Sustainable Materials and Green Buildings Professor B. Bhattacharjee Department of Civil Engineering Indian Institute of Technology Delhi Lecture: 11-Strength of Concrete with Supplementary cementitious materials with composite cements

(Refer Slide Time: 00:19)



So we are looking at strength of concretes as you can design with the supplementary cementitious materials like fly ash concrete. I think we were looking at this in the last class and we said that if the strength of OPC is somewhere here and we design the system for 28 days similar strength, similar 28 days strength, you will find that this would be true for ground granulated GGBFS, also GGB, Fly Ash Ground Granulated Blast Furnace Slag etc. etc. Even metakaolin or you know like barn clay pozzolana. So they would show strength, long-term strength better.

Silica fume, of course behaves slightly differently because as I mentioned in the previous class, maybe sometime, that they are very fine. So they go into the intestacies of the cement itself. For example, if these are your cement clinker, these are your cement clinker, and there, once they the silica fume will go somewhere there, silica fume will go in between them because they are still finer than, finer than the cement particle. And this happens also at the aggregate, also happens at the aggregate interface or boundaries.

If this is my aggregate, so this is, generally these are the weakest link, near the aggregate packing of cement particles are not the best, very best you know like the aggregate particles let us say, they would be packing would not be very good and we call it interfacial transitional zone where the packing near the aggregate, packing is not very good.

But when you put silica fume, let us say, a fine material which is finer than cement, which is finer than cement, they will go into those space, They will go into this space and once hydration of cement takes place, once hydration of cement takes place, let us say, this hydrates, some of this will be used up and the hydration product will occupy more volume; outer product which is outside the original green boundary, they will occupy more volume because.

So these are all the hydration product, original ones are the black, similarly here also this is the unhydrated portion, this is the hydration product and this hydration product have got calcium hydroxide which can react with this fine silica fume. So densify this particular zone itself because this material is very fine and since they are fine, right in the beginning going into the intestacies of the cement particle themselves they reduce down the porosity and pore sizes.

So silica fume can show even somewhat early strength improvement while fly ash and GGBFS as we have seen, GGBFS we have seen that it shows, early strength would not be there. And later on long term strength will be there.

(Refer Slide Time: 04:10)



So GGBFS and fly ash or any other kind of similar pozzolana which have more of silica alumina system, barn clay system, etc. etc. having particle size larger, they do not show this kind of they show this kind of behavior that is early strength is relatively low. So you need, also their reaction process being slower, you need more curing. So curing time required is more for this material. Silica fume also require high curing, that is not, and that is there.

Rice husk ash as I told you, they are cellular in structure, they form cell sort of things. They are cellular in structure, structural cells, something like this cellular in structures. I think I have shown in, I might have shown you electro micro graph, which showed that they are actually cellular in structure. So, but these are, this can, they are very reactive because SiO content is very high. SiO2 is content is very very high which is reactive and pozzolanic reaction can initiate as soon as calcium hydroxide starts liberating.

That means your C2S or C3S starts reacting because C3S reacts earlier. So these materials can show even, can show somewhat not, not diminished strength during the early age, might similar strength almost because of their pore filling effect. Rice Husk Ash also does same thing but Rice Husk Ash has got other problems because they are cellular in structure, although they have large surface area, they consume a lot of water in the system. So they have, issues related to mouldability.

(Refer Slide Time: 06:02)



So generally one would prefer GGBFS and Fly Ash etc. for moderate strength concrete. It can be used for slightly higher strength concrete but you have to design this and this is used for very high strength concrete or high strength concrete. Silica fume is for high strength. You can have judicious combinations of all this to make it, make it higher strength. Cost issue is also there. So all that makes a good sustainable material. All that makes good sustainable material. Now one issue of sustainability as we shall see later on when you come that it should be as much as possible maintenance free.

(Refer Slide Time: 06:47)



So in that context just I was showing you that, this is my aggregate, let us say this is my aggregate portion, this is another aggregate. Cement clinker is here and this is the hydration product at a stage, this is unhydrated cement. This space between, this aggregate bit and the space between this will be filled with by non-sealing precipitate of calcium hydroxide, if it is only ordinary cement clinker, this is the hydration product of the cement because cement hydrates.

Some of the original grain volume that is occupied by hydration product, the size will reduce and it will go outside also and there will be some precipitation outside, calcium hydroxide etc. will precipitate outside So this calcium hydroxide particularly is a non-sealing precipitate, does not seal but go there. So this is the scenario of cement clinker.

If you look at, let us say, this is for slag. Slag can react because as I said slag has got about 40 percent calcium oxide, right and nearly 40 percent SiO2. Now since it is rich in calcium and also been heated up together, it can show cementitious reaction. But not on its own, only when it is activated by some alkalis. So generally alkali activation is done. Cement if you add, replace part for example 50 percent slag and 50 percent OPC, in fact you can go upto 70 percent by score.

Now this one, this one will activate the slag reaction also. So slag, hydration products of slags would also be there and if you look at it, if you look at it, hydration products of slag also would be there, right. Hydration products of slag also would be there so hydration products of Slag, hydration products of OPC, clinker, additional because it has got 40 percent, this has got 40 percent C, 40 percent near about 40 percent. Now if you see in this one 65 percent C, 21 percent around 20 percent you know 21-22 percent S, so roughly around one third.

So, 40 and its one third is about 13, 12-13 percent. So 12-13 percent of this will go into cementitious scenario. But still I am left with around 25-26 percent, this will react with the calcium hydroxide produced probably. So you have both cementitious and pozzolanic reaction in ground granulated blast furnace slag and this fills in the product that makes it more dense. So hydration products of clinker with water, hydration products of slag with water and impermeable precipitate of calcium silicate now calcium silicate hydrates.

So that is how they actually show and these reactions continue for longer period of time. They are initially slow process but later on also they continue and therefore they densify the structure. If you calculate out from the stoichiometry, then specific gravities of calcium hydroxide and calcium silicate hydrate, water, etc. plus water etc. if you see the specific gravity of the initial product, I mean density of the initial product, or volume occupied by the initial product and final product will be similar, they are not much different, unlike cement.

Cement is a solid portion, volume of the solid increases, cement and water, volume of the solid increases. Density of the final product is less than that of original unhydrated cement but more than that of water. So, therefore hydrated cement particle occupies the space occupied by water and therefore solid portion increases.

So that is why the capillary porosity etc. As you know the water feed space which is you know from which is not occupied by hydration product when water evaporates that leads to capillary process in case of ordinary Portland cement but in case of clinker, this will, this was filled with non-sealing calcium hydroxide precipitate, non-sealing calcium hydroxide precipitate but the same space now gets filled with sort of similar volume changes are not there but now it is sealing material, calcium silicate hydrate which has got a binding property or sort of.

So these are sealing. So impermeable, impermeable precipitate, impermeable to water but not to vapour of course because gel pores are there, very fine pores are there in cement hydrate system through which vapour can permeate but not water. So this is how, this is this is how, this is the reason why they show better strength development in the long run and possibly a densified structure with less water penetration potential.

(Refer Slide Time: 12:05)



So therefore, from this point of view one could have something like composite cement as well. Composite cement is a combination of a cement by inter-grinding Portland cement clinker with granulated sag and fly ash or intimately and uniformly blended ordinary Portland cement, finely ground granulated slag and fly ash with required addition of gypsum. So you can grind them or may not grind them. So composite cement combines all, therefore you are able to use a large quantity of waste material which were otherwise would not have been used and reduced on the carbon dioxide because the more you know lesser you use the clinker is better because clinker is a one which produces a lot of carbon dioxide.

(Refer Slide Time: 12:57)



So this is what the current code gives. Fly ash around 15-35 percent, slag from 20-50 and Portland cement, so this is extreme case would be you would not like to have this much so you can go upto 35-40 and use this kind of combination so that is what cement factories, those who are producing composite cements. So you see, now it was, earlier I was talking of two, now we are talking of 3, 3 components in the cement itself to cut down mainly on the CO2 issue of this particular one.

(Refer Slide Time: 13:29)



If you look at fly ash hydration reaction, fly ash does not, it is not cementitious because it is SiO2 Al2O, what is this, Al2O3 system Fe2O3 etc. etc. NO lime, lime is very little, lime less than CaO, less than 10 percent in type F fly ash. So this is cementitious reaction but the calcium hydroxide here would consume this and again form impermeable calcium silicate and calcium aluminate hydrate.

So, calcium hydroxide which you are can leach out if you add this material judiciously, appropriately system designed correctly designed system then you can reduce down that non-sealing precipitate which can leach out and create more pores so therefore durability issues and strength issues both comes into picture. So cement, such supplementary cementitious material can be used in cement to cut down onto the clinker and that is what is being attempted now.

(Refer Slide Time: 14:32)



If you see all cementitious material in this diagram, triangular diagram, this is the lime, 100 percent lime is here100 percent, 90 percent etc. 0 percent lime is this line and 100 percent SiO2 here, this is 0 percent SiO2. 100 percent so, if you take this slag for example, slag will have lime whatever percentage is, silica this much percentage is, and alumina small percentage.

So, if you see you know this is slag and let us see, we are looking at various clays. Silica fume because its reach in silicon oxide so it is somewhere there. Rest of the materials are very small, so it is somewhere here. So as you can see silica fume is somewhere there, let me use another colour, red colour let me use. So this is silica fume because low quantity of SiO, I mean low quantity of CaO and lower quantity of, lower quantity of CaO is 100 here, lower quantity of Al2O3 as well reach in silica fume, 100 percent silica fume. So you can see that Portland cement somewhere is here, Class C fly ash, class F fly ash (15:48). So judicious combination of all these are possible.

So cement today is not the cement or in future obviously the clinker would be replaced in a much much bigger way to cut down on the carbon dioxide scenario because otherwise you need that much amount of land, earth surface and greeneries to capture that carbon dioxide. You know that is how we calculate the carbon dioxide. So if you see, this is actually the European code has already identified this over the years and they have come out with more 27 combinations of cement system.

(Refer Slide Time: 16:25)



So if you look at this, it is kind of a snapshot sort of, not much I mean although I have worked with it. CEM I in EN in British Standard because we were associating ourselves with British Standard because I can understand that language as well. So it is EN 197, all Europeans they have now combined single code and these are appendixes. Anything additional from BS will be appendixes, anything additional from German DIN will be also.

So it will be called DIN EN 197 you know if it is the German one. Something specific to the German from the German code they have added that would be the part of appendix. This is common. So they have identified 27 combinations. CEM I is Portland cement, the only one. Now if you see 95 to 5-100 percent is a clinker there. This is a clinker line, others are not there. This is one cement, sometimes you might be using for some specific purposes. You come to then CEM II which Portland stag cement, Portland silica fume cement, Portland pozzolana cement, various combinations are there CEM 2AS etc., so one can go into this and you can see percentage of slag or silica fume or pozzolana, these are increasing as you go down.

(Refer Slide Time: 17:42)



So CEM I, CEM II if you can see then minor radiation factor should be there, there are other kind of you know for example, crasher, there are other kind of things, property enhancers are added sometimes into the cement system, so they are alloying. CEM II continued, Portland fly ash cement, Portland shale burnt shale cement, Portland limestone cement and Portland composite cement, so composite cement will have 6-20 percent of all of them. The fly ash, slag etc. etc. burnt all slag and pozzolana. Right, so these are.

(Refer Slide Time: 18:18)

-	<u> </u>	CTV DA	truce	tind.	<u></u>	-		-					in a
CTM I	Ballman omet	CEMINE	The lat	an unt	¥ .							-	0.01
		CEMING	5 10 19	en 10-95	-	-	-	-	-	-	-	-	0.001
CEMIN	anet*	CEMINA	1010-00	-	c						-	0101	
		CEMINE	4510-54	-	c					-	-	-	0.10.1
	Composite connent *	CEMIVA	4010-54	1010-30	- c 18 to 30> -							-	0.61
CENT		CEMIVIE	20 to 38	D1 84 50	-	-	- 31 No 5	(-	-		-	0.61
1 1 1 1 1	- teenvi	who perments and CEW V plane FL	CEM BA	M and CE	M 105-M	in Poza	sianit ca ker shal	ments CE	nd by O	nd CEN nigradi	n d'he	nd in or	npost 4

Then you have got CEM III, blast furnace cement which will have much less clinker content but lot more slag content. This is pozzolanic cement, will have more of this pozzolana here than composite cement other combinations. So you have such 5 cements means subsections totally 27 combinations there proposed which is to be used in what kind of situations, some guidelines are also there. And all this does what, this reduces this component as much as possible. When you do not need, you do not use that. So that is the idea, that is the idea of cements, that is the idea of varieties of cements but this is not all about the cements, this is not all about the cements.

There are other kinds of cements which I shall discuss next. In the same ordinary Portland cement, there are changes being done in order to have, less energy requirement less carbon production. Also there are cements like magnesia base cement, so you do not have lime at all and you know the whole reaction system is different, therefore you are not depending upon the clinkerisation of the way you do. Then there are other activated slag and activated fly ash or activated silica, silica alumina or pozzolana system.

(Refer Slide Time: 19:42)

High Belite Cement C₂S formed at 1200C, against 1400C for other clinker compound, less carbonation, slower strength gain Lower carbonation in process, may reduce the carbon emission by 20-25% Slower initially but Adequate strength development in the long run Typically 40-42% alite (C₃S) by 32-33% belite (C₂S) instead of 55 and 20% respectively Slower initially but Adequate strength development in the long run DEPARTMENT OF CIVIL ENGINEERING, IIT DELHI

So, let us look at them, some of them right now. High Belite Cement is one of them, high Belite cement is, and high Belite cement is one of them. What is belite? Belite is C2S. Belite is C2S. So high Belite system is one of them. Now this is formed at 1200 degree centigrade, now this is not new, this has actually been tried up on earlier also to cut down onto the cost.

Now, we know that C2S strength development is slower. First C3S is a first one which gives us strength.

If you look at the strength component you know strength contributor or I rather like to say strength is not the right, it is strength potential because cement does not give the strength of concrete. Cement gives you strength when I test specification of cement when I look at, I look at the strength potential in concrete. So measurement we do by Mortar test. So this is not correct to say strength of cement because we do not really mean, I mean this is what is used but I am looking at actually strength potential of cement.

So strength potential in terms of that C3S is a one which starts reacting in the beginning and there is a reason also because we have produced it at higher temperature if you remember. If you remember the phase diagram we talked about which I will talk again, C3S is produced at higher temperature, it has got higher heat of hydration than this. C3S got the higher heat of hydration. Therefore this is the one, which will react immediately. C3S reacts next so this gives you higher strength or rather you know reacts faster while this reacts late.

So if I use, if you increase this one, which I can do by changing the calcium oxide proportion. (21:34) there is something called lime saturation factor, after that there will be of course free lime but you know the amount of C3S or C2S produced depend upon how much calcium oxide I have put into the system. So temperature will be lower for production of this, so this forms at 1200 degree centigrade while 1400 degree centigrade for C3S in another one.

So therefore I need lesser energy, lesser energy thermal energy to (22:08) and it generates less carbon dioxide, calcium hydroxide also as we know calcium hydroxide generates less. IN fact this, it is, it is less since calcium hydroxide is less generally calcium is CH is less actually, so you will have less chances of, I mean it is less alkaline in the beginning itself but if you can design the system, carbon dioxide of course it will not absorb much but it has got slower strength gain so that is the thing.

So one can use this, lower carbonation process may reduce the carbon emission by, because carbon dioxide, clinkerisation process also reduce the calcium carbonate in the scenario. Right in the beginning, calcium carbonate content can be less in this one. So it can reduce the carbon by 20-25 percent. Slower strength initially but adequate strength development in the long run so it is almost like similar pozzolanic cement or so on.

Typically 40-42 percent C3S as against 55 percent C3S in ordinary Portland cement. 30-33 percent C2S as against around 20-21 percent in ordinary Portland cement in OPC instead of 55 and 20 percent respectively. So you can see that this is increased, this is reduced. So this is increased, this is reduced. So slower strength in hydration process initially but adequate strength that is what you get in the long run.

(Refer Slide Time: 23:39)



So this is what the phase diagram, I might have shown you earlier, I am just repeating. So alite is formed here in this temperature that is your say 3S, belite forms somewhere there , therefore your temperature you know almost it is formation is almost there within this zone so that we do not go to that high temperature. So that is the thing, carbon dioxide evolution. Naturally calcium carbonate content if you reduce down, the carbon dioxide evolution will reduce down. There you are not using carbon dioxide evolution will somewhat reduce down.

(Refer Slide Time: 24:20)



So lime saturation factor, I think I might have, you might have come across this terminology somewhere in concrete technology. So lime saturation factor is a basically a ratio of calcium oxide to rest of the material. So some formula basically depending upon their density as well. And density and reactivity and etc. etc. So proportion of lime, proportion of lime C divided by this is silica proportion, alumina and iron. So if this is high, supposing this is high then beyond 1 or 100 percent you will have free lime that is what we know.

But we control this, one can control this to generate high Belite cement, so some reaction has been there. Similarly there are silica ratio, alumina ratio, etc. So lime saturation factor greater than 100 results in free lime, hence is generally maintained in ordinary Portland cement clinker 95 to 98 percent and higher silica ratio means more C3S etc. etc. So you can combine this, so compound one can approximately find out from one of the empirical formula given.

(Refer Slide Time: 25:37)



This is the kind of formulae well, accuracy is not very high obviously, so today you can do external deflection and another analytical technique to find out more accurately how much is a C3S content, how much is the C2S content etc. in a given cement but earlier days one would have used or even now people use roughly to find out how much is the C3S. So the amount of C3S that is your alloyed will depend upon lime, 4.07 lime 7 minus more silica means this will be less, so high rest all are minus you can see, so if this is high, lime is high, you will have more alloyed and C2S if you see, more, more silica of course, so if reduce down the lime, increase the silica this will increase and C3S will reduce and more the C3S, less will be C2S, so less C3S means more C2S.

So this the, this is how people have tried to control and this has got a renewed interest now because it can reduce your carbon emission by 20-25 percent energy deduction everything put together. C3S is given by this formula, C4AF is given by this formula so this is, this is what is I said 55 it goes to about 40, 30 to 40. This was, if this is one calculate out it goes to around 30 or so, so that is the thing.

(Refer Slide Time: 27:06)

High Belite Cement LSF 78-83 Chemical content of Fe, Cr. B) and Ba) oxides are important (Doping) Rapid cooling and quenching for Belite stabilization HBC has good freeze thaw resistance, lower shrinkage, Lower permeability and resistance against chemical attacks vis-à-vis OPC DEPARTMENT OF CIVIL ENGINEERING, IIT DELHI

So lime saturation factor used is 78-83 percent in this kind of cement not 95 to 98 which would have been ordinary Portland cement clinker and Fe, Cr, B etc. you know like iron, chromium, boron, barium oxides are important, important because you have two melting point. You would have heard of what is called elevation of boiling point, depression of freezing point.

So in a, in a solution if you put a solute its boiling point changes so when you put some other material melting point, when melting temperature at which it will melt to control it and lower it down, they also add these ones in controlled conditions as a part of the research, so people have actually done this then rapid cooling and quenching for belite stabilization, so they quench it after rapidly cooled and quenched cooling, essentially cooling, so high balanced cement has good free thaw resistance, lower shrinkage, lower permeability and resistance against chemical attacks vis-à-vis OPC, almost similar to performance of pozzolanic cement and similar ones actually they more densified structures and all that.

(Refer Slide Time: 28:33)

Reactive Magnesia Cement $Mg(OH)_2 + CO_2 + H_2O = MgCO_33H_2O$ 5Mg(OH), +4CO₂ + H₂O Higher water demand PC-MgO blend, hydrates independently Porous blocks, concrete, ground improvement DEPARTMENT OF CIVIL ENGINEERING, IIT DELHI

Then the next cement I will talk about is reactive magnesia so by the way this, this is this some, some research quite done in 1980s-90s in fact in, in fact when I look at literature in channels I find the most referred paper comes from ACC. Dr. AK Chatterjee's paper, it is referred very well all over the place, done in 1990s. They have tried this but then now the Chinese are popularizing.

They have started producing things of this kind of cement, because of this carbon issue. Carbon issue was not an issue earlier in 1980s-90s, they possibly wanted to have another cement and you know cost reduction and things like that. Reactive magnesia cement been a quite of bit is being attempted in Australia and New Zealand.

So, essentially what it relies on? Magnesium hydroxide reacting with carbon dioxide of atmosphere forming this and this further reacting with you know these are the kind of reaction, this, that other reaction to be something like this. This is one reaction, this could be other reaction. So essentially the cement will have magnesium hydroxide right in it which will absorb carbon dioxide from the atmosphere and therefore it will solidify, it will solidify

So that is, that is the thing but this has got higher water demand to make it more, make it more flow-able, the water demand has been high that is what is seen and people have tried to attempt, these are all attempted not yet come in to the market, this will possibly take some time. Portland cement, magnesium oxide blend, they have of course two of them, Portland cement hydrates independently and this one magnesium oxide will work separately right so people have tried with this.