Admixtures And Special Concretes

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Lecture -41

Mineral Admixtures : GGBS - Part 3 : Hydration of slag & Durability of slag cements

Recap:

Hydration of slag:

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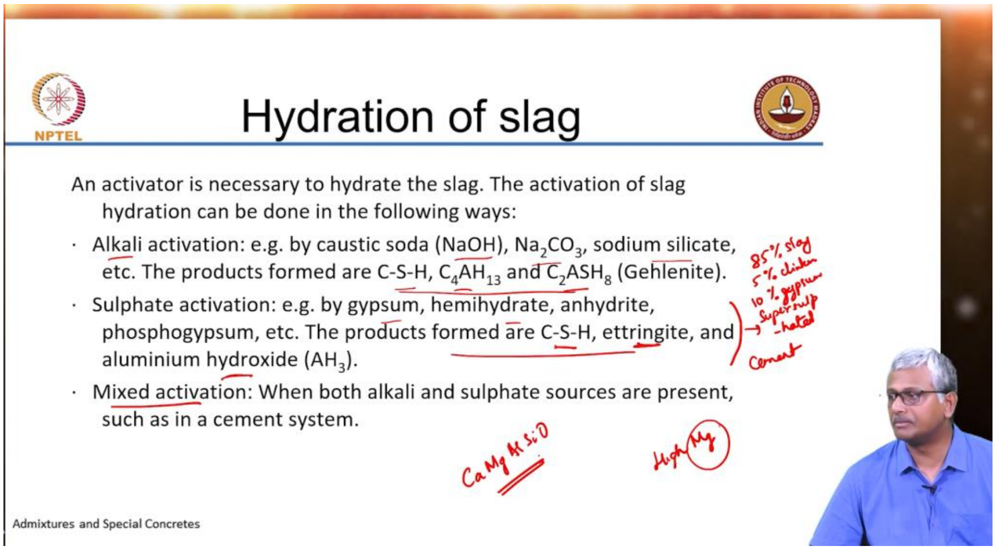

Hydration of slag

An activator is necessary to hydrate the slag. The activation of slag hydration can be done in the following ways:

- Alkali activation: e.g. by caustic soda (NaOH), Na_2CO_3, sodium silicate, etc. The products formed are C-S-H, C_4AH_{13} and C_2ASH_8 (Gehlenite).
- Sulphate activation: e.g. by gypsum, hemihydrate, anhydrite, phosphogypsum, etc. The products formed are C-S-H, ettringite, and aluminium hydroxide (AH_3).
- Mixed activation: When both alkali and sulphate sources are present, such as in a cement system.

85% slag
5% clinker
10% gypsum
→ Supersulphated cement

CaMgAlSiO

High Mg

Admixtures and Special Concretes

So let us resume our discussion on ground granulated blast furnace slag. In the last class, we were talking about the hydration of slag. Hydration is enabled by activation. This activation can happen with the help of alkalis or sulphates but when it is used in combination with cement the activation is with the help of both alkali and sulphate which are provided by the cement. So mixed activation is what we typically have. As I said slag also has a high magnesium so generally a number of phases in slag are basically calcium, magnesium, aluminium, silicates.

Complex phases which have all these elements present calcium, aluminium, magnesium, silica. The difficulty with these phases is that because of magnesium the solubility of these phases becomes very limited. So the greater the amount of free amorphous silica that is present the faster will be the reactivity. But for these phases getting them to react in any short period of time is very difficult.

It is only a long-term process and by then your water available for curing or water available for hydration will have already got depleted mostly. So most of the reaction will happen because of the amorphous phases that are present. So all the slag is amorphous but then this amorphous phases containing magnesium are not that easy to come into solution and undergo the reaction because of which you will generally find slag concretes as having many unhydrated particles of calcium, magnesium, silicate phases.

Effects on concrete properties:

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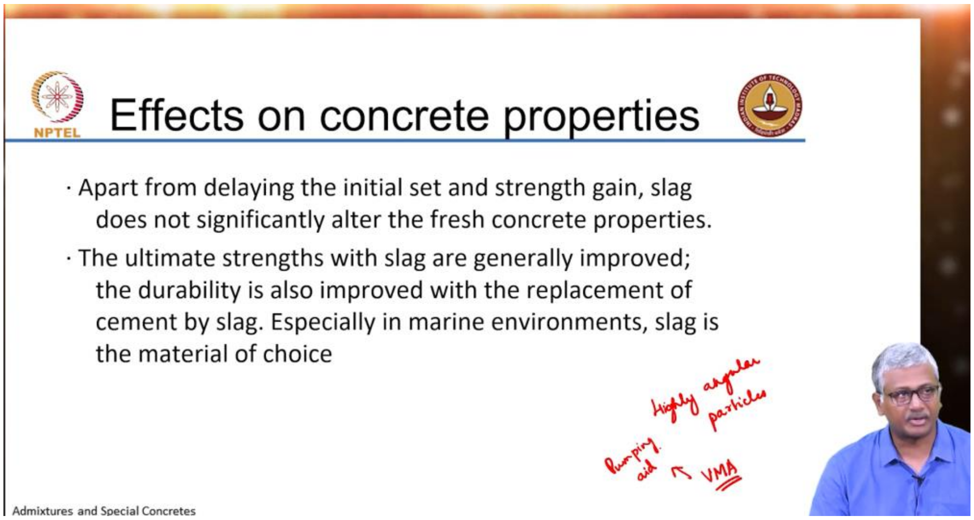

Effects on concrete properties

- Apart from delaying the initial set and strength gain, slag does not significantly alter the fresh concrete properties.
- The ultimate strengths with slag are generally improved; the durability is also improved with the replacement of cement by slag. Especially in marine environments, slag is the material of choice

Now in terms of how slag affects concrete properties it is not very difficult to visualize that because your slag reaction is slower there will be a delayed rate of strength development. Apart from that you will really not see too much effect on fresh concrete properties when cement is replaced by slag.

But one thing that may happen, please remember slag is a ground version of the granulated slag that comes out after quenching the molten slag. Now when you grind it these particles become highly angular. Of course, cement grains are also angular but please remember that slag is much harder than cement. We talked about it from the perspective of intergrinding versus interblending. So because of this hardness, these slag particles can actually increase the harshness of your system.

So when you are trying to pump slag concrete through a pipe the frictional resistance offered by the concrete will be more and people have reported from the site that when slag concrete is used the pipes seem to get worn out much faster as compared to plain cement concrete. So you are basically pumping a harder material so wear and tear of the pipe is going to be much more. So that is one thing to keep in mind when you are trying to use slag concrete for pumpability try to design it with a slightly higher slump so that you can reduce this extent of wear and tear on the pipe. Alternatively, we can use an admixture such as what kind of admixture should we use if you want to push concrete easily through a pipe without too much resistance- viscosity modifying agent VMA can be used in such instances where VMA basically helps in pumping it is also known as a pumping aid. VMA is also called pumping aid when it is used primarily for the purposes of making pumping easier.

So slag concrete is difficult to pump because of the wear and tear increase of the pipe because of hard slag particles and you can make it easier by designing with the highest slump or using a VMA. Now when you talk about continuous curing the ultimate strength with slag will be generally improved and durability we already talked briefly about that earlier that because of the presence of alumina, there is a large proportion of binding of chlorides that actually happens and because of this in marine environments slag concrete is almost always the material of choice almost always. More often than not people will be using slag concrete in marine environments.

Hydration and microstructure of slag cements:

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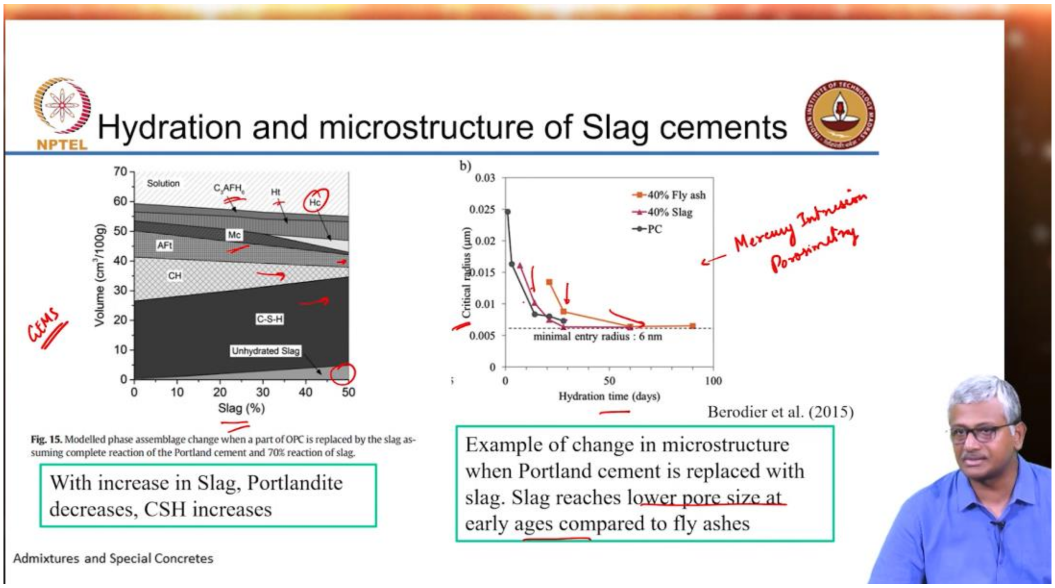

Hydration and microstructure of Slag cements

Fig. 15. Modelled phase assemblage change when a part of OPC is replaced by the slag assuming complete reaction of the Portland cement and 70% reaction of slag.

With increase in Slag, Portlandite decreases, CSH increases

Berodier et al. (2015)

Example of change in microstructure when Portland cement is replaced with slag. Slag reaches lower pore size at early ages compared to fly ashes

Admixtures and Special Concretes

Now some aspects of hydration are presented here. Now there is some reactive silica so portlandite consumption will be there but please remember that slag has enough calcium on its own the decrease in calcium hydroxide content or portlandite content with the presence of slag is not going to be as substantial as with other active elements of alumina silicates let us say like calcium clay.

So here this is actually a model for hydration which is called the GEMS model or Gibbs free energy minimization model. It is a model that has been put forward based on how the thermodynamics of the system evolves and what are the possibilities of the products that could form from a given mixture of reactants. So here they are talking about slag, portlandite, ettringite I mean whatever remains in the first phases of cement hydration. So with time your formation or with the increase in slag content the formation of CSH is going up but because a lot of slag is not going to react there will be still very high amounts of unreacted slag when you obviously have a greater amount of slag in your mix. You consume calcium hydroxide to some extent and you see that the calcium hydroxide content is continuously reducing as you go to higher slag replacements but very often in actual experimental evidence, this is a thermodynamic model.

This is basically the if equilibrium is attained in this reaction what is the potential for the product formation but in reality, all this may not actually happen. Your unreacted slag may be much more than what is predicted, your calcium hydroxide depletion may be much less as compared to what is predicted by the thermodynamic model. Generally, ettringite will get converted to monosulphate more in a slag concrete or a flash concrete why? Because why does this happen? Why do you expect more conversion of ettringite to monosulphate? There is more alumina present, so alumina silica balance is going to get affected when you replace cement by slag. Very often when we prepare blended cements we ensure that we modify the sulphate content also to really make it suitable to be used with the alumino silicate mineral admixture. So sulphate optimization is often done whenever mineral admixtures are used to ensure that we do not get too much of a change in the balance and the sulphate optimization also helps you to attain the early strengths.

Early strengths you know the partially because of ettringite formation and that you can obtain by doing some sulphate optimization. There are other phases that could also form in the system calcium alumino ferrite hydrates, hydro-talsite, hemicarbonate could form in some instances or monocarbonate could also form provided there is some calcite available in the system or calcium carbonate available in the system. Because there is alumina from your slag there is carbonate from your calcite or limestone and that can combine to form carbo-aluminates. Just like what we discussed earlier carbo-aluminates are forming when you have alumina and calcium carbonate in the presence of portlandite calcium hydroxide. Now this is a result from mercury intrusion porosimetry.

So in this experiment what is done is you take a sample of your hardened cement paste or cement mortar and subject that to continuously increasing pressures of mercury. So you put it inside immerse it in mercury and pressurize the mercury to get into the pores. Mercury is chosen in this experiment because it does not wet the surface it is a non-wetting liquid. It has a obtuse contact angle if you remember your surface chemistry. So mercury is able to penetrate the pores without getting stuck to the pores.

So the higher the pressure the smaller will be the diameter of the pores that the mercury will penetrate. So you can actually get a range of pore sizes from this experiment called mercury intrusion porosimetry. So here what they are saying is as the hydration time increases the critical radius that means the radius exhibited by majority of your pores continuously reduces. Why? Because more and more hydration is happening. So more pores are getting filled up.

When pores start getting filled up with CSH they become smaller and smaller. And what you can clearly see is for Portland cement there is some extent of reduction that happens but with slag and fly ash this reduction in your critical radius of the pore keeps increasing or reduction keeps increasing that means the pore size keeps reducing as hydration proceeds further. So and generally it may happen that you will not be able to reduce the pore size beyond a certain limit because it is not physically possible to continue the hydration beyond a certain point. There is not enough space for the hydrated materials to start growing. So your hydrated materials need some space to start nucleating and growing and that is not going to happen if your pores become smaller and smaller.

And generally, slag will reach lower pore size at early ages compared to fly ashes. Why? You can see from here that slag is the red curve. The lowering of pore sizes in slag is faster than in fly ash because of higher reactivity of slag. Because of higher reactivity of slag fly ash is not as reactive so it takes some time so you need to give prolonged curing for fly ash reactivity to continue happening. But after a certain period of time it is almost going to be at the same level of critical pore size as the slag mix.

And both these concretes may have a smaller pore size compared to the plain cement mix.

Durability of slag cements:

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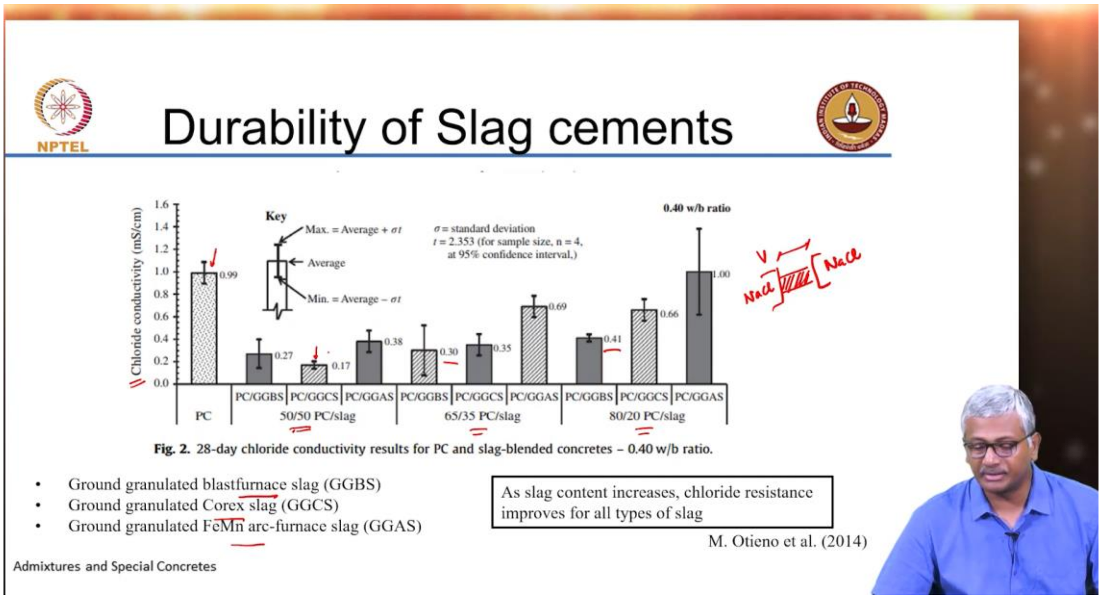

Durability of Slag cements

Fig. 2. 28-day chloride conductivity results for PC and slag-blended concretes – 0.40 w/b ratio.

- Ground granulated blastfurnace slag (GGBS)
- Ground granulated Corex slag (GGCS)
- Ground granulated FeMn arc-furnace slag (GGAS)

As slag content increases, chloride resistance improves for all types of slag

M. Otieno et al. (2014)

Now this is a result from University of Cape Town and this talks about the durability of slag cements in terms of a durability parameter called Chloride conductivity. So in this experiment what is typically done is you have 2 electrodes and you have a concrete sample sitting between the 2 electrodes. Sample is like a disc of concrete sitting between 2 electrodes and both sides are having saturated sodium chloride solution. The concrete also is completely saturated in sodium chloride solution.

This is a little bit different as compared to the rapid chloride permeability test that I discussed earlier. So here you do not want your chlorides to diffuse anymore but you fill up your pores with chloride and then you apply a voltage, you apply a potential difference between the 2 electrodes and measure the current. You measure the current and determine the conductivity. So all you are doing is determining conductivity of the system which is completely saturated with sodium chloride. So there is no transport of chlorides that is happening in this experiment.

It is only a transport of charge that is happening. Why is that important? What does it tell us? Transport of charge. If the pores are highly connected there will be more charge passing. If the pores are less connected there will be less charge passing. So here chloride conductivity of plain cement, you see that it is about 1 millisiemens per centimeter but as you use your mineral additives like for instance 50-50 blend of cement and slag 65-35 and 80-20.

You can clearly see that there is a reduction in your conductivity when slag is used. So that clearly shows that you have much better resistance to ionic penetration or better resistance implying a less interconnected pore network. There is a less interconnected pore network in the case of slag. And you can see that depending upon the type of slag, there are 3 slags that were tried blast furnace slag, corex slag and another ferromanganese arc furnace slag. In this case you can see that the corex slag which is the second one in the series seems to have fairly good activity but the blast furnace slag is essentially more or less the best at least in the case of the 65-35 blend and the 80-20 blend.

But in 50-50 you see a slightly better result with corex slag. But your ferromanganese arc slag is not really giving you a very good result in this experiment. But in general, the chloride resistance is better as compared to your plain Portland cement mixture.

Carbonation of Portland Slag Cements:

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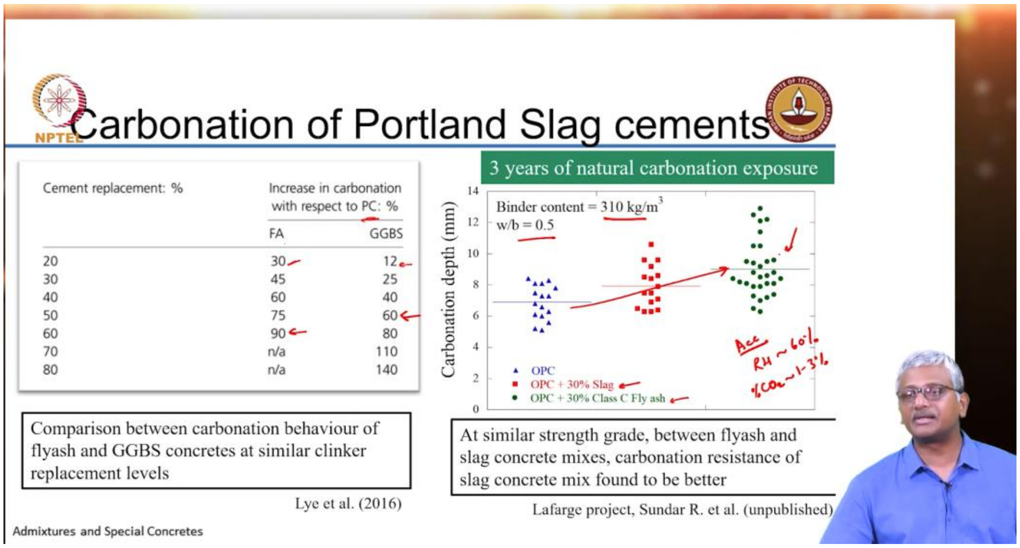

Carbonation of Portland Slag cements

Cement replacement: %	Increase in carbonation with respect to PC: % FA	GGBS
20	30	12
30	45	25
40	60	40
50	75	60
60	90	80
70	n/a	110
80	n/a	140

Comparison between carbonation behaviour of flyash and GGBS concretes at similar clinker replacement levels

Lye et al. (2016)

3 years of natural carbonation exposure

Binder content = 310 kg/m^3
w/b = 0.5

At similar strength grade, between flyash and slag concrete mixes, carbonation resistance of slag concrete mix found to be better

Lafarge project, Sundar R. et al. (unpublished)

Admixtures and Special Concretes

Now we talked already about this briefly earlier that when you replace cement with any mineral additive your carbonation is likely to increase because you have less calcium hydroxide present as an alkaline buffer that can combine with carbon dioxide to form calcium carbonate that forms a layer on the surface and prevents easy entry of CO2 into the concrete. But generally with increased amount of cement replacement by fly ash or slag you expect that your carbonation depth will go up.

So generally here what you see is increase in carbonation with respect to Portland cement when fly ash is used at 20% the increase is about 30%. That means if the carbonation depth with plain Portland cement is 20 mm with fly ash at 20% it will be 26 mm. So 30% increase is happening. But what you see is at high volumes of slag you are getting a 90% increase in carbonation depth when you use 60% cement replacement by fly ash. Slag generally the numbers are smaller you see that at 20% you hardly get any major increase.

But when it comes to the typical slag mix that is 50% replacement you get a 60% increase in carbonation depth and that is substantial that could be substantial. Now in IIT, we had a long term study done in conjunction with Lafarge. Lafarge holds them that is. So this study involved natural carbonation our exposure site was essentially the terrace of BSB we kept specimens on the terrace of BSB and from time to time after 1 year, 2 year, 3 years, 5 years and so on we have extracted these specimens and checked the depth of carbonation in these specimens. So what you see here is after 3 years of natural carbonation what is the natural carbonation or CO_2 concentration, approximate CO_2 concentration in natural environment? 0.04% or 400 parts per million.

What is the carbonation or CO_2 environment in this room? Obviously more. So it depends on the number of people sitting inside, it depends on the kind of air circulation that we have because of air conditioning and that is one reason why you start feeling sleepy in an air condition room. Depending upon the type of air conditioner if the air exchange is not sufficient the CO_2 content basically goes up it increases your drowsiness. Of course, there are many other reasons that cause you to sleep but that is one of the reasons. At least we teachers like to believe that is the reason that you are sleeping.

So this result is presenting the comparison of OPC and OPC replaced with 30% slag and with 30% class C fly ash. So high calcium fly ash system. So you see that there is some increase as you go from cement to slag to fly ash but if you check the scatter it is not tremendous, it is not really such a huge increase that you see. The same experiment when you conduct it in an accelerated carbonation environment. Accelerated means people try to increase the CO2 concentration and fix the humidity in such a condition that the rate of penetration is maximum.

So generally RH for accelerated conditions, RH is typically around 60% and your CO2 is around 1 to 3%. So that means you are going significantly higher than atmospheric carbonation when you do accelerated carbonation. So when you read papers with carbonation measurements make sure you understand what is the condition that has been adopted for measurement of carbonation. Not everybody can afford to do a natural carbonation. Imagine if you are doing a PhD, if you do a natural carbonation test and stay for 5 years just to measure 3 or 4 sets of data you are basically done.

It has to be done over several PhDs. So that is why people adopt accelerated means of testing because accelerated testing can get over in a matter of 4 to 5 months even if it is accelerated it takes 4 months. That also tells you that if you really have to check carbonation resistance of a concrete for a construction project you need to have at least 6 months to do your mix design. Not many people allow you to do that. So, anyway, at similar strength grade between fly ash and slag concrete mixes carbonation of slag concrete is lesser than that of fly ash concrete at the same strength grade levels. That is also important to consider when a structural engineer tells the concrete producer that a particular strength concrete is required you can design for that particular strength with different combinations of additives.

The design is supposed to satisfy that the strength at 28 days should be met or if there is an early strength requirement that also needs to be met. But what happens is then you start comparing at an equivalent strength level. This study here however has been done at an equivalent binder content and water binder ratio. So there is a difference in results when you do studies at equivalent water binder ratio and binder content or if you do the study at equivalent strength. Why do I say this? When you do the 30% class C fly ash mix, obtaining the same strength as that of an OPC mix may require you to get a lower water-to-cement ratio.

Because this is 28 days strength we are talking about. Well this is class C fly ash so maybe 28 days it may become equal. Imagine if you have class F fly ash you may want to go for a lower water-to-binder ratio to get that same strength. Now when you start checking the rate of carbonation at equivalent strength levels is when you will get the correct picture of what is going on when cement is replaced by fly ash or slime. So it is very important to again be careful about what you are reading in papers so that you can get a clear estimate of what is going to happen in your actual construction project.

IITM results on durability with SCMs:

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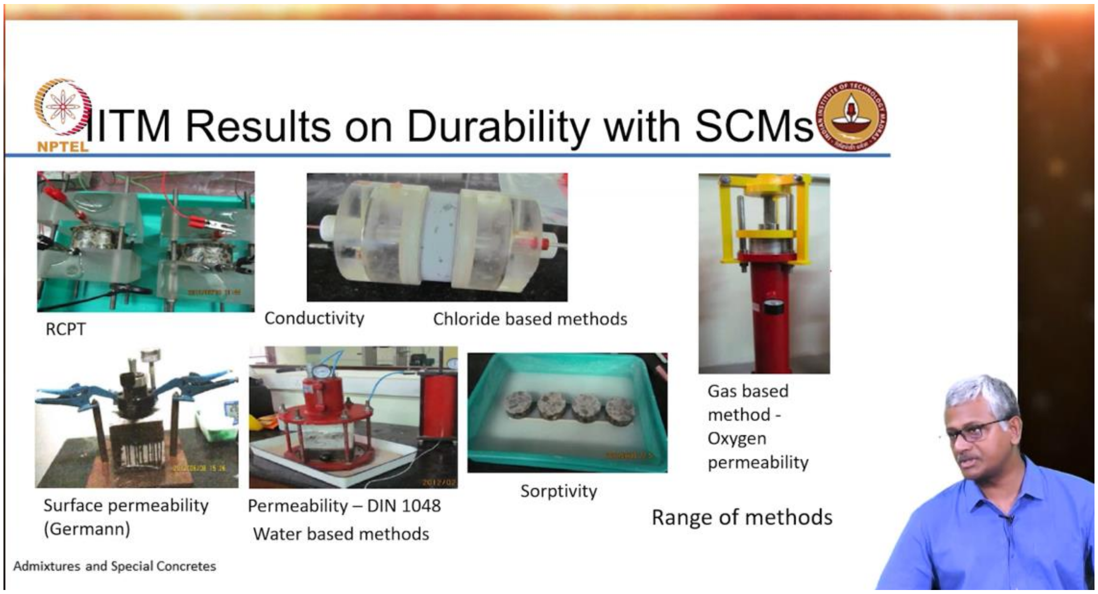

IITM Results on Durability with SCMs

RCPT

Conductivity

Chloride based methods

Gas based method - Oxygen permeability

Surface permeability (Germann)

Permeability – DIN 1048

Water based methods

Sorptivity

Range of methods

Admixtures and Special Concretes

Now we not only did carbonation but we did a whole range of other durability studies ranging from chloride-based tests to gas penetration tests to water penetration tests. So all of these tests were conducted over this long-term study. This was over a period of 2 years that we actually did the study. The idea was to see what kind of limiting values we need to propose for construction projects when concrete mixtures have these mineral additives. And how do we control quality of concrete based on durability. So I am not going to go through the details of these test methods because that is not really the scope of this course but I will give you some general results.

Influence of SCMs in chloride penetrability:

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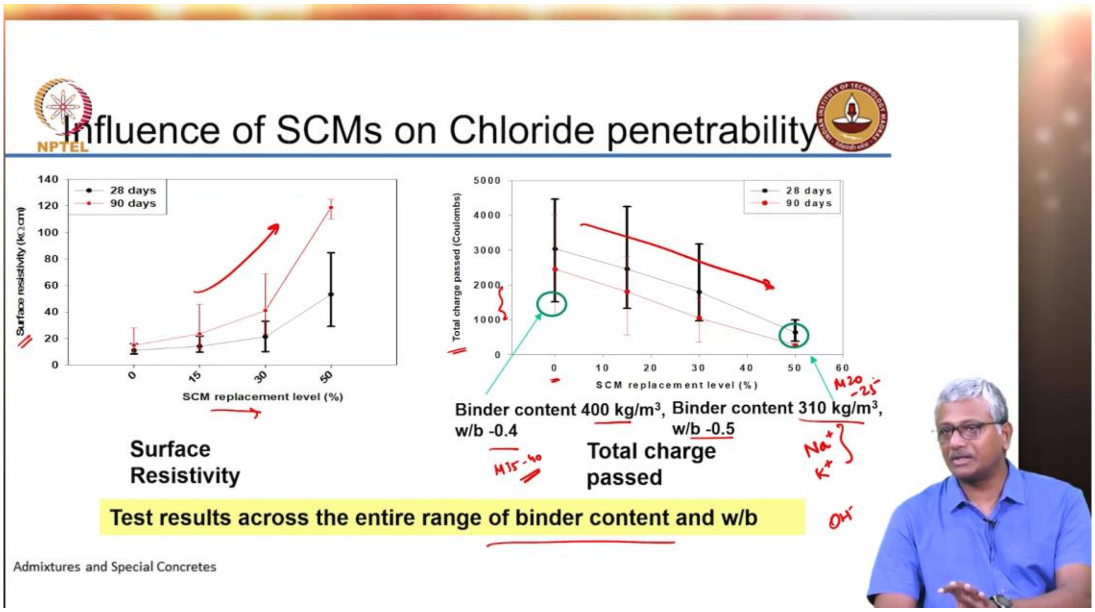

Influence of SCMs on Chloride penetrability

Binder content 400 kg/m³, w/b -0.4

Binder content 310 kg/m³, w/b -0.5

Surface Resistivity

Total charge passed

Test results across the entire range of binder content and w/b

Admixtures and Special Concretes

So here what is presented is test results across the entire range of binder content and water binder ratio. Over this study we had nearly about 40 to 45 concrete mixes which had varying degrees of binder content and water binder ratio and replacement levels of supplementary cementing material. So what you see here, the surface resistivity measurement is typically done in a moist concrete and you are basically trying to assess the properties of the cover concrete by passing a current and then measuring the potential difference and converting that to the resistivity of the concrete. In this kind of a test what you see that as you increase the supplementary cementing material your resistivity is going up. What implications does this have on your durability? If your resistivity is higher what does that talk about your durability? Durability goes up, why? So resistivity is the inverse of conductivity.

So the less conductive the material it indicates that the pore structure is less interconnected. So resistivity is a good measure for quality assessment of concrete mixtures with respect to durability and what you see here is that as you increase replacement level your resistivity is going up. But what does that indicate? Does it always indicate higher durability or could it be because of some other reasons also? Same thing opposite you are talking about total charge passed in a rapid chloride penetration test as you increase the replacement level the charge passed drops in other words the conductivity of the system is going down. But is this only because of improved durability or could there be something else contributing to this result? We talked about this when we had a discussion on silica fume. What happens when you replace cement by siliceous mineral additives or glassy or amorphous mineral additives? Why would it have an impact on conductivity? Because it starts binding the alkali ions.

The siliceous phases bind the alkali ions lower the overall concentration of ionic species in your pore solution. What does that do? Obviously it will lower the conductivity of the pore solution that is present in the concrete. We talked about this silica fume always does well in the rapid chloride penetration test and that is why the promoters of silica fume always used RCPT to show the result and never other durability tests and that is why this test has become so popular all across the world. Anycase, partly the result is also due to the fact that your cement is getting diluted so you do not have as much alkali present in your system. Alkali loading of your system has come down so pore solution has become less concentrated with respect to ionic species.

What does your pore solution have? It has sodium, potassium and to balance that what is the other ionic species present in the pore solution? To balance you need to have a negatively charged species. What should that be? OH^-. So you have sodium, potassium, and OH^-. You may have some calcium but not too much. Generally, in your pore solution, this is what will be the concentration in the long term.

So how do you extract pore solution? You just have to compress your concrete with a great deal of pressure. Triaxial compression has to be done and then you will be able to extract the pore solution. You can analyze that for pH, you can analyze that for your concentration of these species and you will find that whenever cement is replaced by mineral additives the content of sodium and potassium is coming down. But what about hydroxyl? It is a balancing species. So if the positive species comes down the negative also will come down.

There will not be too much of stabilization and in any case you are also consuming your calcium hydroxide. So the net charge balance is such that your pore solution becomes less conductive. So some of these results that rely on electrical methods need to be looked at carefully to possibly see the influence of this lowered conductivity of the system. Now what is interesting here is that since RCPT is often used for durability level assessment of concrete mixtures, it is interesting to see that even at 0% replacement that means with plain Portland cement we are able to get between 1000 and 2000 RCPT value but this is with 400 kilogram binder and 0.4 water to binder ratio.

So what approximate grade of concrete could this be? 400-kilogram binder and 0.4 water cement ratio. Similarly this will be around M35 to 40. Of course in laboratory studies with the Chennai materials, this will produce about 40 MPa but in the field, we can think of that as an M35 mix. Now what is interesting to see is that you are able to produce even lower chloride permeability at 50% replacement for mixtures that have binder content 310 and water binder ratio 0.5.

So we are talking about M20 to M25 mixtures here. Which is typically used for your residential construction. So what does this show? What is the primary impact of this result? When you use only Portland cement to get higher durability you need to go for higher strength. But when you use blended cements you can get good durability even at low to moderate strength levels. That is the major impact of this result. You can prove now that for concrete mixtures which have blended cements you will get decent level of durability even with lower grade of concrete. But all of this is assuming you are doing adequate curing. That is the main aspect here. You need to do adequate curing without which you are not going to get this result.

Influence of SCMs on water sorptivity:

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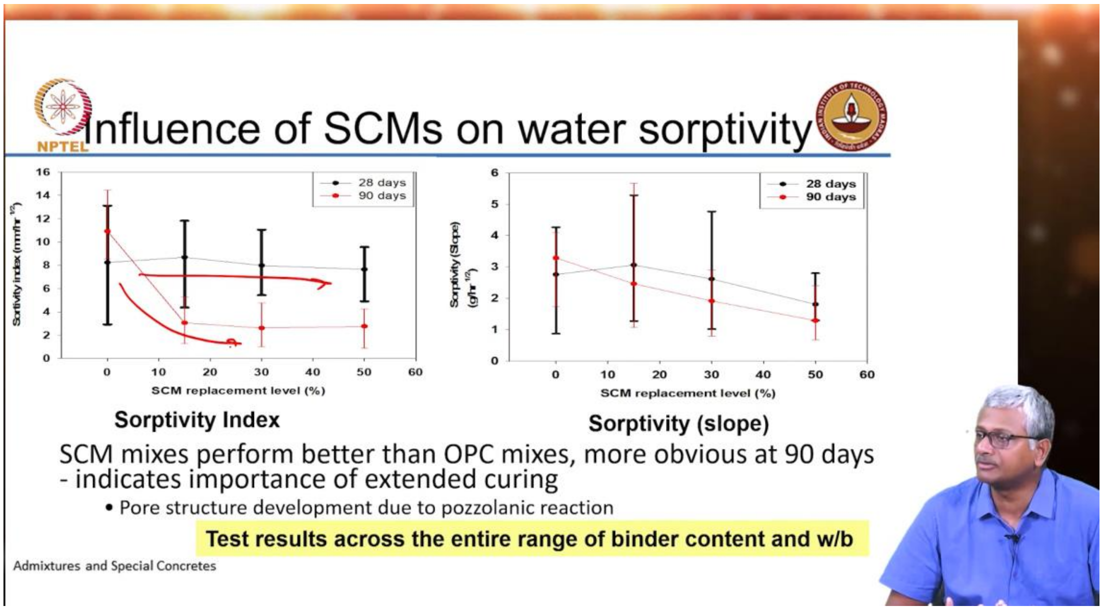

Influence of SCMs on water sorptivity

Sorptivity Index

Sorptivity (slope)

SCM mixes perform better than OPC mixes, more obvious at 90 days - indicates importance of extended curing

- Pore structure development due to pozzolanic reaction

Test results across the entire range of binder content and w/b

Admixtures and Special Concretes

Water sorptivity result also indicates that at 28 days there is not that much of a difference. But at 90 days you clearly see that the water sorptivity level is reduced when higher levels of symmetry placement are done. Again it goes to show the impact of extended curing on concretes with mineral admixtures.