Advanced Concrete Technology
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Lecture – 21
Mineral admixtures – Part 4

In the last lecture, we discussed about silica fume and its various available forms. So, what we get is a condensed or dry densified silica fume. But as we discussed also that sometimes silica fume may also be made available as slurry in which case it is easy to disperse in the concrete mixture. If it is in dry densified form what you need to do is have a good mixing strategy and use a very good super plasticizer to completely mix the material into the concrete. Otherwise these agglomerative silica fume will sit in the system without really reacting and you may actually end up having a scenario quite similar to alkali silica reaction, in which small condensed particles of agglomerate of silica fume can start acting like reactive silicious aggregate rather than the reactive mineral admixture that silica fume is known to be. In fact, this research worldwide which shows that these silica fume condensed particles that they are not able to disperse properly and react pozzolanically, then in the long term you may get some risks of alkali silica reaction.

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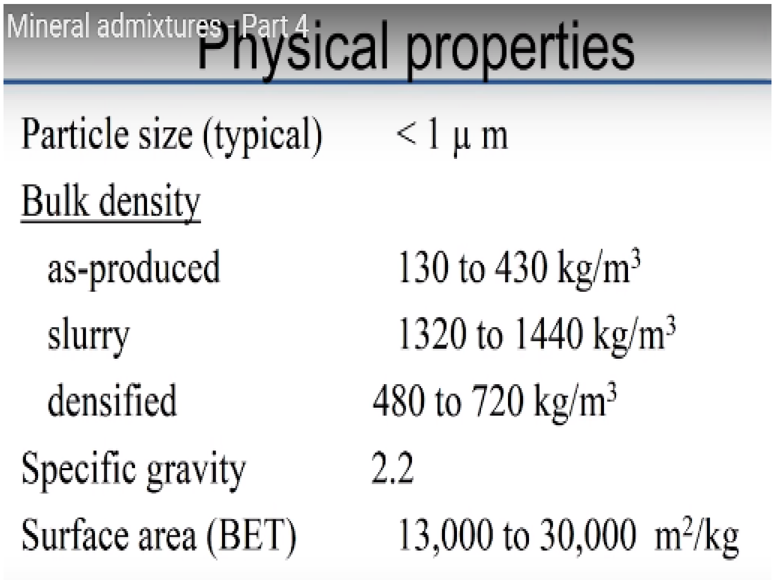

Mineral admixtures - Part 4

Physical properties

Particle size (typical)	< 1 μ m
Bulk density	
as-produced	130 to 430 kg/m^3
slurry	1320 to 1440 kg/m^3
densified	480 to 720 kg/m^3
Specific gravity	2.2
Surface area (BET)	13,000 to 30,000 m^2/kg

So, in terms of physical properties, the particle size typically is less than 1 micron. Cement has an average particle size of around 15 microns. So, here were talking about a completely different order of magnitude in terms of the particle sizes where the average size is close to about 0.3 to 0.5 microns. The bulk density of ‘as produced’ state is 130 to 430kg/m^3.

When it is dry densified, it can almost triple to about 500 to 700 kg/m^3. So, because of that since it is bulky even after dry densifying it we do not typically get it in bags of 50 kilograms. We get in bags of 25 kilograms.

Specific gravity of the particles is quite similar to what you have for fly ash, about 2.2. The surface area cannot be measured with the help of Blaines air permeability test because the air simply cannot permeate through a bed of the silica fume particles since they are so fine. So, you do not really have the spaces in between for the air to flow through and because of that we have to adopt other techniques to determine surface area and this is called the BET technique which is based on the principle of adsorption. In this case nitrogen gas is made to condense on the surfaces of these particles. When can nitrogen condense? When it is extremely at a low temperature. So typically temperatures of about 77K are used in this instrument where nitrogen basically forms a layer on the particles. So, the more the surface area the greater the adsorption of the nitrogen. Similarly you can also do adsorption studies using water vapor. But most commonly preferred methodology is to use liquid nitrogen to condense on the surface of these fine powders.

So, based on that a surface area between 13000 and 30000m^2/kg is worked out. It is sort of a completely different range as compared to your cement particles.

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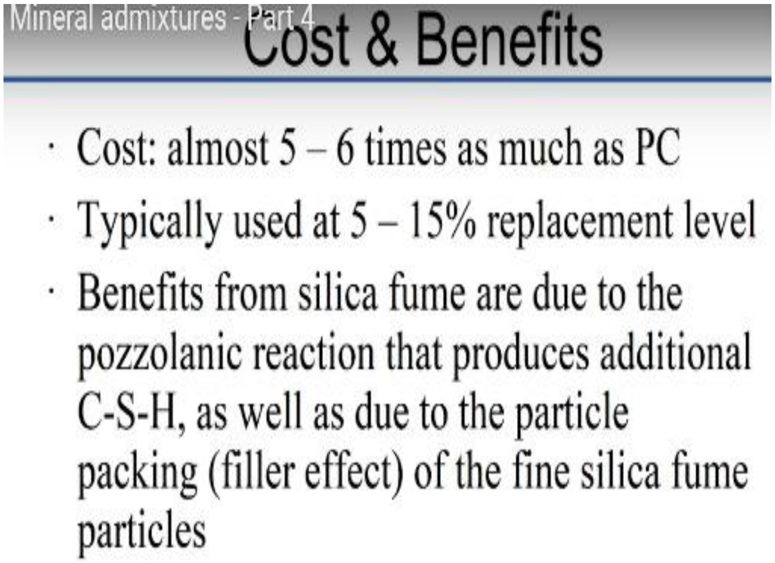
Mineral admixtures - Part 4

Cost & Benefits

- Cost: almost 5 – 6 times as much as PC
- Typically used at 5 – 15% replacement level
- Benefits from silica fume are due to the pozzolanic reaction that produces additional C-S-H, as well as due to the particle packing (filler effect) of the fine silica fume particles

Since silica fume is a material that is coming out of very highly specialized industry because of which the cost is very high, about 5 to 6 times the cost of Portland cement and that is because silica fume is a material that is obtained from a specialized industry and the conditions of usage of silica fume are also quite different as opposed to fly ash or slag.

So, you really need to justify why you use silica fume in concrete gets only the situation demands and you would need the kind of performance that you get from silica fume. So, because of that we also need to maintain a low replacement level. Typically 5 to 10% is what is usually done but there have been instances when 15% replacement also is being used. But cost is not the only thing because of which the replacement is low the other aspect is you are using extremely fine particles so if there is going to be a massive increase in the water demand even if you compensate with super plasticizers, the mix is going to get exceedingly sticky because you have such fineness in the mix.

Performance benefits are obviously from the extremely fast pozzolanic reaction because of the fine particle size as well as the high purity of the silica in the silica fume. Nearly 90% silica is present because of which there is a very large degree of pozzolanic reaction and this happens quite quickly also. So silica fume replaced mixes can get the same strength performance as ordinary Portland cement mixes within the first 3 days itself, sometimes as early as 1 day.

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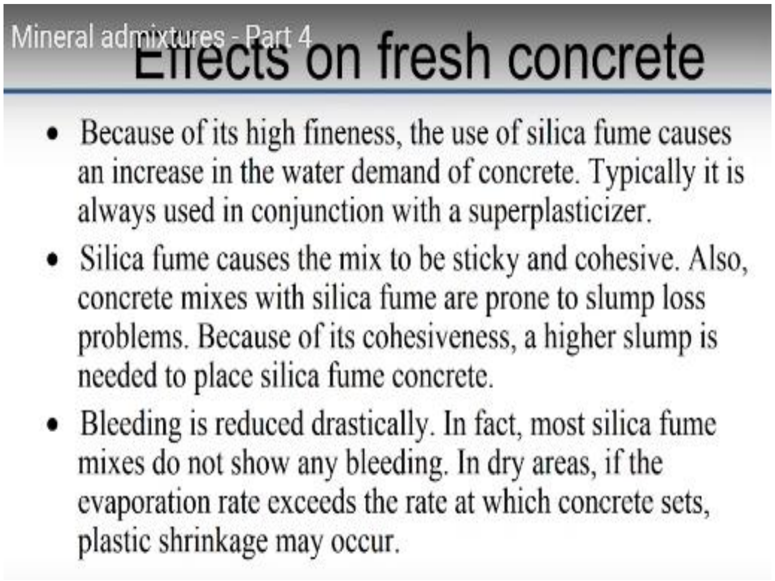

Mineral admixtures - Part 4

Effects on fresh concrete

- Because of its high fineness, the use of silica fume causes an increase in the water demand of concrete. Typically it is always used in conjunction with a superplasticizer.
- Silica fume causes the mix to be sticky and cohesive. Also, concrete mixes with silica fume are prone to slump loss problems. Because of its cohesiveness, a higher slump is needed to place silica fume concrete.
- Bleeding is reduced drastically. In fact, most silica fume mixes do not show any bleeding. In dry areas, if the evaporation rate exceeds the rate at which concrete sets, plastic shrinkage may occur.

The main problem when silica fume is used is its effects on the fresh properties of the concrete. In terms of fresh concrete, because of the extreme fine nature of the particles there is an additional degree of cohesion in the concrete. While that may be a positive attribute in certain cases, for example, when you are doing flowing concrete, in that case self-compacting concrete is able to maintain the cohesion and prevent segregation. Or if you are making a grout for a post tension application where your grout has to actually flow through very small constructed spaces without getting segregated, the silica fume particles do very well in actually reducing the segregation.

When you do a regular concrete construction if your mix becomes highly cohesive and sticky, compaction and finishing become a difficult task. So, that is one major issue and the other aspect is that the slump loss is also large because a lot of the water gets lost in adsorbing at the surface of these extremely fine particles.

Because of silica fume being so fine there is no question of any bleeding from silica fume mixes. bleeding is obviously a negative thing to happen in concrete but there is one positive attribute. A little bit of bleeding from the concrete provides a sheen on the surface of concrete that protects the internal water from of evaporating. In-situ concrete when we typically cast it especially in horizontal elements like slabs or beams there is a rise of water to the top. The detrimental part of that is obviously that this water is going to increase the local water-cement ratio at the cover concrete zone. But the advantageous part is that when this water comes up to the surface it prevents the atmospheric drying of the internal water from the concrete.

With silica fume, since there is going to be no bleeding, concrete is going to be susceptible to drying from early stage itself. The problem with that is the plastic shrinkage; essentially shrinkage of the concrete while it is still fresh. This will lead to cracking because only the surface of the concrete wants to shrink and the rest of the concrete is dimensionally stable, because of which there is a restraint which causes the cracks to appear on the surface. This is not a structural issue, but you do not want surface cracks to appear because aesthetically it is a problem secondly, durability may be an issue because if there is cracking obviously water can get in into the cracks.

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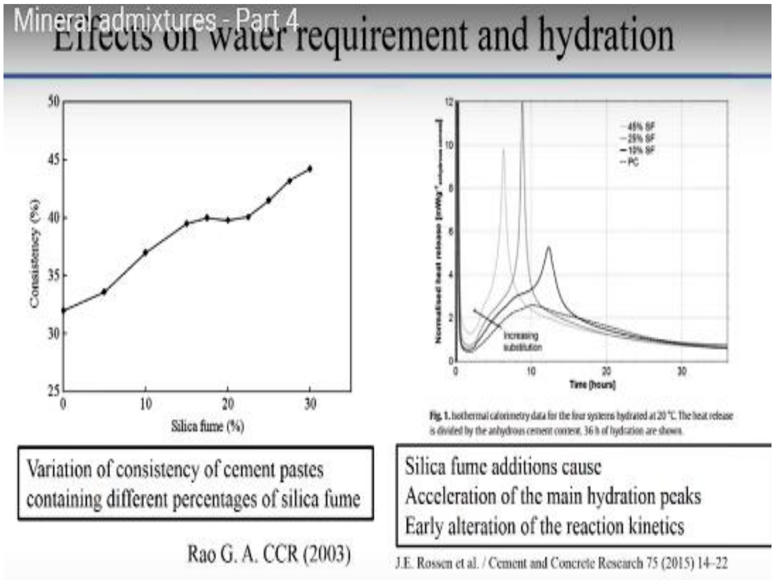


Mineral admixtures - Part 4

Effects on water requirement and hydration

Fig. 1. Isothermal calorimetry data for the four systems hydrated at 20 °C. The heat release is divided by the anhydrous cement content. 36 h of hydration are shown.

Variation of consistency of cement pastes containing different percentages of silica fume

Silica fume additions cause
Acceleration of the main hydration peaks
Early alteration of the reaction kinetics

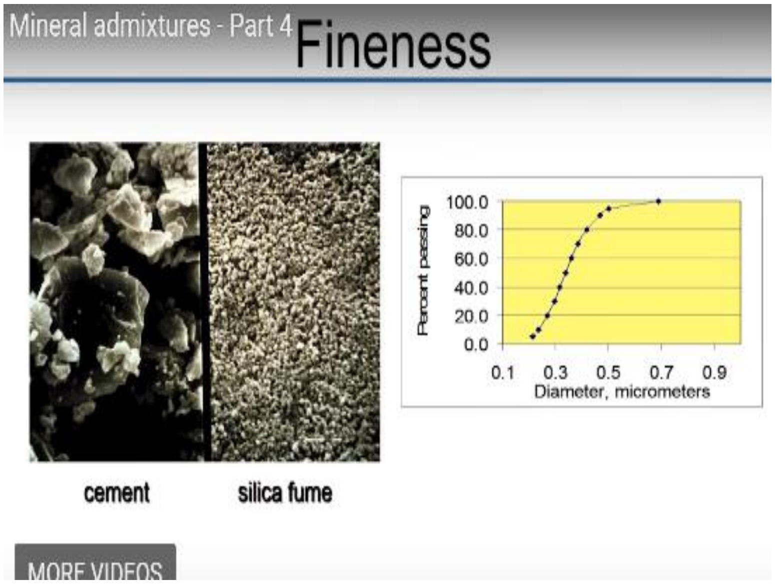
Rao G. A. CCR (2003)

J.E. Rossen et al. / Cement and Concrete Research 75 (2015) 14–22

With silica fume, the consistency is going up extremely high. So, with 0% silica fume or just plain portland cement is there, the consistency is of the order of about 30 to 32%. With 30% silica fume, that inordinately a high amount of silica fume as a replacement, it goes up all the way to about 40 to 45%.

We are mostly concerned in the range of replacement level of cement of 5 to 10%. But even there, there is a substantial increase in the cohesiveness of your mix which causes the consistency or water requirement to go up. Some research results are presented on right side with respect to the effects on the heat evolution patterns. We discussed that the dormant period relates to the early period of cement hydration beyond which starts the mean silicate peak and with very high amounts of silica fume you can actually get a situation where the peaks beyond the silicate peaks are getting excessively enhanced. So now in this case mean hydration peaks are also getting severely accelerated.

Why is this happening here? Silica fume requires the presence of lime for production of CSH because it is a pozzolanic binder. What is happening here is the silica fume particles, being extremely fine, have a very large surface area around them. Because of the high surface area, they give a space for your regular cementitious hydrates like CSH to nucleate to grow and because of that whenever any fine material or fine additive is added to a blend with Portland cement you will start seeing an increase in the rate of hydration. This is because more and more CSH is now capable of forming on the new sides which are provided by these fine particulate matter. Silica fume may not be reacting in that stage but the services of silica fume particles which are very high surface area, are providing sites for nucleation. **(Refer Slide Time: 11:02)**



Mineral admixtures - Part 4

Fineness

This is a picture showing the fineness of silica fume particles; you can see cement particles are of this size shown on left. But compared to that on the right hand side you see silica fume particles which are much smaller. A typical particle size distribution curve is given here and if I pick up the D50 from this curve it will be around 0.3 to 0.4 microns.

Because of this you get all these interesting problems with silica fume primarily plastic shrinkage.

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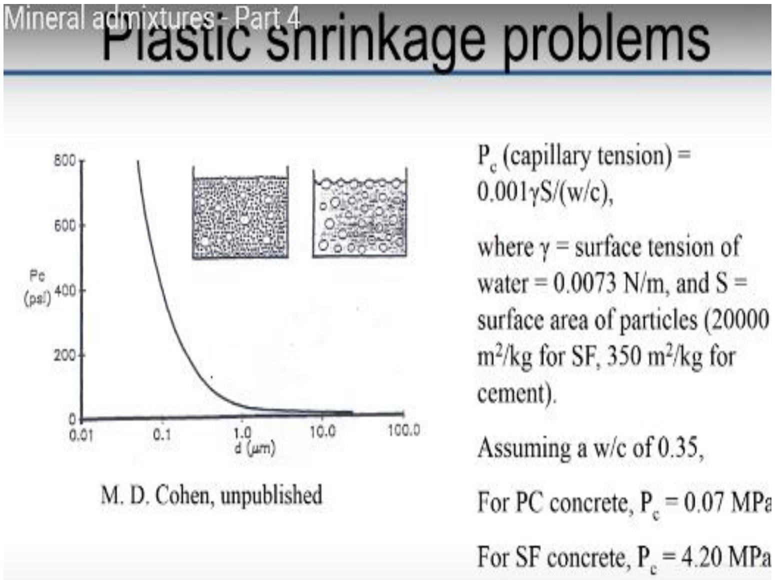

Mineral admixtures - Part 4

Plastic shrinkage problems

M. D. Cohen, unpublished

P_c (capillary tension) = $0.001\gamma S/(w/c)$,

where γ = surface tension of water = 0.0073 N/m, and S = surface area of particles (20000 m^2/kg for SF, 350 m^2/kg for cement).

Assuming a w/c of 0.35,

For PC concrete, P_c = 0.07 MPa

For SF concrete, P_c = 4.20 MPa

Let us consider this blend here which is a blend of cement+silica fume and another blend which is just cement. So, when water starts drying out between the cement particles in the case of a plain cement mix, the capillary pressure that is caused by the drying out of this water can be worked out to some extent by this capillary equation. The pressure is related to the surface tension, related to the surface area of the particles as well as the water to cement ratio. So if you consider particular water cement ratio and use this equation assuming the surface tension of water to be a constant amount 0.0073N/m. Just substituting different surface area of cement and silica fume particles gives you a results like shown in picture. For cement it is 0.07 MPa. That means if you make a concrete with plain cement, the plastic shrinkage related capillary pressure, which is caused when you drive the water from between the particles is less 0.1 MPa. So, it is a very small pressure that is not resulting in any cracking. With silica fume, the same capillary pressure rises to about 4MPa. Obviously in the fresh state or when concrete is in the semi solid state, it simply not going to have enough resistance to resist this kind of a stress 4.2 MPa.

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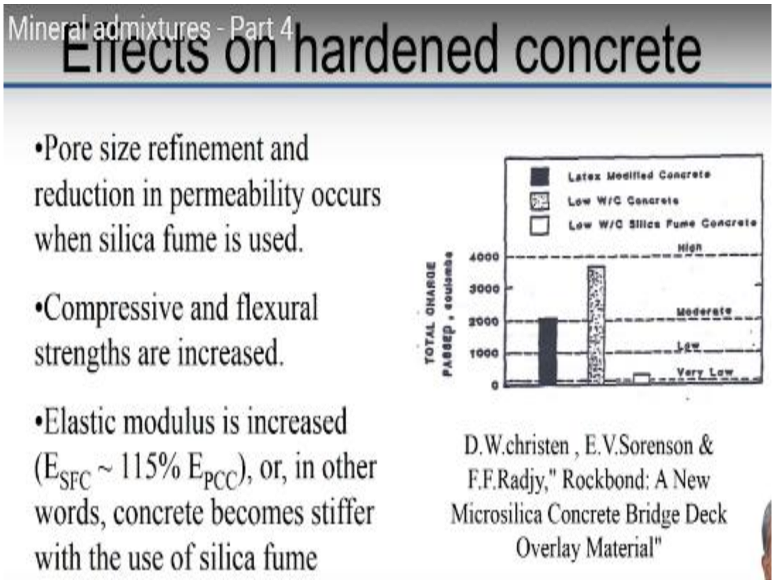

Mineral admixtures - Part 4

Effects on hardened concrete

- Pore size refinement and reduction in permeability occurs when silica fume is used.
- Compressive and flexural strengths are increased.
- Elastic modulus is increased ($E_{SFC} \sim 115\% \ E_{PCC}$), or, in other words, concrete becomes stiffer with the use of silica fume

D.W.christen , E.V.Sorenson & F.F.Radjy," Rockbond: A New Microsilica Concrete Bridge Deck Overlay Material"

With hardened concrete properties, because of the extremely fine particle sizes it works as filler. Secondly because of the pozzolanic reaction there is additional CSH formation because of which most of the characteristics are enhanced. Primarily because silica fume is such a fine material it is able to fill the extremely small voids between the cementitious hydrates and that enhances the strength of concrete and also it enhances the modulus of elasticity of the concrete. The resistance to deformation with silica fume concrete is much higher than that with just Portland cement concrete, about 15% more than portland cement concrete. In the case of durability most results are positive for example, a research study which explains the influence of silica fume on the rapid chloride permeability charge passed. The higher the charge that is passed through the concrete the more permeable that concrete is. So, if you pass a low charge, that is what happens with silica fume concrete, you get a very low charge passing through the concrete implying the concrete is highly durable.

There is a story behind this. After this test was developed in the US, the manufacturers of silica fume founded this test was really very helpful to promote their product and that is essentially because when you have very fine grain silica particles in your mix, you trap all the ionic species in the glassy particles itself. RCPT or rapid chloride permeability test is in which basically you apply a 60-volt potential difference between 2 phases of a concrete specimen that is 50 millimeters thick.

One phase is exposed to sodium chloride the other phase to sodium hydroxide. The science is that because you are driving this potential the chlorides are driven through the concrete towards the anode. The chloride being negatively charged goes towards a positively charged electrode. The problem here is when you have concrete which is saturated, there are ions in the pore solution of the concrete. When you apply a potential obviously those ionic species also start moving around. The charge carrying ability of the concrete will depend on the amount of ions present in your pore solution. So, when you introduce finely graded silica in the system amorphous silica in the system these ionic species sodium potassium and hydroxyl ions get trapped inside the glass. So, when you test a concrete with silica fume it is no surprise that you are actually getting a result that is extremely good..

But nevertheless even with other test methods like water sorptivity test and things like that you can still prove that when you use fine particulate mineral additives like silica fume as replacement of cement, your performance definitely improves. But RCPT somehow has become a test that silica fume manufacturers have used tremendously to their advantage. If you look at their brochures and publications, you will often see the mention of this test because this brings out their material in a far superior way as compared to any other test that can be used for durability applications. But anyway nevertheless it still goes to show that silica fume concrete is more durable as compared to plain cement concrete.

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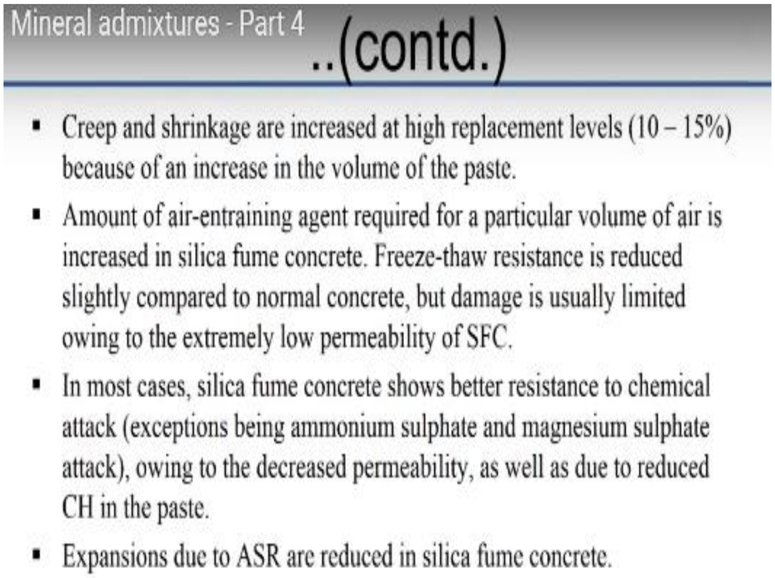

Mineral admixtures - Part 4

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- Creep and shrinkage are increased at high replacement levels (10 – 15%) because of an increase in the volume of the paste.
- Amount of air-entraining agent required for a particular volume of air is increased in silica fume concrete. Freeze-thaw resistance is reduced slightly compared to normal concrete, but damage is usually limited owing to the extremely low permeability of SFC.
- In most cases, silica fume concrete shows better resistance to chemical attack (exceptions being ammonium sulphate and magnesium sulphate attack), owing to the decreased permeability, as well as due to reduced CH in the paste.
- Expansions due to ASR are reduced in silica fume concrete.

Now apart from strength enhancement and durability enhancement, most of the hardened concrete properties are good when silica fume is used. Expansions due to alkali silica reaction are definitely improved or reduced when silica fume concrete is used. The same is true for any mineral additive, even fly ash or slag, when you use it as a cement replacement you are going to be reducing the alkali silica reactivity.

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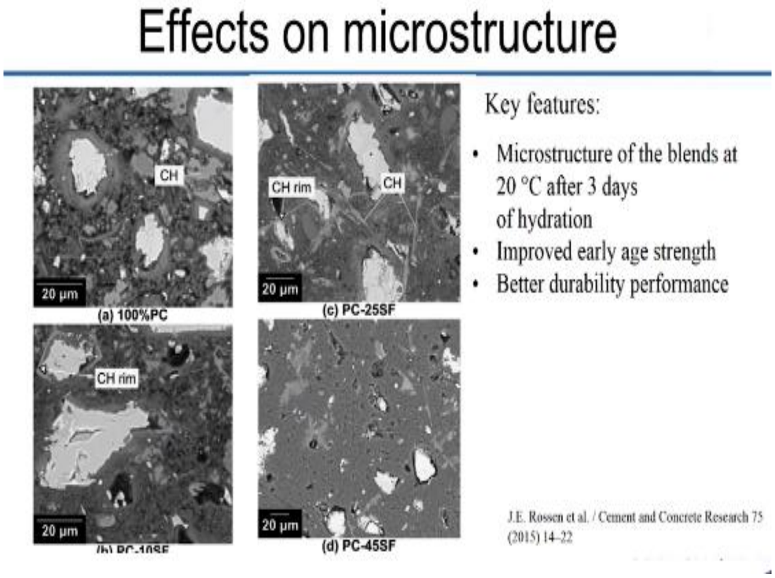

Effects on microstructure

Key features:

- Microstructure of the blends at 20 °C after 3 days of hydration
- Improved early age strength
- Better durability performance

J.E. Rossen et al. / Cement and Concrete Research 75 (2015) 14–22

This is a back scattered electron image of concrete which is showing on the left top side 100% Portland cement. Next is is 10% silica fume, 25% silica fume and 45% silica fume. So, you see very clearly as you replace more and more cement with silica fume, you are increasing the level of packing of your cement paste and you would you essentially end up with a system which does not show much porosity. Interestingly there is also other research which shows that the effects of silica fume can be better demonstrated in mortar and concrete as opposed to paste. What could be different in mortar which is not happening in paste?

You do not have any interfacial transition zone (ITZ) in paste. So, in mortar and concrete the ITZ is responsible for most of the negative effects of cement concrete. So, if you are strengthening the ITZ or if you are increasing the particle packing around the ITZ you are obviously going to get much more benefits when silica fume is used. This will have an increase of strength in the order of 30% to 40%.o So, that is why when you look at research papers they look at the effect on paste with silica fume. You will see that there is not that much of an enhancement in properties whereas in mortar and concrete you can definitely see the distinct benefits of using silica fume.

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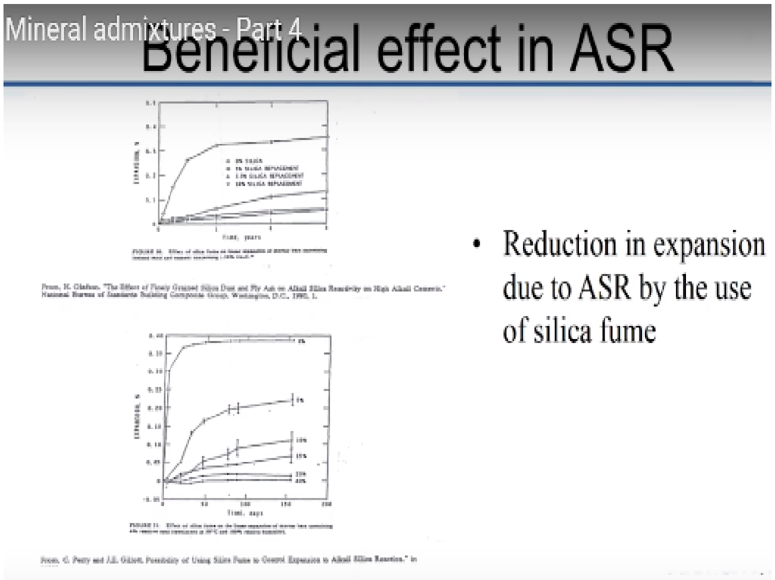

Mineral admixtures - Part 4

Beneficial effect in ASR

- Reduction in expansion due to ASR by the use of silica fume

From, H. Olafsson, "The Effect of Finely Grained Silica Dust and Fly Ash on Alkali Silica Reactivity on High Alkali Cements." National Bureau of Standards Building Components Group, Washington, D.C., 1985, 1.

From, G. Perry and J.E. Gillott, Possibility of Using Silica Fume to Control Expansion to Alkali Silica Reaction." in

This is just showing you the expansion due to alkali silica reaction and the reduction when more and more silica fume is used as a replacement for cement.

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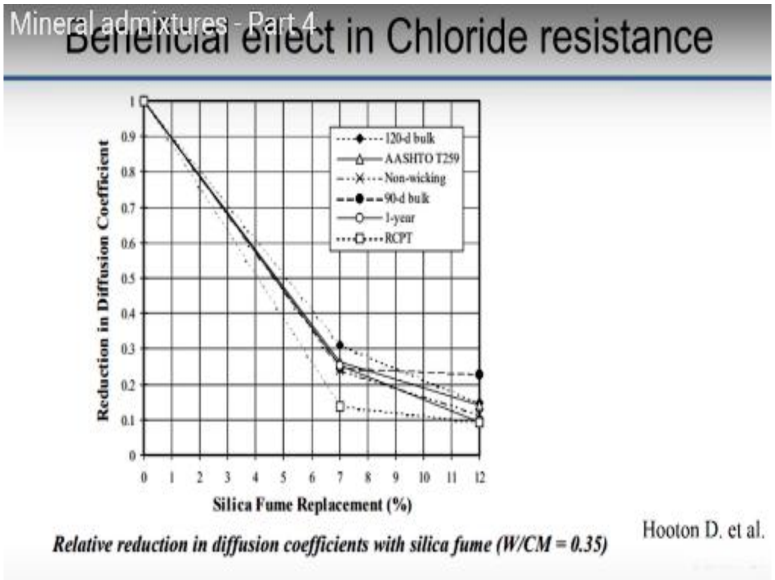

Mineral admixtures - Part 4

Beneficial effect in Chloride resistance

Relative reduction in diffusion coefficients with silica fume (W/CM = 0.35)

Hooton D. et al.

This is showing a real chloride test called chloride diffusion test. Chloride diffusion is basically the movement of chloride from a zone of high concentration to low concentration. So, this means that if you subject a concrete to chloride environment, the chlorides from the external environment penetrate the contract because of the concentration difference.

This assumes that your concrete is saturated. This test is done with a concrete a specimen that is placed inside a chloride solution and after some time you remove this specimen and you start removing material from the surface according to the depth. And each of the sample that you collect from the specimen you grind it to a powder and measure the amount of chloride. So, what that tells you is how much chloride is at the top, how much chloride is in next 1 millimeter, 5 millimeters 10 millimeters and so on. Then you plot the chloride concentration against the depth and from the curve that you get you need to calculate something called ‘diffusion coefficient’, which is a material characteristic at that particular age. So, if you are measuring this at 28 days we call it the diffusion co efficient at 28 days. Why should we be specific with respect to time?

Because with increased number of days the microstructure of the concrete changes. Because of which you may get a completely different result. So here what is being shown is when silica fume replacement level is increased you have a massive drop in diffusion coefficient. That means your capability for chloride to diffuse through the concrete keeps reducing as you increase the level of silica fume in the concrete.

So, this is actually a true positive result. In the case of RCPT you may get a false positive also but for the most part it also reflects the fact that the concrete is more durable with silica fume.

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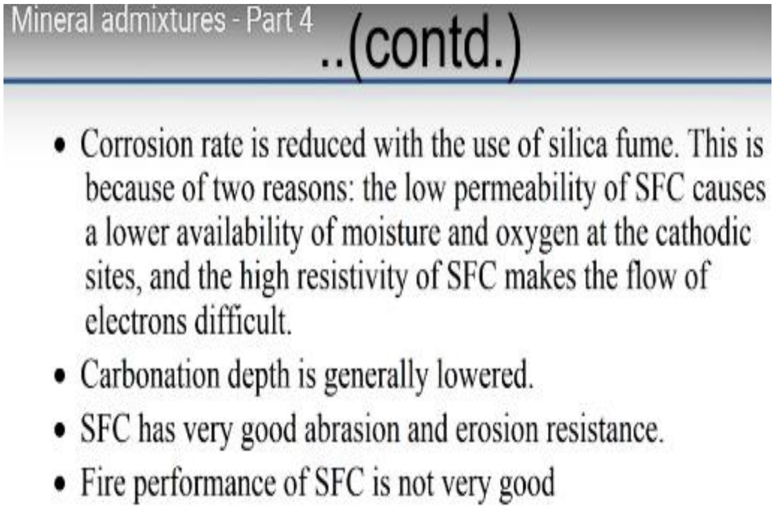

Mineral admixtures - Part 4

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- Corrosion rate is reduced with the use of silica fume. This is because of two reasons: the low permeability of SFC causes a lower availability of moisture and oxygen at the cathodic sites, and the high resistivity of SFC makes the flow of electrons difficult.
- Carbonation depth is generally lowered.
- SFC has very good abrasion and erosion resistance.
- Fire performance of SFC is not very good

Generally, corrosion rate is reduced significantly when silica fume is used, because there is low permeability of silica fume concrete because of which oxygen and moisture cannot be easily available to propagate the corrosion. Then you also do not have sufficient points for the chloride to enter to really cause the steel corrosion to happen. The resistivity of concrete becomes so high with silica fume that the ions which are needed to mobilize for corrosion to happen simply do not get the opportunity to do that. So, high resistivity and high impermeability are the reasons why concrete with silica fume performs very well with respect to corrosion resistance.

Carbonation depth may be a matter of dispute but in general it is lowered because the permeability is of a much different magnitude much lower as compared to ordinary corrosion. Abrasion and erosion resistance are very good and that is one reason why silica fume concrete can be quite suitable for applications in hydraulic facilities. Wherever you expect a lot of aggregate or large boulders of stone to drop from massive heights that causes a lot of erosion and abrasion on the surface of the concrete and for that purpose utilizing silica fume could be a very beneficial thing.

Fire performance of silica fume is not very good. When heat is generated there is moisture on the concrete that has to come out immediately while transforming to steam. In normal concrete there is enough connectivity and ITZ for the steam to come out without any difficulty. With silica fume concrete the steam can actually build up within the system and cause explosive failures happening to the concrete. This was found when the tunnel linings in the channel tunnel between England and France, connecting by road. There was a petrol tanker that actually caught fire inside. So, there was very high level of heat inside and the tunnel linings which were made with high performance silica fume concrete collapsed almost instantly because the water inside started converting to steam and it caused the concrete to burst out. So, all the linings were simply destroyed.

What people started doing is looking at how we can learn from this and make silica fume concrete also fire resistant; in which case what they did was they started putting plastic fibers in the silica fume concrete. What happens is that at high temperature the plastic fibers would melt leaving behind the voids and then the water will be able to come out as steam through those voids.

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Mineral admixtures - Part 4

Ground-granulated blast furnace slag (GGBFS)

Actually, slag should not be classified as an admixture; it is a hydraulic cement!!

Let us look now at granulated blast furnace slag. We discussed earlier that it is typically not included as one of the mineral admixtures or pozzolanic additives, it is called a hydraulic cement on it is own. That is because slag can react on it is own. But then the reaction is extremely slow and needs some activation and this activation typically happens in the presence of Portland cement.

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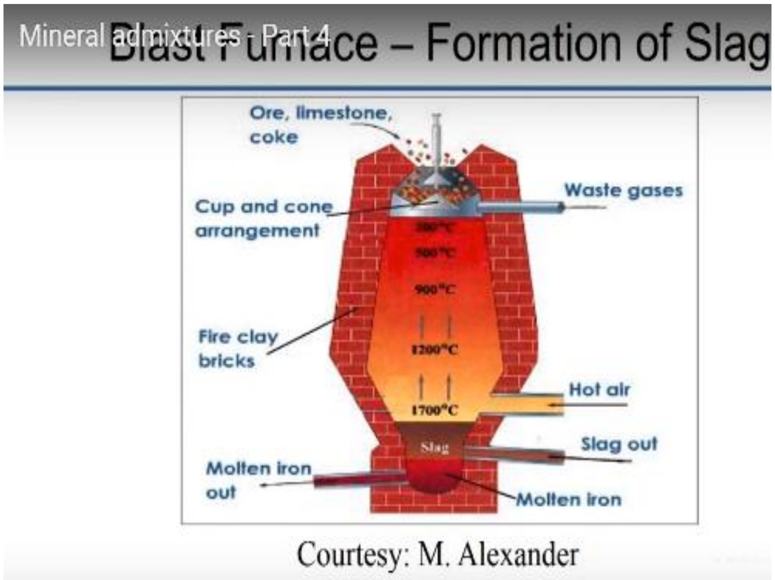

Mineral admixtures - Part 4

Blast Furnace – Formation of Slag

Courtesy: M. Alexander

The iron ore wich is fed into the blast furnace along with limestone and coke. The limestone essentially is a flux that reduces the temperature at which the ore will melt and ultimately all the impurities in the ore are collected along with the limestone and brought out as slag.

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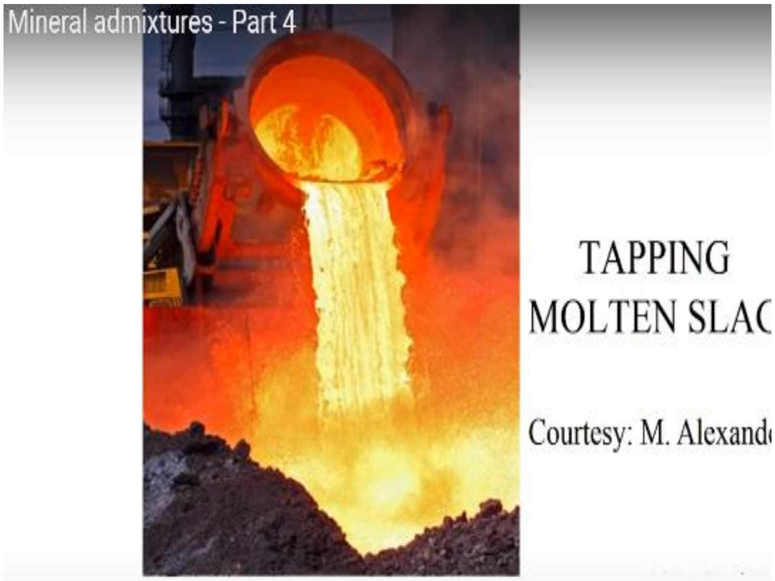

Mineral admixtures - Part 4

TAPPING
MOLTEN SLAC

Courtesy: M. Alexand

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This slag is in molted form and it has to be immediately removed and quenched to form the blast furnace slag clinker. Quenching means a sudden cooling of the molten material and that leads to the formation of blast furnace slag clinker

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And then or if you let it cool very slowly you get the air cooled slag which ultimately forms a very hard and good aggregate. Okay people can use air cooled slag also as aggregate.

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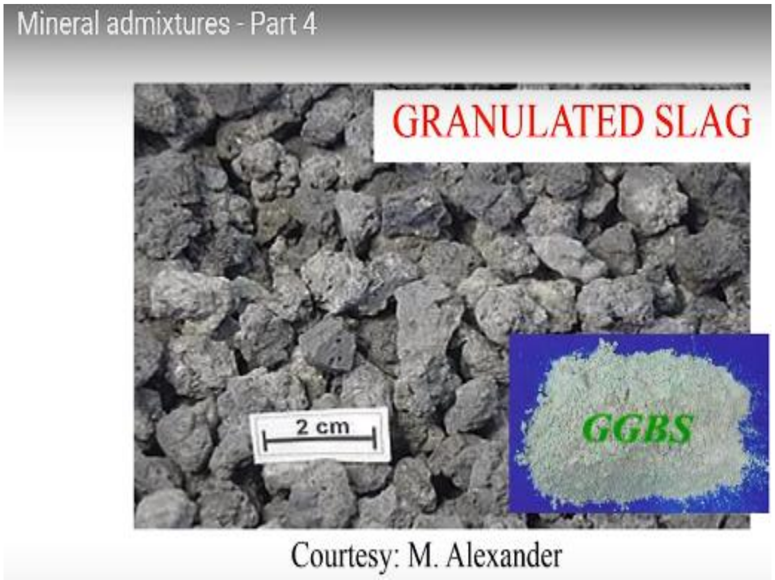

Mineral admixtures - Part 4

Courtesy: M. Alexander

But what we are interested in, from the perspective of supplementary materials, is the use of slag in the granulated form. This is the quenched slag which is then ground into a fine powder and used as ground granulated blast furnace slag. So, you will often see slag represented as GGBS or GGBFS, ground laminated blast furnace slag.

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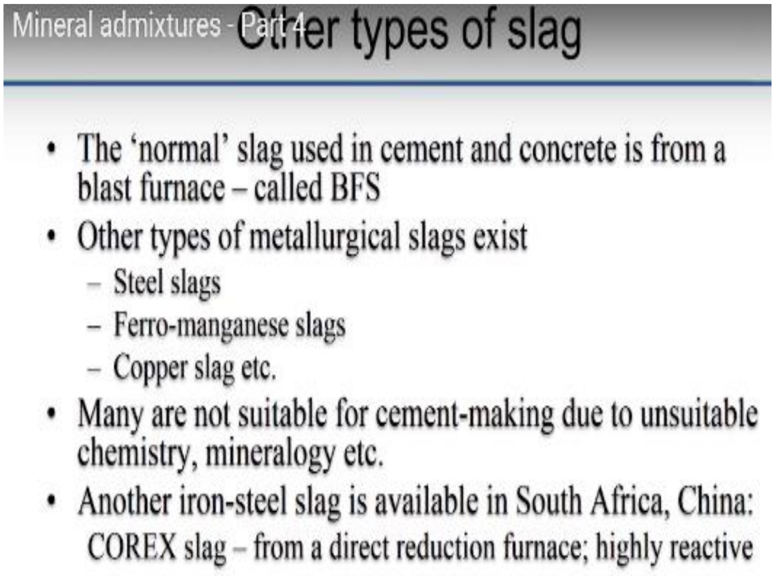

Mineral admixtures - Part 4

Other types of slag

- The 'normal' slag used in cement and concrete is from a blast furnace – called BFS
- Other types of metallurgical slags exist
  - Steel slags
  - Ferro-manganese slags
  - Copper slag etc.
- Many are not suitable for cement-making due to unsuitable chemistry, mineralogy etc.
- Another iron-steel slag is available in South Africa, China: COREX slag – from a direct reduction furnace; highly reactive

There are other types of slags also which you find from the industry increasingly and a lot of research papers are also coming out from other type of slags like steel slags, Ferro manganese slags, copper slag and so on. In fact, copper slag is also allowed as a partial replacement for fine aggregate in concrete. In IS383 which is basically the Indian specification for aggregates and concrete, it tells you the different sources of aggregate that are actually permitted to be used in concrete and you can also see the amounts to which they are allowing you to do the substitution. Unfortunately many of these slags that are obtained in different processes are not very suitable for cement making. Because their chemistry could be unstable, for example they may be able to help in the initial stages, but in the long term their chemicals or the ingredients that may be found in these slags may not be suitable for reaction or may not be suitable for proper performance of the concrete. So, you need to be very careful with the kind of material that we use as cement replacement. The steel slag which is also available from a different kind of furnace is called COREX slag. It is a very reactive form of ground granulated blast furnace slag and this high reactivity slag is obtained in certain types of manufacturing units is and it is also quite suitable for being used as a cementitious replacement. So you need to be quite sure what is the process from which you are getting your slag, so that you know exactly what reactivity you may be likely getting from the kind of slag that you are using.

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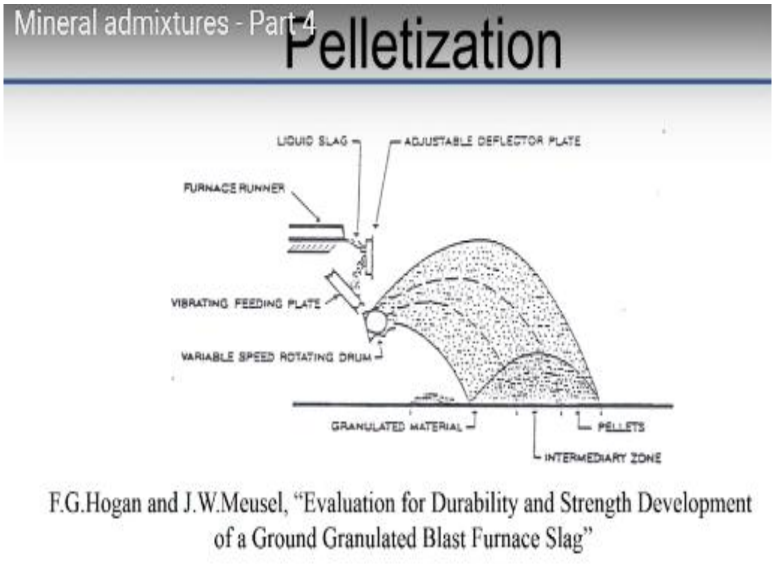

Mineral admixtures - Part 4

Pelletization

F.G.Hogan and J.W.Meusel, "Evaluation for Durability and Strength Development of a Ground Granulated Blast Furnace Slag"

There is another process possible to produce slag, it is called pelletization. So what happens here is this liquid slag which is coming out from the from the blast furnace is fed out to a vibrating feeding plate and then it is thrown by a rotating drum and this process of getting thrown from a rotating drum is able to form slag pellets and depending upon the size of the pellets you can collect the granulated material at one side and the large pellets on the other side okay. Because granulated material will be the small pellets which get cooled very rapidly because of this fall and then once they are cooled they form the granulated slag. You can take this pelletized slag and also grind it to get reactive blast furnace slag. But you must be careful about not calling it GGBFS it should be still called pelletized slag as the reactivity may be quite different as opposed to what you get from the quenching process.

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Mineral admixtures - Part 4

COREX Slag from South Africa

Courtesy: M. Alexander

This is a COREX slag from South Africa and you can see the highly angular nature of the slag particles. Slag is ground from the quenched material so obviously it is going to be quite angular and in this case COREX slag is showing high reactivity primarily because it has gojt a very highly irregular structure.

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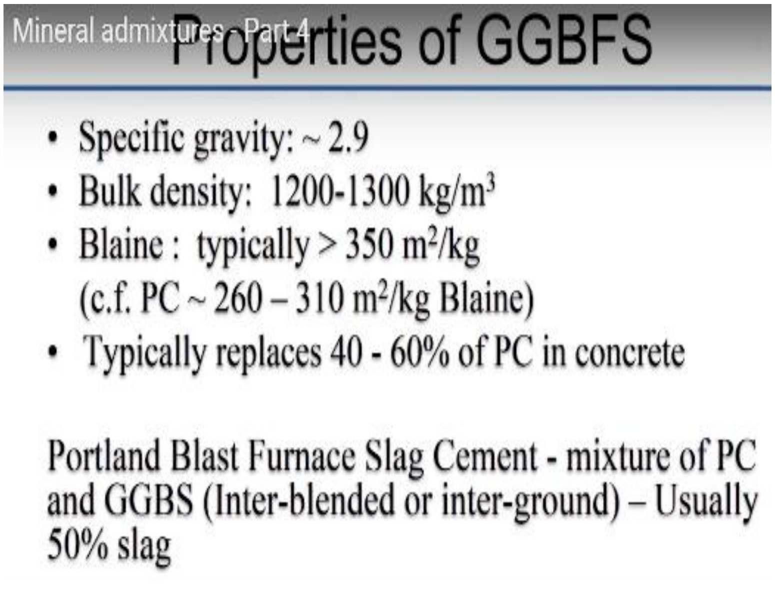
Mineral admixtures - Part 4

Properties of GGBFS

- Specific gravity: ~ 2.9
- Bulk density: 1200-1300 kg/m^3
- Blaine : typically > 350 m^2/kg
  (c.f. 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

Specific gravity of slag is close to cement at about 2.9. So when you replace cement with slag you do not see that much of a change in the volume of the powder that you have. Because all of the mineral additives which are silica based like fly ash or silica fumes may end up increasing the volume of the paste significantly in the early stages. Bulk density is also about similar to that of cement though slightly less..

Fineness depends on how much you grind the slag. Typically it is ground to a fineness which is similar to that of cement at about 350m2/kg and it typically replaces about 40 to 60% of the cement and concrete. The standards for Portland slag cement allows upto 70% cement replacement with slag.

That is because it is a hydraulic cement and not a pozzolanic additive because of which it can substitute a larger fraction of cement. So, most of Portland slag cements that you get in the market would have about 50% slag in them and generally if you go to any concreting application also they would be using slag usually at a 50% replacement level.

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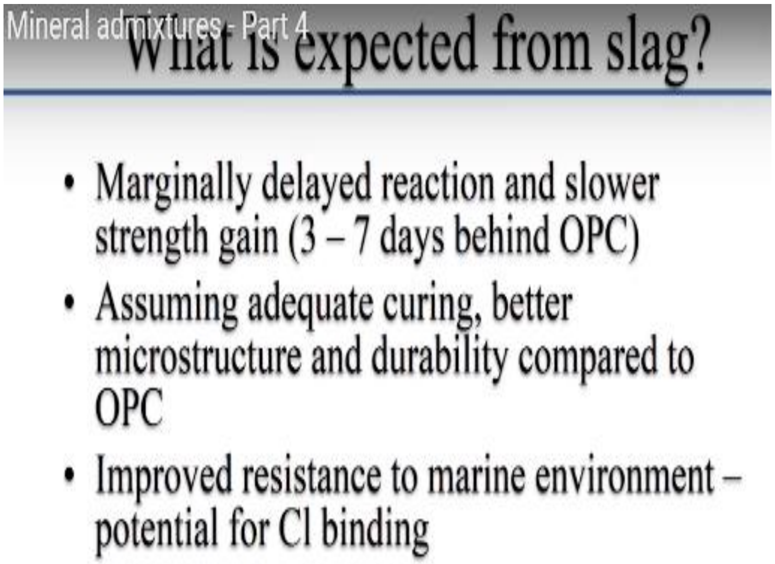

Mineral admixtures - Part 4

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

So, we expect from slag generally a marginally delayed reaction. I discussed this earlier that the effective time that the slag mix may need to reach the level of the potential development of Portland cement maybe about 3 to 7 days. But it may also not be true as you may actually get slags that are much more reactive and sometimes equally reactive as cement and lead to very good performance at very early ages itself. Assuming again that you do adequate curing, in the long term you can expect better microstructure and durability as compared to ordinary Portland cement concrete.

Primarily when we are talking about slag we are talking about it is potential for chloride binding. The aluminates that are present in your cement react with sulphates in the early stages of cement hydration to form ettringite, which later gets converted to the AFm phases. If you have a large amount of aluminate in the system, it also shows an affinity for chloride ions. So, generally if you look at the design for concrete in a marine environment where lot of chlorides are present, the choice of a high C_3A is cement is usually good because C_3A can actually bind the chloride ions.

But another way of doing this is to use mineral additives which are have a high alumina content especially alumina that is reactive. In slag you get that reactive alumina which is able to bind the chlorides. So, because of high binding of the chloride you end up reducing the extent of chloride that can get to the level of the reinforcing steel and that obviously enhances the performance in a chloride environment. So, for marine applications generally slag is known to be the best substitute for cement and up to 50% slag is almost routinely used as cement replacement for all marine applications.

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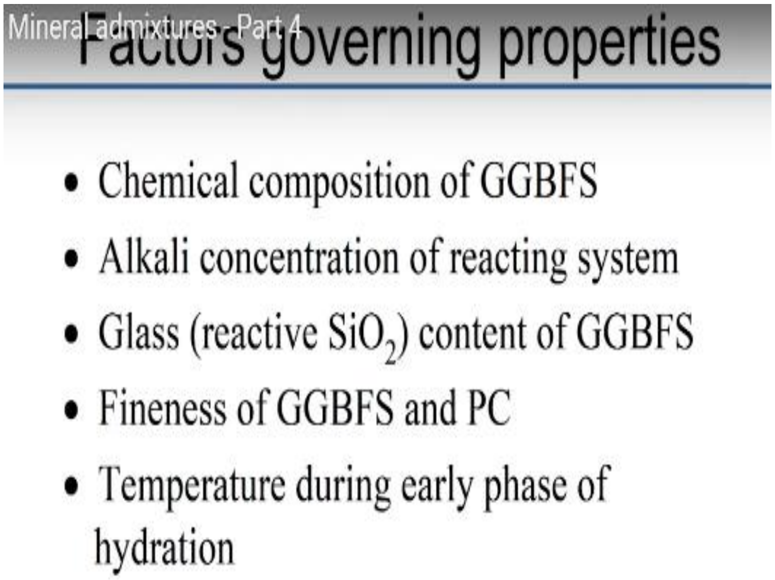

Mineral admixtures - Part 4

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

Slag is a latent hydraulic system. If you let slag react in it is own with water it may take a substantial period of time before that reaction gets anywhere. So, if you do some activation of the slag it leads to a faster reaction and activation is happening primarily because of the alkalis that are present in the system. For example, the alkalis that are contributed by the cement and also the sulphates that are contributed from the cement.

That is basically gypsum that is present in your system also acts as an activator for the slag. The amount of reactive silica in the slag is obviously important from the perspective of how fast it will actually end up reacting and produce the CSH. The fineness of the slag; just like in the case of Portland cement system, higher the fineness the faster will be the reactivity of the system. And in the early stages of hydration if the temperature is high that causes a further acceleration of the hydration process of the slag.

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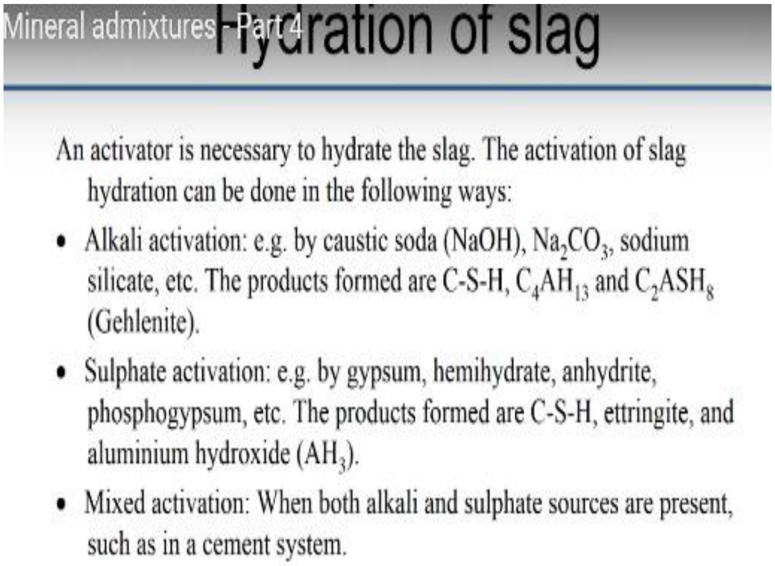

Mineral admixtures - Part 4

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.

So, hydration of slag basically happens because of alkali activation or sulphate activation or mixed activation. It can actually have a mixed activation in which both alkalis and sulphates are present just like in the case of ordinary Portland cement replaced partially by slag, and that is where you get mixed activation. Alkalis like sodium hydroxide, sodium carbonate, sodium silicate these could be used for activation. Sometimes even combination of the materials can be used to actually hydrate the slag and this hydration of the slag leads to the formation of CSH, C_4AH_{13} and the gehlenite phase (C_2ASH_8) which is a calcium aluminate silicate hydrate. People often call this system as alkali activated slag system, and you may refer to this in literature as AAS.

This is also from the same family of materials that is sometimes called Geopolymer. Most of you would have heard the term Geopolymer; but alkali activated slag is truly not a geo polymer. What is happening in an alkali activated slag system is that the alkalis are activating the hydration of the slag. Whereas in the Geopolymer what the alkalis are doing are the polymerization of the alumino silicate.

For example, if you choose calcine clay, or fly ash which has alumina and silica., you will get a binding between the alumino silicate chains or alumino silicate molecules and lead to the formation of a 3 dimensional polymer network. So, that is called geo polymer. Slag based systems are not geo polymers; they are simply alkali activated slag systems.

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Sulphate activation leads to the production of slightly different kind of products. You can activate it using gypsum, hemihydrate, anhydrite and or other alternative forms of gypsum like phosphogypsum and the products that are forming obviously will include CSH. In this case you may also form ettringite and aluminum hydroxide. So you form a completely different hydration assemblage as opposed to the case of alkali hydration. So, what will happen in the mixed activation when both alkali and sulphate sources are present? Obviously it will form all of these compounds. You may end up forming all of these compounds depending upon the reactivity of the slag. So, all the compounds CSH, calcium aluminate hydrate, alumino silicate hydrate, calcium sulpho aluminate, aluminum hydroxide can be formed.

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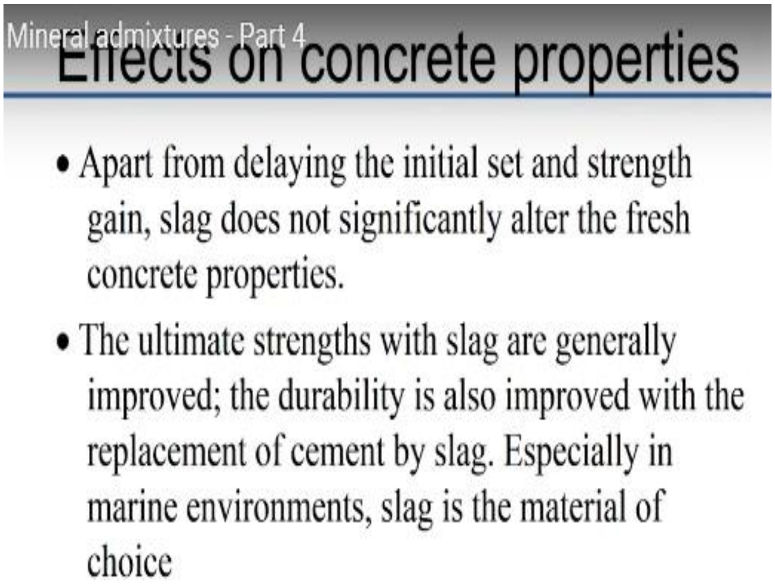

Mineral admixtures - Part 4

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

So, again concrete properties, the effects are quite similar to what we discussed earlier for general mineral replacements of the cement. Apart from delaying the initial certain strength gain, slag simply does not cause much of change in any of the other concrete properties with respect to mechanical characteristics. But sometimes you may see that the ultimate strengths with slag are generally improved when you are doing curing. The longer you cure the better the potential development of the strength. What is most important is durability, especially in chloride environment, is increased when slag is used as a replacement for cement. That is the main aspect that we want to consider slag for. I will show you some research results later which will capture the performance of the concrete with the slag and fly ash as opposed to cement.

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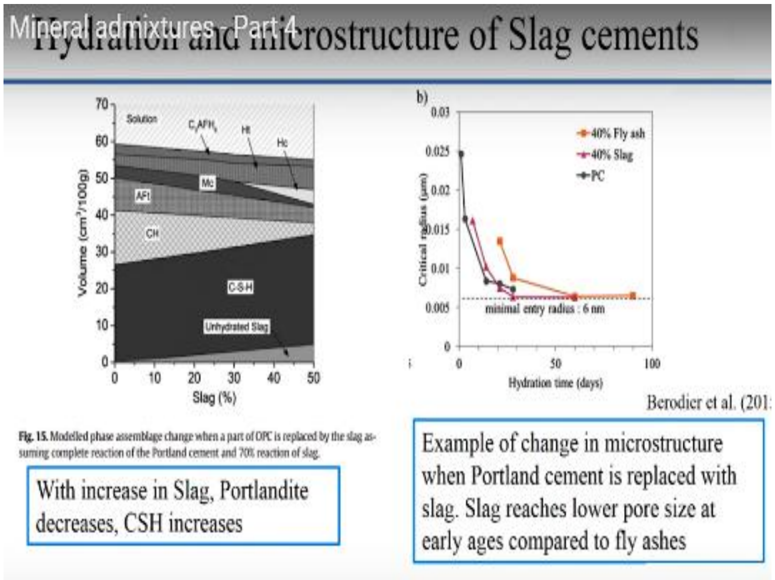

Mineral admixtures - Part 4

Hydration and microstructure of Slag cements

Berodier et al. (201

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

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

This is one of the results which is actually showing you the size of the porosity with increasing level of hydration. So on the right hand side you have this image which is showing portland cement replaced by slag. It is also showing the size of the pores with increasing levels of hydration and you can see very clearly that the critical radius, that means the largest pore that is still available in the system through which liquids can penetrate your concrete, is decreasing significantly with more and more time of hydration and for systems with fly ash and slag the pore entry radius is becoming smaller as opposed to that of Portland cement. These are measured using Mercurry Intrusion Porosimetry or MIP. One important characteristic is, for Portland cement there is not much of a change in the pore radius after sometime. For Portland cement after some time there seems to be a stabilisation with respect to the pore radius.

Slag system is quite similar to cement; slightly lower as compared to Portland cement system but almost it is happening at the same time. With fly ash you see that there is a tremendous benefit of additional curing in the case of fly ash. Because again fly ash is much slower to react as opposed to slug. So, more you cure the fly ash system the higher will be the level of enhancement or reduction of the porosity in your system.

What is shown on the left is actually a modeling of the hydration assemblage that actually ends up forming in a slag system. So, here what is shown is the volume of the initial ingredients that are present in your system and as you increase the level of the slag that is there, your hydration products keep changing from the beginning till the end.

So, you have other phases that are forming; essentially your calcium hydroxide phase is getting lower because most of that is getting bound in the other hydration products including calcium silicate hydrate. You may also form some other species like hemi carbonate or mono carbo-aluminate because of the alumina in the slag

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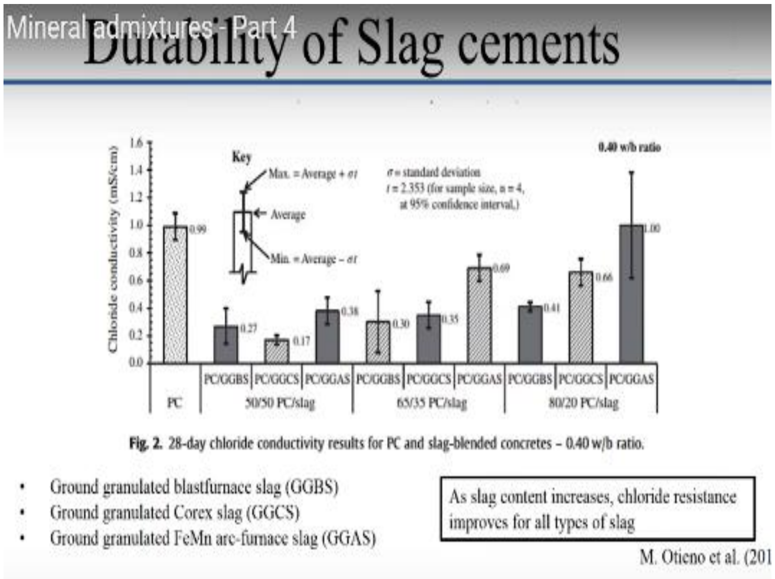

Durability of Slag cements

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. (201

This is some research results which look at the durability of slag cements in terms of chloride conductivity. This is not the same test as chloride permeability. But here what you are simply doing is you have chloride solutions at both ends of the concrete that means there is no diffusion. Concrete is saturated with respect to chloride also that means the chloride from outside are simply not going to get into the inside.

What you are doing is measuring the charge passing through this or charge carrying ability or the conductivity of the concrete system. So, more permeable it is, the greater will be the conductivity. The less permeable the material less will be the conductivity. So, chloride conductivity is expressed here and if you are replacing cement with slag your conductivity is going down tremendously.

especially with 50%, 35% and 20% replacement you can see very clearly that you can maximize the benefits when you are going for 50% replacement with slag. These are shown for different types of slags like the ground granulated blast furnace slag, COREX slag as well as the Ferrous manganese arc furnace slag.

So, you can see that the kind of performance you get may be quite different based upon different slags; especially when you are using this ferro manganese arc furnace slags, the performance is not as good as the cement when you are using only 20%. Only when you are using a high amount you can actually bring it to a level which is better than that of plain Portland cement concrete. Okay so again you have to be careful about what slag you are using.

Nowadays, number of people are trying to explore different means of replacing cement with other materials that may be found in different applications. Oftentimes these are done without preliminary characterization of these materials people simply add this in the concrete and say okay I added 10% the strength changed by 20%. But that kind of the research we need to be a little bit careful about because the data may look quite different if you investigate from a different perspective. So, be very careful when you are trying to look at data which is presented which talks about cement replacement with mineral additives, make sure that you understand what kind of characterization has been done for the additives to bring out the properties and the behavior of these additives first, before you understand how that is affecting concrete properties. Very often that initial characterization is not done satisfactorily because of which you cannot explain the results very easily and you know very well from your testing of concrete cubes that your are even allowed a 15% deviation between specimens.

So, if you have a research paper which is producing a major result with conclusion at the end saying that my strengths are 15% different, it is really nothing to go down about it. So, you are not really showing anything new as this 15% difference could be because of regular testing practices itself. So you need to be very careful about how you investigate these claims made by people that they are coming out with new additives.

These days especially the amount of research in construction materials has enhanced tremendously. Most people who have been doing structural engineering earlier are totally into materials research now. Because there is a lot more scope for doing all kinds of stuff with much lesser cost. At the same time what is happening in construction material research is that there is another branch of people, the chemists and the material scientists who have come in from a completely different background. And they have given a totally different outlook for concrete. Those people are doing their research at the cement paste or maximum mortar level and their results never match with what we actually see in terms of concrete performance. Because they do not understand concrete variable and the structural engineers do not understand the cement chemistry variable. So, ultimately we have lot of scope for research.