Admixtures and Special Concretes

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Lecture -39

Mineral Admixtures: Silica fume - Part 3: Effects on Microstructure + GGBS - Part 1: Introduction

Effects on hardened concrete:

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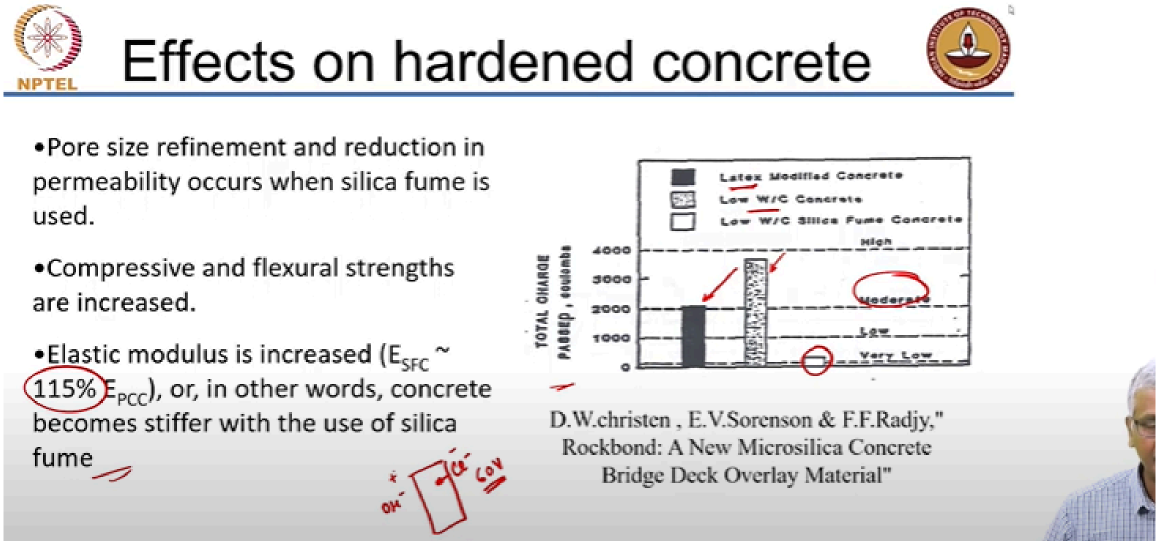

Effects on hardened concrete

- 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} ~ 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"

So, we were talking earlier about the effects of silica fume on hardened concrete and as we had discussed primarily the effect will be on enhancing the hardened properties of concrete primarily the strength and modulus of elasticity because the fine particles of silica fume are able to densify the interfacial transition zone and that helps in further reducing the extent of penetrability of the concrete and also adds to the stiffness of the material.

Now there are specific instances of the contribution of silica fume to the volume of the paste which may lead to some different conclusions with respect to the tendency to creep or shrink, but the increased resistance to deformation caused by the highest stiffness when silica fume is used to cement replacement may tend to overcome those effects. One important aspect obviously like any other mineral additive the expansions due to alkali silica reaction are reduced when silica fume is used as a cement replacement.

Effects of Microstructure:

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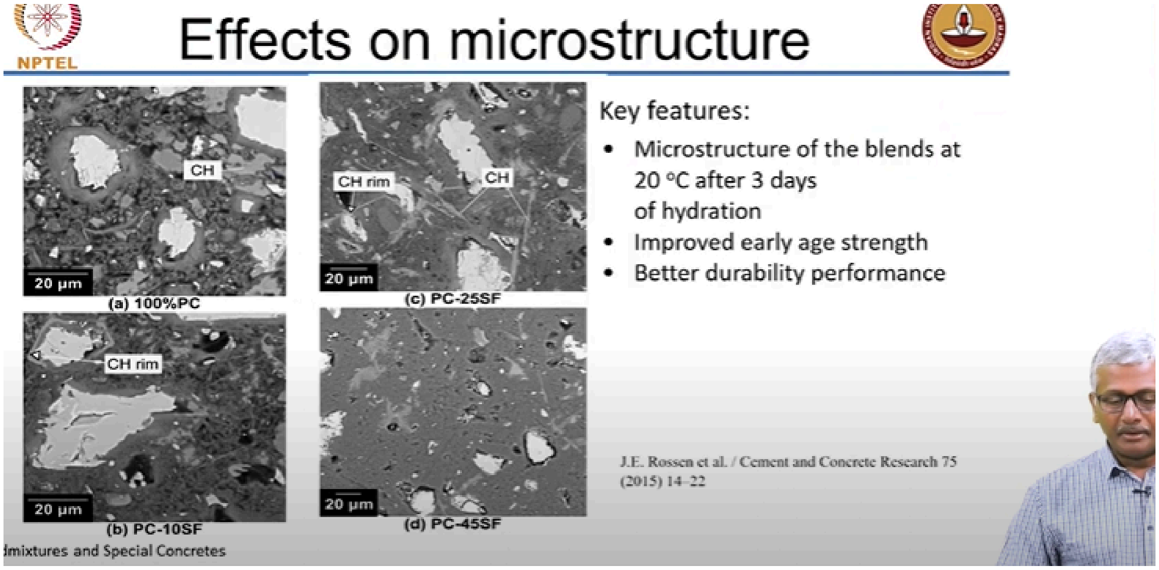

Effects on microstructure

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

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Now just to give you some examples of research studies that have been done with silica fume this is a study by Ross and Natal published in 2015 where you can see clearly that in the microstructure of cement paste when silica fume is used as a cement substitute you can see increased densification that is actually happening. So this is your 100 % Portland cement on the top left and this is a structure shown by backscattered scanning electron microscopy. The technique is quite similar in terms of interactions with the sample. The technique is similar to your optical microscopy which many of you are familiar with except that instead of light we use electrons to image the surface of an object.

Now here the denser the object the greater will be the reflectivity of the electrons. So the whiter phases that you see here are the denser phases, denser implying which do not have much voids in them. So here the denser phases are the ones which are unhydrated cement grains and the grey basically refers to all kinds of hydration products that are actually there. The calcium hydroxide is represented by these whitish phases whereas the CSH is the dark grey phases that you see and also the light grey phases which are right outside the unhydrated cement grains. But what you also see is the large number of black spaces, the black spaces are the ones which offer very little reflectivity because they have the least density that is your porosity in your system. So as you go from 100% PC to 10% silica fume to 25% silica fume and to 45% silica fume of course it is a totally impractical mix to do in real situations but nevertheless if you can produce a good mix with 45% silica fume what you see is almost a complete elimination of the porosity in your system.

Because the silica fume particles have actually filled up the porosity quite nicely and these are all at room temperature at 20°C after 3 days of hydration. You also can noticeably see that the extent of calcium hydroxide is getting reduced significantly as you increase the percentage of silica fumes.

Beneficial effect in ASR:

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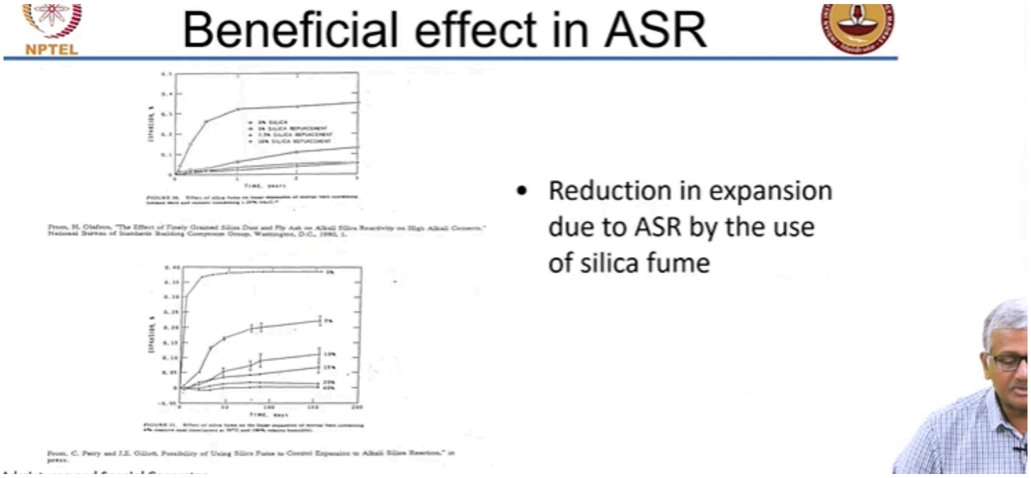

Beneficial effect in ASR

- 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 Composites Group, Washington, D.C., 1980, 1.

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

This is another research study which explains the expansion in alkali aggregate reaction. As more and more silica fumes are used the expansion is falling to levels which are much lower than what can be characterized as a reactive aggregate. So whenever you have reactive aggregate the use of cement replacement by mineral admixtures is the first line of defense to restrict the expansion to a level which is controllable.

Beneficial effect in Chloride Resistance:

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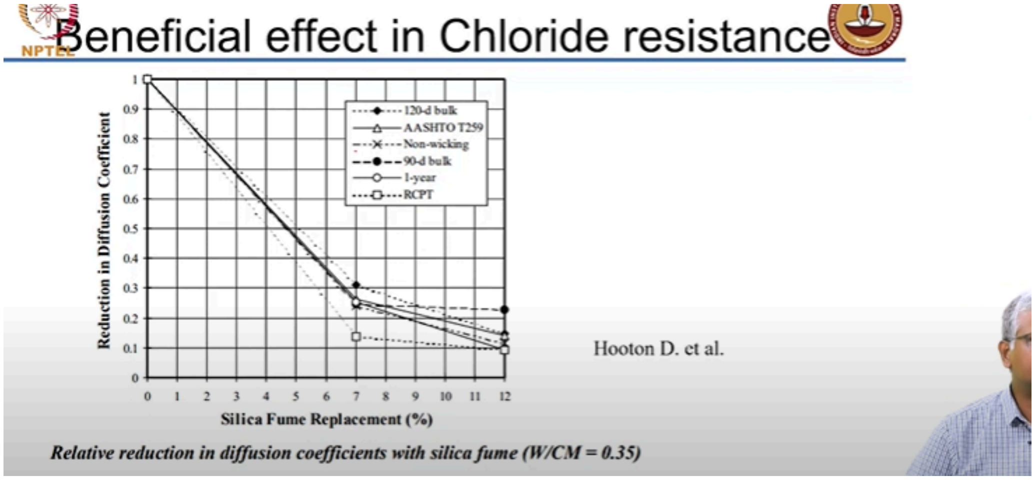

Beneficial effect in Chloride resistance

Hooton D. et al.

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

And chloride resistance effects are usually very good again because we are affecting the permeability of the concrete. So the concrete becomes less permeable and that leads to a better resistance to chloride penetration.

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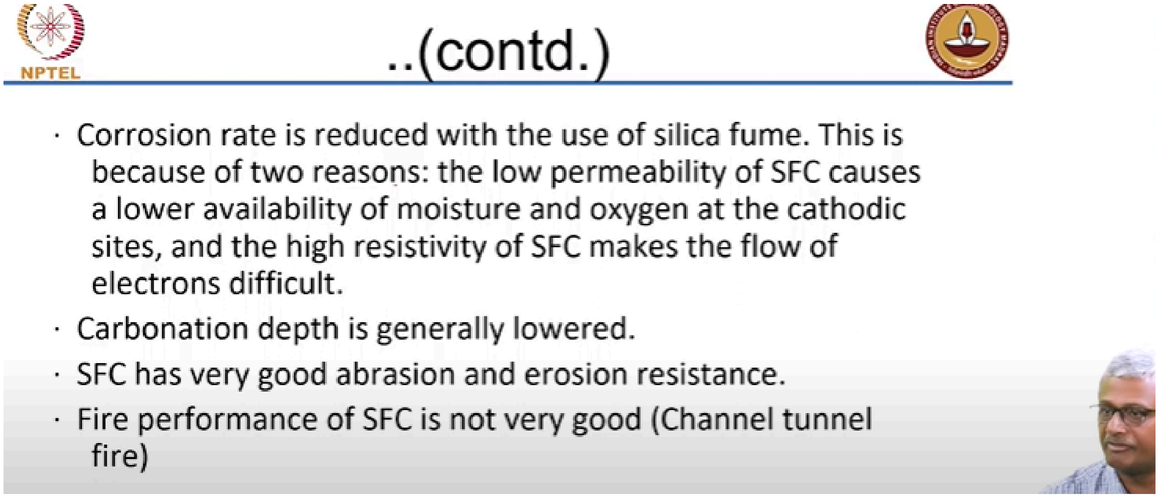

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- Corrosion rate is reduced with the use of silica fume. This is because of two reasons: the low permeability of SFC causes a lower availability of moisture and oxygen at the cathodic sites, and the high resistivity of SFC makes the flow of electrons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

Again the direct effect on chloride because of permeability is also the reason why silica fume concrete becomes less prone to corrosion problems. Very low permeability so oxygen and moisture that are required for cathodic reaction may not be able to get in easily because of the concrete being very dense and impermeable. And then because ionic transfer has to happen in the conducting medium that is your concrete the conductivity of concrete gets reduced significantly whenever you substitute cement by other pozzolanic materials. Because you are binding the alkalis conductivity is reducing and because of which your ionic passage in the electrolyte or the medium surrounding the concrete or surrounding the steel is going to be restricted significantly so your corrosion rate also will reduce whenever any mineral admixtures used and particularly so when a high reactivity mineral additive like silica fume is used.

Now carbonation is a tricky situation. We talked earlier that carbonation happens when CO_2 enters concrete from the external environment and interacts with calcium bearing phases to convert those to calcium carbonate. The problem with carbonation is not the chemical reaction, the problem is the fact that this reaction lowers the pH and that lowering of the pH makes the steel susceptible to corrosion. Issue is when you substitute cement with mineral additives we know that we are converting calcium hydroxide into CSH. So in carbonation of blended cementitious systems you have very little calcium hydroxide available to offer some initial resistance to the passage of carbon dioxide. So your CO_2 will be able to penetrate greater depths in blended cementitious systems irrespective of the fact that blended cements have lower permeability as compared to concrete with ordinary Portland cement. So there are two effects at play here one is permeability the other is your lime content or calcium hydroxide content.

In the case of silica fumes we use very little of it and a lot of it may not even get a chance to react and may be simply functioning as a filler. So silica fume although it is highly reactive pozzolan it is going to consume calcium hydroxide to some extent. In ideal situations it may be able to consume all of calcium hydroxide but that may not actually happen because each and every grain of silica fume may not have access to calcium hydroxide depending on how it is spread out in the microstructure. So the effect of the permeability when such small quantities of silica fume are used can be more dominant than the consumption of calcium hydroxide. When fly ash or slag is used, how much percentage are we talking about? 30 to 50% we are talking about at least 30% fly ash 50% slag. So a lot more is available in the microstructure so the possibility of calcium hydroxide interaction and consumption is much greater in such instances. But it only happens over a longer period of time.

Now we talked about this earlier that when your system is lime rich when it has more calcium hydroxide the calcium hydroxide starts forming calcium carbonate and that almost forms a barrier on the surface of your concrete through which CO_2 cannot further penetrate easily. But whenever mineral additives are used since calcium hydroxide is not available in large quantities your CO_2 is able to penetrate into the CSH or other calcium varying compounds CSH also will start carbonating. And carbonation of CSH leads to more porosity.

So if it leads to more porosity obviously more CO_2 also goes in. So your penetration depths with concrete with blended cements is generally going to be more than penetration depth with OPC. But in the case of silica fume concrete there may be an exception. You may have sufficiently low permeability with silica fume concrete to avoid the effects of reduction of calcium hydroxide content. Well it depends on a case by case basis we need to take that but on the whole silica fume concrete may show a lower carbonation depth.

Now in terms of abrasion and erosion resistance silica fume performs very well again why? Because it is increasing the hardness of your concrete by filling up the porosity well enough because of its extremely small particle size. Where is hardness and abrasion resistance or abrasion erosion resistance? In what kind of structures is it important? Pavements you need good abrasion resistance where else?

Under water construction especially sea construction. For the sea you need very good abrasion and erosion resistance. Dams you need good resistance for spillways not for the entire gravity dam because that is usually low grade concrete but for the spillways you need high grades of concrete which need good abrasion resistance. So in such cases silica fume can be a very good material to use.

The interesting part is the fire performance of silica fume concrete is not very good. An example is a channel tunnel fire. How many of you know about channel tunnel fire? This channel tunnel is basically the tunnel which goes from England to France in the English Channel under the English Channel. And this tunnel had a lining which was made with high performance concrete. The lining of the tunnel was HPC with silica fume high performance concrete with silica fume. It was a very high strength concrete that was used for the lining and one truck which was bearing petrol caught fire inside the tunnel. And because of the sustained fire the concrete lining made with high performance concrete completely spalled. And there was a major repair to be done for the tunnel.

Now what could be the cause of poor fire resistance of silica fume concrete? When concrete heats up water will convert to steam. The steam needs to come out of the concrete like a pressure cooker. The weight goes up and the pressure gets released and that is exactly what is happening here. There is no release of pressure that is possible in concrete that is extremely dense. So, steam which has very less porosity may not have sufficient pressure to push out the water or may not have sufficient passage to push out the water or the steam because of the pressure that is getting built up your concrete starts getting stressed and completely spalled out. Later what people talked about is you can produce high performance concrete with silica fume but use polypropylene fibers inside that will reduce the spalling. Why? This type of polypropylene fiber when temperature rises then this fiber gets melted down. It creates a hole. Exactly. So, at the temperature of the fire the polypropylene fibers start melting and it allows the passage of steam to the external environment. So polypropylene fibers as an additive to concrete used in the tunnel linings is a very popular choice these days. But with silica fumes we can expect that there is going to be very high pressures because of the steam generated inside the concrete. Of course that does not mean we can start making concrete more porous. It is only an extenuating circumstance like a fire where we put fibers inside the concrete.

GGBFS – Ground granulated blast furnace slag:

So most of the aspects that we discussed about resistance to chemical attack and corrosion and carbonation will sort of repeat in our discussion of other chemical additives or other mineral additives also. But nevertheless we have to understand the basic chemistry of these materials as to what goes into making the system different from a plain Portland cement based mix. So we have discussed earlier that ground granulated blast furnace slag is not really a mineral admixture, it is a hydraulic cement on its own because it has the potential to react with water. However, it needs some activation for the reaction. It can react on its own but it happens very slowly but in the presence of the activators it can actually react much faster. So that is why we call it a latent hydraulic binder. In terms of cement chemistry you may hear different terms for cement. Sometimes it is called cement but that is only when plain Portland cement is used. Sometimes we call it cementitious material and sometimes we call it binder.

Mineral admixtures are also sometimes called supplementary cementing materials; actually that is the more common name these days. They are sometimes also known as extenders. SCMs, mineral admixtures, and extenders are sometimes also called CRM’s. What is CRM? Cement replacement materials. So you have to be careful about what the authors of papers and books are referring to when they refer to all of these materials.

Extenders is a term that is used in Europe for defining the properties of special cements which have more and more of these mineral additives as replacements of cement. So this is something that you know very well.

GGBS:

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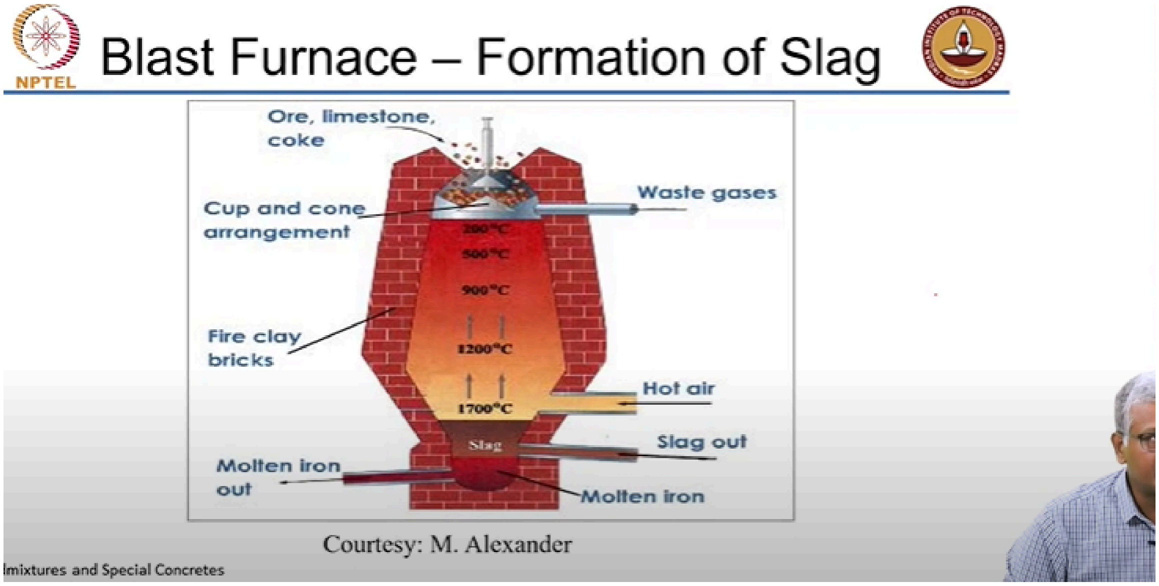

Blast Furnace – Formation of Slag

Courtesy: M. Alexander

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Slag is collected in the blast furnace process that is why the name blast furnace also comes in the name of the slag ground granulated blast furnace. Slag is the full name of slag. So we know that we add limestone in the blast furnace process. Why? What does limestone do? It produces lime, but what is the function of limestone? All this can be done without limestone also. All you are doing is burning the iron ore or heating the iron ore at a very high temperature. It reduces the temperature of melting iron. So it is a fluxing material. It reduces the temperature of the melting of the iron.

So here what we are simply trying to do is melt the iron ore and iron ore melting is happening across the range of temperatures. Now what really happens here is that the limestone is contributing to your calcium oxide. It is combined with the impurities present in iron ore which are in the form of silica, alumina and so on and gets collected as molten slag which is lighter than molten iron. So it is collected in a basin above the molten iron and then it has to be cooled to produce the granulated slag. Now molten slag of course is at very high temperatures. It can be cooled in various ways. You can cool it in air, you can cool it by throwing water on it or putting it in water completely which is called quenching or you can pelletize and then cool it slowly.

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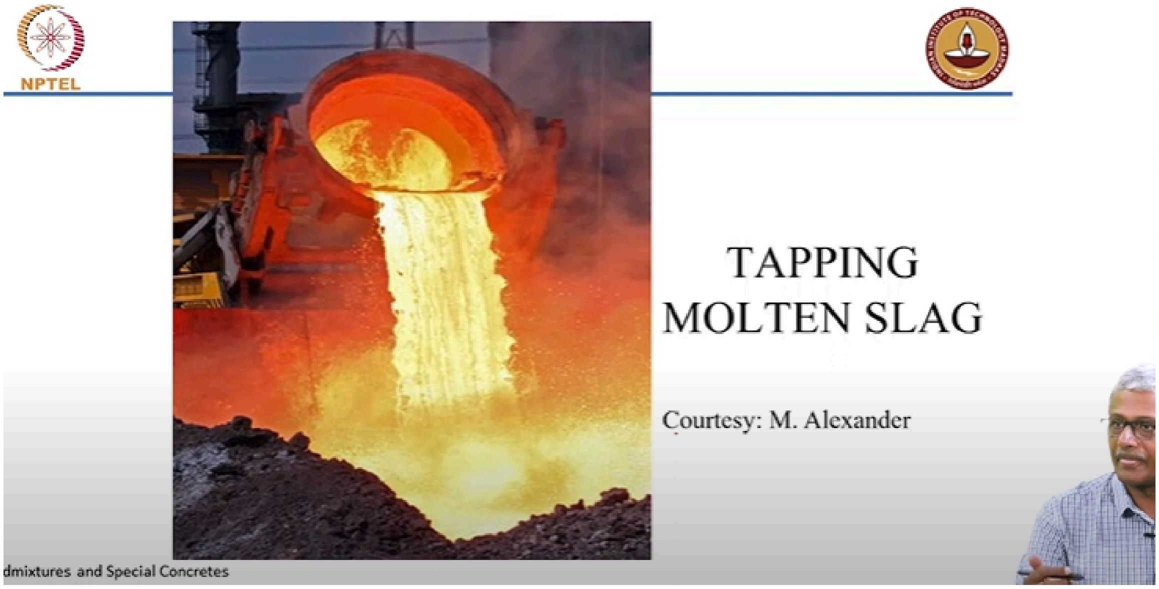

TAPPING MOLTEN SLAG

Courtesy: M. Alexander

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So there are different ways of cooling, but to produce a concrete or produce a material that is highly amorphous, what methodology should you choose? Cool fast or cool slowly? We need to cool very fast in order to make the material amorphous. If you cool slowly, just remember the same thing with your molten magma which makes your rocks. Granite is intrusive igneous rock, basalt is extrusive, and all of these are forming from cooling magma. So extrusive is above the earth's crust or outside the earth's surface where there is air cooling happening there. So it is relatively faster as compared to the cooling that happens under the earth's crust. That is why granite has a crystal size or grain size which is much larger than that of basalt which is formed on the earth's surface. So the same way here, if you cool very fast, you lead to a more amorphous nature. If you cool slowly, it becomes more crystal and in that case it will not be reactive.

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BFS CLINKER

Courtesy: M. Alexander

So you have to cool fast. Generally quenching is done to get what is called the BFS clinker. So quenching or cooling by water is done to get the BFS clinker and this BFS clinker, blast furnace slag clinker is further ground.

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AIR-COOLED SLAG

This is the other form of slag which is air cooled slag. Air cooled slag is what would not be reactive like a blast furnace slag, regular blast furnace slag which is quenched. This is out of quenching and this is from air cooling.

Air cooled slag is a material that is fairly hard and can be quite useful as an aggregate in concrete. Only problem is slag is a material that may have large iron content. Obviously, it is obtained in the process of removal of iron from iron ore and because of that it may also contain significantly high iron content. So what will be the relative hardness of slag as compared to cement clinker or as compared to limestone? Slag will be less or harder. Harder it has got iron in it, it is going to be harder. So crushing slag into aggregate sizes from the large bulk may be quite energy intensive.

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GRANULATED SLAG

Courtesy: M. Alexander

Similarly crushing slag into very small sizes to become a cementitious material is also fairly energy intensive. So granulated slag is the smaller pieces of the cement clinker or slag clinker that are obtained by quenching and then those are ground. That is why we call it ground granulated blast furnace slag.

Pelletization:

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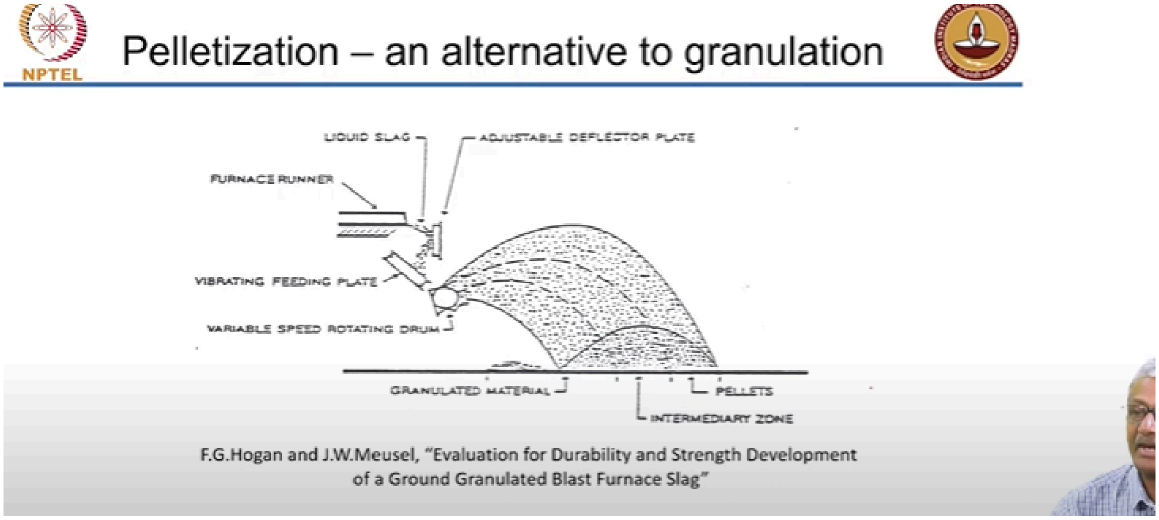
Pelletization – an alternative to granulation

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

The process of pelletization is another alternative to granulation where the liquid slag is made to fall on a vibrating plate and this vibrating plate feeds it to a variable speed drum and the particles of slag which are cooling because of the air interaction are thrown by this drum to different distances. So what happens is there will be some pellets that form which are larger in size, there will be some particles of slag which are smaller which may fly further.

So you collect the granular material over here which is of the size of the granulated slag size, you can see about 1 to 2 cm is the size and then the pellets, the small pellets are basically getting formed on the other side. So you can then further grind this to make the reactive slag. The only thing is here the pelletized slag may not have the same reactivity as your quenched material because air cooling is happening here, the air cooling is happening of very small specs of the liquid slag. That is why it cools much faster than the entire slag together. But in spite of all of this there may still be enough slag available which people are not able to cool by quenching or pelletization, they may actually be cooling it by just storing it outside. They may be dumping the liquid slag outside in areas which can receive such material where it will get slowly cooled by air. And these are the ones where air cooled slag can be formed, air cooled blast furnace slag ACBFS. Why do we keep bringing the name blast furnace inside? Because there are other types of furnaces in steel manufacture also like the electric arc furnace, there is also an LD furnace, all kinds of slags can be actually produced in the overall process of iron and steel manufacture. But the other slags that you get from other furnaces may not be as reactive as what you see with the blast furnace. Blast furnace is where you get the highest reactivity because of your calcium addition in the form of limestone.

Other types of slag:

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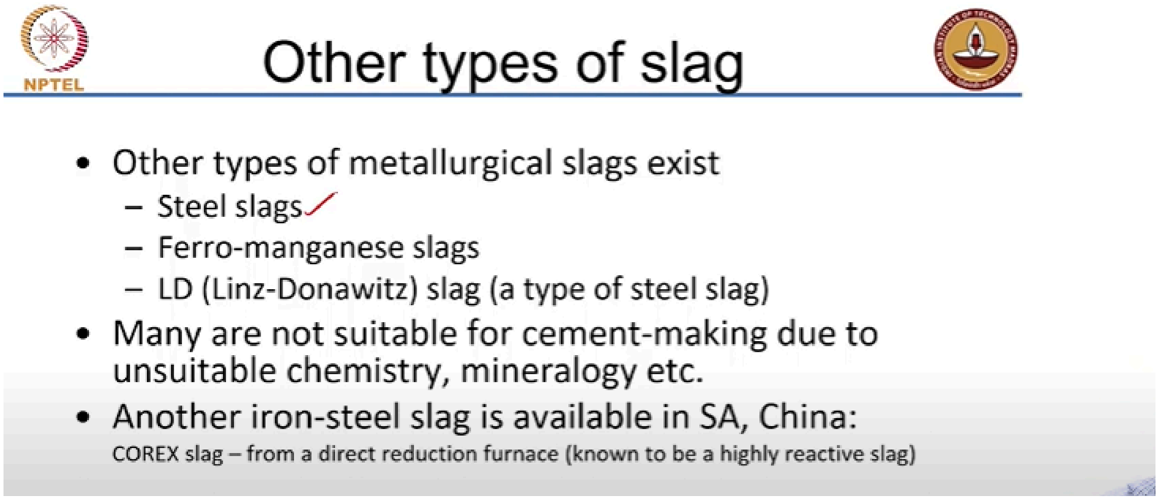

Other types of slag

- Other types of metallurgical slags exist
  - Steel slags✓
  - Ferro-manganese slags
  - LD (Linz-Donawitz) slag (a type of steel slag)
- Many are not suitable for cement-making due to unsuitable chemistry, mineralogy etc.
- Another iron-steel slag is available in SA, China:
  COREX slag – from a direct reduction furnace (known to be a highly reactive slag)

So again the other slags are overall known as steel slags, because they are produced in the other processes that may come beyond the blast furnace. There are also other slags called ferromagnetic slags from other industries and Linz Donawitz process slag, LD slag which is also a type of steel slag which is posing a large problem for many of the steel companies because this is not a material that can be used either as cement replacement because it is not reactive nor it can be used as an aggregate because it has got large amount of free lime. What is free lime? Lime oxide, if you remember in cement we want to restrict free lime because otherwise it produces unsoundness, it produces expansion upon setting. So this LD slag tends to have a high amount of free lime and that makes the use of LD slag even as aggregate quite difficult. Air cooled blast furnace slag you do not have that problem, but LD slag the process involves production of the slag which has a large amount of free lime. You have to be careful about where the slag is getting collected from and what kind of approach you may have towards utilizing it. So again many of the steel companies have this problem of LD slag and means of disposal.

COREX slag:

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COREX Slag from South Africa

Courtesy: M. Alexander

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There is also a different type of iron steel slag that is available called corex slag. It turns out to be very highly reactive, it is from a direct reduction furnace and the structure of corex slag is a lot finer and a much more sharp angular texture is shown which makes it quite reactive as opposed to the regular blast furnace slag.

LD slag:

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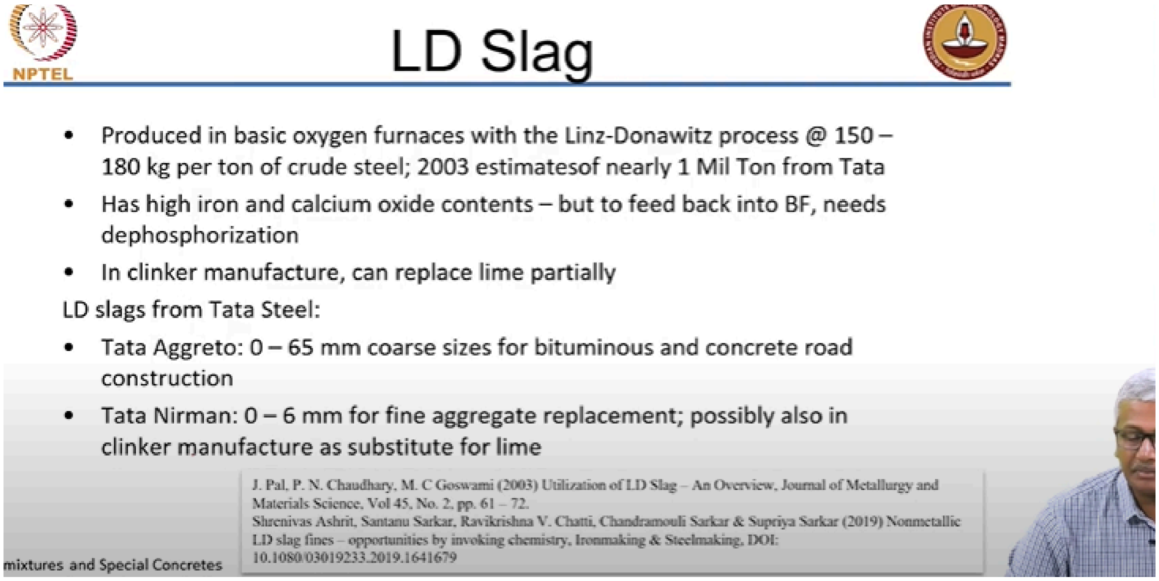

LD Slag

- Produced in basic oxygen furnaces with the Linz-Donawitz process @ 150 – 180 kg per ton of crude steel; 2003 estimatesof nearly 1 Mil Ton from Tata
- Has high iron and calcium oxide contents – but to feed back into BF, needs dephosphorization
- In clinker manufacture, can replace lime partially

LD slags from Tata Steel:

- Tata Aggreto: 0 – 65 mm coarse sizes for bituminous and concrete road construction
- Tata Nirman: 0 – 6 mm for fine aggregate replacement; possibly also in clinker manufacture as substitute for lime

J. Pal, P. N. Chaudhary, M. C Goswami (2003) Utilization of LD Slag – An Overview, Journal of Metallurgy and Materials Science, Vol 45, No. 2, pp. 61 – 72.
Shrenivas Ashrit, Santanu Sarkar, Ravikrishna V. Chatti, Chandramouli Sarkar & Supriya Sarkar (2019) Nonmetallic LD slag fines – opportunities by invoking chemistry, Ironmaking & Steelmaking, DOI: 10.1080/03019233.2019.1641679

So as I was saying LD slag is from a basic oxygen furnace, the process is called the Lenz Donovitz process and you can imagine the extent of material that we are creating 150 to 180 kg per ton of crude steel is produced. So 2003 estimates of nearly 1 million ton from Tata steel alone, this is the figure from Tata. 1 million ton per year from Tata steel alone, so now this must have grown to probably 4 to 5 million tons because the capacity of Tata steel also would have enhanced. As I said, the primary problem with this is the high calcium oxide content. The other aspect is it has got a lot of phosphorous content and phosphorus content is not very good in terms of your steel corrosion. You want to restrict the phosphorus content significantly.

Now what people have tried to do is because it is giving calcium oxide content, you can put this back into the cement clinker manufacture process. It can give a little bit of more lime, but the problem is it is also giving along with that lime it will also give silica. So you have to keep adjusting that calcium silica ratio that comes out of your cement clinker production.

Tata steel has tried to produce aggregate with it. They have various names for it also Aggreto and Nirman, but the problem is again that you have to precondition the material so that the free lime gets converted. What will you do? How can you take care of the free lime before you use it in new concrete? What can you do with the free lime? What is the unsoundness reaction of free lime?

Reaction with water to form calcium hydroxide. So why don't we have that reaction even before putting this aggregate into concrete? Convert as much of the calcium oxide to calcium hydroxide which upon exposure to the environment should convert to calcium carbonate. So essentially what you are trying to do is mineralize the free lime that is present into a phase that is not going to be affecting the properties of the concrete which is made with the aggregate. So that is the kind of approach that people are trying to follow before selling this material as an aggregate.

Problem still exists that you cannot easily crush this material because it has much higher iron content than even your blast furnace slag because it is further up in the process than blast furnace. So more iron content will actually come out with the slag and it gets harder and harder to crush this material and process it to an aggregate size. Now very often we talk about industrial processes where we are producing waste which we would like to use as aggregate because it is a good material as aggregate, it is hard, durable and so on. But that very hardness which makes it suitable as aggregate makes it difficult for the production process of the aggregate. So we need to crush the aggregate, energy is involved, you need to justify whether the extent of energy that you are putting in to make this aggregate is really giving you the kind of performance that you expect in new concrete.

So it is not just technical aspects that we need to look at from the performance perspective, the processing and production of the material also are equally important to consider. As engineers we need to make decisions that are considering all of these aspects together. In the blast furnace slag process there will still be CO_2 emission, some CO_2 is going to get evolved. In the blast furnace process you are having temperatures which are high enough 900°C for instance where your CO_2 can get excited from your $CaCO_3$ that you are adding. Well it depends on how this waste gas is utilized, yes slag production will also lead to some CO_2 formation. But see again what people justify is that you are not producing slag, slag is an eventuality that happens during the production of pig iron. So this slag that is collected is treated as a waste. So very often in sustainability analysis you will see that the amount of CO_2 emission or energy for slag removal is not even considered. All of that is attributed to the steel, the CO_2 that is getting emitted in this process is attributed to steel not to the slag. So you have to remember that this is the production process of steel not of slag, slag is collected as a waste. But yes you have to expend energy and that expenditure of energy also either electrical energy or whatever to grind the slag to produce the ground granulated slag that involves significant bit of energy and the associated CO_2 emissions have to be taken into the account of slag when you are actually trying to substitute cement with slag.

Phases of LD slag:

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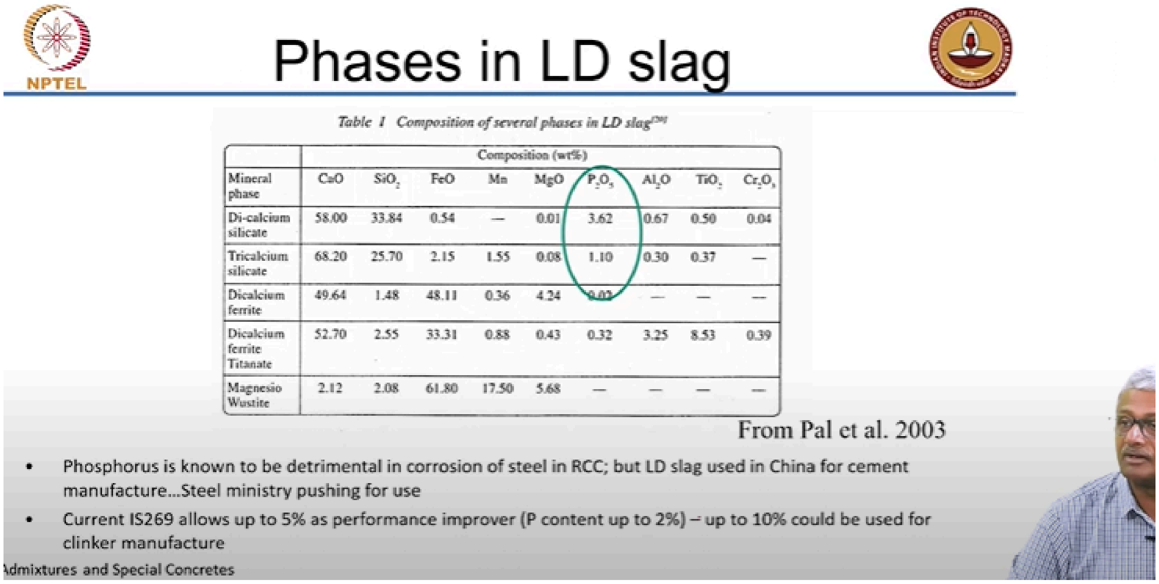

Phases in LD slag

Table I Composition of several phases in LD slag[30]

Mineral phase	Composition (wt%)								
	CaO	SiO_2	FeO	Mn	MgO	P_2O_5	Al_2O	TiO_2	Cr_2O_3
Di-calcium silicate	58.00	33.84	0.54	—	0.01	3.62	0.67	0.50	0.04
Tricalcium silicate	68.20	25.70	2.15	1.55	0.08	1.10	0.30	0.37	—
Dicalcium ferrite	49.64	1.48	48.11	0.36	4.24	0.02	—	—	—
Dicalcium ferrite Titanate	52.70	2.55	33.31	0.88	0.43	0.32	3.25	8.53	0.39
Magnesio Wustite	2.12	2.08	61.80	17.50	5.68	—	—	—	—

From Pal et al. 2003

- Phosphorus is known to be detrimental in corrosion of steel in RCC; but LD slag used in China for cement manufacture…Steel ministry pushing for use
- Current IS269 allows up to 5% as performance improver (P content up to 2%) – up to 10% could be used for clinker manufacture

Again as I said LD slag has higher phosphorus content which is not very good for steel corrosion in concrete. If you look at current IS 269, what is IS 269? This is standard for Portland cement. Now there is only one standard, earlier they used to have different standards for different grades of cement, there is now only one standard that is IS 269. It allows up to 5% as performance improver provided you can control the phosphorus content to less than 2%. And when the same material can LD slag is available to be used as a raw material into clinker manufacture up to 10% is permissible for that. So 5% is a performance improver.

When is the performance improver added to the Portland cement? After the clinker formation in the final grinding in the ball mill or vertical roller press whatever it is, in that process the performance improver is added. So if you are adding this material as a performance improver, what is going to happen? The grinding of the slag particles, LD slag particles is going to be very less as compared to the grinding of cement particles which are much or clinker particles which are much less harder. Here there is a lot of iron present, so many iron bearing phases are actually present in the LD slag. So because of this you have obviously a preferential grinding of clinker that will happen and slag will not really get ground much. So it may be okay as a performance improver but again you have to look at the efficiency of grinding.