Admixtures And Special Concretes

Prof. Manu Santhanam

Indian Institute of Technology Madras

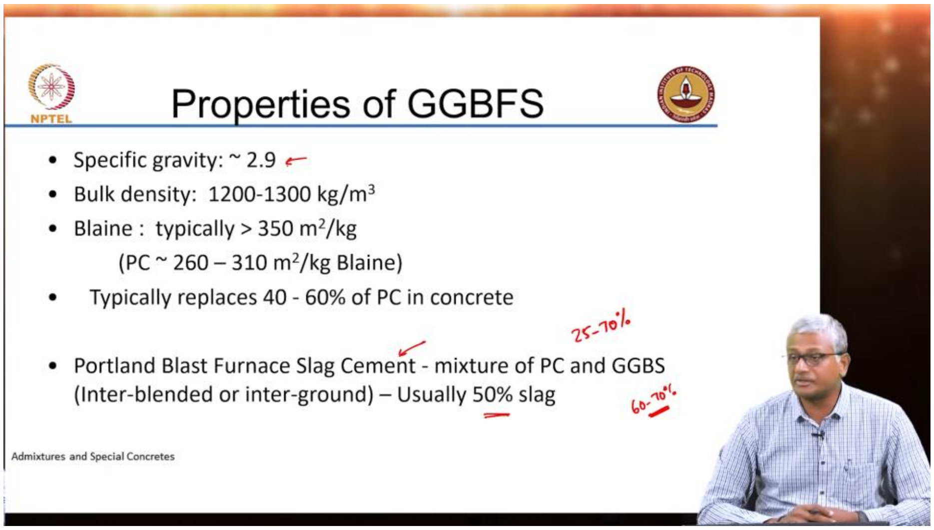
Department of Civil Engineering

Lecture -40

Mineral Admixtures: GGBS - Part 2: Properties

Properties of GGBFS:

(Refer to slide time: 00:18)



Properties of GGBFS

- Specific gravity: ~ 2.9
- Bulk density: 1200-1300 kg/m^3
- Blaine : typically > 350 m^2/kg
  (PC ~ 260 – 310 m^2/kg Blaine)
- Typically replaces 40 - 60% of PC in concrete
- Portland Blast Furnace Slag Cement - mixture of PC and GGBS (Inter-blended or inter-ground) – Usually 50% slag

25-70%

60-70%

Admixtures and Special Concretes

The same problem comes when we talk about Portland blast furnace slag cement. So here we are talking about high quantities of slag about 50% replacement of cement by slag up to 70% is permitted. So if you look at the slag cement standard, the cement clinker replacement by ground granulated blast furnace slag is permitted between 25 to 70%. So most cements will have 50% formulation, but more and more people are trying to shift towards 60 to 70% these days. But the problem there again is if you are doing intergrinding of the cement clinker and slag, the slag fineness may not be achieved to the same extent as the cement fineness because slag is not, slag is much harder than clinker. So you have to take that into account.

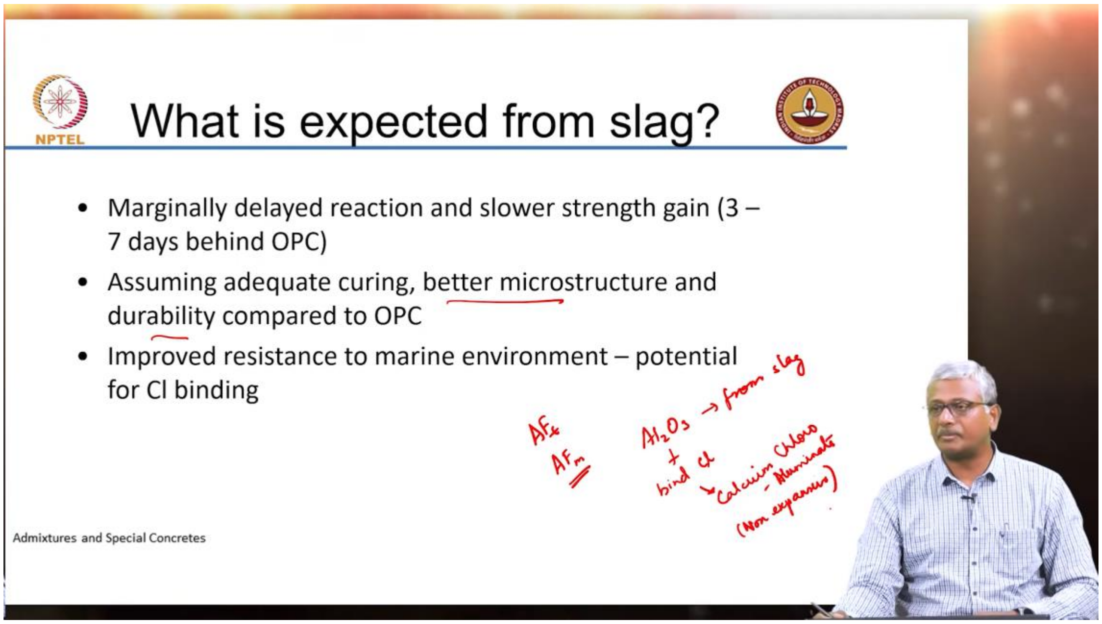
So in this case will intergrinding be a good option or interblending be a better option? Interblending may be better because you can then grind cement separately, slag separately and then combine them together to make your blast furnace slag cement. But then there are other problems with that process you need to have separate silos for ground slag, ground clinker and then you need to have the equipment for interblending to produce interblended slag. So mostly, you will see that intergrinding is typically done because it reduces the extent of infrastructure required in a cement plant. What we are not covering in this entire discussion is the use of grinding aids that is again a very important technology these days.

There are grinding aids that make the grinding much easier for cement and the additive phases that are added in the ball mill or the vertical roller press mill process. So again this is again a cement production technology which is assuming a lot of importance these days because all of this affects the way that the cement behaves in concrete especially the way that it interacts with super plasticizers also. So all of those things need to be considered when you are actually looking at performance. It is not just the basic hydration reactions or pozzolanic reactions. In terms of properties, slag is less dense as compared to cement but not much less unlike fly ash or silica fume which were having densities which were 2.2 to 2.4. Here the density is about 2.9. The bulk density packing in a bag more or less similar to cement slightly less but more or less similar.

So you can actually get bags of slag which are 50 kg which have nearly the same size possibly, but generally, slag is sold in bulkers you do not really get commodity slag available from the market. Slag is available for projects directly but not in the market you do not get bags of slag in the market. Blaine value of slag is typically around 350 square meters per kilogram as compared to cement which is a little less fine as compared to the slag. Now slag is ground finer primarily because people wanted to react faster when it is used as a cement replacement because it is used in such large quantities of replacement.

Expectations from slag:

(Refer to slide time: 03:41)



What is expected from slag?

- Marginally delayed reaction and slower strength gain (3 – 7 days behind OPC)
- Assuming adequate curing, better microstructure and durability compared to OPC
- Improved resistance to marine environment – potential for Cl binding

AF_t
AF_m

Al_2O_3 → from slag
+
bind Cl
→ Calcium Chloro-Aluminate (Non expansive)

Admixtures and Special Concretes

Again expectation from slag is easy to understand we can expect that there will be marginally delayed rate of strength gain because slag reaction is delayed as compared to cement reaction. And we discussed earlier that the effective time can be between 3 to 7 days within that time the slag mix should catch up with the Portland cement mix assuming that there is sufficient curing that is happening.

And assuming that good curing is happening you can get better microstructure and durability as compared to Portland cement concrete. Better microstructure and durability especially in the marine environment because you have alumina from slag and alumina bearing phases can actually combine or rather bind chlorides that are coming in from sea water to form what? You have calcium alumina and chlorides so you form calcium chloroaluminate. Now in ordinary concrete what happens? You form calcium sulfoaluminate because there is sulphur from gypsum available, sulphate from gypsum available you form calcium sulfoaluminate which could be either ettringite or monosulphate mostly it is monosulphate because ettringite is not stable beyond a certain time period because there is excess of alumina that is available in the system. What you are simply doing by replacing cement by slag is that you are further increasing the alumina ratio and when you do this you have more alumina in the system to bind with chlorides to form calcium chloroaluminate.

It is the same kind of reaction. What kind of name did we give for the monosulphate? AF_m, alumina ferrite monosulphate and ettringite was given the name AF_t, trisulphate. So AF_m can refer not just to the monosulphate phases but also to the monochloroaluminate phases. So AF_m is a general family of products that can form when calcium aluminates interact with either sulphate or with chloride. The difference being when they interact with sulphate they lead to the formation of ettringite which is expansive.

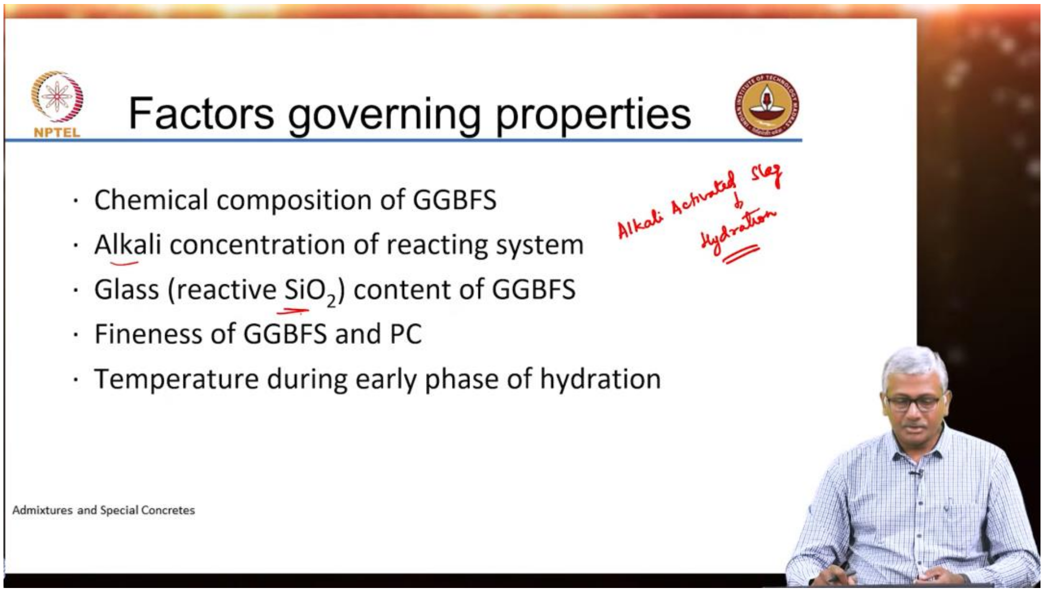
Ettringite leads to expansion but chloroaluminates are not expansive. That is the difference between a chloride and a sulphate attack on a concrete is that when you have aluminous phases interacting with sulphate they lead to expansive products. Aluminous phases interacting with chlorides lead to non-expansive products. As a result of this binding of chloride what happens to the total chloride content of the concrete? It reduces, free chloride reduces so the amount of chloride that can build up on the steel comes down. So, if you can, in the cover zone if you have a lot of these aluminous species, any species that gives more alumina will tend to have greater chloride binding and prevent chlorides from reaching the steel surface.

Of course that is not the only reason why you get better performance. You also get better performance because lower permeability. You have lower permeability in your system when cement is replaced by slag or silica fume or whatever it may be. Silica fume is not doing this binding because it does not have sufficient alumina to contribute. Whereas slag can do binding, fly ash can do binding because it is also contributing alumina.

And we will see later calcium clays can really do a great job at chloride resistance. So, as far as carbonation was concerned the entire process was governed by permeability and presence of calcium hydroxide. As far as chloride resistance is concerned permeability is still very important perhaps even more important than carbonation. But added to that you have this instance of chloride binding which is brought about by the presence of greater aluminous contents in your system.

Factors governing properties:

(Refer to slide time: 08:11)



Factors governing properties

- Chemical composition of GGBFS
- Alkali concentration of reacting system
- Glass (reactive SiO_2) content of GGBFS
- Fineness of GGBFS and PC
- Temperature during early phase of hydration

Alkali Activated Slag
&
Hydration

Admixtures and Special Concretes

So generally slag performance will be affected by many factors. One is obviously the chemical composition, how much is the calcium content, how much is the silica content and so on. The greater the calcium content the faster will be the activity of slag. The alkali concentration of reacting system because the alkalis are leading to the hydraulic reactions of the slag. So we call the system which does not have Portland cement but only slag with alkalis as alkali-activated slag system. Alkali-activated slag is when you do not have any cement but you only use alkalis to activate slag hydration.

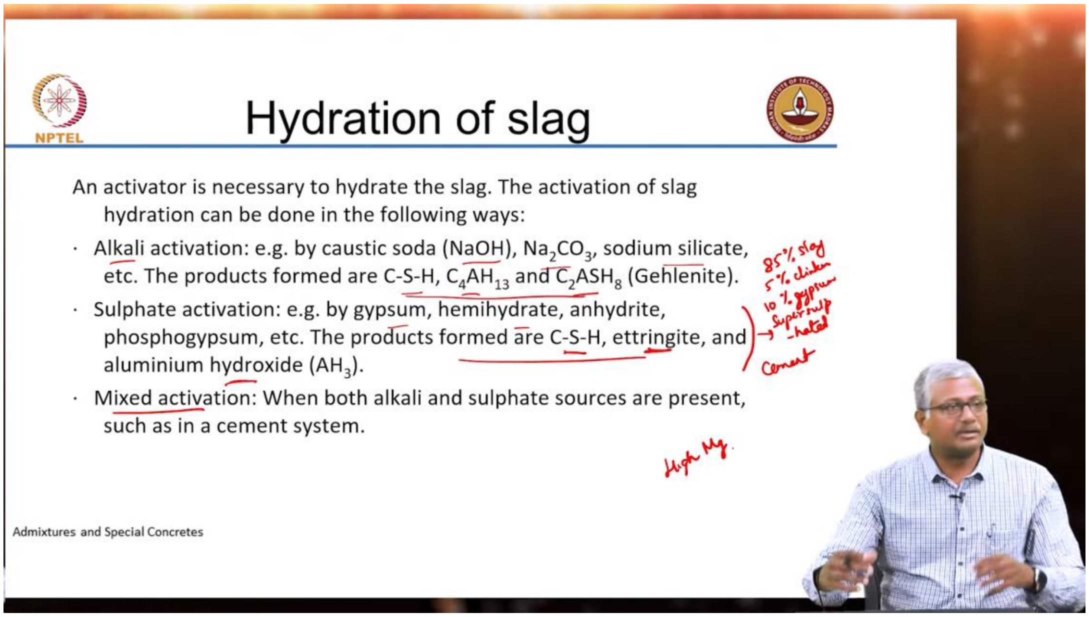
Now many people wrongly call this as geopolymer. You may have heard the term geopolymer. Geopolymer is any aluminosilicate-bearing compound which in the absence of cement gets dissolved by a very highly alkaline solution and then recrystallizes in a three-dimensional network which we call as a geopolymer. If you read some articles in geopolymer people have made some claims that even the blocks that are used in the pyramids were geopolymerized materials. But that theory was debunked because there is sufficient amount of stone available that was brought in to make those.

Most people understood earlier also that this is a large blocks of stone that were naturally occurring stone that were actually put together to make the pyramids but somebody came up with this theory that these were just aluminosilicates which were geopolymerized to make those blocks. Anyway, that was debunked. Anyway, but that is a possibility that you can actually take an active aluminosilicate when it is crushed in the form of a powder which makes more surface area available for reaction and such materials can be dissolved in a highly alkaline solution and re-precipitate to form a three-dimensional structure which is called geopolymer. That is not the same with alkali activation of slag because what this does is it leads to hydration of slag and not geopolymerization. What is the difference between hydration and geopolymerization? What do you form in hydration? CSH, you form CSH. Hydrated phases are formed whereas geopolymeric phases are basically polymeric structures involving alumina and silica.

There is no hydration there, there is no water which is associated with the structure formation of geopolymers. Now the extent of reactive silica present in slag will obviously be an important factor which determines the rate of reactivity. The fineness of slag in Portland cement, the finer the material the faster will be the reaction just like you see in typical Portland cement and temperature during early phase of hydration. What will happen at high temperatures? If the temperature is higher what is going to happen? You will have a faster reaction because the initial dissolution of phases is increased when you decrease the temperature. So all of these factors will affect properties of slag but very important to understand how does slag hydrate.

Hydration of slag:

(refer to slide time: 11:37)



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

High Mg.

Admixtures and Special Concretes

As I said slag needs to be activated and activation can be done either by alkalis. Alkalis are either in the form of caustic soda, sodium hydroxide, sodium carbonate, sodium silicate all of these can be used or the equivalent potassium compounds could also be used for the alkali sources. That is when you make alkali-activated slag and in such instances the products that are formed are because of hydration of the slag and that could be your CSH, CAH calcium aluminate hydrate and CASH calcium alumino silicate hydrate. All these compounds can be formed as a result of slag hydration caused by alkalis. You could also do a sulphate activation even in the presence of excess sulphate you form I mean excess sulphate could be from gypsum, hemihydrate or other forms of gypsum and the products that you end up forming by this are CSH because of the calcium silica present in the slag.

The alumina and the slag will combine with the sulphate to form ettringite phases and you may also precipitate aluminum hydroxide and this is the basis of what we call as super sulphated cement. Typically, this has about 85 percent slag for 10 percent gypsum and 5 percent clinker. As the name implies it is very high amount of gypsum, so that is why it is super sulphated and that is because the sulphate is directly activating the slag and the clinker is just added to provide the initial kick to really get the process going. But these days you would not get super sulphated cement in the market. What will be the primary products here? CSH, ettringite and aluminum hydroxide.

So again you have very stable phases to begin with, so if this concrete that has super sulphate cement is subjected to sulphate attack, the ettringite is already present in its own form. The external sulphate is not going to change that in any way, so because of that you will not get any expansion because of ettringite formation. So the performance of such cements will be good in chemical attack cases in sulphate attack cases and because of so many alumina varying products present even in chloride attack you will certainly have a better performance. But again what people discovered was such cements in the long term were tending to lose their strength. These cements were losing their strength because of the ettringite slowly decomposing in the long term because of temperature and carbonation and that led to poor performance in the long term.

Same thing with calcium aluminate cements, you may have heard about the special cements called calcium aluminate cement. Now calcium aluminate cement right after the Second World War, I mean there was a major necessity for rebuilding at a very rapid pace because many buildings were destroyed. So in England and Germany and all that they were working out strategies to build very fast. At that time this calcium aluminate cement became very popular because the strength came even at one day is extremely rapid with calcium aluminate cement. You can produce like 30, 40 MPa or more in just one day with the cement.

But the problem was in the long term upon exposure to environment and to moisture the strength kept on dropping significantly as much as 80 percent drop in strength actually happened for many of these structures. And why did that happen because the hydration products that form in the early stages of calcium aluminate cement are not stable. They convert into other forms which are much more porous. So again these special cements have their own necessities and needs. For instance, calcium aluminate cement is a very good fire-resistant material so it can be used in refractory linings.

In the cement kiln also because the temperatures are very high, we need to have some sort of a system to protect the lining of the protect the steel in the kiln. So for that either we can use a brick which is highly temperature resistant or you can use calcium aluminate cement. Nevertheless, when slag is mixed with cement you get a mixed activation because cement contributes both alkali and sulphate. So if you are able to react the slag you will be able to produce all of these products in some way or the other.

But it is very difficult to completely react the slag. You can react the very fine particles within slag but a lot of slag will not react at the rate that you want and not really produce extensively cement-bearing compounds, cementitious compounds as much as you produce from your plain Portland cement. Now that is because there is also a very high magnesium content in slag. Most of the phases that are available in slag are bound forms of calcium and magnesium silicates and those when you see and probably have some microstructural images later, you will only see reactions happening at the edge of the particles are not really completely reacted particles that you see in the system even after long period of hydration.