Hydration, Porosity and Strength of Cementitious Materials
Prof. Sudhir Mishra and Prof .K. V. Harish
Department of Civil Engineering
Indian Institute of Technology, Kanpur

Lecture – 19
Heat of Hydration of Portland Cement

[FL] and welcome to this lecture 19, which deals with heat of Hydration of Portland Cement as part of our course on Hydration, Porosity and Strength of Cementitious Materials.

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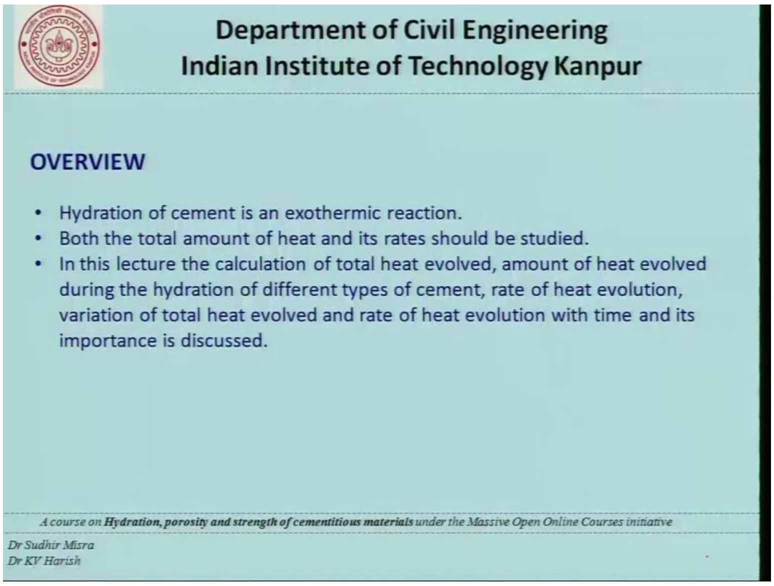

An overview of what we will do today. We must understand that hydration of cement is an exothermic reaction which means that it involves liberation of heat. Now once we are talking of liberation of heat there are 2 aspects to it. One is the total amount of heat that is liberated and the second is the rate at which it is liberated. We would see how both these parameters are important for us to understand and differentiate. In this lecture the calculation of the total heat evolved, the amount of total heat evolved during the hydration of the different types of cement the rate of heat evolution and the variation of the total heat evolved along with the rate of heat evolution with time and it is importance we will be discussed.

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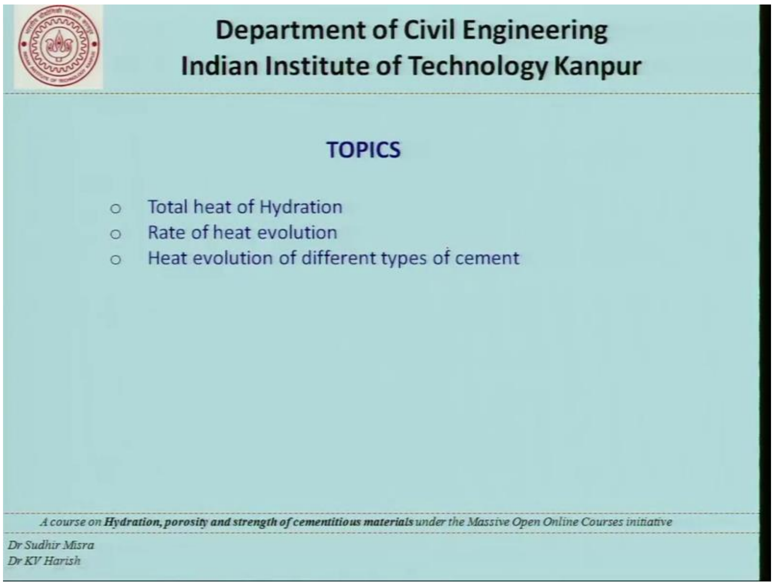

This discussion is divided in to total heat of hydration, the rate of heat evolution and the heat evolution in different types of cement.

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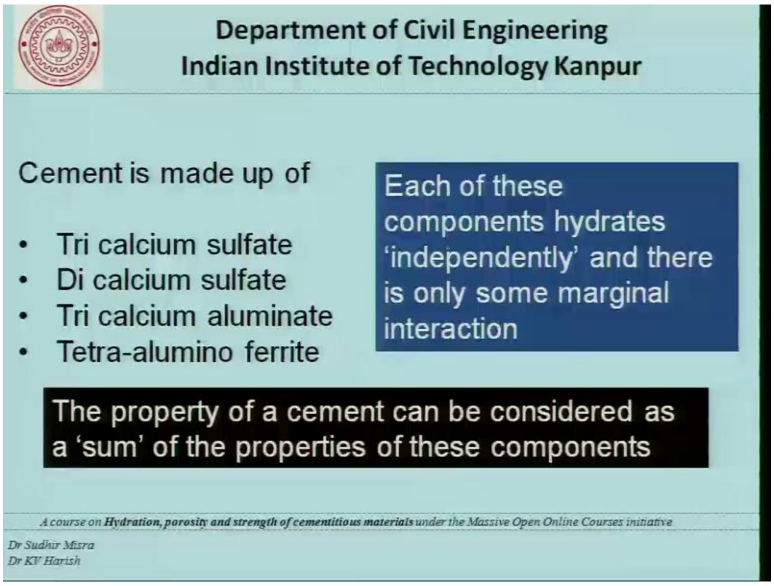

Before we get in to a detail discussion on the heat of hydration of cement, we must remember that cement is made of tricalcium sulfate tricalcium cement is made of tri calcium sulfate. Di calcium sulfate tri calcium aluminates and tetra alumino ferrites, this we know from the discussion that has been happening in this course or this while. Now each of these components hydrates almost independently and there is only marginal interaction.

Now, what this hydration independently means is that the chemical reaction of each of these 4 components with water leading to the formation of hydration products is almost an independent process. It happens simultaneously, but for the ease of understanding it can be taken to be occurring independently, with marginal interaction has been mentioned. Therefore, the property of cement can be considered as the sum of the properties of these components. We must also keep in mind that the heat of evolution and the heat evolved is related to the reaction and the reaction kinetics of each of these 4 components. This issue is also related to other properties such as strength setting and so on and so forth.

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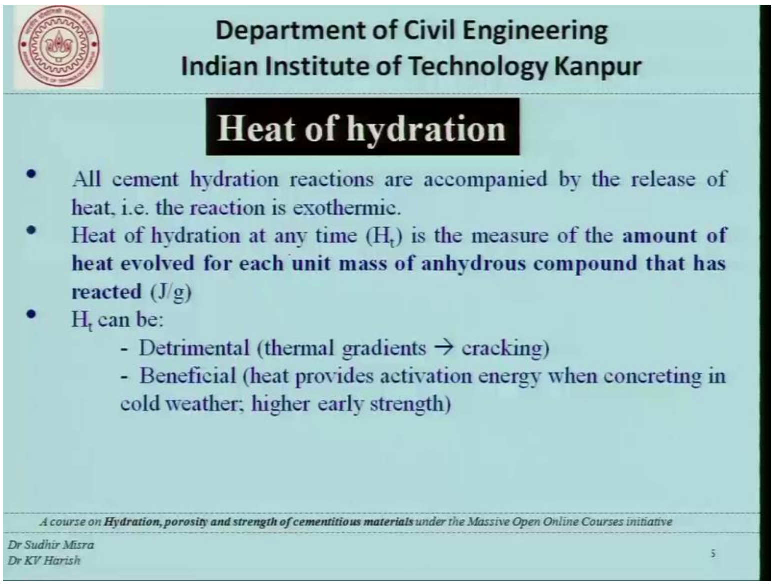

With this background let us try to understand the heat of hydration a little more technically. All cement hydration reactions are accompanied by release of heat and the reaction is exothermic.

Now, the heat of hydration at any time since this process goes on for several awards several days, at any time which is given as Ht in the slide is a measure of the amount of heat evolved for each unit mass of anhydrous compound that has reacted. That is the unit for heat of hydration is something like joules or gram or kilo joules per kilo gram and so on and so forth. So, basically what it means is that if a gram or a kilo gram of cement hydrates how many joules or kilo calories of heat is evolved. This is; obviously, related to the type of composition of cement and so on. And we will see later on in the discussion in this lecture.

Now, this heat of hydration Ht can be detrimental, it can be harmful because it leads to be setting up of thermal gradients in the concrete and which finally, leads to crack in and that extremely undesirable. However, in certain cases the heat of hydration could also be beneficial. For example, the heat provides the activation energy, when concreting on cold weather or when we require higher early strength.

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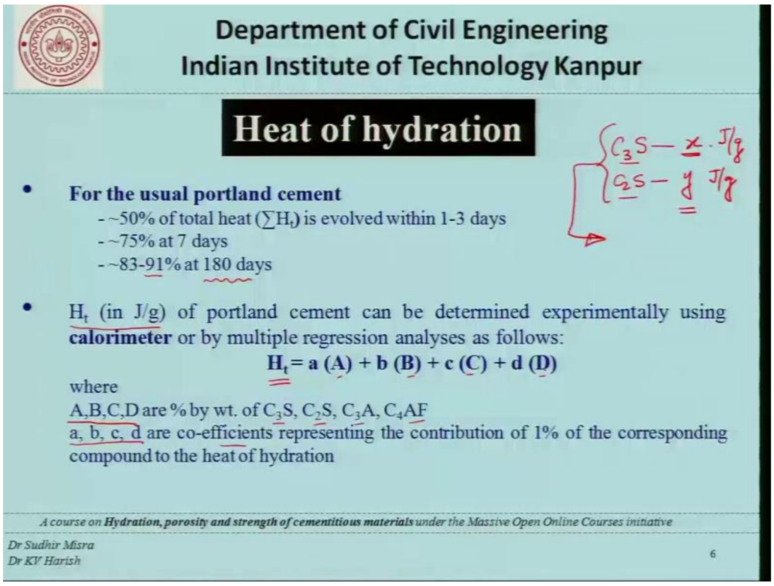

We see a part of the slide before for the normal Portland cements; it has been found that up to 50 percent of the total heat is evolved within 1 to 3 days. 75 percent is evolved in 7 days and 83 to 91 percent at 180 days.

What this effectively means is that at the end of even something like 6 months, we are still talking of only 91 percent of the heat having been evolved, meaning there by that 9 percent which almost one-tenth of the total heat evolution takes place beyond 6 months. And that has something to tell us as for as hydration is concerned hydration is not over at 28 days or 7 days and so on. It continuous for a long period of time, coming to the composite nature of cement, Ht which I said is measured in terms of joules or gram of Portland cement can be determined experimentally using a calorimeter or by multiple regression analysis which is in the form Ht is equal to a A plus b B plus c C plus d D where the capital A B C and D are the weight percentages of the C3S C2S C3A C4AF and the small a b c d is are coefficients which represent the contribution of one percent of the corresponding compound to the heat of hydration.

Basically what we are saying is, that if from a chemical stand point of with a stand point cement chemistry, we knew that C3S evolves a certain amount of heat in joules per gram, C2S evolves a certain other amount of heat in joule per gram, a compound which contains a certain percentage of C3S and the certain percentage of C2S, we can determined by heat of hydration of that compound if we know this x and y and we know the composition of that compound in terms of C3S and C2S. This is exactly the kind of thought process which goes when we say the total heat of hydration that evolves in a gram of cement hydrating is related to the individual heats of the hydration of the 4 principle components and their percentages.

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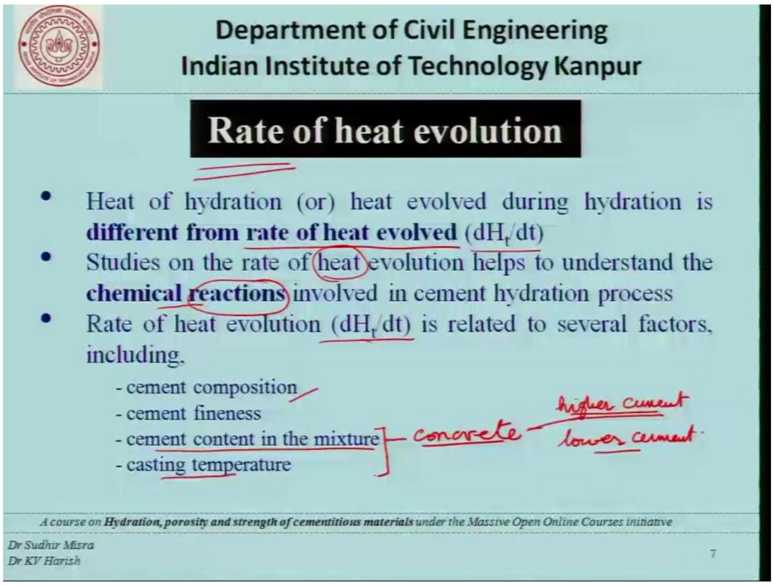

Now, it is not only the total heat that is involved, it is not only the total heat of hydration which is important, but also the rate of heat evolution. It is not enough to know that hundred kilo calories of heat will be evolved. It is also important to know at what rate will be evolved will all the heat evolution we completed in one day or it will go on for the period of 7 days or 14 days or whatever. From that point of view we will talk in terms of the rate of heat evolution, which is basically d Ht by d t. And studies on the rate of heat evolution help us understand the chemical reaction or the reaction kinetics involved in the hydration process of cement.

In fact, as I said before the reactions of the individual components, and the heat evolved in different reactions are extremely closely related. And this rate of heat evolution is related to several factors. It is related to cement composition that is reverse component of cement, which liberate the heat early. If they are higher in proportion then for that cement the rate of heat evolution will be higher in the initial stages. It depends on the cement fineness, because if the fineness increases the surface area which is available for hydration increases and therefore, all these chemical components whether it is C2S C3S or C3A more of them are reacting at the same time.

However, the fineness of cement higher is the rate of heat evolution cement content in the mixture and here we are really talking about concrete. We must remember that cement is rarely used in it is own right it is almost always used for all engineering applications as concrete sometime is more, but we are mostly concerned with concrete now; obviously, a concrete which has higher cement compare to a concrete which has lower cement this concrete will have a higher heat evolution compare to this concrete. So, as for as the d Ht by d t concrete is concerned it is related to the cement content of the mixture as well. The temperature at which the concrete is passed that also has an important vary, we will try to discuss these aspects when we talk about the issues and evolving the heat of hydration and concrete in a subsequent discussion.

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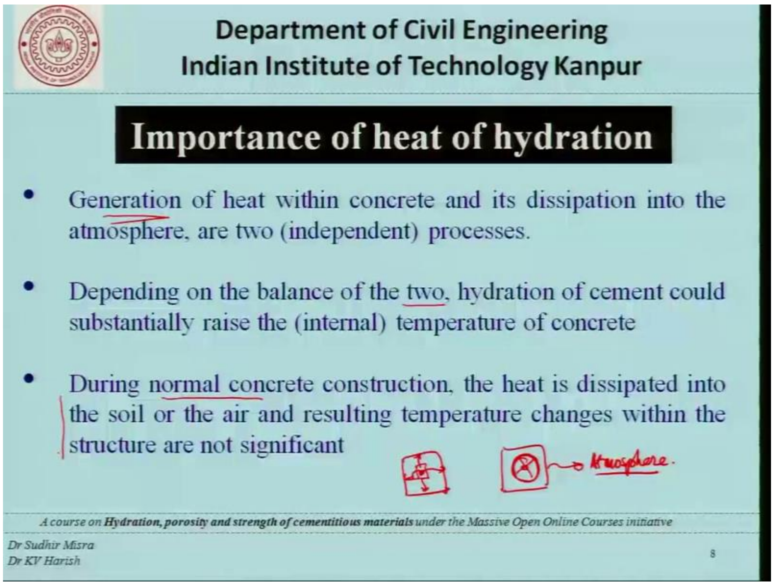

As for as the importance of the heat of hydration is concerned, the generation of heat within concrete and it is dissipation into the atmosphere are 2 independent processes, but we must understand is that if we take a block of whether it is cement paste or it is mortar or it is concrete, this block has a certain amount of cement which has a certain amount of heat which will be liberated if complete hydration was to taking place. So, this is what is called or what is beam called as the generation of heat within the concrete. Now this heat once it is generated here dissipates into the atmosphere. All our concrete construction happens in the atmosphere sometimes takes place and the water and so on.

But in any case the heat evolved within the concrete is dissipated into the atmosphere. Which means that the heat evolved within this block here it is dissipated into the atmosphere and this dissipation is more less and independent process and has to be looked upon independently, from the heat generation process. And now depending on the balance of the 2 the 2 meaning the heat generation, and the heat dissipation hydration of cement could substantially raise the internal temperature of concrete. Now what this means is that if heat evolution within concrete takes place at a rate which is higher than the rate at which the dissipation takes place that is what will lead to an increase in temperature of the concrete or an increase in the internal temperature of the concrete. In cases where the dissipation can take care of the amount of heat that is evolved we will not see any substantial change in the temperature of the concrete which has been caused.

Now, this difference between the heat evolved and the heat dissipated is important for us to understand when we talk of implications of heat of hydration as for as concrete engineering is concerned. In normal concrete construction the heat is dissipated into the soil or the air and the resulting temperature changes within the structure are not significant now the reason for that is something which we need to is spend a little time on and think, why that happens we will answer this question later on in this lecture or perhaps the next one.

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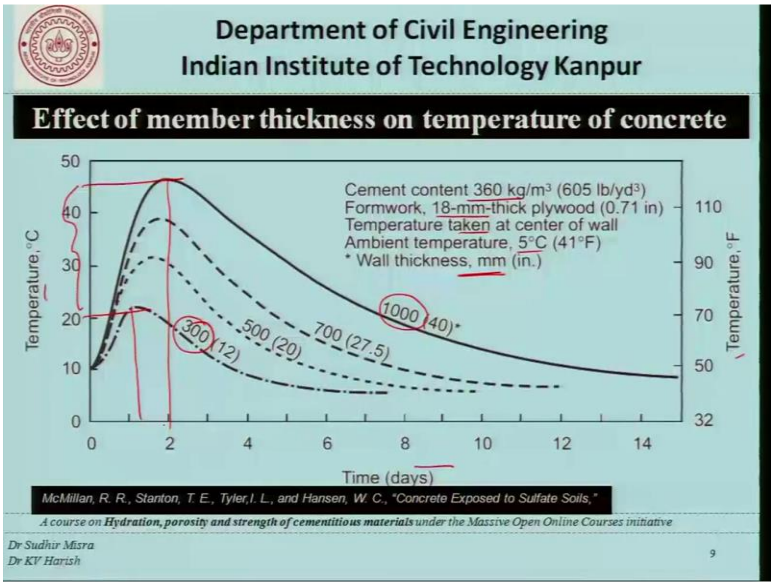

Now, this slide shows the effect of member thickness on the temperature of concrete now this side is in degree centigrade and this side is an far an height and here we are talking in terms of time in days.

So, if we see that for a cement content of 3 and sixty kg is per cubic meter having a form work of 18 mm thick plywood the temperature taken at the center of a wall with an ambient temperature of 5 degree centigrade if the wall thickness was varied from 300 mm to 1000 mm now 1000 mm is the meter and 300 mm is about a 40 it is about 12 inches this about 40 inches. If the thickness is changed the maximum temperature that is reached that changes by as much as about 25 to 27 degree centigrade. Secondly, the time at which this speak occurs is also not the same in the 2 cases. What it effectively shows is really the answer for the previous question, as to why we do not see substantial temperature rises in normal concrete construction.

I am still not answering the question in a every quantitative manner and I would like you to think about this a little more.

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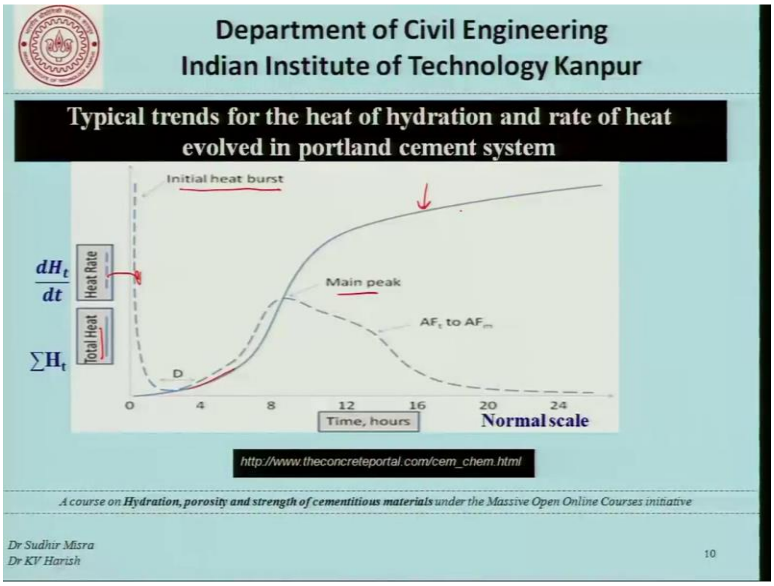

Now, if you look at the typical trends for the heat of hydration and the rate of heat evolved in Portland cement systems, this one here is the total heat and this one is the rate. So, in a manner of speaking this graph here which is the dotted line is just the derivative of the firm line. And we can see that there is an initial high rate which goes down which is called an initial heat burst the main peak and so on. And here we have the total heat of hydration being shown for typical cement systems.

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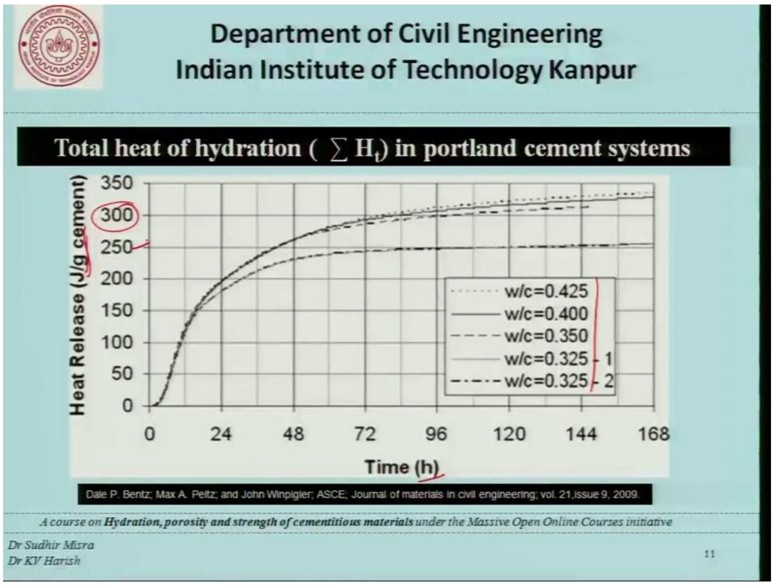

If you look at this a little more closely here we show the total heat of hydration in Portland cement systems for different water cement ratios, and the heat released in terms of joules per gram of cement at different points in time. So, here we see the depending on the water cement ratio and so on. The heat liberated could be of the order of about 300 to 350 or in some cases 250 joules per gram.

It is important for us to have a feel of the numbers which are involved because these numbers become the basis for characterization of different cements.

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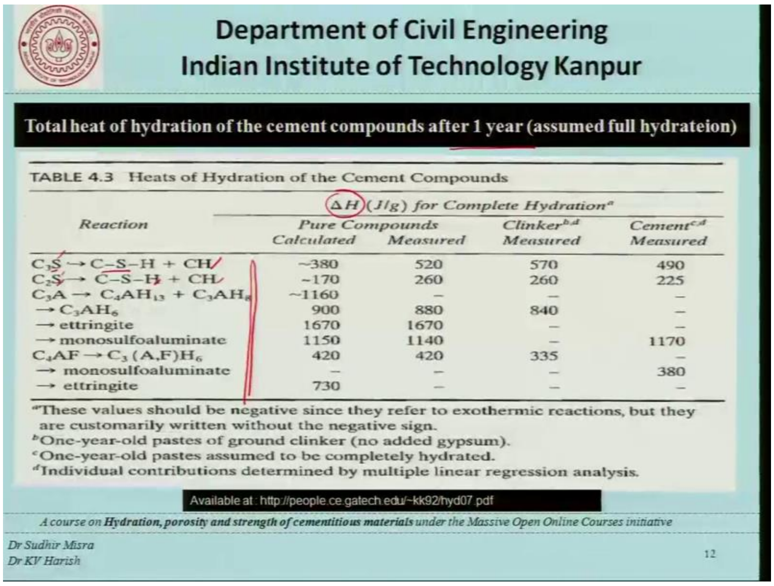

TABLE 4.3 Heats of Hydration of the Cement Compounds

Reaction	ΔH (J/g) for Complete Hydration[a]			
	Pure Compounds Calculated	Pure Compounds Measured	Clinker[b,d] Measured	Cement[c,d] Measured
$C_3S \rightarrow C\text{-}S\text{-}H + CH$	~380	520	570	490
$C_2S \rightarrow C\text{-}S\text{-}H + CH$	~170	260	260	225
$C_3A \rightarrow C_4AH_{13} + C_3AH_8$	~1160	–	–	–
$\rightarrow C_3AH_6$	900	880	840	–
$\rightarrow$ ettringite	1670	1670	–	–
$\rightarrow$ monosulfoaluminate	1150	1140	–	1170
$C_4AF \rightarrow C_3(A,F)H_6$	420	420	335	–
$\rightarrow$ monosulfoaluminate	–	–	–	380
$\rightarrow$ ettringite	730	–	–	–

[a]These values should be negative since they refer to exothermic reactions, but they are customarily written without the negative sign.
[b]One-year-old pastes of ground clinker (no added gypsum).
[c]One-year-old pastes assumed to be completely hydrated.
[d]Individual contributions determined by multiple linear regression analysis.

Now, here this table shows the total heat of hydration of cement compounds after one year assuming full hydration and we can see that as C3 has hydrates into CSH gel and the formation of calcium hydroxide c 2 as goes into CSH gel and hydration and calcium hydroxide and so on. If these are the reactions that are taking place these are the kind of heats which are evolved upon complete hydration these numbers here for C2S C3S and so on help us determine the total heat which will be evolved for particular cement which may have different compositions of C2S C3S and all that.

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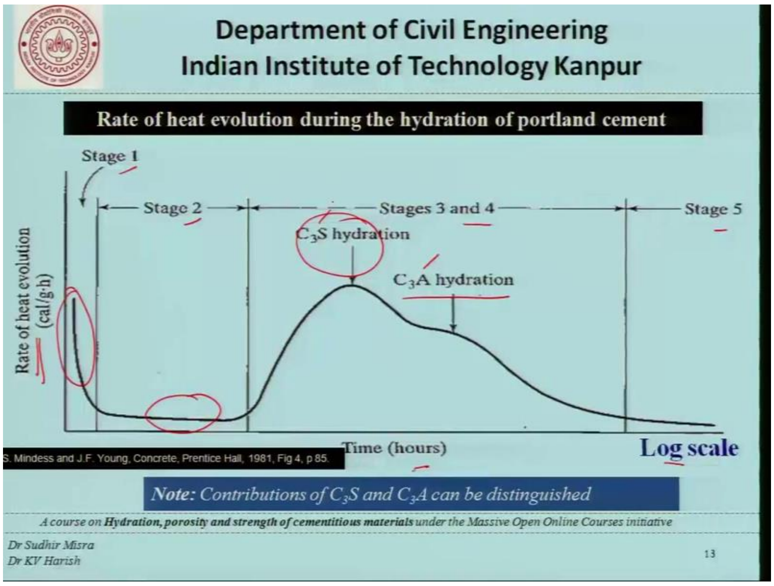

This one here is another schematic representation relating the heat evolution to the hydration process. So, this is the stage 1 2 3 and 4 and 5 where time on the log scale is plotted versus the rate of heat evolution and we have a the burst here a dormant period here this is where the C3S hydration is taking place the C3A hydration is taking place and so on. I would like you to look at cement chemistry literature, and tried to see how individual components of cement what are their graphs what is the pattern or the trend that we see in the rate of heat evolution for the different components. That is an assignment.

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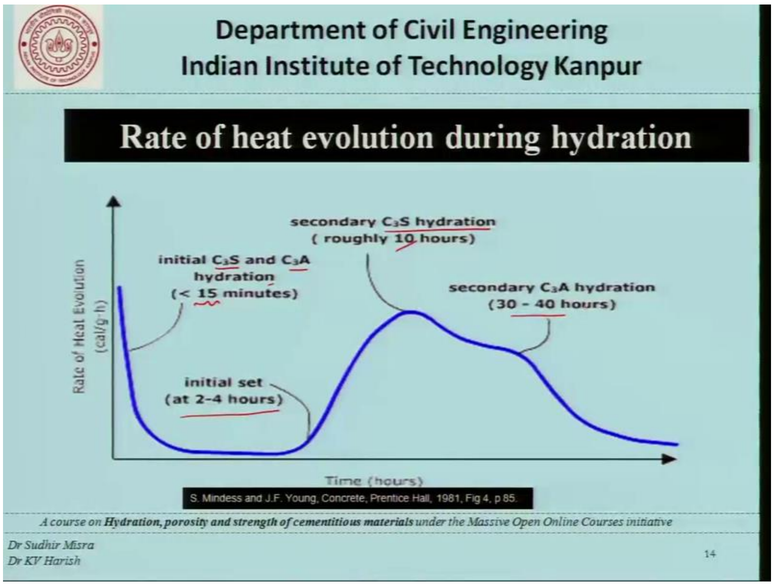

This again is another representation of more or less the same things which says that in the initial part we have the initial C3S and C3A hydration, and that takes place within the first 15 minutes. Then we have a process where the hydration is dormant and we have initial set in about 2 to 4 hours, and then we have secondary reactions or the secondary hydration of C3S which carries on for about 10 hours and then we have secondary C3A hydrations for about 30 to 40 hours and so on. So, those of first were interested in the chemistry of cement hydration.

For them these are very interesting graphs as a engineers, we must know about these graphs and also try to understand them in the light of how we will use this information when it comes to concrete constructions.

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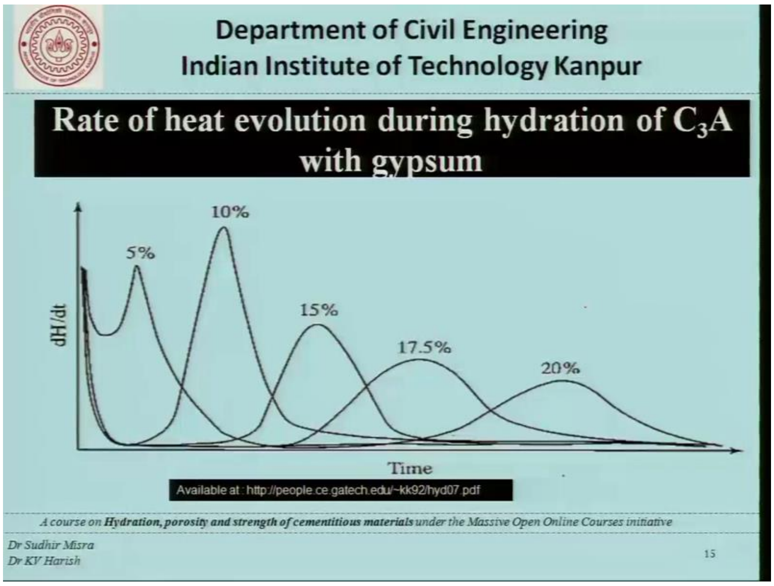

This here shows the rate of heat evolution during hydration of C3A with gypsum. So, these are the different percentages of gypsum and we can see that the d h by d t for C3A is quite different if the gypsum percentages are changed. And this is something which cement chemists and concrete technologies can use to their advantage if we know where we want to use particular cement or what is the application that we have in mind for a concrete.

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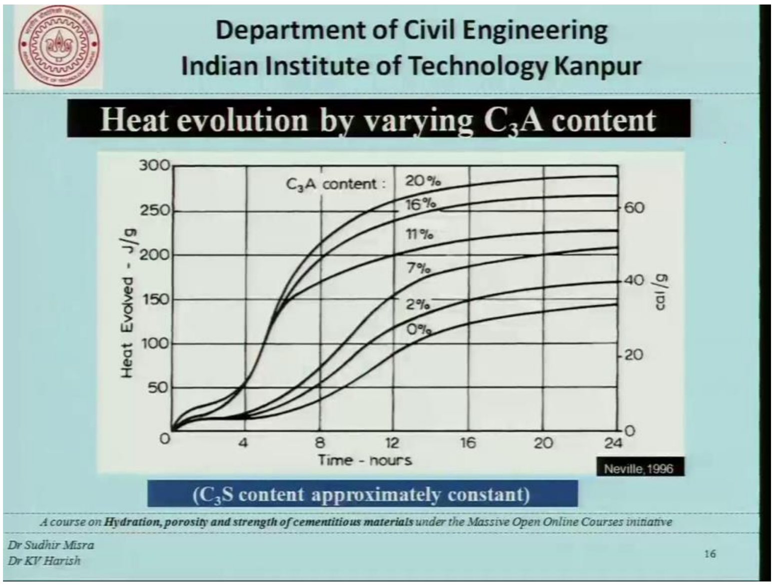

This slide shows the heat evolution where the C3A content of the cement has been changed. So, we can see that if the C3A content changes from 0 to 20 percent. The heat evolved changes dramatically. And that is again something which we have to understand or we have to know if you want to characterize the cements, if you want to understand the cement from the point of view of mass concrete applications as we shall see later on.

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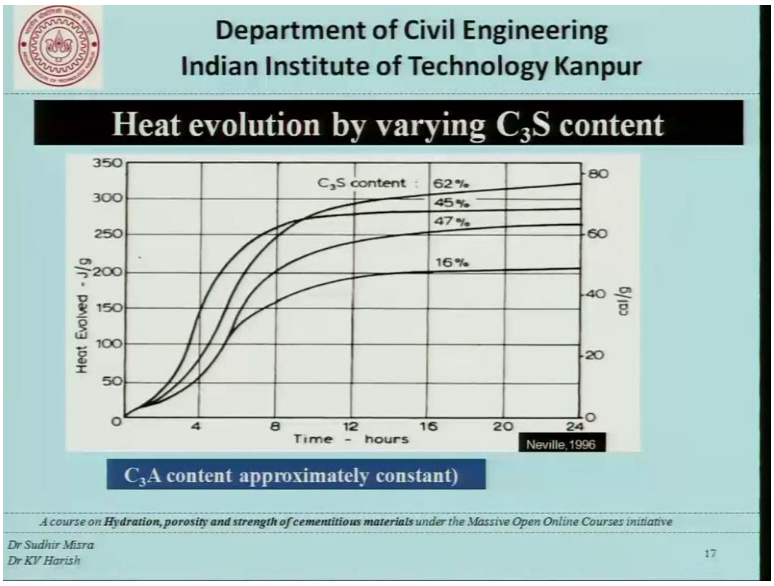

This diagram is an illustration of heat evolution by varying the C3S content, the previous one was C3A and this is C3S.

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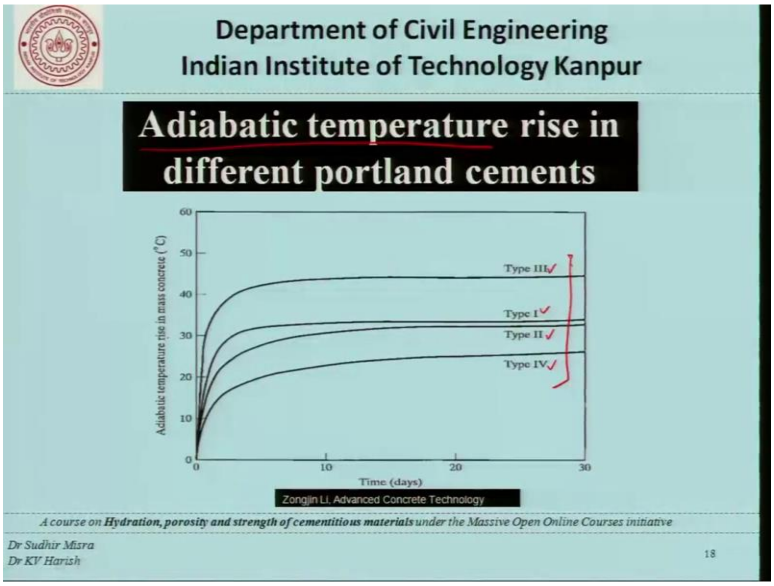

This here introduces the concept of an adiabatic temperature rise in different Portland cements. What we are talking about is different cements tested under adiabatic conditions will have different temperature rises, because different amounts of heat will be evolved. This kind of a discussion or study helps us actually to classify the cement.

For example, here we see that cement type one type 2 type 3 and type 4 they have very different adiabatic temperature rises.

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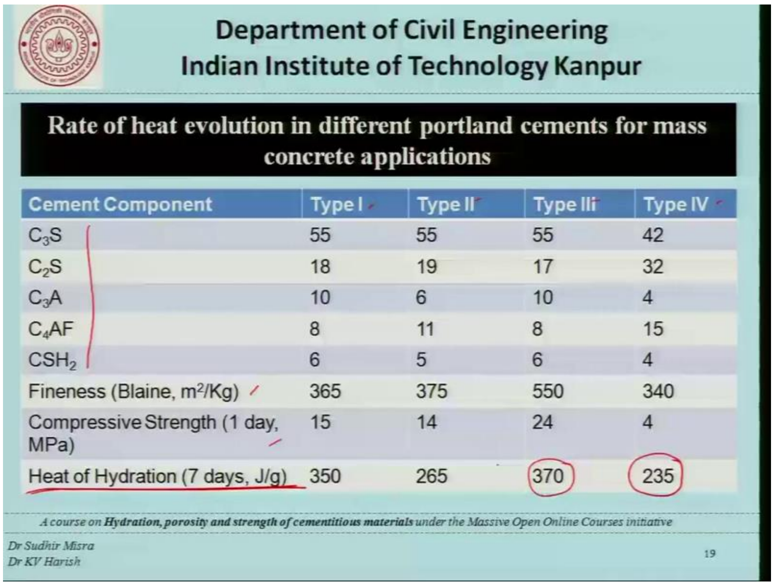

Cement Component	Type I	Type II	Type III	Type IV
C_3S	55	55	55	42
C_2S	18	19	17	32
C_3A	10	6	10	4
C_4AF	8	11	8	15
CSH_2	6	5	6	4
Fineness (Blaine, m^2/Kg)	365	375	550	340
Compressive Strength (1 day, MPa)	15	14	24	4
Heat of Hydration (7 days, J/g)	350	265	370	235

And this table here is a comparative statement of the rate of heat evolution in different Portland cements for mass concrete applications.

So, this type one type 2 type 3 and type 4 are the different kind of cement and we can see that depending on the type of cement be proportion of the constituents is different and the SOS there blaine fineness source there compressive strength and So, is the heat of hydration. In this case what is given is at 7 days. So, if we look at this table carefully we find that the heat of hydration at 7 days would vary from 23 5 joules per gram to as much as 370 joules per gram depending on the type of cement.

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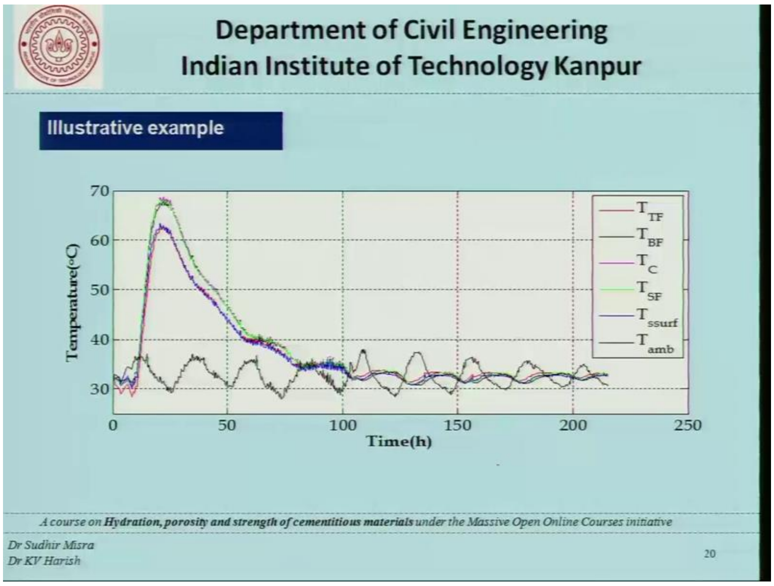

This picture is an actually illustration where the temperature of a block of concrete was monitored in the lab, and we found that the temperature starting at about 30 degrees goes up to as much as 70 degrees and this rise happens in about 25 27 hours.

Now, this actually is worth noting that depending on the size of the block depending on the constitution of the concrete the temperature rise is not very small, it is a substantial temperature rise and this happens not at the surface of the concrete, but in the core of the concrete. And that is the essence with which we discuss mass concrete definition and how to handle mass concrete.

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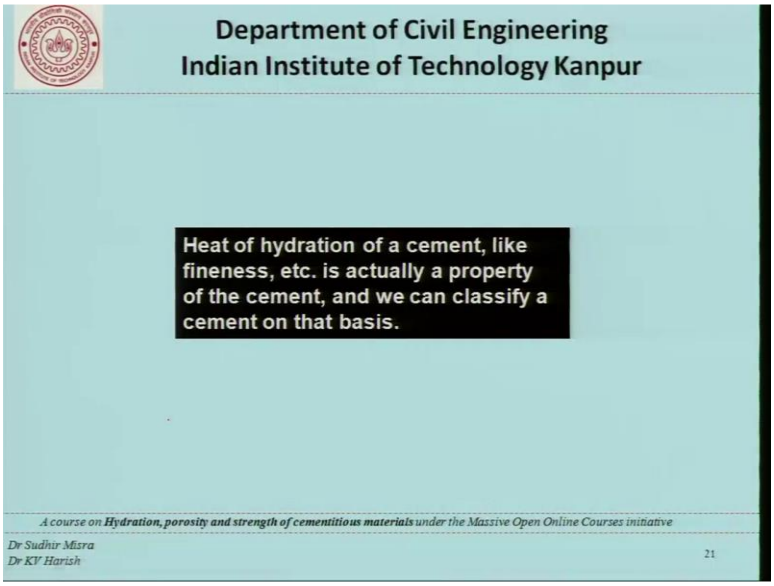

Now, trying to close the discussion for today heat of hydration of a cement like fineness is actually a property of the cement, and we can classify a cement on that basis we can say that a low heat of hydration cement will be such that the heat evolved in that cement will be less than a certain number of joules per gram. Or in other words unless a cement meets certain criteria it cannot be called low heat of hydration cement.

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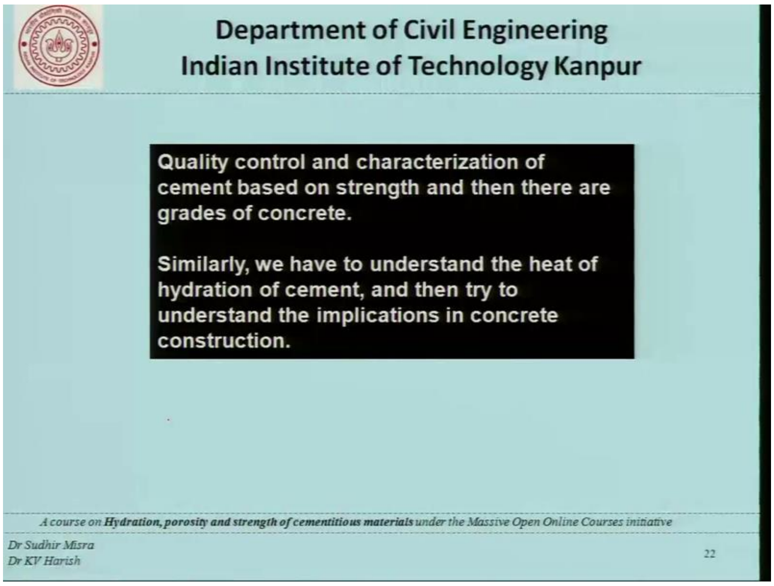

Let me give you another illustrative thought quality control and characterization of cement based on strength and then there are grades of concrete. We talk of cements in

India which are OPC grade 33 43 and so on. So, we have grades for cement and then there are grades for concrete. Similarly, as for as the heat of hydration is concerned we have to understand it in similar lights that heat of hydration or the amount of heat evolved during the hydration of gram of cement is a property of that cement. And how that property affects the total heat evolved or the temperature rise that happens in a particular concrete is something quite different it is related, but it is not really the same thing.

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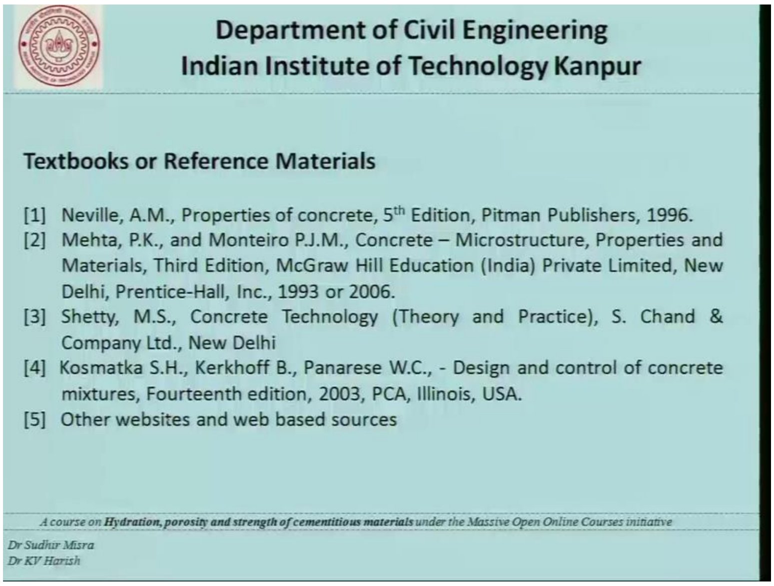

With this we are more or less at the end of this discussion and these references and text books will help you understand the topic better.

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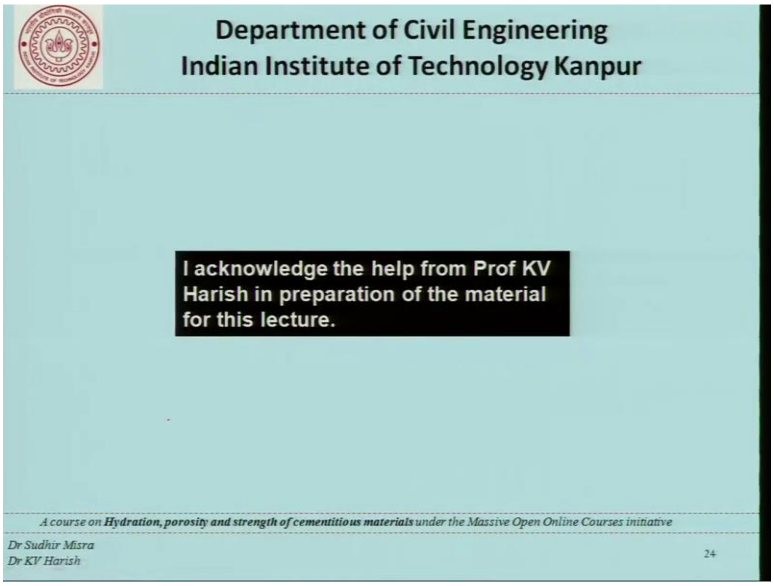

And I must say that I acknowledge the help from Professor Harish in preparation of the material for this lecture and I would like to thank you.