Sustainable Materials and Green Buildings
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Lecture: 9- Fuel for Cement

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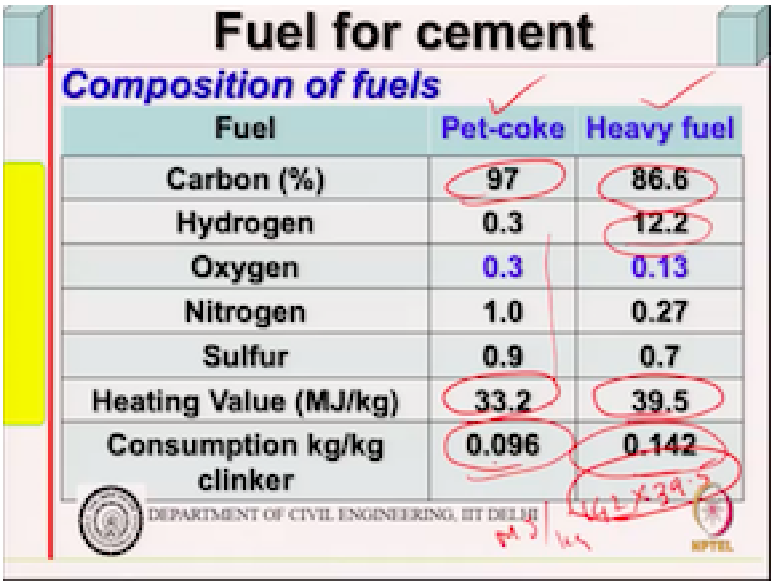

Fuel for cement

Composition of fuels

Fuel	Pet-coke	Heavy fuel
Carbon (%)	97	86.6
Hydrogen	0.3	12.2
Oxygen	0.3	0.13
Nitrogen	1.0	0.27
Sulfur	0.9	0.7
Heating Value (MJ/kg)	33.2	39.5
Consumption kg/kg clinker	0.096	0.142

.142 × 39.5

MJ/kg

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Ok, so remember last class we were looking at fuel for cement, right and if you remember we looked at two case, at two fuel for example one of them is a pet-coke, Pet-coke and another is heavy fuel for example now, carbon is 97 percent and rest all material are there. In this one it is around 86.6 percent now finally the heating value is 33.2 mega joules per kg and this is 39.5 mega joules per kg because this hydrogen must be contributing, whatever it is.

So the consumption kg per kg of clinker is 0.096 is 0.142, 0.142 kg per kg of clinker, So, if I look at it I can actually calculate out because it will be 0.142 multiplied by 39.5 because this is the amount of fuel consumed per kg of cement and this is the calorific value so this is the mega joules produced used up for per kg of cement mega joules used up for per kg of cement.

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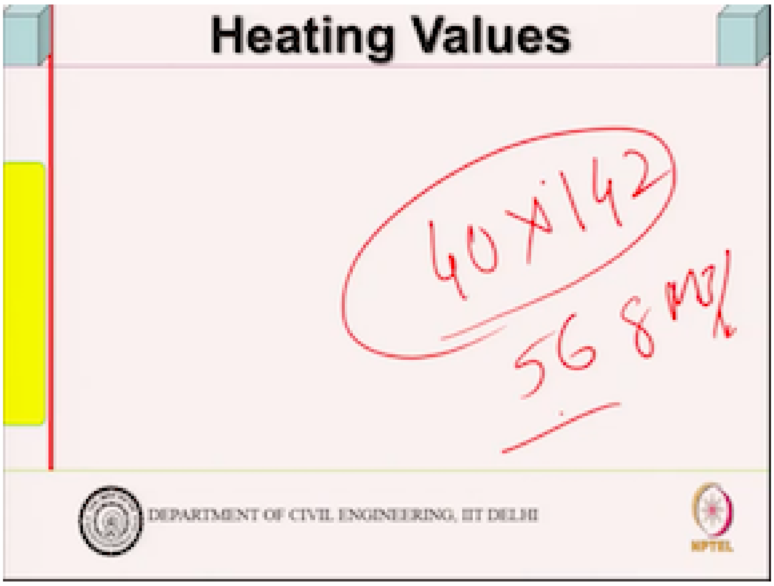

Heating Values

40×142

$56\,8$ MJ/kg

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So, the embodied energy if somebody is trying to calculate out right from the all ingredients and things like that, one can actually get some idea for how much is the energy actually used for clinkerisation of cement. So something like 39.5 let se 40, 40 into 14, 140 into 40 into142, that would be mega joules per ton because 0.142 was there multiplied by 1000, so 40 into 142 mega joules per ton actually and if I am trying to find out for per kg this will be something like this, which will be how much something like 56 point something ya mega joules, per kg of cement. So that is what energy consumed for clinkerisation

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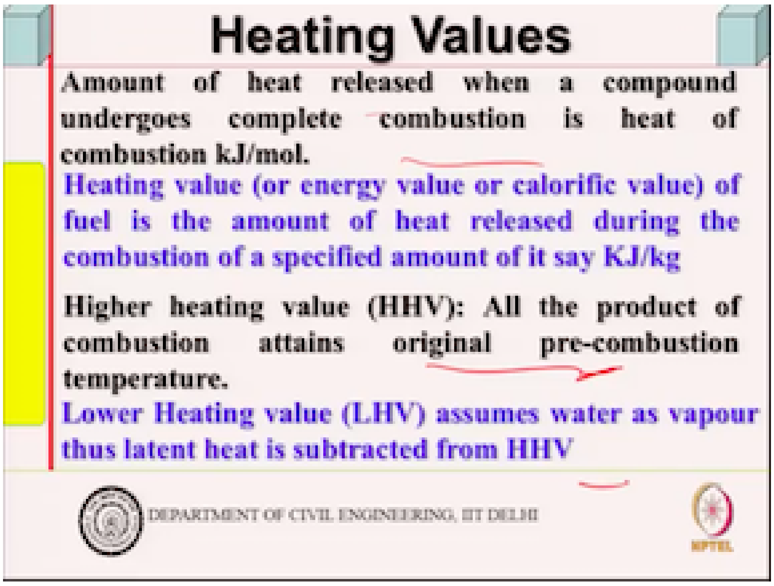

Heating Values

Amount of heat released when a compound undergoes complete combustion is heat of combustion kJ/mol.

Heating value (or energy value or calorific value) of fuel is the amount of heat released during the combustion of a specified amount of it say KJ/kg

Higher heating value (HHV): All the product of combustion attains original pre-combustion temperature.

Lower Heating value (LHV) assumes water as vapour thus latent heat is subtracted from HHV

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Anyway so, that is, this I already mentioned in the last class the amount of heat released when heating value is that how we define and we have two of them high heating value higher heating value and the lower heating value. In this one we are assuming everything it generate the heat and then everything is in the original state, for example there will be some moisture which will vaporize so latent heat is absorbed by the moisture vapour now, if it comes back to the water state then the heat value you get because then the all the heat released and it will have gone for clinkerisation process.

So higher heating value corresponds to no water moisture vapour this also at the state of water as it was combined in the free will itself. Because , so that is why it's higher lower means water has gone as vapour therefore that heat is not available, now using for clinkerisation or whatever it is.

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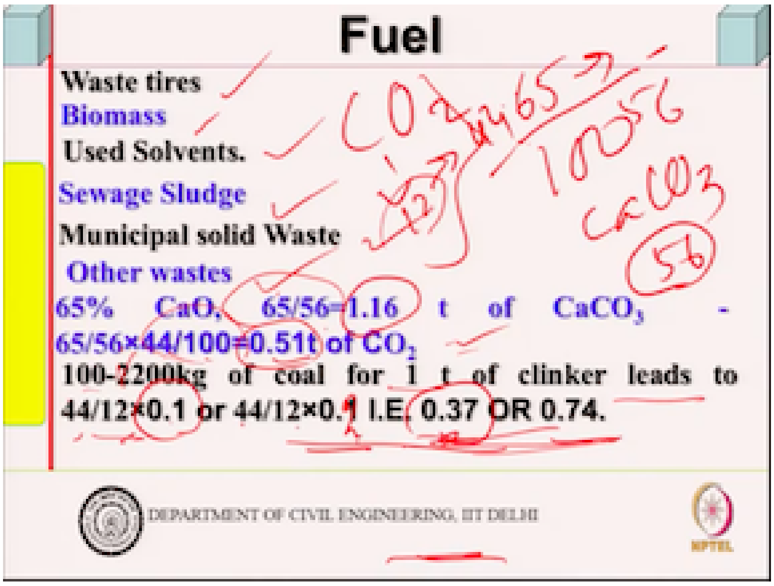

Fuel

Waste tires
Biomass
Used Solvents.
Sewage Sludge
Municipal solid Waste
Other wastes

65% CaO, 65/56=1.16 t of $CaCO_3$ - 65/56×44/100=0.51t of CO_2

100-2200kg of coal for 1 t of clinker leads to 44/12×0.1 or 44/12×0.1 I.E. 0.37 OR 0.74.

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So, that is what fuel cells is so that is what the additional fuel, lot of people are trying to use like waste tires, Biomass, used solvents and sewage sludge, Municipal solid waste, other waste and in all this cases in all these cases you get an advantage because this are waste material, you will not use it otherwise so in accounting this will not go to my carbon accounting actually.

This was already there, waste material I do not know I would had to have some bio productive land for depositing them or doing something , so this one's do not go into daily accounting, so that is an advantage from environment point of you, both accounting point of vies otherwise also because we are reducing down the waste generation.

Because all kind of if you see many cement plants during the like during the preheater they use all kind of waste materials and this calculation we have done already that the amount of carbon dioxide generated, from the fuel because it is 100 to 200 not 2200 kg of coal for 1 ton off clinker if you are using coal and that generates gives you around point this.

So, this calculation we have looked before earlier and that is why we say because this is from stoichiometric relationship, supposing I have got 65% calcium oxide in my Portland cement then for 100 calcium carbonate 56 kg of 56 kg is a calcium oxide, 40 is the carbon dioxide. So 65 by 56 I have to use 1.16 tons of calcium carbonate for in one ton of cement. 1.16 tons of calcium carbonate will go in 1 ton of cement.

So this produces this if you look at it 65 by 56 into 44 by 100 so it gives you about 51 tons, because from 65 in 100 kg or 100 ton or 1 ton you will have point 0.65 calcium oxide, corresponding to 0.65 calcium oxide this divided by 56 will give you how much calcium carbonate is required and from that, that much amount of calcium carbonate we produced 40 point this 40 by 100, 44 carbon dioxide.

So, therefore this is the carbon dioxide that you produce from one ton of cement because of clinkerisation but fuel also produces carbon dioxide and this is because if you use 44 because you already means, if it is all carbon, so one carbon produces CO2, one carbon 12 is 44 carbon dioxide 44 carbon dioxide one because 12 mass of carbon will produce 44 mass of unit of mass carbon dioxide.

So, 44 divided by 12 and if you are using 0.1 ton that is 100 kg or in the extreme case 0.2 tons this is 0.2 tons, 0.2 tons then this will be 0.37, 44 by 12 into 0.2 or 44 by 12 into 0.1 so 0.37 to 0.74.

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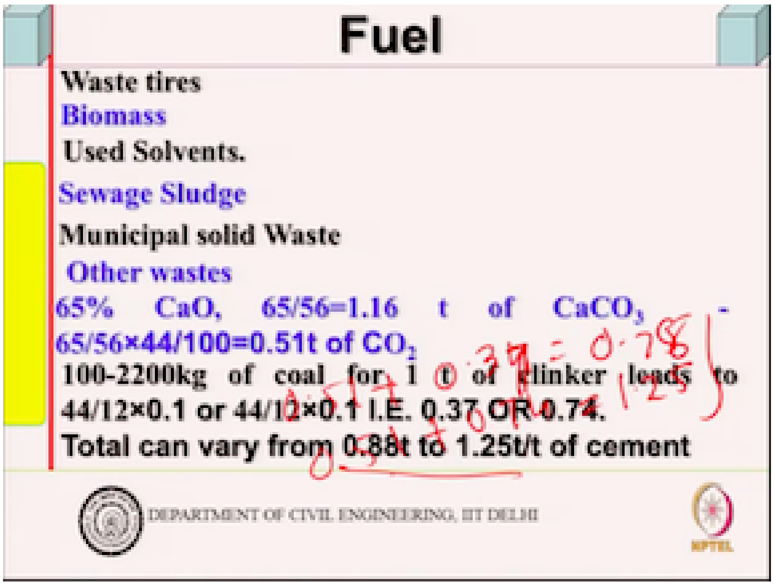

Fuel

Waste tires
Biomass
Used Solvents.
Sewage Sludge
Municipal solid Waste
Other wastes
65% CaO, 65/56=1.16 t of $CaCO_3$ -
65/56×44/100=0.51t of CO_2
100-2200kg of coal for 1 t of clinker leads to
44/12×0.1 or 44/12×0.1 I.E. 0.37 OR 0.74.
Total can vary from 0.88t to 1.25t/t of cement

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That is why we were saying that my total carbon is carbon emission for 1 ton of cement will be 0.51 plus 0.34 which will make it 0.75 or 0.51 plus point how much was it double of it actually 37, this was 37, so 37 means 78 and this was 74 so how much this will make it 1.25, so on an average if you look at it I can say a that one ton of cement produces one ton of carbon dioxide.

So that is the issue actually and that means you need more carbon land for sequestration of this carbon, to have this carbon you need more plants to absorb this carbon dioxide and that is why you produce so this is the contribution to carbon land and ecological footprint.

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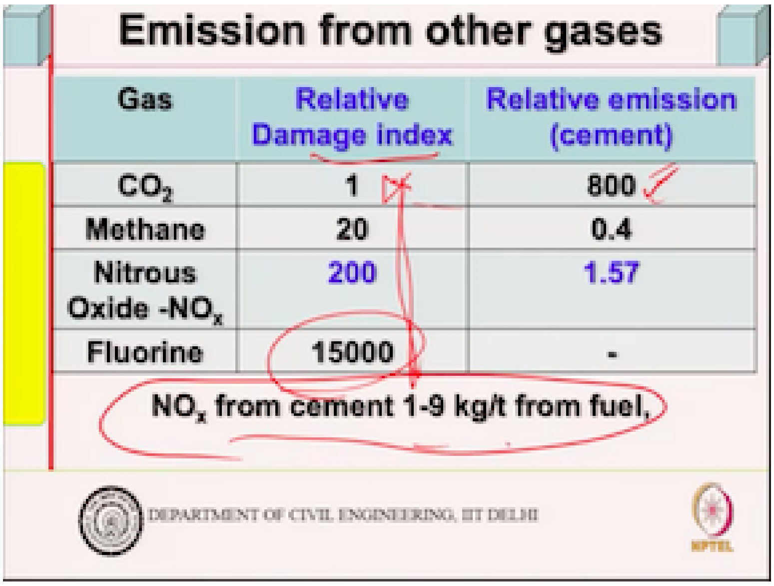

Emission from other gases

Gas	Relative Damage index	Relative emission (cement)
CO_2	1	800
Methane	20	0.4
Nitrous Oxide -NO_x	200	1.57
Fluorine	15000	-

NO_x from cement 1-9 kg/t from fuel,

So that is why people are so much bothered about so much bothered about the carbon issue in cement, other than of course fossil fuel very much it is there and we know of course the green house gas effect emission from of course other gas relative emission from cement is 800 if I take this this is the emission relative damage index related to this is 1 to 15000 but emission from cement is something like 800 we have seen earlier in a table. So, NOx from cement is around 1 to 9 kg per ton from fuel because nitrogen gets oxidized to nitrous oxide at high temperature and something of this kind.

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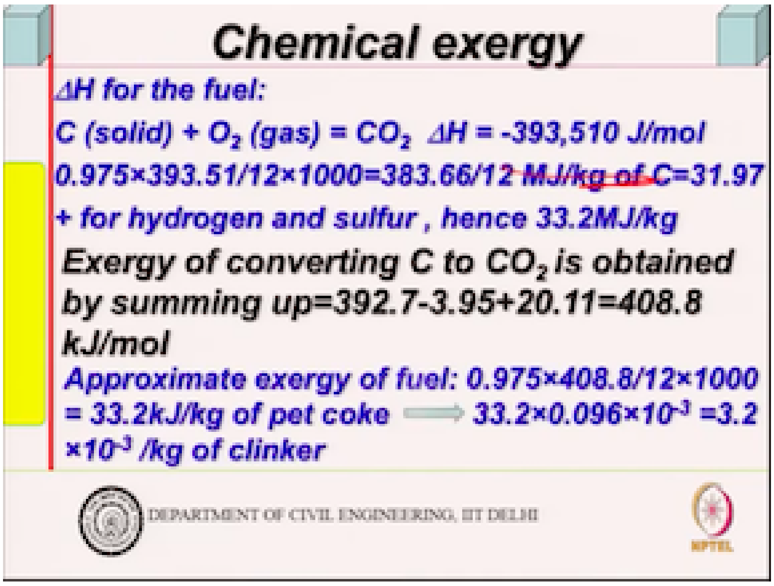

Chemical exergy

ΔH for the fuel:

C (solid) + O_2 (gas) = CO_2 $\Delta H = -393{,}510$ J/mol

$0.975 \times 393.51/12 \times 1000 = 383.66/12$ MJ/kg of C=31.97

+ for hydrogen and sulfur , hence 33.2MJ/kg

Exergy of converting C to CO_2 is obtained by summing up=392.7-3.95+20.11=408.8 kJ/mol

Approximate exergy of fuel: $0.975 \times 408.8/12 \times 1000 = 33.2$kJ/kg of pet coke $\Longrightarrow$ $33.2 \times 0.096 \times 10^{-3} = 3.2 \times 10^{-3}$ /kg of clinker

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So that is what it is. So that is what we have seen it, carbon this is the kind of joules per molecule I think I have not look into this the chemical exergy part this is not important now looking at that, that is why I am not looking at that and heating values is what I am interested in heating value so I am interested in.

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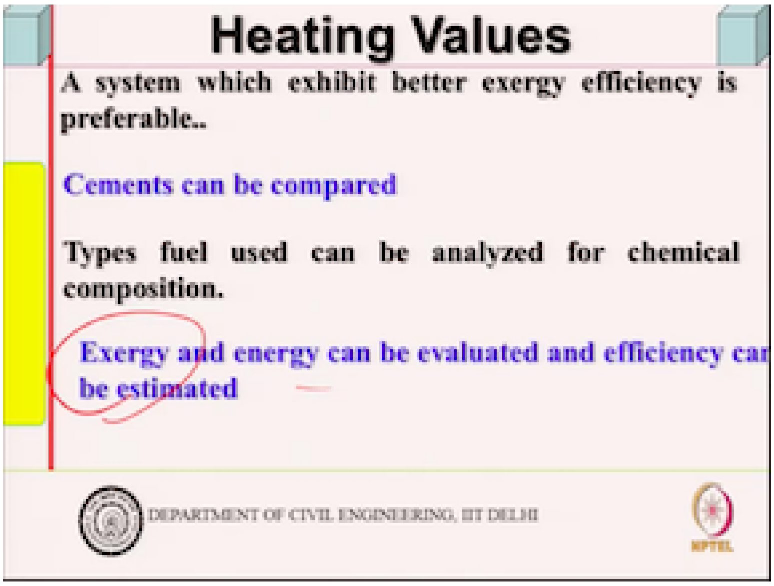

Heating Values

A system which exhibit better exergy efficiency is preferable..

Cements can be compared

Types fuel used can be analyzed for chemical composition.

Exergy and energy can be evaluated and efficiency can be estimated

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Now in case of process one is interested in the exergy part where we find out the even remove out the entropy losses because wherever you are producing you are converting energy into work or something there we will energetic efficiency is there this much energy produce the work, but there is some work efficiency as I showed in case of coal because you are bringing down to from the mine to when you are producing the power there is a lot of losses every stage.

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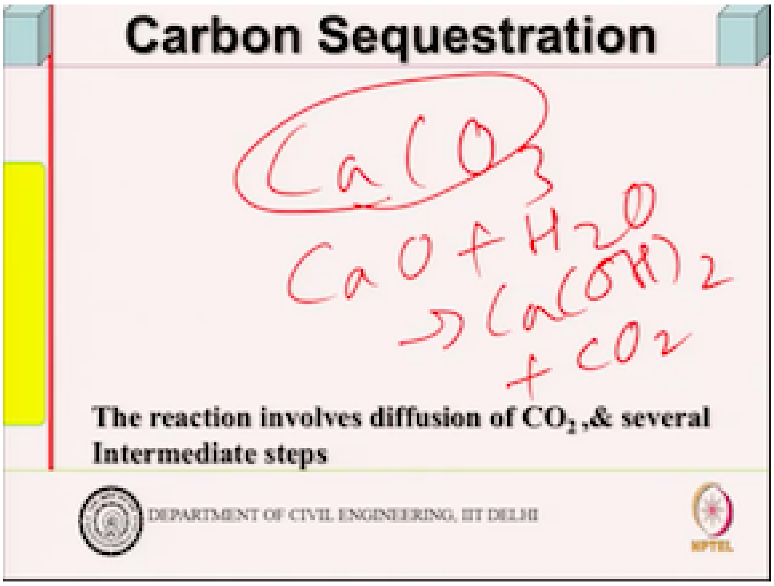

Carbon Sequestration

$CaCO_3$

$CaO + H_2O \rightarrow Ca(OH)_2 + CO_2$

The reaction involves diffusion of CO_2 ,& several Intermediate steps

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So carbon dioxide produce calcium carbonate is a natural material it is stable calcium carbonate is stable magnesium carbonate these are carbonates are stable, calcium oxide is not stable the moment you bring in contact with water it will form calcium hydroxide and if you leave it to the atmosphere it will then convert it into calcium carbonate because calcium oxide plus water lead to calcium hydroxide and this in added to carbon dioxide to form calcium carbonate so finally stable state exist, So you give energy to convert calcium carbonate into calcium oxide in the cement.

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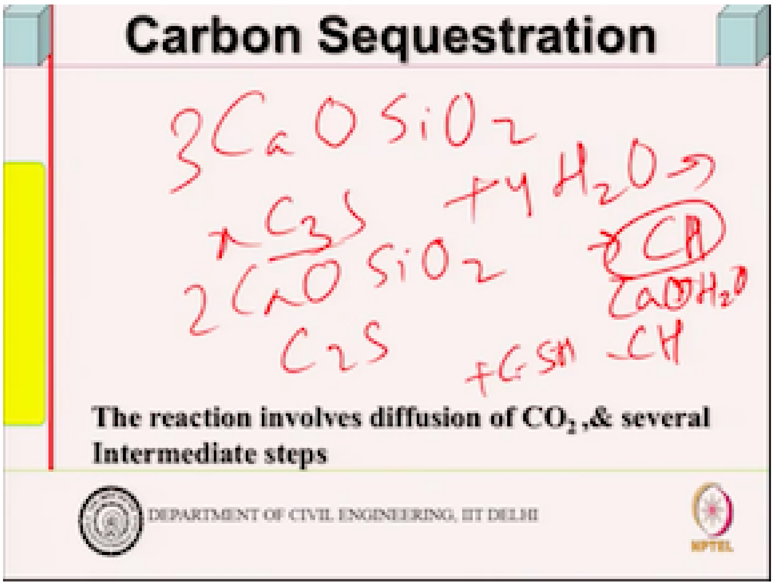

Carbon Sequestration

$3CaO\,SiO_2$

$\rightarrow C_3S \quad + y\,H_2O \rightarrow$

$2CaO\,SiO_2 \quad \rightarrow CH$

$CaOH_2O$

$C_2S \quad + CSH \quad CH$

The reaction involves diffusion of CO_2 ,& several Intermediate steps

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And therefore it will have always a tendency to go back so hydration reaction you add water to cement for when you add water to cement when you add water to cement that tri calcium silicate which you call C3S then di calcium silicate with you call C2S this one reacts with water you can actually have the X and Y or whatever it is.

It produces some amount of calcium hydroxide which you denote as calcium hydroxide we calcium oxide and water something like this so you write it as CH in the abbreviated form we write calcium hydroxide as CH. It produces some CH plus some calcium silicate hydrate as you call it this will be CSH here.

So, calcium hydroxide is produced so calcium state in the cement reaction I get calcium hydroxide and in the long-run calcium hydroxide absorbs carbon dioxide from the atmosphere in presence of moisture and goes back to calcium carbonate state and that in concrete technology you call it carbonization process which reduces down PH etc but that is not the issue here, issue is that cement in the long run thousand years or millions of years cement hydrates will again tend to some of it will tend to go back to calcium carbonate from where it has come, .

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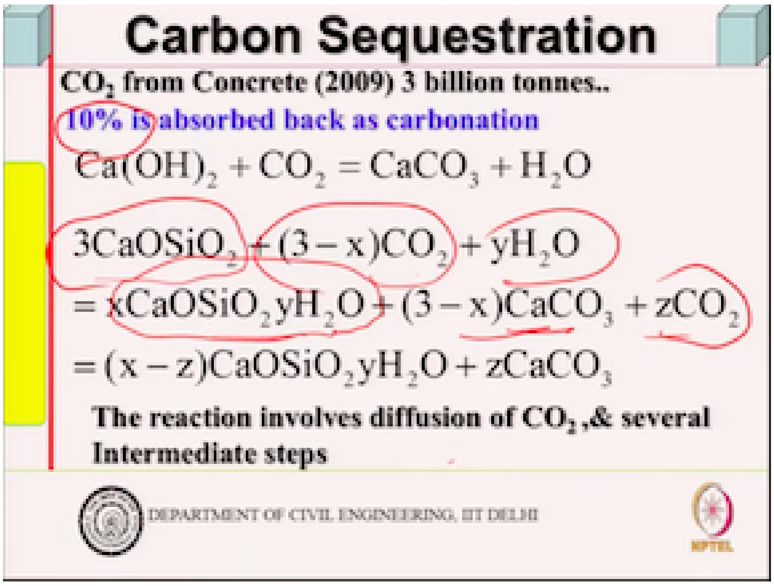

Carbon Sequestration

CO_2 from Concrete (2009) 3 billion tonnes..

10% is absorbed back as carbonation

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

$$3CaOSiO_2 + (3-x)CO_2 + yH_2O$$

$$= xCaOSiO_2yH_2O + (3-x)CaCO_3 + zCO_2$$

$$= (x-z)CaOSiO_2yH_2O + zCaCO_3$$

The reaction involves diffusion of CO_2 ,& several Intermediate steps

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Let us see what happens actually so this is carbon dioxide from concrete 3 billion tons 10 percent is absorbed back as carbonation, immediately after some time I mean after a short period of time. In 2009 it was world produced 3 billion tons and 10 percent because as I said calcium hydroxide in the cement will absorb carbon dioxide in presence of course water and form this.

Now, not only that this will make our this is this will make this system makes when I have reduced down my calcium hydroxide the CSH, as I said that is your calcium oxide SiO2H2O some xyz this will be the calcium silicate hydrates now this itself is not stable at low PH not stable at low PH, stable at low PH.

So, even this when calcium hydroxide is consumed by carbon dioxide from atmosphere through carbonation process even this is not stable this tends to get converted into carbonates so that is the reaction, so that is the reaction you see so this is the calcium silicate carbon dioxide and water and it will form calcium silicate of this kind calcium carbonate directly also calcium silicate tri calcium silicate reacts with carbon dioxide to form calcium carbonate and of course silicate hydrates and besides that in the long run all of them can get converted into calcium carbonate back but it will be very very long time because it is starts the reaction process physical process is also involved.

The carbon dioxide must reach to the cement hydrates and at the surface it can reach, surface is exposed to carbon dioxide but to penetrate it into inside carbonation front must penetrate inside and if all the concrete are to be getting they should be carbonated and CHS had to be broken in into calcium carbonate it will take very long time.

So therefore 10 percent absorption one can take globally for the whole year different ones which you are constructed earlier etc. So some carbon carbonation occurs and this reaction process involves division of carbon dioxide at several intermediate steps, so philosophically we can understand it has come from calcium carbonate it will go back to the, it will again go back to the calcium carbonate state which is table but it will take very long time, millions of years.

If everything is to be carbonated ok so this was so this is the carbon issue of cement is important so people have been trying to actually work with various other types of cement various other types of cement this is one issue since so far we are looking at cement and relative issue related to cement we are looking at, we will go to concrete later on.

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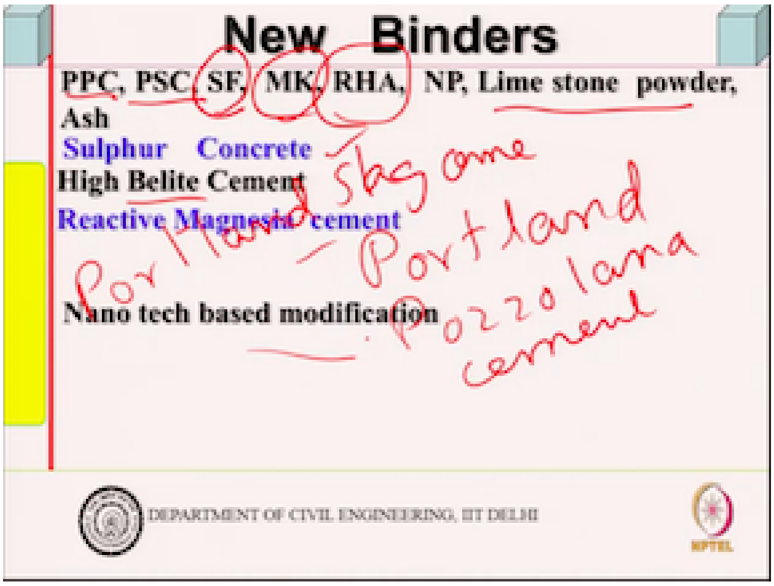

New Binders

PPC, PSC, SF, MK, RHA, NP, Lime stone powder, Ash

Sulphur Concrete

High Belite Cement

Reactive Magnesia cement

Nano tech based modification

Portland slag ceme

Portland pozzolana cement

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So if you look at cement of the other kind there are varieties of cement that has been actually attempted you will be familiar with something called Portland pozzolana cement. Portland pozzolana cement this is PPC Portland pozzolana cement for those who are not familiar with concrete technology so much I will just we will talk about this also. This is Portland slag cement, these are very well known cements then, silica fume has also been meta kaolin, these are added to the cement, system rice husk ash and limestone powder.

Various other kind of ashes, Sulphur concrete there are other types of cement has been tried like High Belite cement, I will come to all of them, reactive magnesia cement and then nanotechnology-based modification these are attempt made to reduce down the carbon dioxide production from cement because, ordinary Portland cement if you have you will have one ton producing nearly one ton of carbon dioxide.

So if you can get something diluted with something else one way and then a newer type of cement are not new there are many of them are old but they have been now re-looked into alkali-activated cement so will look into each one of them.

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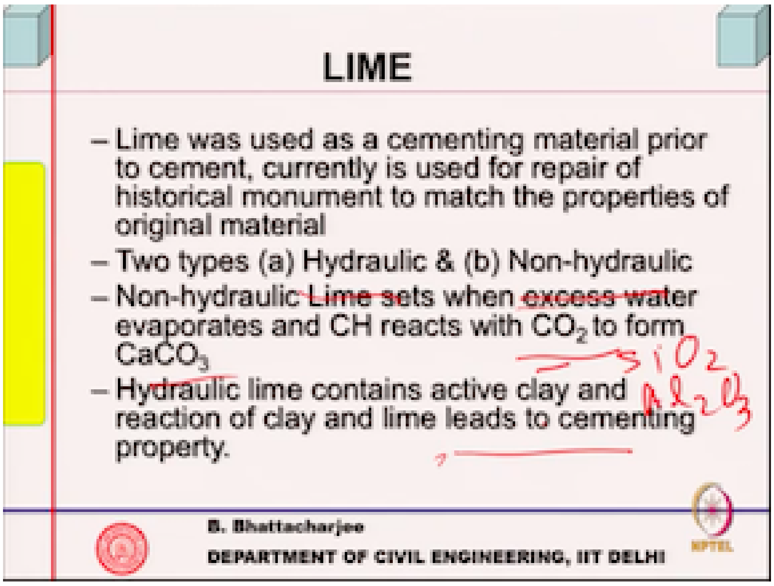

LIME

- Lime was used as a cementing material prior to cement, currently is used for repair of historical monument to match the properties of original material
- Two types (a) Hydraulic & (b) Non-hydraulic
- Non-hydraulic ~~Lime sets~~ when ~~excess water~~ evaporates and CH reacts with CO_2 to form $CaCO_3$
- Hydraulic lime contains active clay and reaction of clay and lime leads to cementing property.

SiO_2
Al_2O_3

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Now if you want to look into this then first you must understand we are dealing with the lime system, , we are dealing with lime and silica system. So lime has been there cementing material for long long back and currently also people use it for archaeological restoration of monuments, archaeological monuments.

There are two types of lime, hydraulic and non-hydraulic lime. So, non hydraulic lime sets when excess water evaporates and calcium hydroxide so what you do you take the lime stone, produce the lime it might have more quantity of calcium oxide which with water will react form slag and lime, calcium hydroxide and when exposed to water it absorbs carbon dioxide to form calcium carbonate there for its solidifies.

So, use of lime is very old, in fact it is recorded is that first used was possibly in Israel somewhere they did the recording, it might have been elsewhere but they found out, traced it somewhere around 8000 BC. So nearly around 10000 years ago using lime.

Hydraulic lime is the other one which contain some active clay because clay will be the impurity in lime as well, so it contain some active clay so as you add water the clay reacts with the silica reacts with the lime but this process is relatively slow. As long as your clay is reactive, clay would be means clay would means silica and alumina and if it is reactive then if it is reactive not all clay or silica are reactive for example Quartz is not reactive.

Quartz is crystalline, very stable material. You have silica all over the place and there in the nature therefore they are stable they would not react further. You see man made materials are not stable natural materials are stable because man made material would be produced with the expense of energy so you raise what is called chemical potential. It will have a tendency to react so clay, all clay are not reactive, there are some who react so some play reactive and how they become reactive let us see a little bit.

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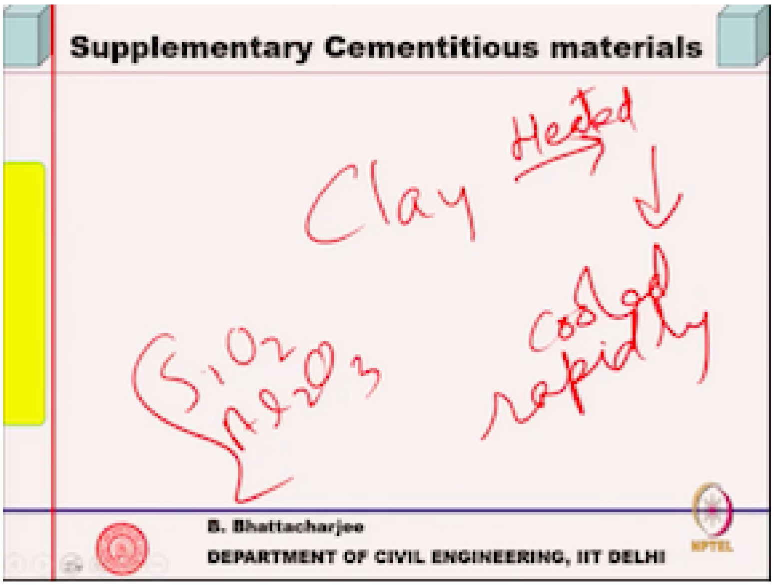

Supplementary Cementitious materials

Clay $\xrightarrow{\text{Heated}}$

↓

cooled rapidly

SiO_2
Al_2O_3

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So this, pozzolana name came from volcanic ash. Now volcanic ash is the ash that comes out in the volcanic eruption in the beginning so what would have happened actually the clay would have subjected to lot of heat. Hot powdery like thing ash and this would settle to the atmosphere that means around 25-30 degree centigrade, suddenly it is exposed to 25 to 30 degree centigrade.

So, clay heated and cooled rapidly volcanic eruption so that is that is that clay again because you have heated it up silica and alumina system and cooled it rapidly that means certain amount of energy would be trapped in that it will not form it will not dissipate all the energy which is gone in heating and it would it would be therefore its chemical protection is increased.

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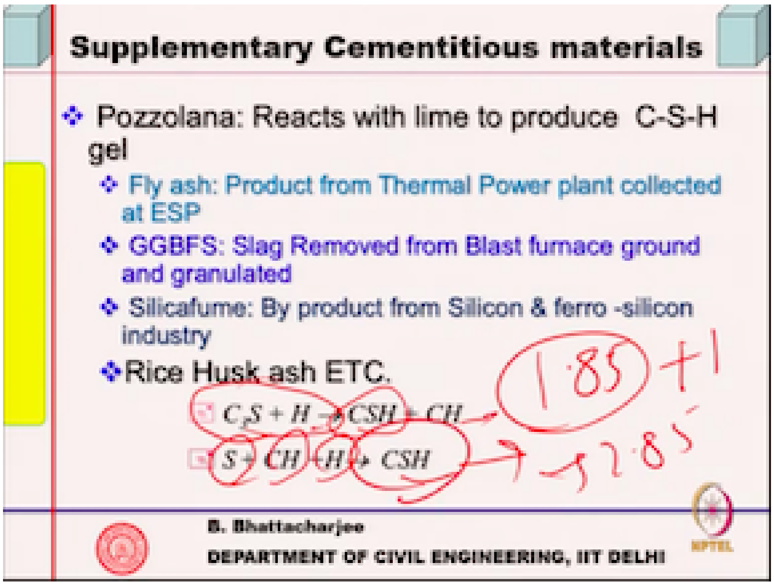

Supplementary Cementitious materials

- Pozzolana: Reacts with lime to produce C-S-H gel
  - Fly ash: Product from Thermal Power plant collected at ESP
  - GGBFS: Slag Removed from Blast furnace ground and granulated
  - Silicafume: By product from Silicon & ferro -silicon industry
  - Rice Husk ash ETC.
    - $C_2S + H \rightarrow CSH + CH$
    - $S + CH + H \rightarrow CSH$

1.85 + 1

→ 2.85

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It will have a reacting tendency so that will give rise to reactive silica and alumina system it will give rise to reactive alumina system and this was actually discovered long back. So Romans used this for their (21:14) and things like that and that is why the name pozzolana came into being.

So this reacts with lime because, this is reactive so same reaction as I was just mentioning this one this one lime some active clay reacts, so basically what is happening is your calcium hydroxide reacting with some sort of silica forming calcium silicate hydrate sort of thing or other if I write it in that for CH plus S in presence of some water would form CSH, so that is pozzolanic reaction is something of this kind, it reacts.

So this is what has been so this has been used so pozzolana therefore fly ash you can use GGBFS you can use the product from thermal power plant collected electrostatic precipitator, product from thermal power plant collected at electrostatic precipitator. Now, you can see that coal when burnt it is grinded and burnt grinded to find powder like powder condition so that its surface area is large and it can burn now but the clay as impurity which comes from mines along with it that also get heated up and the fine ash that goes we call it fly ash.

Fine ash that goes towards the chimney along with the flue gases that you fly ash. The larger ones you call bottom ash they go down below but this fly ash we cannot leave it to the atmosphere and they are charge, very fine particle colloidal form suspension when you put it to the electrostatic precipitator they are collected as powders.

So this is as a reactive clay same reactive material, reactive silica and alumina because we have heated it up and then cooled it very rapidly something like volcanic ash itself. Similarly ground generator blast furnace slag, now slag is removed from blast furnace and grinded and granulated. Now what is when you are producing iron so steel production iron would be the ore will be molten, it will melt it.

It will contain lot of clay impurities how do you remove it lime is added to this so lime is added, lime is added to remove clay to remove impurity or silica alumina as I go to SiO2 system Al2 system from iron. Now iron is very heavy 7.85, molten iron so this material lime and this in hot condition they are actually form a slag and floats over the molten iron. This is drained out then this is grinded and granulated and this is also granulated to fine sizes, almost cement sizes and this is also reactive because same issue same issue it has been heated up and then cooled rapidly.

Now, this will have lime also so this will have lime also while this may have lime or may not have lime it will depend upon how much impurity was there in the ash in the form of lime but in this one lime will definitely will be there so this is other one this silica fume come from as a byproduct from silicon and Ferro-silicon industry.

What they do, they heat up quartz, quartz is heated up to high temperature of the around 2200 degree centigrade and to actually get silicon metal now in the process some silicon oxide. Very rich silicon oxide around 85-90 percent silicon oxide which fumes or gases comes out which is condensed and you get what is called micro silica or silica fumes condensed fume and this is also a material which will react with calcium hydroxide easily so this will also react with calcium hydroxide easily, we will see some of them.

Rice husk ash if you burn anything now which is rich in silica and alumina and found that ash rest of the material will go out carbon etc will go out so rice husk if you burn it you can actually produce some sort of pozzolana and you will see quickly some of their reaction. So the essential reaction in this pozzolana are, C3 something like calcium same tri calcium silicate reacting with water.

Some calcium hydroxide now this calcium hydroxide reacting with silica in present of water forms CSH, that is the kind of essential reaction in this called pozzolanic reaction essential pozzolanic reaction. The stoichiometry here is not very difficult around 1.85 calcium hydroxide is required to react with one unit of silica to produce 2.85 this product, this product, so we might look into this again.

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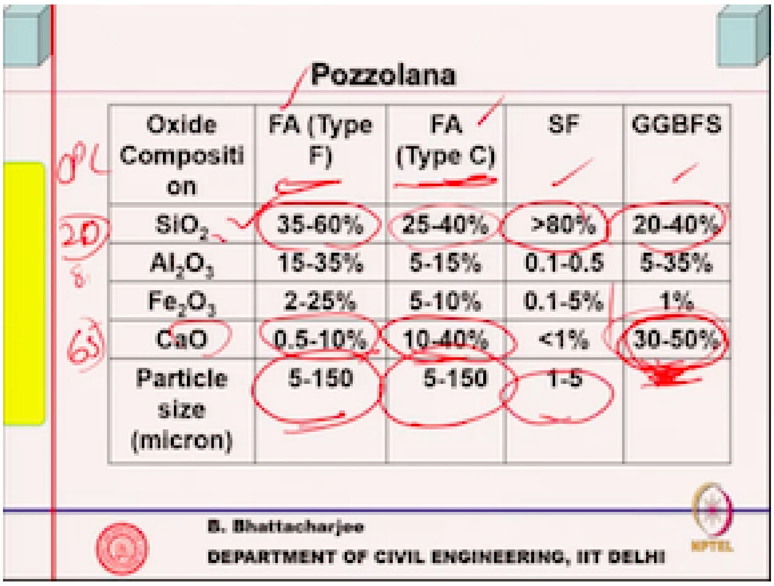

Pozzolana

Oxide Composition	FA (Type F)	FA (Type C)	SF	GGBFS
SiO_2	35-60%	25-40%	>80%	20-40%
Al_2O_3	15-35%	5-15%	0.1-0.5	5-35%
Fe_2O_3	2-25%	5-10%	0.1-5%	1%
CaO	0.5-10%	10-40%	<1%	30-50%
Particle size (micron)	5-150	5-150	1-5	

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So, there are various type of pozzolana, fly ash or varieties kind silica fume ground grinded blast furnace slag. Now, two types of fly ashes has been classified according to HTM classification, one is called type F other is called type C. Type C has got high amount of calcium hydroxide that is what calcium oxide, that was I telling you because the impurity in the carbon or coal system it contains sufficient lime calcium carbonate can be also be an impurity.

So when it is 10 to 40 percent, this is called type C, type F has got this less while this is higher obviously this is less here, rest all some are different so if you look at it here this is 80 percent silica rest all are very small silica fume ground granulated blast furnace you will have this much higher because you have added lime to remove the impurity out from it.

So therefore this has got lime, now cement if you compare just like for OPC let me it here this will be about 21 percent 20 percent or so, this will be around 65 percent or so this about how much? 8 percent or something of that order.

So there is small, these are larger ones so, if you look at this this has got somewhat less lime, this is also what is still lesser lime and they do not have lime so therefore this one GGBFS can show some sort of cementitious reaction also, because both this is active this is also active but they do not exhibit this reaction on their own you need a catalyst or an activator to start this cementitious reaction in lime, cementitious reaction in lime so therefore if you activate them GGBFS you can make new kind of cement will come to that. One more important aspect is that the physical characteristic this is 5 to 150 micron, similar size, particle size micron and this is very small 1 to 5 micron.

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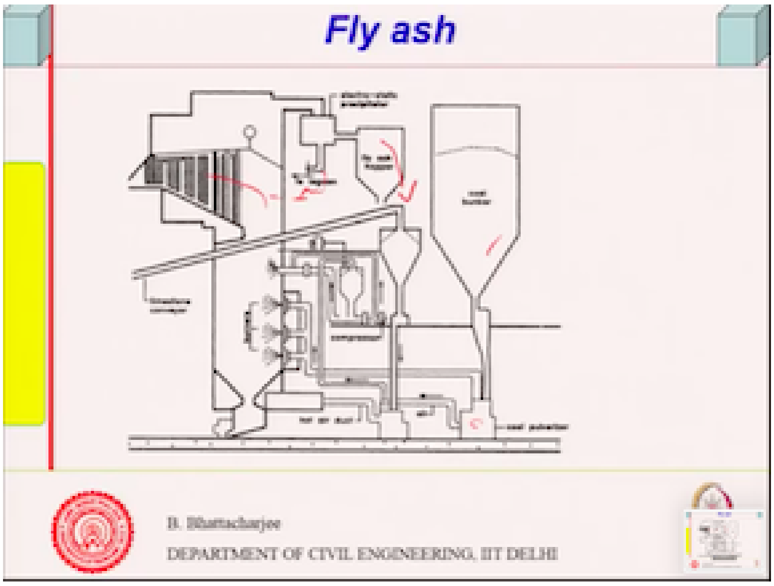

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Some more comparison we will have quickly this is how fly ash is produced schematic diagram, coal bunker, this is coal pulverizer, this is crust, fine powder it is made then hot air, hot air and then this is hot air duct etc and then essentially the essentially the burning occurs somewhere here and then the fluid gases go these are B and electrostatic precipitator collected here, this is to either to a lagoon where they are stored because this is a waste, fly ash is a waste.

So you will find somewhere there are what is called is ash ponds, ash pond and other would be in a Hopper so bottom ash goes to the ash pond generally together with some fly ash but now a days it is not recommended that fly ash should be sent to the ash pond because there when you mix it up then they are not useful. So if you mix two things up it is not useful.

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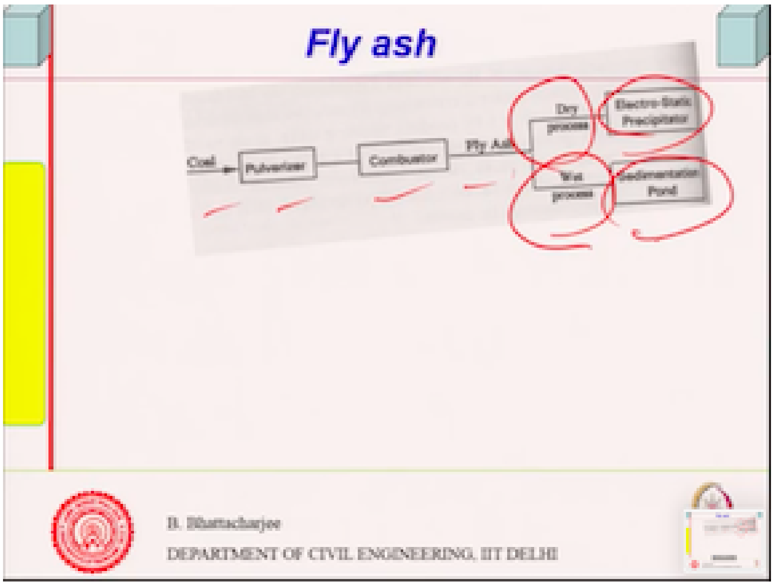

Fly ash

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So this is how it is so, so this is how it is produced actually this is what is so coal pulverizer, combustor, fly ash, dry process, electrostatic precipitator. If you have bottom ash usually meets slurry with water through wet process of transport and sedimentation in the pond it is done but you see it has got a double effect now.

Double effect is if the waste are not utilized you need space, you need space, so where to store them. So if you have visited some thermal power plant you will find huge ash ponds all around many places because old days there would actually mix up fly ash and bottom ash together make a slurry out of it and put it in the ash pond that is not the best way to use them because then what you do the pond gets all full you need more land or it might make a mound out of it or a hill then what you do the hill actually gets and then the hill and then you have greeneries on top of it so that it does not fly away.

Stability of this one, there are several issues involved so this is a problem and this is again shown in the similar manner, the fuel gas goes here, fuel gases precipitator's collector etc. So (31:29) oversize pulverize ash, use as that can be a classifier which can separate out the final once from the course around the process fly ash.

So this is the (31:38) where they can be stored, this can from this is the chimney flue gases go out and through electrostatic precipitator goes PFA is stored in the bunker and then one can separate them, classify them to all sort of things. So we will see that this can be used in cement. So look into other cementitious material or as you call it in they are classified as cementitious, they can give cementing property and we will look into them we can have some question after having a small break