Hydration, Porosity and Strength of Cementitious Materials
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Lecture - 04
Portland Cement

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

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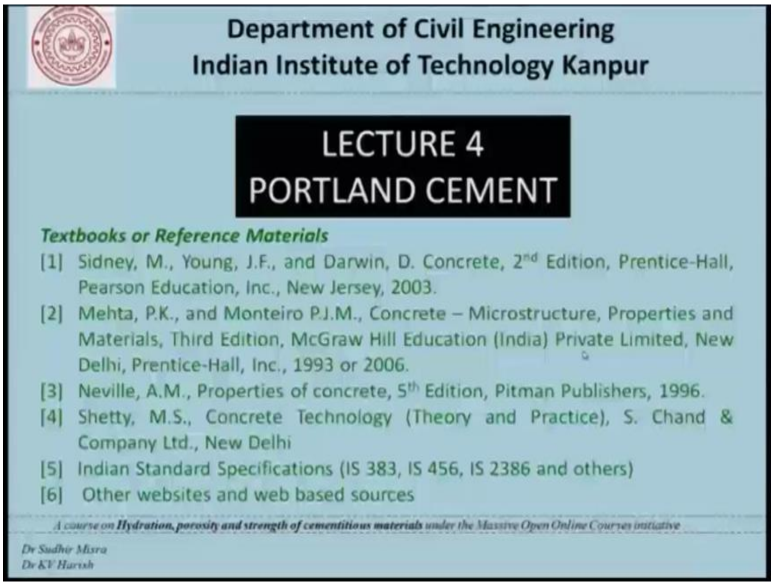

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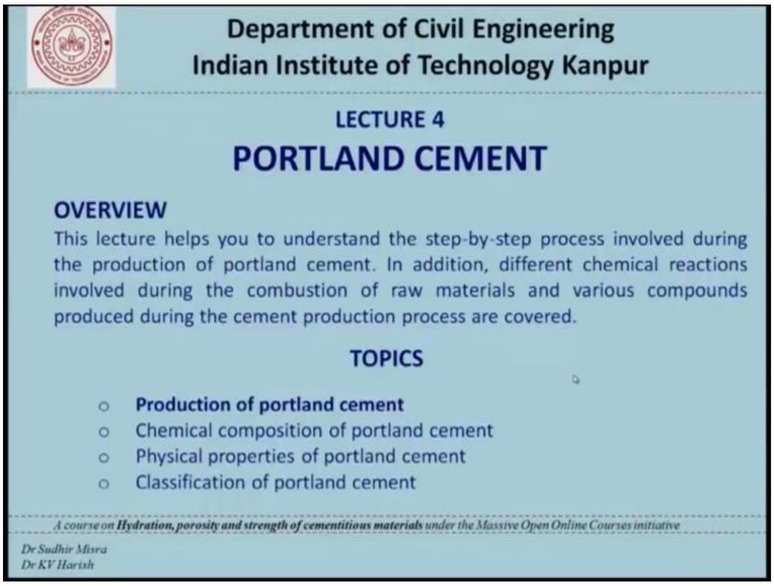

We will see lecture 4; Portland cement, the textbook and reference material for this course is provided. The overview of the course is as follows; this lecture helps you to understand the step by step process involved during the production of Portland cement, in addition the different chemical reactions involved during the combustion of raw materials and various compounds produced during the cement production process are covered. So, the primary topic in this lecture is production of Portland cement.

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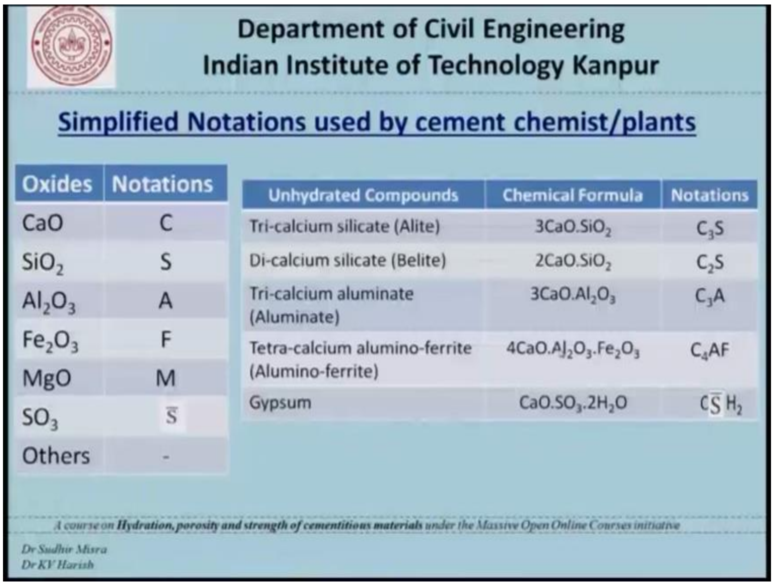

Portland cement is a very commonly used material and concrete is a very important product from Portland cement, Portland cement is produced from several raw materials primarily limestone, clay and other materials. Portland cement consist of oxides and some compounds, the oxides are shown in the left side, some important oxides are calcium oxide, silicon dioxide, aluminium oxide, iron oxide, magnesium oxide, sulphur trioxide and others. Some simplified notations that are used are as follows; the oxides namely calcium oxide will be abbreviated as C, silicon dioxide as S, aluminium oxide as A, iron oxide as F, magnesium oxide as M and sulphur trioxide as S bar.

You also have compounds present in Portland cement and remember that oxides are does not exists as oxides in Portland cement, rather they exist as compounds. There are 4 main compounds in Portland cement namely tri-calcium silicate and many times tri-calcium silicate is also called as Alite, second one is Di-calcium silicate; many times it is also referred as Belite, third one is tri-calcium aluminate; many times generally referred as aluminate the fourth one is tetra-calcium alumino-ferrite; many times referred as alumino-ferrite, in addition to the 4 compounds, we also have gypsum the role of gypsum and other things will be explained at a later stage.

Now, tri-calcium silicate or Alite the chemical formula is 3 CaO dot SiO2 and in simplified notations, we call it as C3S. Likewise Di-calcium silicate or Belite; the formula is 2CaO dot SiO2 and it is many times denoted as C2S. Tri-calcium aluminate 3CaO dot Al2O3; C3A and tetra calcium alumino-ferrite 4CaO dot Al2O3 dot Fe2O3, referred as C4AF and gypsum which has a chemical formula of CaO dot SO3 dot 2H2O is many times abbreviated as C S bar, now these notations C3S, C2S, C3A, C4AF and CS bar they are generally called as cement chemist notations.

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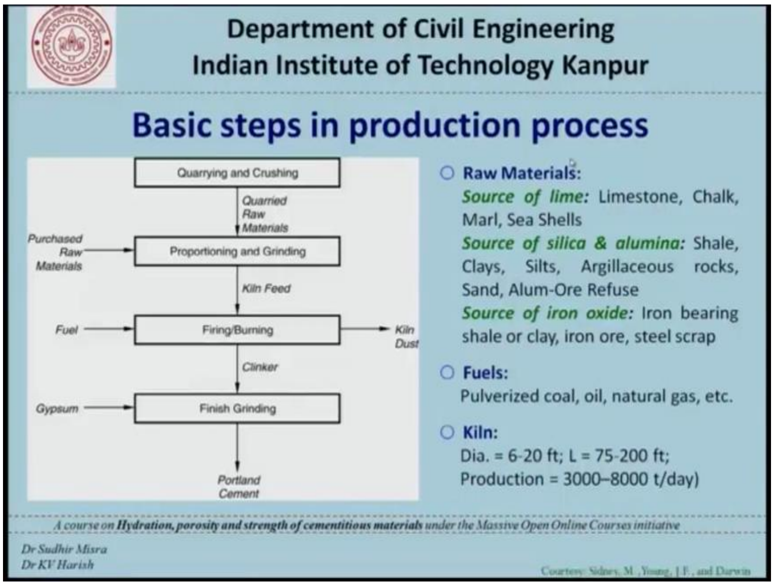

Now, the basic steps involved in the production process are as follows, there are 5 different process, one is quarrying and crushing, the second one is proportioning and grinding third one is firing or burning and fourth one is finish grinding and finally, what you get is the Portland cement. So, the raw materials in the Portland cement could be from sources such as lime silica and alumina and iron oxides sources of lime maybe limestone chalk marl sea shells etcetera most popularly known sources of lime is limestone sources of silica and alumina includes shale clays silts argillaceous rocks and other sources of iron oxide includes iron bearing shale or clay iron oxide and some steel scraps. So, these raw materials are initially quarried and they undergo crushing process and we will see all these steps at a later stage in detail.

Now, during the burning process fuels are used and the primarily pulverised coal oil and natural gas are popularly used in addition the burning process takes place in a rotary cube many times referred as a kiln. And the typical dimensions of the kiln are also provided for information purpose the diameter of the kiln ranges from 6 to 20 feet the length of the kiln ranges from 75 to 200 feet the production of the plant typically ranges from 3,000 to 8,000 ton per day which means 3,000 to 8,000 tonnes of cement is produced per day.

Now, in the steps involved what you see is the materials are basically quarried the raw materials are basically quarried and then they are proportioned and taken to a kiln for firing and burning and then whatever comes out of the kiln is called as a clinker and then further gypsum is added to get Portland cement.

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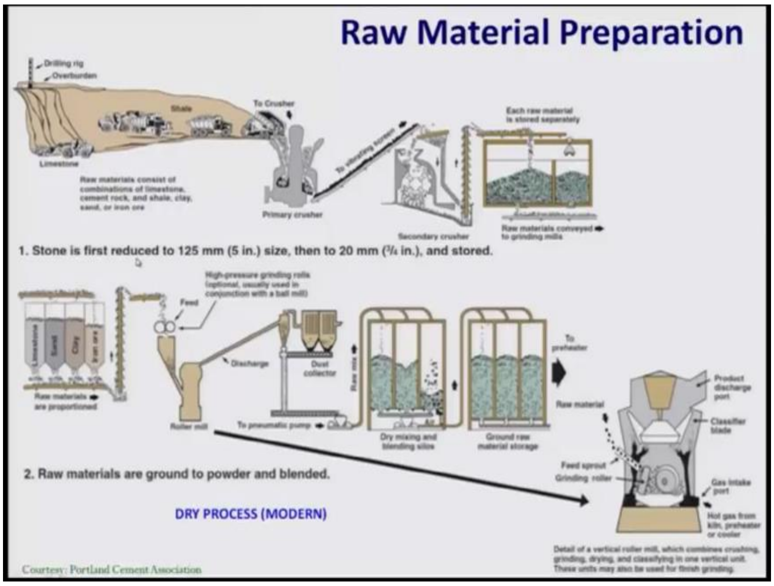

Now, let us see the step by step process, in the first step; the stone is first reduced to one 25 mm size and then to 20 mm size and then stored. So, in the figure what you see is this is the quarrying process where sometimes we may have to drill if the sources of rocks are very hard we have to drill it or sometimes we have to blast it and finally, dump trucks carry all these material and put everything in a primary crusher the primary crusher reduces the bigger particles to smaller particles and finally, it will take it to a secondary crusher for further reduction of particle size and again the secondary crusher reduces to about twenty mm size and the entire material is stored.

The materials are stored separately from different sources. So, as you can see in the next step raw materials are ground to powder and blended. So, you can see that the raw materials are separately kept in silos and appropriate proportioning takes place and then finally, it goes to a roller mill where the materials together are ground to a fine powder and then during this process you may have substantial amount of dust that is formed. So, there is a dust collector and the remainder of the material goes for the mixing process.

Now, in the recent days die mixing is preferred which means we mix all the materials in the dry state which also means that no water is added to the entire mixture in the previous days wet process is used where the entire mixture is added with water converted into a slurry and then mixed well and then taken to the kiln for further burning dry process and wet process has their own advantages and disadvantages.

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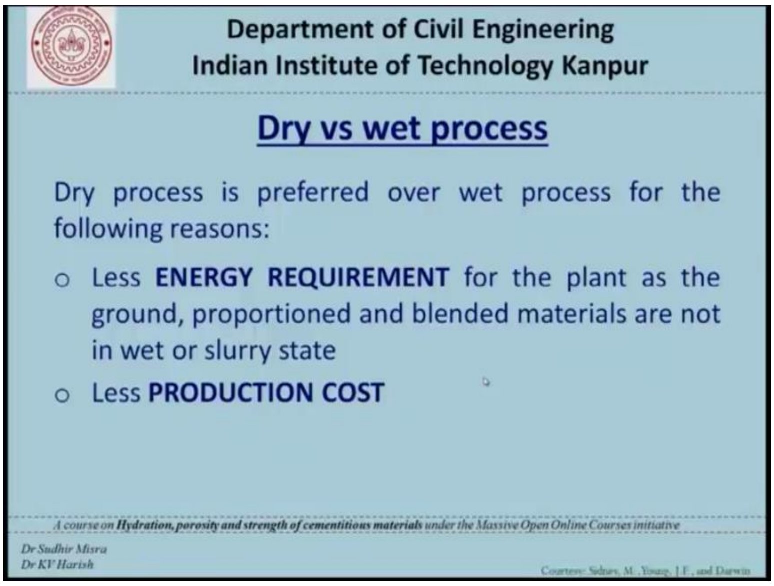

So, dry process is preferred over wet process for the following reasons in dry process the energy that is required is much less for the plant as the ground proportion and blended materials are not in the wet or slurry state in addition in the dry process the production cost is very low.

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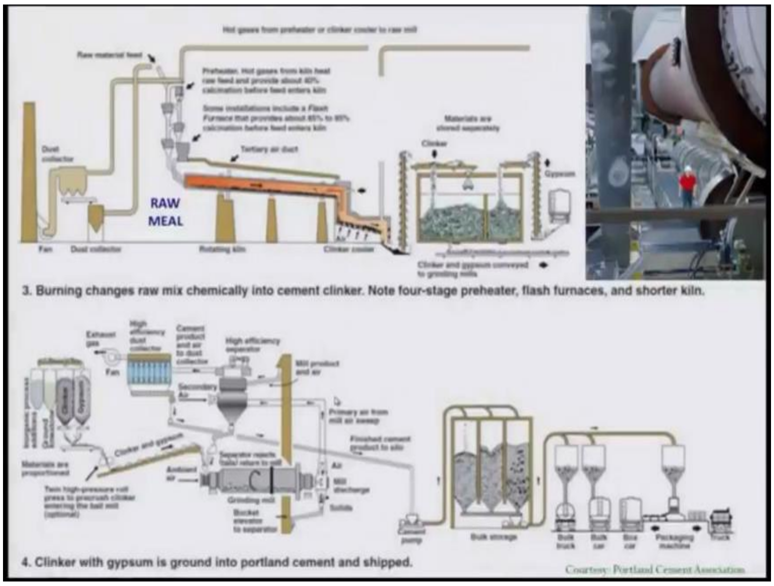

The third step involves burning changes raw mix chemically into cement clinker note fourth stage pre heater flash furnaces and shorter kilns. So, what you find is that the raw material that which is proportioned previously is fed into a kiln; kiln is a tube which contains refractory phases because the temperature of the kiln usually varies from room temperature to about 1,500 degree Celsius and hence the refractory phases of the kiln provide essential properties for the kiln to withstand such high temperatures.

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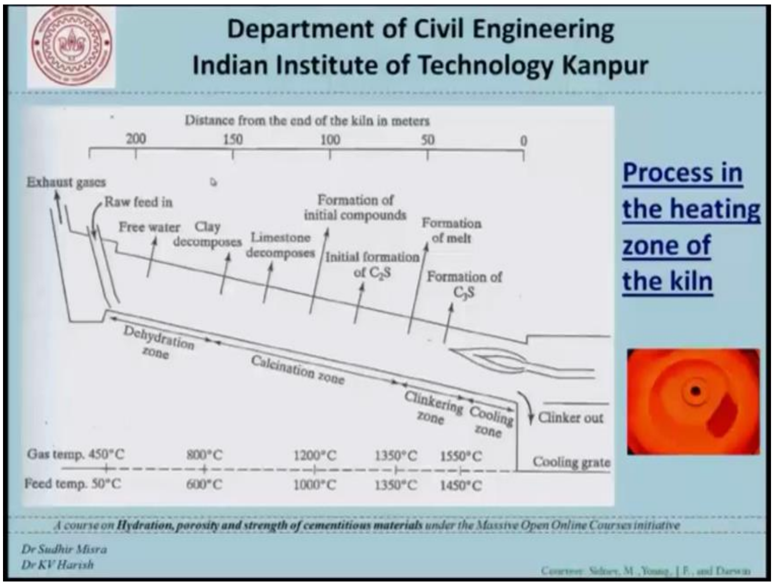

So, what you see in the figure is the kiln which is inclined at some angle and at one end of the kiln you will see the fire that is provided for which you need some fuels which is already discussed in the previous slide and at the other end the raw materials are fed.

The process that takes place inside the kiln is very important and it is dealt in the next slide once you get the material that comes out of the kiln somewhere here the material is cooled and then further gypsum is added and the cooled material is called as clinker and gypsum is added to clinker and then it goes to ball mill grinders for blending of gypsum and clinker and finally, what you get is Portland cement the fourth step is clinker with gypsum is ground into Portland cement and shipped and finally, final product Portland cement is put in a packed baggage and then shipped to different places for distribution

Now, what happens in the kiln is very important because the raw materials are primarily converted to different reactive compounds. So, in this figure what you see is a kiln which is inclined at some angle and what you see at the bottom is the temperature that is varying from somewhere about 50 degree Celsius to about 1,450 degree Celsius and on the top what you see is the horizontal distance of the kiln ranging from 0 to above 2 hundred metres and in the figure what you see is at one end of the kiln you have the burning we are taking place and the other end of the kiln where the raw material is fed.

So, the kiln is basically divided into 4 parts one is called as the dehydration zone the other one is called as the calcination zone the other one is called as the clinkering zone the final one is called as the cooling zone. So, what happens in each of the zone is very important. So, in a hydration zone free water in the raw material escapes in addition clay compounds decomposes in the calcination zone the limestone decomposes some compounds are formed and primarily C2S which is Di-calcium silicate starts forming in the clinkering zone where typically the raw materials starts melting and also you get the formation of C2S more information about what happens in the kiln is discussed in the next slide.

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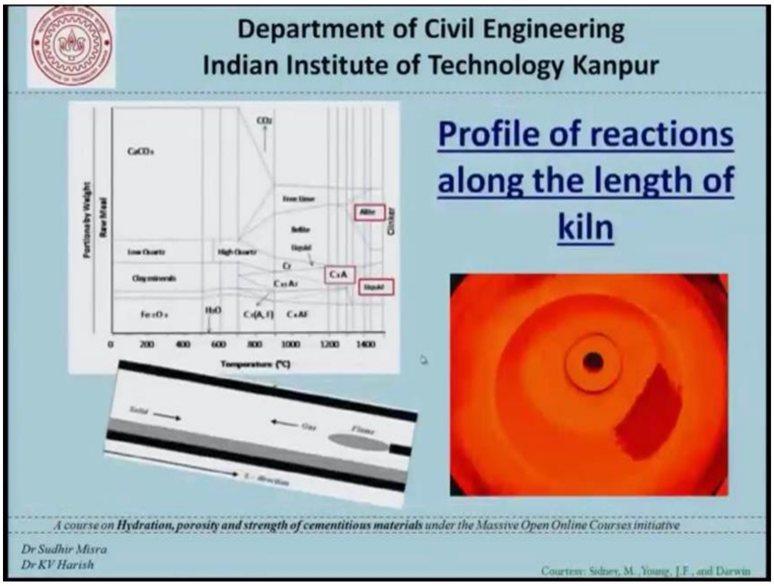

So, the profile of reactions along the length of the kiln is shown in the figure what you can see is this is the kiln that is inclined at some angle to the horizontal and what you see in the figure is that the y axis shows the proportion of weight proportions by weight and in the x axis it shows the temperature ranging from normal temperature to above 1,450 degree Celsius and what you can see is that calcium carbonate which is present in large amounts low quartz or quartz related materials present in some minor amounts. Clay minerals present in substantial amounts iron oxides or iron ore materials which are also present in substantial amounts all these together reacts from 0 degree Celsius to about 450 degree Celsius or 500 Celsius, but not much reactions happen only thing is the water in these materials get evaporated.

Say from temperature between 5 degree Celsius to about 800 degree Celsius water again gets evaporated in addition low quartz become high quartz primarily indicating that there is some phase change in the quartz related material in addition to that you also see that some quantity of carbon dioxide is getting liberated from the combustion of limestone and at temperature between 800 to about 1000 degree Celsius, you have the initial formation of C2AFC 2 AF which is unstable compound and further heating say beyond thousand degree Celsius the first compound that forms is C4AF. And at the same time you also have Belite which is formed and remember that a portion of the liquid at this temperature range becomes liquid and you also see that the limestone is converted to free lime in this temperature and the free lime is available for reactions further and at temperatures above 1,200 degree Celsius, C3A that is tri-calcium aluminate C3S for Alite and these 2 compounds are primarily formed through sustained heating and at temperatures of the order of 1,400 degree Celsius typically the entire mixture is in the form of liquid.

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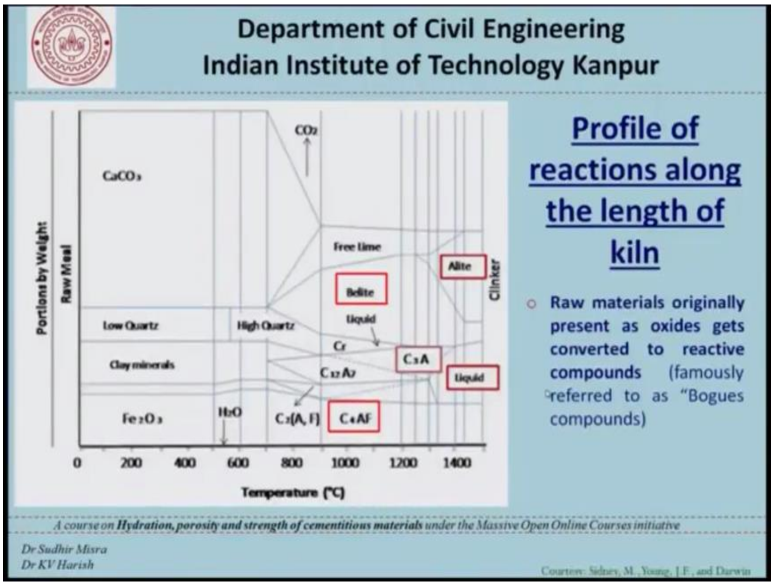

Bigger picture is shown for clarity. So, overall the raw materials originally present as oxides gets converted to reactive compounds and these reactive compounds are famously called as Bogues compounds.

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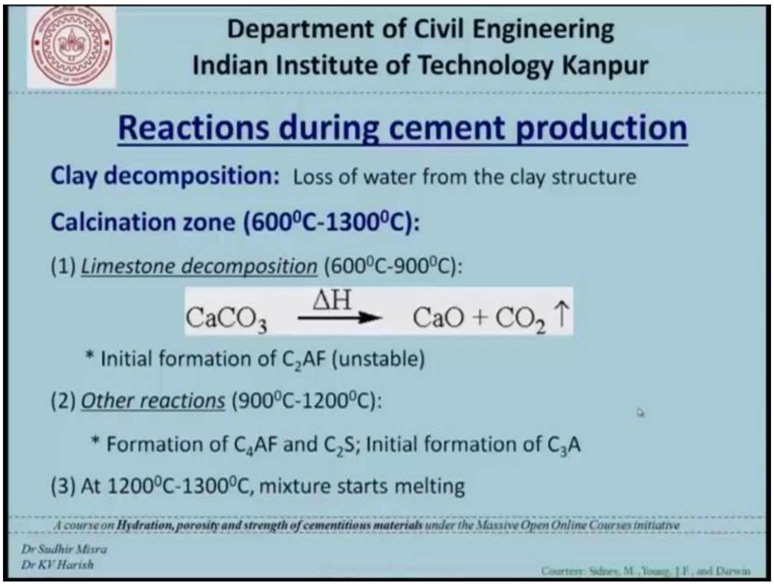

Now, the summary of the reactions that is happening during cement production are provided clay decomposition where loss of water from the clay structure takes place calcination zone typically between 600 degree Celsius to 1,300 degree Celsius, 3 reactions happen limestone decomposition at temperatures between 600 to 900 degree Celsius where calcium carbonate forms calcium oxide and carbon dioxide its looses water and you also have initial formation of C2AF, but C2AF is unstable other reactions 900 degree Celsius to 1,200 degree Celsius you have the formation of C4AF and C2S together in addition to that you have initial formation of C3A at temperatures 1,200 degree Celsius to 1,300 degree Celsius mixtures start melting.

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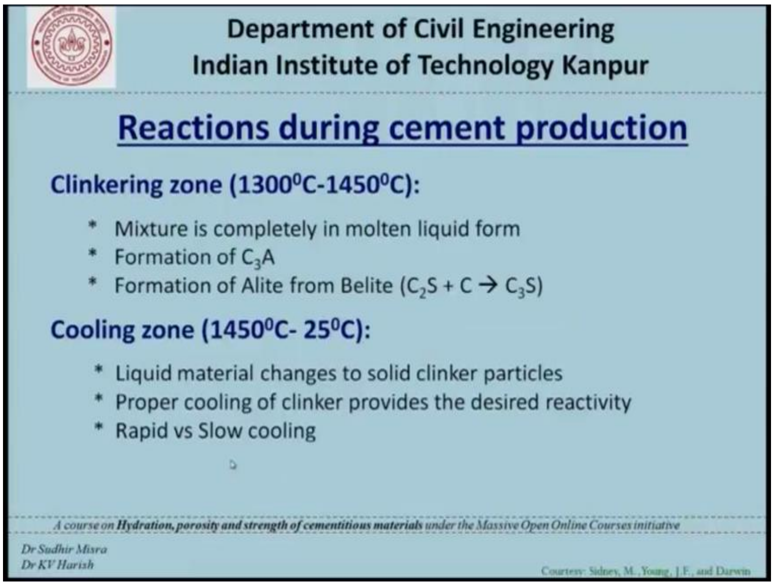

In the clinkering zone, 1,300 degree Celsius to 1,450 degree Celsius, the mixture is completely in molten liquid formation of C3A takes place formation of Alite from Belite that is C 2 S reacts with C to give C3S remember that C does not refer to carbon C refers to calcium oxide.

Cooling zone 1,450 degree Celsius to 25 degree Celsius, you can see that the temperature difference here is very high and hence the cooling can be done either rapidly or slowly. So, in the cooling zone liquid material changes to solid clinker particles proper cooling of clinker produces the desired reactivity you can either do rapid cooling or slow cooling in the plant usually rapid cooling is followed.

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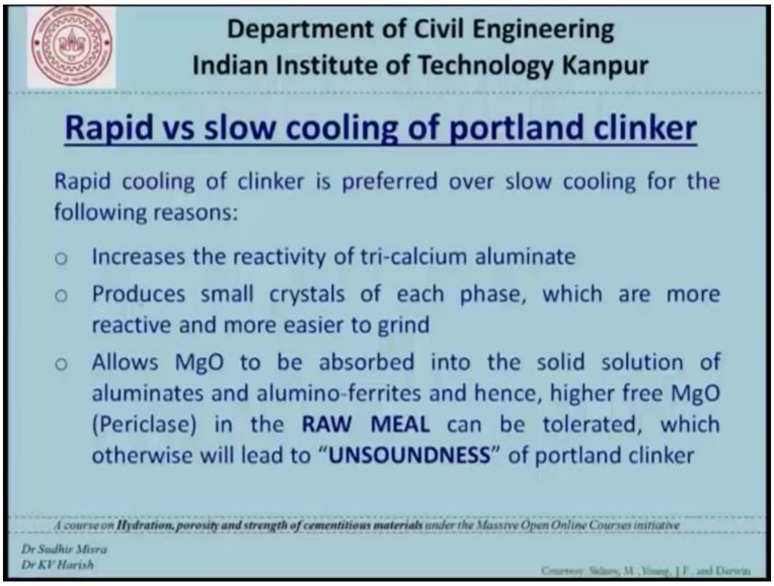

Some of the advantages of rapid cooling over slow cooling is discussed rapid cooling increases the reactivity of tri-calcium aluminate rapid cooling produces small crystals of each phase which are more reactive and more easier to grind it also allows magnesium oxide to be absorbed into the solid solution of aluminates and alumino ferrites and hence higher free magnesium oxide in the raw meal can be tolerated which otherwise will lead to unsoundness of Portland cement what is unsoundness is discussed in the next slide.

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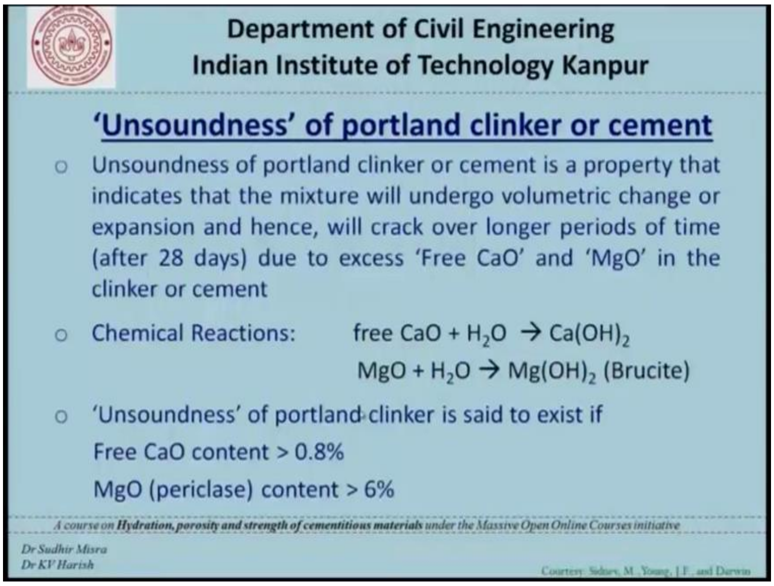

Unsoundness of Portland cement is a property that indicates that the mixture will undergo volumetric change or expansion or cracking over longer periods of time usually after 28 days due to excess amounts of either free calcium oxide which is not properly burnt or magnesium oxide that is present in the clinker or due to both free calcium oxide and magnesium oxide.

The chemical reactions which cause expansions are shown here free calcium oxide plus water gives calcium hydroxide magnesium oxide plus water gives magnesium hydroxide which is also called as Brucite. So, these 2 reactions are expansive in nature and causes cracking in concrete at later stages and hence we do not want our cement to be unsound unsoundness of Portland cement is said to exist if free calcium oxide content is greater than 0.8 percent and magnesium oxide content is greater than 6 percent these limits are specified clearly in Indian standard specifications.

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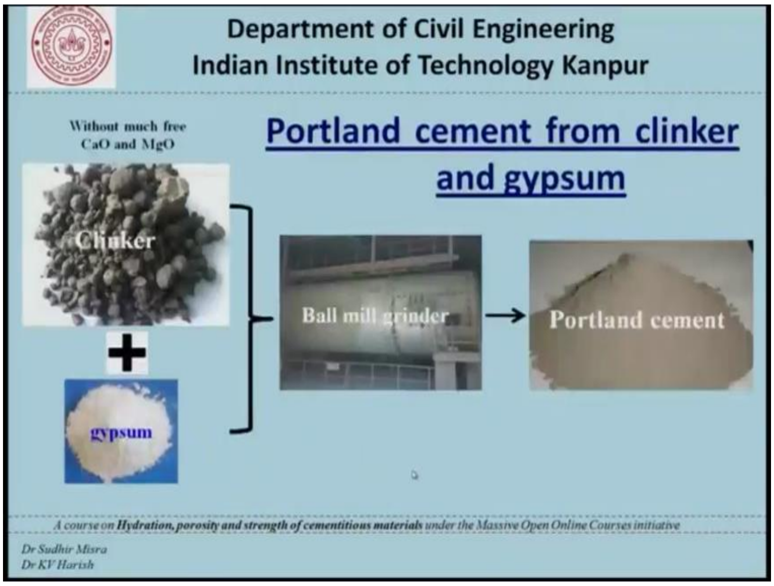

So, once the raw materials comes out after the burning process it is called as clinker and we need to make sure that it does not contain too much of free calcium oxide or magnesium oxide and then it is added to gypsum and both are fed in ball mill grinders and once it is ground well then you get the material called Portland cement which will be in fine particle form and they are packed in bags and distributed.

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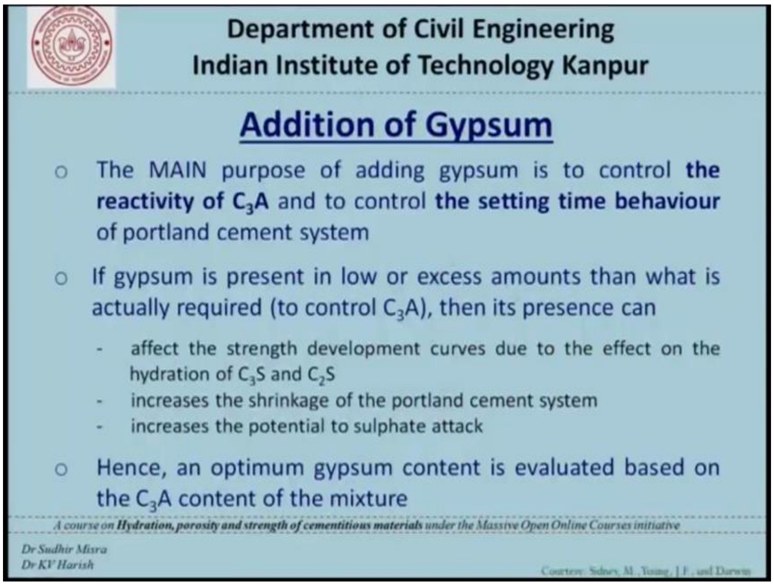

The purpose of adding gypsum is discussed the main purpose of adding gypsum is to control the reactivity of tri-calcium aluminate and to control the setting time behaviour of Portland cement system if gypsum is present in low or excess amounts than what is actually required to control C3A. Then its presence can affect the strength development curves due to the effect on the hydration of C3S and C2S increases the shrinkage of the Portland cement system increases the potential to sulphate attack the role of gypsum will be explained at a later stage when we deal with hydration of Portland cement hence an optimum gypsum content is required and it is usually evaluated based on the tri-calcium aluminate content in the mixture.

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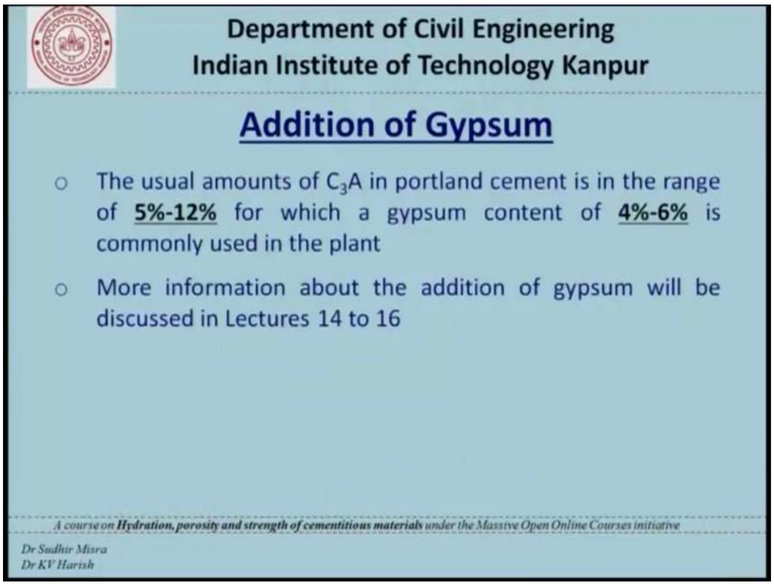

The usual amounts of tri-calcium aluminate in Portland cement is in the range of 5 to 12 percent for which the gypsum content is in the range of 4 to 6 percent and hence this quantity is used commonly in the plant more information about the addition of gypsum will be discussed in lectures 14 to 16.

Thank you.