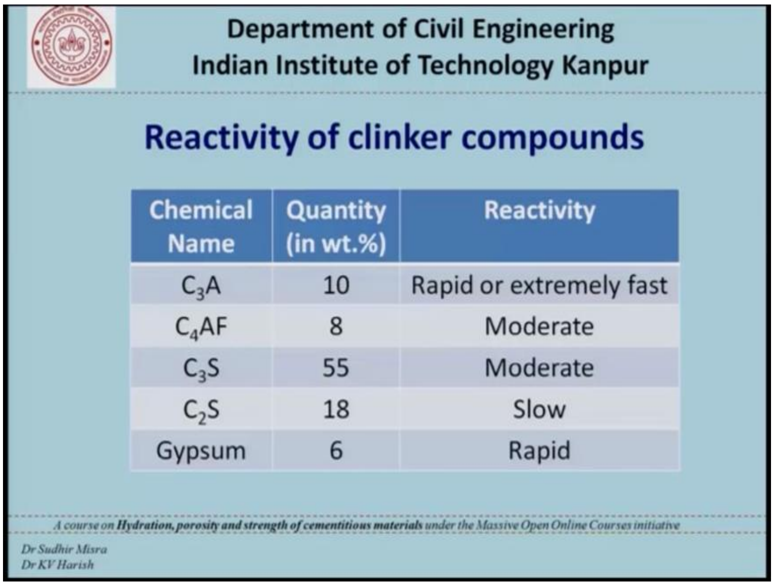

Now, in general we should also know that under the reactivity of clinker compounds which compound is more reactive which compound is less reactive. So, this table helps you in that. So, here you find 3 columns in the left side you have the compounds present in cement in the middle column you have the quantities and in the right column you have approximately the reactivity. So, C3A remember that is approximately 10 percentage in the entire Portland cement composition and the reactivity is explained as rapid or extremely fast in a case of C4A f it is approximately 8 percent and the reactivity is explained as moderate and in the case oFC3S approximately explained as moderate and C2S approximately 18 percent and reactivity is explained as slow and gypsum approximately 6 percent remember that the percentage of gypsum is always taken in proportion with C3A the reactivity is rapid similar to C3A.

So, with this the reactivity of clinker compound gets over we will now get on to the chemical reactions in Portland cement.

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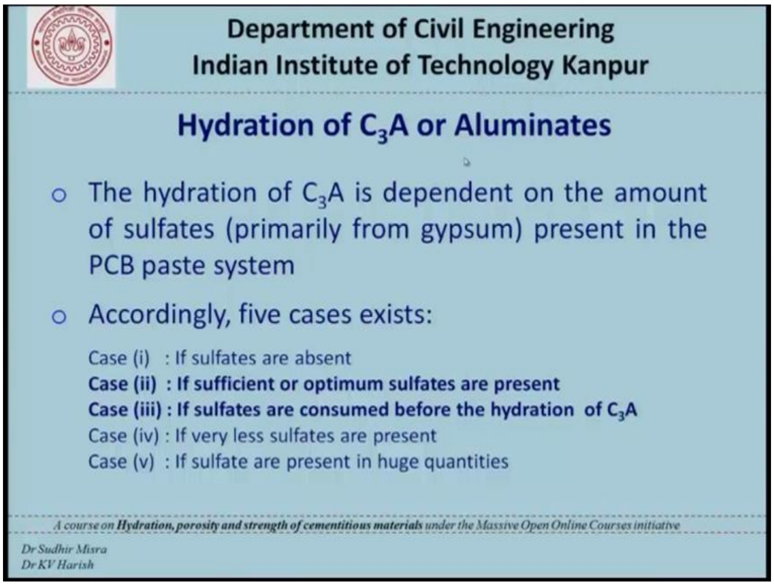

So, there are primarily 4 reactions that take place. So, the first one tri-calcium aluminate the hydration of C3A is dependent on the amount of sulphates primarily from gypsum present in the Portland cement based paste system accordingly you have 5 different cases which exist and each of the 5 cases are extremely important and hence it is requested that please pay attention now case one if the sulphates are absent which means what we are creating a situation that assume that gypsum is completely not present.

So, in that case how does tri-calcium aluminate behave or what is the reaction with water in the second case if sufficient or optimum sulphates are present in the third case if sulphates are consumed before the hydration of C3A, in fourth case if very less sulphates are present remember it is not completely absent sulphates not completely absent, but you have less sulphates compared to eliminates and in the fifth case if sulphates are present in huge quantities compared to aluminates. So, these 5 cases you have 5 different reactions. So, each of these reactions are extremely important and primarily this defines the setting time of cement.

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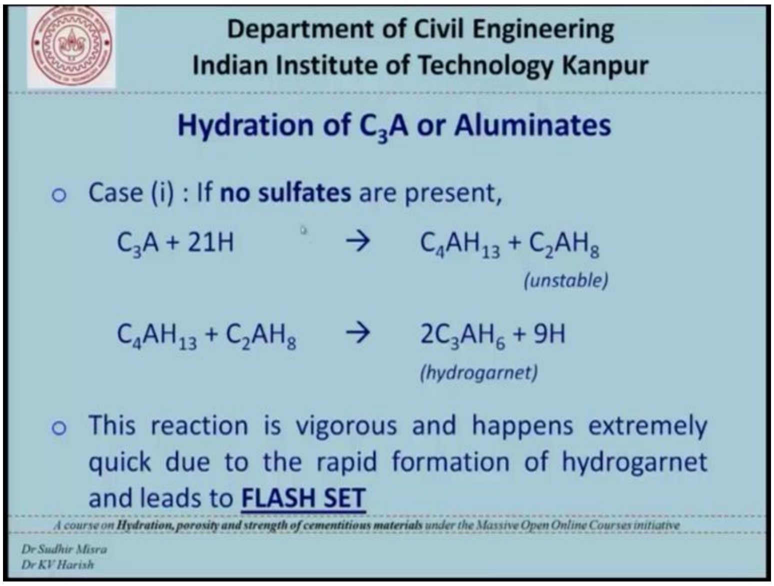

So, let us see the first case if no sulphates are present the tri-calcium aluminate reacts with water remember that here H refers to H2O to form C4A H13 which is generally described as calcium aluminate hydrates in addition to that you also have another form of calcium aluminate hydrate C2aHO which is unstable and hence this immediately converts through a compound called hydrogarnet the chemical formula is C3AH6 and you have some water now the problem with this equation is that the hydrogarnet is extremely hard material and the entire reaction is extremely quick. So, this reaction is vigorous and happens extremely quick due to the rapid formation of hydrogarnet and this leads to a condition called as flash set.

Heat evolved at the stage is extremely high and hence the terminology flash set comes along with it and at a later stage when we see about setting and hydration we will see what happens to this flash set.

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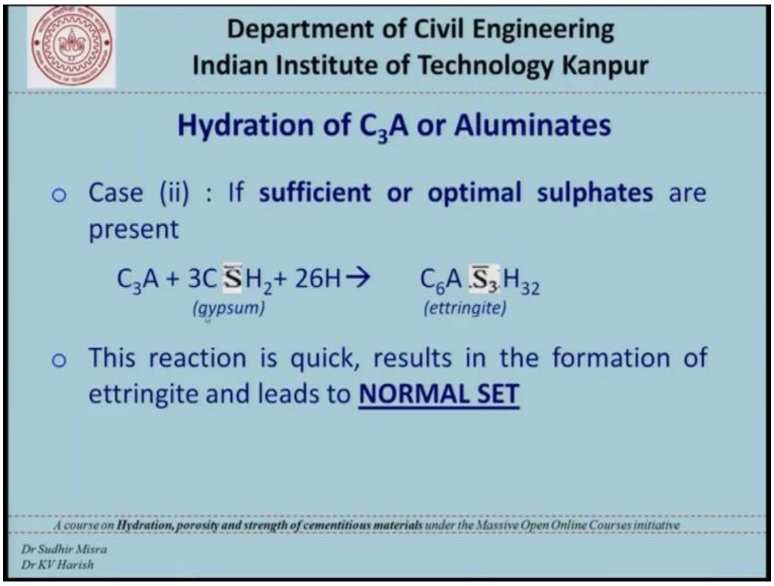

In the second case we have a situation where amounts of sulphates and gypsum are optimal in such cases C3A reacts with gypsum and here gypsum is referred as 3CS bar H2 plus water a compound called ettringite or ettringite C6AS3 bar H 32, this reaction is also quick, but not that quicker compared to the previous case and results in the formation of ettringite and finally, we have the condition called normal set remember that normal set is obtained only when you have sufficient or optimal sulphates when we say normal set the Portland cement paste typically takes 2 to 4 hours to achieve initial setting time now the third case is when sulphates are consumed before the hydration of C3A.

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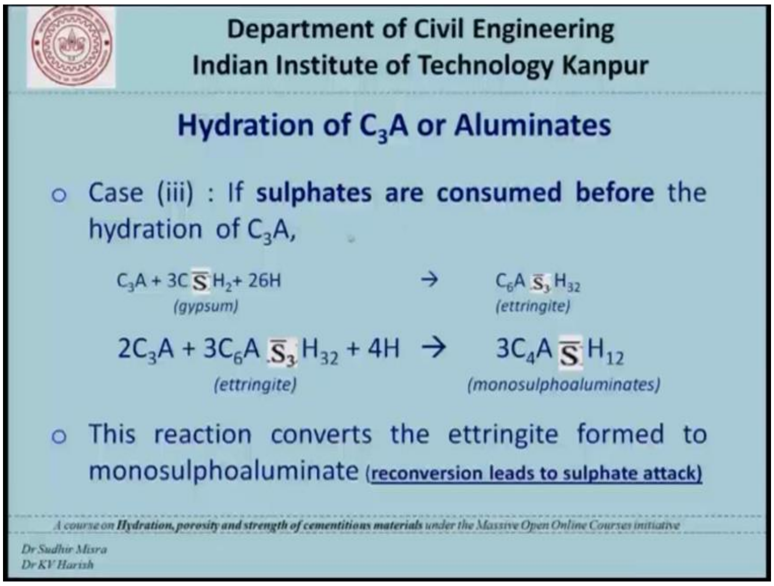

So, what are you mean by that assume that we have either sufficient sulphates or we have less sulphates or we have more sulphates whatever may be the case if sulphates are consumed before the hydration of C3A which means you have these reactions C3A plus gypsum plus water giving ettringite which is taken from the previous case and now that you have those ettringite available and C3A is also present in such cases C3A reacts with this ettringite in the presence of water to give another compound called monosulphoaluminates which is denoted by C4A s bar H 12 this is very very important.

When we discuss about sulphate attack we will see that later this reaction converts the ettringite form to monosulphoaluminates usually we do not prefer this compound and we prefer the aluminates the hydrated aluminates to be in the form of ettringite the formation of monosulphoaluminates as such does not cause any deterioration, but at a later stage if there are more sulphates or external sulphates coming from outside then it creates a cracking in concrete and those are primarily or popularly referred as sulphate attack which we will deal at a later stage.

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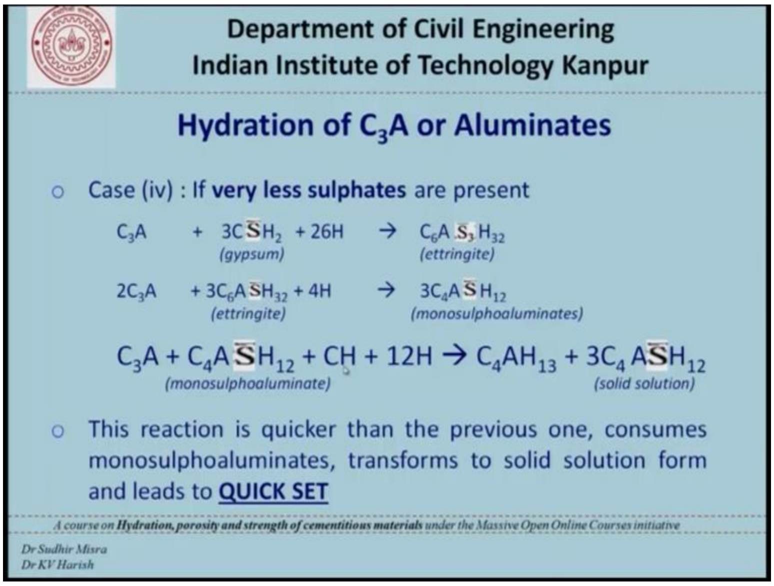

Now, moving on to the fourth case if very less sulphates are present then C3A reacts with gypsum plus water which would have formed some ettringite some portion of C3A if ettringite are available they will form monosulphoaluminates like what we have seen in the previous main equations this one and this one. So, those 2 things happen, but if very less sulphates are present C3A reacts with monosulphoaluminates that is formed along with calcium hydroxide and water remember the mere presence of calcium hydroxide is sufficient in order to trigger this reaction.

So, you will have C4A H 13 plus C4AS bar H 12 and both of them will be in the form of solid solution remember that this compound is again monosulphoaluminates the difference between this and this is that this will be in the form of solid solution this will be only in the form of hydrated solid this reaction is quicker than the previous one and consumes monosulphoaluminates and transforms to solid solution. And many times referred as quick set remember that in the hydration of Portland cement based paste systems we usually target only at normal set we do not want flash set we do not want quick set and we also do not want the next case which I will discuss right away.

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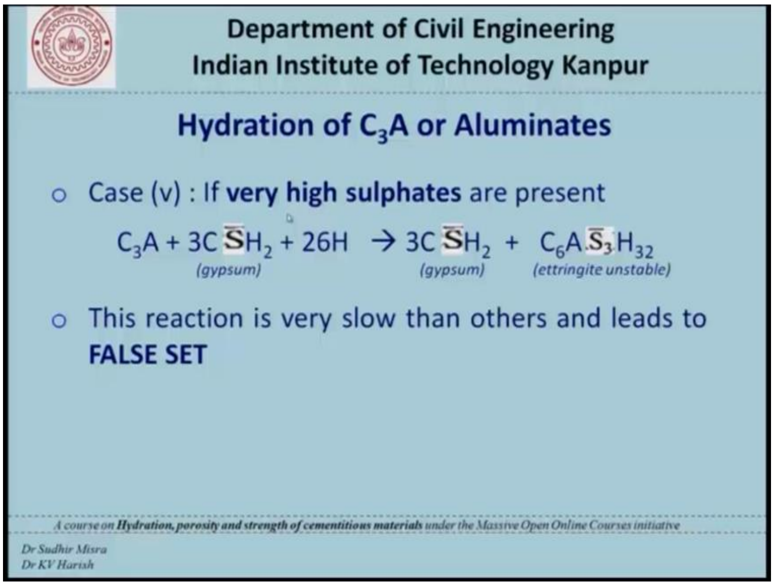

In the fifth case if very high sulphates are present tri-calcium aluminate reacts with gypsum to form in the presence of water to form gypsum and ettringite, but remember that since substantial amount of gypsum is present the ettringite will not be stable. So, in this case the Portland cement based system will not sit at all and it is many times referred as fall set. So, as I already mentioned in Portland cement based system we do not prefer flash set we do not prefer quick set we do not prefer fall set will only prefer normal set now coming onto the second set of hydration reactions.

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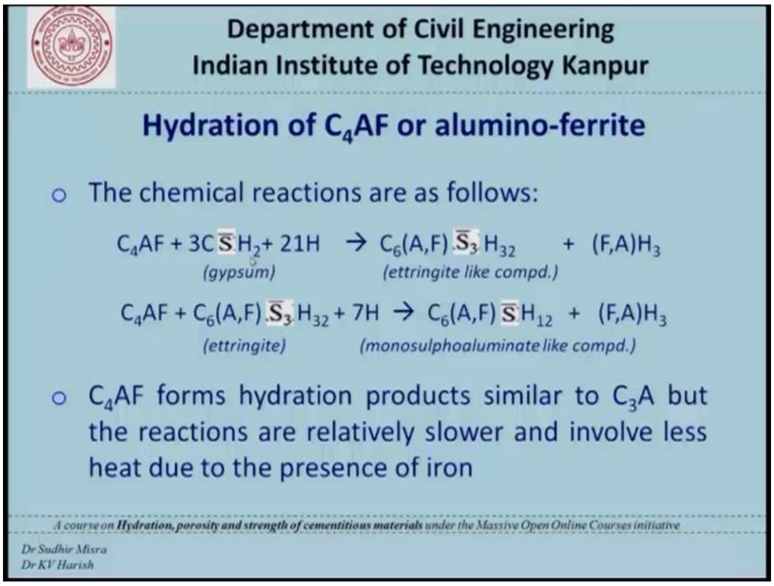

Where tetra-calcium alumino-ferrite reacts with gypsum in the presence of water to form this compound and if you carefully look into the compound you see that instead of a; which you find in aluminates you find AF. So, this compound is similar to ettringite accept that instead of a you have AF and you also have some aluminate ferrite hydrates and likewise when tetra calcium aluminate ferrite reacts with ettringite in the presence of water you get monosulphoaluminates except that instead of a you have a f and you have iron aluminate hydrate C4AF forms hydration products similar to C3A, but the reactions are relatively slower this is extremely important of the presence of iron the presence of f in these equations helps a lot to reduce the rate of reactivity.

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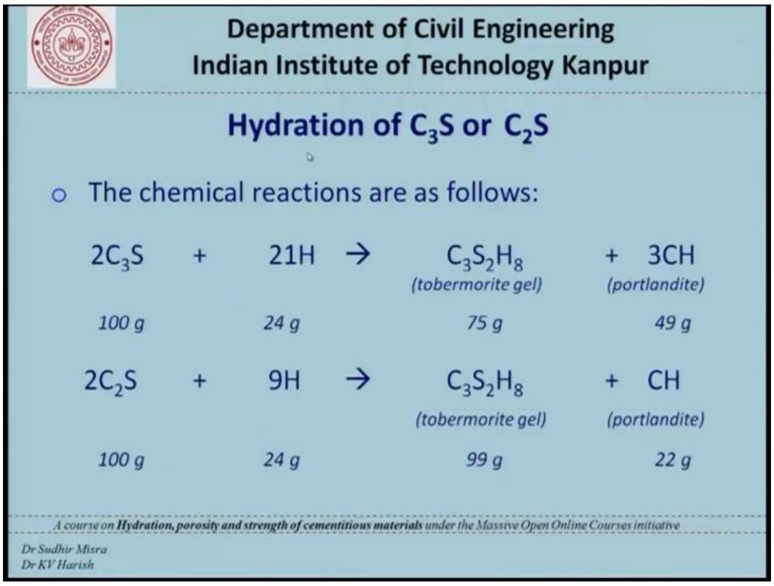

In this slide we see the hydration of tri-calcium silicate and hydration of di-calcium silicate together the chemical reactions are as follows tri-calcium silicate reacts with water to form calcium silicate hydrate gel which is many times referred to as tobermorite gel or CSH gel and you also have calcium hydroxide which is many times called as Portlandite likewise C2S reacts with water and form the same compound tobermorite gel and calcium hydroxide. But there is a difference between the hydration oFC3S and C2S in the case of hydration oFC3S the amount of calcium silicate hydrate gel formed is much lower compared to the calcium silicate hydrate gel formed from the hydration of C2S.

So, here in this case if you take 100 grams OFC3S 24 grams of water you result in 70 5 grams of CSH gel and 49 grams of calcium hydroxide where as in C2S 100 grams plus 24 grams gives 99 grams which is much higher than 75 grams plus 22 grams which is much lower than 49 grams.

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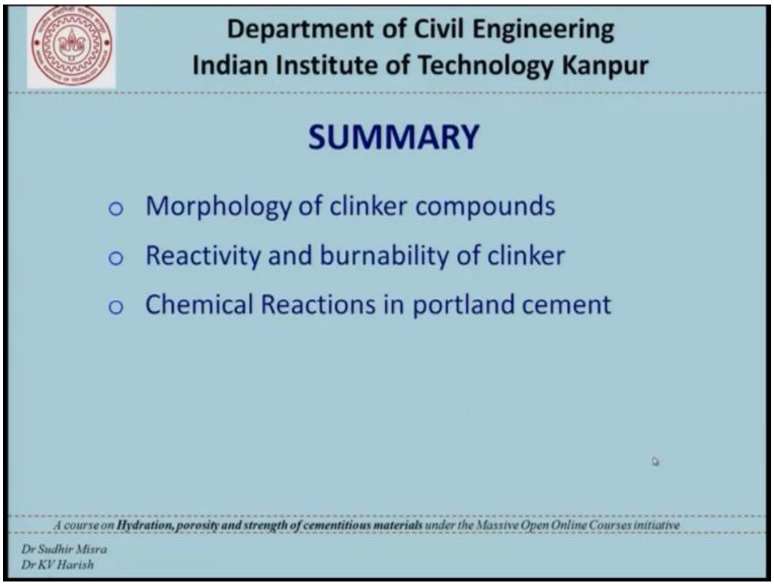

So, in summary we have seen morphology of clinker compounds the reactivity and burn ability and the importance of the reactivity and burn ability of clinker and some of the most famous reactions chemical reactions in Portland cement with is this lecture gets completed.

Thank you.