Characterization of Construction Materials
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Lecture 10
Calorimetry: Sample Preparation, Practical Note and Heat of Hydration Part 2

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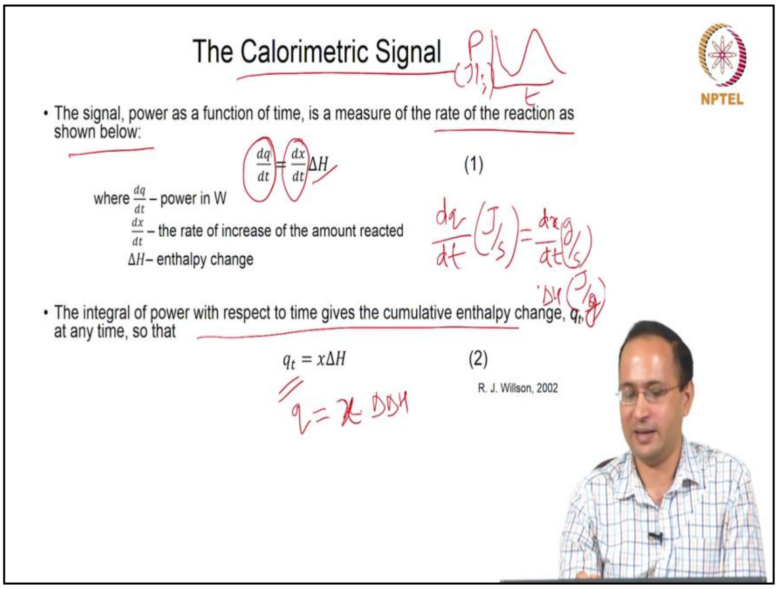

The Calorimetric Signal

- The signal, power as a function of time, is a measure of the rate of the reaction as shown below:

$$\frac{dq}{dt} = \frac{dx}{dt}\Delta H \qquad (1)$$

where $\frac{dq}{dt}$ – power in W
$\frac{dx}{dt}$ – the rate of increase of the amount reacted
ΔH– enthalpy change

- The integral of power with respect to time gives the cumulative enthalpy change, q_t, at any time, so that

$$q_t = x\Delta H \qquad (2)$$

R. J. Willson, 2002

So, now we look into the calorimetric signal, what do we get from calorimeter. Yesterday when we talked about the thermodynamics, we saw that you can get the enthalpy. So, whatever heat measurement you get, can relate to enthalpy of a reaction. So, the signal what we get is the power as function of time, so keep in mind you have this for isothermal calorimeter, for an example, this kind of plot. You get this power output. So, that signal is power as the function of time, is a measure of the rate of reaction.

Now you look, we will see how we can use that signal to know more about the kinetics, kinetics means how fast reaction is going. We are interested in the rate, because that is very important. Two different reactions at different temperatures, will have different rates. So, it is very important to know the rate of reaction. So, let us see what it is. So we are saying ($\frac{dq}{dt}$), we are getting this power, and q is heat.

So, it is easier to understand it is Joule per second (J/s) ; power is what you are getting, that is output ($\frac{dq}{dt}$). Whatever power you are getting, is because of some reaction, you can relate it to

($\frac{dx}{dt}$) which is the rate of increase of the amount reacted. Obviously you start with 0% when nothing has reacted. Now if you monitor that ($\frac{dx}{dt}$) will give you the rate of increase of the amount, dx and associated enthalpy change.

So again, ($\frac{dx}{dt}$) this is gram per second (g/s) times ΔH. ΔH again is Joule per gram (J/g). So, ($\frac{dq}{dt}$) is the power signal, equals to this rate of increase times ΔH.

$$\frac{dq}{dt} = \frac{dx}{dt} \Delta H$$

Now if you integrate power with respect to time, you will get the cumulative enthalpy.

So you have this P over t, P is nothing but Joule per second, if you integrate over time you will get Joule, total enthalpy.

$$q_t = x\Delta H$$

Where,

x is the amount of material that has reacted.

When x=0, q=0. When x = 100%, q = ΔH.

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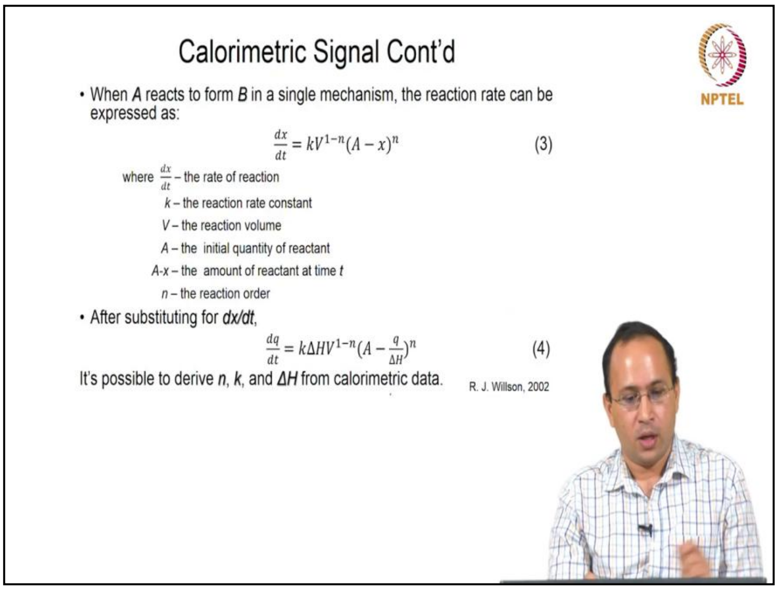

Calorimetric Signal Cont'd

- When *A* reacts to form *B* in a single mechanism, the reaction rate can be expressed as:

$$\frac{dx}{dt} = kV^{1-n}(A-x)^n \qquad (3)$$

where $\frac{dx}{dt}$ – the rate of reaction

k – the reaction rate constant

V – the reaction volume

A – the initial quantity of reactant

A-x – the amount of reactant at time *t*

n – the reaction order

- After substituting for *dx/dt*,

$$\frac{dq}{dt} = k\Delta H V^{1-n}\left(A - \frac{q}{\Delta H}\right)^n \qquad (4)$$

It's possible to derive *n*, *k*, and *ΔH* from calorimetric data.

R. J. Willson, 2002

So, now let us look at the simple reaction, where you get suppose A gives you B and there is a single mechanism, some reaction we are talking about, it could be complicated also, it could be A + B = C; it could be A + B = C + D; this rate of reaction can be related to the amount of A that has reacted simply. So, you start with A, now after some time, part of x has reacted.

So now you have (A-x) and B is x, so we are measuring this change in this amount ‘x’. So, $(\frac{dx}{dt})$ is the rate of reaction, it is proportional (A – x), because that matters, how much is left, and this ‘n’ is the order of the reaction.

$$\frac{dx}{dt} \propto (A - x)^n$$

Then if you get this coefficient, which is reaction rate constant. Remember you have V; here it is present because we are using x in amount, and we are talking about ‘x’ in grams. Lot of times, ‘V’ term gets dropped because you are talking about the concentration. If you talk about ‘x’ like concentration; that means mass per volume, so then you would not see this V term. But here, since we are talking about amount, you have this V term.

But it is basically same expression. So, now you have this relation where you can relate this reaction rate to the amount. Now what we can do, after substituting for $\frac{dx}{dt}$, now we know in the last slide,

$$\frac{dq}{dt} = \frac{dx}{dt} \Delta H$$

Now we can calculate $\frac{dq}{dt}$, that is the signal we are getting from calorimeter, $\frac{dq}{dt}$ is Joule per second (J/s) (Power). Now you replace $\frac{dx}{dt}$, you get this equation,

$$\frac{dq}{dt} = k.\Delta H.V^{1-n}.\left(A - \frac{q}{\Delta H}\right)^n$$

Where,
V is the reaction volume.

So, notice what you have. You know ‘P’ with the time and ‘n’ is the reaction order; ‘ΔH’ is enthalpy; ‘k’ is the rate. So, now suppose you have this power at different time. Basically, you can get a relationship between ‘q’ and function of time. It will be a function of time and also you will have some terms, because you can integrate this, you can write dq equals to this times dt, then you have a term q as a function of time.

Now you have this data point, the point is now you know how much ‘q’ you are getting how much is the heat at different time intervals, so you can plot it. You can plot q versus t; it could be something like this. Now the idea is, you can use any technique, any modelling, the optimization to get these parameters n, k, ΔH, as you know the value of q at different time intervals.

Now it is just matter of getting this n, k and ΔH. That tells you about the reaction, 'n' is the reaction order, you can tell whether it is zero order reaction, first order reaction, second order reaction. 'k' is the reaction rate, how fast the reaction is proceeding, and ΔH is the enthalpy. So, just from calorimetry, like in this case we saw from isothermal calorimetry, we can calculate these thermodynamic and kinetic parameters.

For this obviously you need data. First you have to collect the data, and then you can use this data to get the values.

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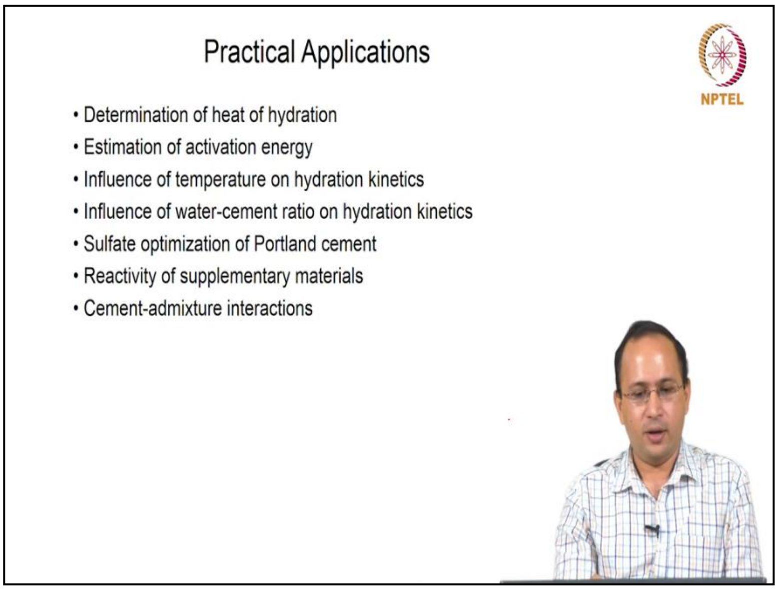

Practical Applications

- Determination of heat of hydration
- Estimation of activation energy
- Influence of temperature on hydration kinetics
- Influence of water-cement ratio on hydration kinetics
- Sulfate optimization of Portland cement
- Reactivity of supplementary materials
- Cement-admixture interactions

Now, we will look into some applications of calorimetry. The focus will be more on isothermal calorimetry, because that is used quite a bit, I will also draw some applications from adiabatic calorimetry, so that you can see the similarity. But most of the time we will talk about isothermal calorimetry because it is a most commonly used technique these days.

So where can we use this? It has a lot of advantages. We can determine the heat of hydration of a reaction at different temperatures. Because, here we can maintain the temperature, we can change the temperature. So, we will know the heat of hydration at different temperatures. If you do that, you can also calculate the activation energy, because when you have a data at different temperatures, you can calculate the activation energy.

Influence of temperature on hydration kinetics - it is very important. Suppose the reaction is taking place at really low temperature, say 5 °C. It is different than the reaction taking place at 30 °C. So we want to understand, how the temperature influences the kinetics. Also, we can use it to understand the influence of water-cement ratio. Simple example, low water-cement ratio high water-cement ratio, you can use this technique, to just see the effect of that.

Sulphate optimization, you must have heard of it. It is nothing but optimization of gypsum. To make cement eventually you grind clinker with gypsum. How do you determine how much gypsum you have to add? Conventionally what we have been doing is we optimize the strength. You add 1%, 2%, 3%, 4%, 5% of gypsum, and then you determine the strength, and see where you are getting the maximum strength. Usually it is around 3 to 5% typically, that number you should know. You can also use isothermal calorimetry to get the optimum sulphate content. So, it is also non-destructive technique, we do not have to do a destructive test, we are making non-destructive measurements.

Reactivity of supplementary materials - very important, these days we are using lot of new materials - pozzolanic materials, supplementary cementitious materials, flag, fly ash, silica fume, metakaolin, calcined clay. How do you understand or examine the effect of these materials on the reactivity of system. So, this technique can be used to understand that.

Also important is cement admixture interaction. Admixture, we are talking about, suppose, chemical admixtures, we are using retarders, we are using accelerators, we are using super-plasticizers, various chemical admixture, there is no concrete which does not have any chemical admixture, these days, when we are talking about high strength concrete, high-performance concrete. We are always using some sort of chemical admixture. So, we want to understand the effect of that admixture; we are interested in understanding the cement-admixture interaction.

If you use a particular admixture, does it delay your setting? Does it accelerate your setting? What is the influence on the main hydration? These things we want to understand. So, this technique can be used to examine those interactions.

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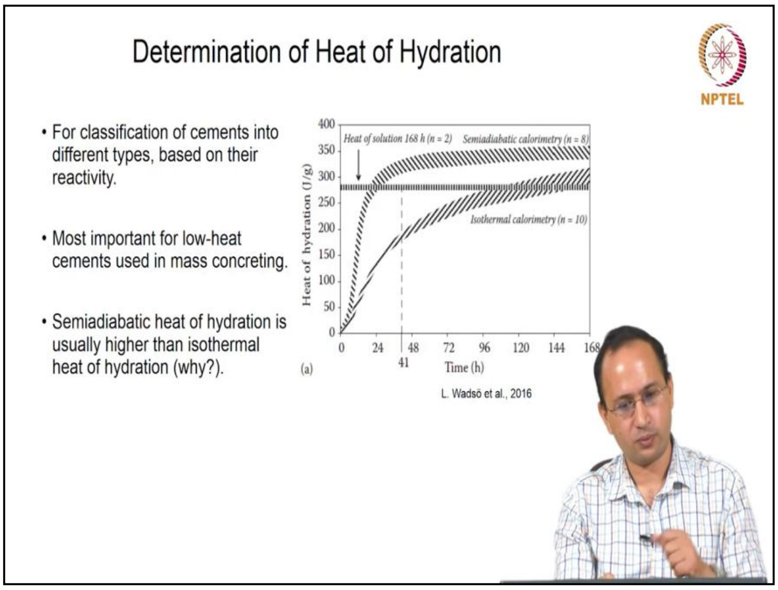

Determination of Heat of Hydration

- For classification of cements into different types, based on their reactivity.
- Most important for low-heat cements used in mass concreting.
- Semiadiabatic heat of hydration is usually higher than isothermal heat of hydration (why?).

L. Wadsö et al., 2016

So, starting with determination of heat of hydration, simply what you do is, you prepare your sample and here, in the plot, you compare 3 different techniques - isothermal calorimetry, semiadiabatic and heat of solution. So, you notice that first of all the heat of hydration from semiadiabatic is higher than isothermal calorimetry. It is again because of that temperature effect, because when you are increasing the temperature, you influence the cement hydration also.

So, these are the things you have to keep in mind. Roughly, this number you should remember, you get 250 to 300 Joule per gram; that is the heat of hydration for the cement. Obviously that will change depending on the temperature, depending on water-cement ratio, but that is a number good to remember. And the heat of solution basically is nothing but, you are dissolving your samples in very strong chemicals like hydrochloric acid, nitric acid.

And then you are measuring the heat of hydration. Since you have to use these hazardous chemicals, not many people use this heat of solution, because you have to deal with hydrochloric acid which is very hazardous. So, but anyway the values you get are very consistent, very similar to what you get from isothermal calorimeter. Semiadiabatic heat of hydration is usually higher than isothermal heat of hydration. Now you know why.

So the idea is, you should appreciate the difference. We cannot just compare, so you have to always know the conditions; like someone says I determined heat of hydration and found it to be 350, someone says 200, you have to always ask how did you calculate? Then they will say, we used the semiadiabatic calorimetry; that is the point. But as you can see, you are able to capture the cement hydration.

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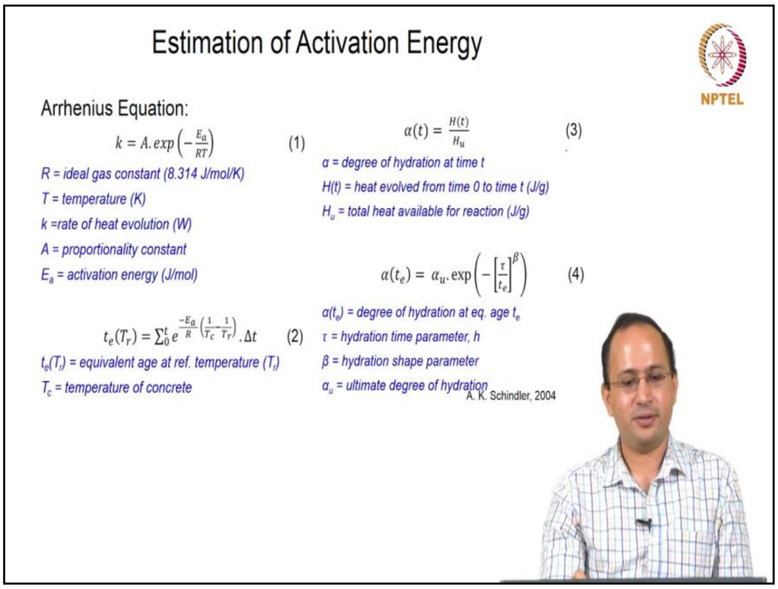

Estimation of Activation Energy

Arrhenius Equation:

$$k = A.exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

R = ideal gas constant (8.314 J/mol/K)
T = temperature (K)
k =rate of heat evolution (W)
A = proportionality constant
E_a = activation energy (J/mol)

$$t_e(T_r) = \sum_0^t e^{\frac{-E_a}{R}\left(\frac{1}{T_c}-\frac{1}{T_r}\right)}.\Delta t \quad (2)$$

$t_e(T_r)$ = equivalent age at ref. temperature (T_r)
T_c = temperature of concrete

$$\alpha(t) = \frac{H(t)}{H_u} \quad (3)$$

α = degree of hydration at time t
H(t) = heat evolved from time 0 to time t (J/g)
H_u = total heat available for reaction (J/g)

$$\alpha(t_e) = \alpha_u.\exp\left(-\left[\frac{\tau}{t_e}\right]^{\beta}\right) \quad (4)$$

$\alpha(t_e)$ = degree of hydration at eq. age t_e
τ = hydration time parameter, h
β = hydration shape parameter
α_u = ultimate degree of hydration

A. K. Schindler, 2004

Also, we can use this technique to estimate activation energy. A small review, already you are familiar with Arrhenius equation, what do we mean? See the reaction rate is dependent on the temperature. So, Arrhenius relationship basically is used to describe this relationship. k is the rate of reaction or in this case you can say rate of heat evolution, is dependent on the temperature, using this. It is the standard relation you use. Here you see E_a is the activation energy, R is ideal gas constant, T is the temperature. This is the relationship between the temperature and reaction rate.

Second thing, suppose you have concretes, for an example, at two different temperatures one concrete is at 15 °C, one concrete is at 30 °C. This is the idea of equivalent age which comes from this maturity method.

I am saying that, so your 20 °C concrete will take longer time to have the same maturity level; 40 °C concrete will get to that maturity early. How do you relate this? This relationship can be used: $t_e(T_r)$ basically is the equivalent age at reference temperature, equals to:

$$t_e(T_r) = \sum_0^t e^{\frac{-E_a}{R}\left(\frac{1}{T_c}-\frac{1}{T_r}\right)}.\Delta t$$

Again it is nothing but, you are using this rate relationship at two different temperatures and using that to calculate the equivalent age, because the temperature will affect the rate.

Now the important thing - how do we calculate degree of hydration? We all want to know what is the degree of hydration, is it 10%, 20%, 30%, 100%, how do we calculate? So, this allows you to calculate that heat of hydration. Suppose you have this hydration curve you have calculated the heat total heat with the time. And I know H_u which is the total heat formed when the reaction completes.

Or you can calculate it also from your composition. Suppose you start with the cement, cement has phase composition, you know pure phase releases so much of heat. So, you know the heat released by pure phases, you can calculate the total heat. Also, you can extend this plot and get the H_u value. Now if I want to know what the degree of hydration is, I do

$$\alpha(t) = \frac{H(t)}{H_u}$$

Where,

α = Degree of hydration at time 't',

H_t is the heat evolved at that particular time *(J/g)*,

H_u = Total heat available for the reaction *(J/g)*.

When H_t becomes H_u, you will get heat of hydration as 1, and when your H_t is equal to 0, heat of hydration is 0, which means no heat has released, that means there is no reaction and degree of hydration is 0. So, based on this curve, you can calculate degree of hydration. Suppose someone gives you the information, he says that he did this calorimetric experiment and he got this heat versus time, then we can give the degree of hydration after 28 days.

You just have to look at that curve, calculate the H_u, go to the time, like suppose 28 days in this case and then calculate this. Because heat is coming from the reaction, as long as there is reaction, there is going to be heat. So, if you know the heat, you can calculate the extent of reaction. Now again this degree of hydration can be related. So, α is the degree of hydration at equivalent age.

Similar concept here, degree of hydration at equivalent age can be related as:

$$\alpha(t_e) = \alpha_u . \exp\left(-\left[\frac{\tau}{t_e}\right]^{\beta}\right)$$

Where,

α_u = ultimate degree of hydration; τ = hydration time parameter, h ; β = hydration shape parameter.

It is again the concept of equivalent age.

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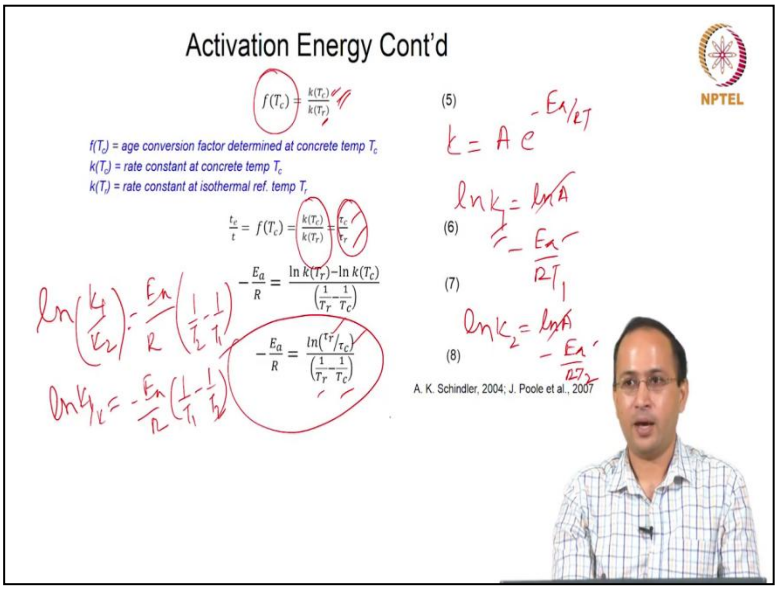

Activation Energy Cont'd

$$f(T_c) = \frac{k(T_c)}{k(T_r)} \quad (5)$$

$f(T_c)$ = age conversion factor determined at concrete temp T_c

$k(T_c)$ = rate constant at concrete temp T_c

$k(T_r)$ = rate constant at isothermal ref. temp T_r

$$\frac{t_e}{t} = f(T_c) = \frac{k(T_c)}{k(T_r)} = \frac{\tau_c}{\tau_r} \quad (6)$$

$$-\frac{E_a}{R} = \frac{\ln k(T_r) - \ln k(T_c)}{\left(\frac{1}{T_r} - \frac{1}{T_c}\right)} \quad (7)$$

$$-\frac{E_a}{R} = \frac{\ln(\tau_r/\tau_c)}{\left(\frac{1}{T_r} - \frac{1}{T_c}\right)} \quad (8)$$

A. K. Schindler, 2004; J. Poole et al., 2007

$k = A e^{-E_a/RT}$

$\ln k_1 = \ln A - \frac{E_a}{RT_1}$

$\ln k_2 = \ln A - \frac{E_a}{RT_2}$

$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$\ln k_1/k_2 = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

So, we are looking at the sensitivity for temperature. These are some calculations, but we are trying to relate. So, suppose you have done experiments at one temperature, how can you translate that to a different temperature? So, we are interested in this factor, $f(T_c)$ this is the age conversion factor which is nothing but the ratio of rate constants ($k(T_c)$ and $k(T_r)$ at different temperatures.

'r' is reference, 'c' is the current temperature or concrete temperature. Reference is usually 20ºC (20 or 22 ºC). So, we are interested in this ratio of rate constants, because rate constant depends on the temperature. So, the ratio of rate constants is nothing but the ratio of time constants$\left(\frac{\tau_c}{\tau_r}\right)$.

So, finally we can get this relationship (Eq.8). Before that, let me just go back, so you have this Arrhenius relationship. $k = A.\exp\frac{-E_a}{R.T}$

Now if I take natural log, and suppose at one temperature I say k_1, T_1, and similar thing I can write at different temperature $\ln k_2 = \ln A - \frac{E_a}{R.T_2}$; now from this, I can just subtract we will cancel (lnA) out; and we can get a relationship between k_1, k_2 and your activation energy. Now we want to calculate the activation energy A, we know T_1, T_2.

Now we get this ratio, suppose you subtract it so,

$$lnk_1 - \ln k_2 \rightarrow \ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Or you can also write it as

$$lnk_1 - \ln k_2 \rightarrow \ln\frac{k_1}{k_2} = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

So, now we have relationship which relates the temperature and rates, so we are interested in this ratio $\left({}^{k_1}/_{k_2}\right)$ at two different temperatures, that is what we are getting from here.

So, we have to calculate this ratio $\left(\frac{\tau_c}{\tau_r}\right)$, through this relationship (Equation 4 on slide number 5). Once you know that for a particular temperature you can use that. So, finally we can calculate this activation energy $\left(\frac{E_a}{R}\right)$ when you know τ_r,τ_c, T_r, T_c. It could be T_1, T_2; simply put if you have a data for two different temperatures you can use this relationship to calculate the activation energy.

How do you get that τ? You already know the temperature; now how do you get the τ? You calculate the degree of hydration (Refer graph on slide 5). You have this plot H vs. t, then you can calculate the degree of hydration, (α vs. t); it will be a similar plot. Now you fit this and you get these parameters τ and β. So, you know τ and β for a particular temperature and you use that to calculate the activation energy. We will stop here and we will pick it up from here in the next class.