Advanced Concrete Technology
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Lecture - 22
Mineral admixtures - Part 5

We discussed about slag cements in last lecture and we were trying to understand what concerns we may have with respect to durability. In most cases, as far as chloride attack is concerned or durability parameters that lead to chloride resistance are concerned, you always get a positive response when cement is replaced by slag. However, there is an obvious issue that can come about whenever cement is replaced by any mineral additive. The fact that you have, lesser calcium hydroxide in the system may lead to conditions of carbonation happening in the system. So carbonation of slag cements is generally higher than the carbonation of plain Portland cements.

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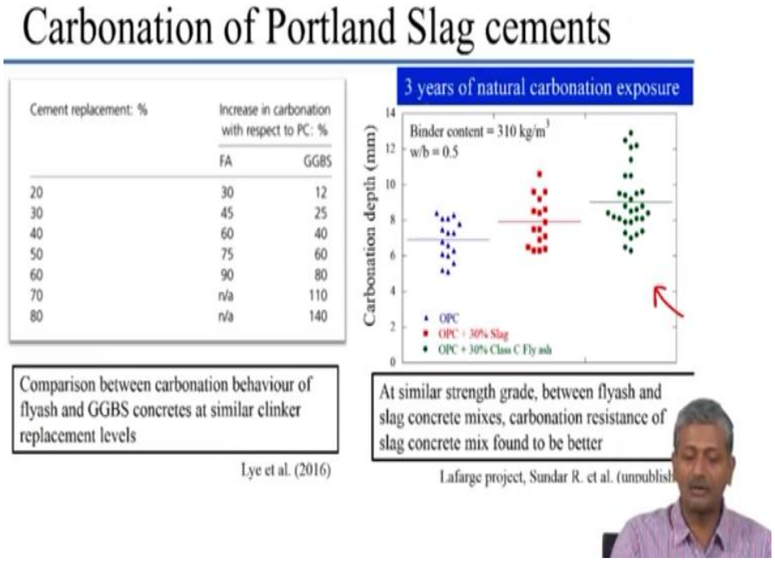

Carbonation of Portland Slag cements

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

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

Lye et al. (2016)

3 years of natural carbonation exposure

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

Lafarge project, Sundar R. et al. (unpublish

For example, here on the right, this is data that is published from a project that has been executed in our lab. So for ordinary Portland cement, the carbonation depth after three years of natural carbonation exposure, they are showing an average carbonation depth of around 7 mm. Whereas the mix with 30% slag was marginally higher probably at around 8 mm. With flyash depth was aroud 9 mm. This is not a significant difference at the end of three years, but if you put this in service life models, you will actually get a factor that is showing a lower service life for slag and flyash phase systems in carbonation environments.

Many service life models are basically restricted to determining the service life as an equivalent of the time it takes for the steel to start corroding. So here the time it takes for steel to start corroding here is assumed as the time that the carbonation front starts from the surface and reaches the level of the reinforcing steel. What does carbonation do? It consumes lime. You have $Ca(OH)_2 + CO_2 \rightarrow CaCO_3$ and there is a water molecule that goes out in this reaction. Some moisture is actually needed to convert this carbon dioxide into carbonic acid that actually consumes the lime. But this lime is already reduced in a pozzolanic system or in a cement substituted system. So if the carbon dioxide cannot react with lime, it will tend to react with other calcium bearing compounds like CSH.

Since the reaction of lime with carbon dioxide leads to the formation of calcium carbonate that almost forms an impermeable layer on the surface of the cement mortar or cement concrete, that becomes a limiting process. It further slows down the rate at which CO_2 actually goes in. In the case of mineral admixture based systems, since you have less lime, there is obviously going to be more CO_2 going inside.

So the carbonation depth generally in mineral admixtures will tend to go up as you increase the levels of replacement of cement with mineral admixtures. So generally with most mineral admixtures, the resistance to chloride induced corrosion is always improved, but the resistance to carbonation or carbon dioxide penetration is generally reduced whenever mineral admixtures are used as a replacement for cement.

That is an important thing, because very many times, if we take the rate of carbonation as an indicator of the possible damage, you can expect in your system, then mineral admixture based concretes will always come out to be poor with respect to ordinary Portland cement based concrete. However, if you link carbonation to corrosion, that may still not be the case. Because for corrosion process to sustain itself, you need the presence of oxygen and moisture.

These are coming from the cover concrete and if the cover is dense and impermeable like what expect concrete with mineral admixtures to have, the moisture will still be limited to propagate that corrosion. So all this is saying is that the risk for corrosion can be greater in the case of concretes with mineral admixtures in a highly carbonating environment, because more carbon dioxide penetration can happen. But that does not necessarily mean that corrosion will actually happen, because the access to moisture could be quite limited. So there is ongoing research, which is trying to explore the humidity of concrete inside systems with different types of binders. So humidity level obviously determines the rate of propagation of corrosion. If you have less humidity, very highly resistive concrete, then obviously you are not going to get great risk of propagation of corrosion.

There is another research data presented here from Lye et al, 2016. which talks about increasing levels of cement replacement and again increasing carbonation with respect to Portland cement and percentage is given in the picture above. For flyash, there is significant enhancement of carbonation extent. For slag also the carbonation extent can go up, but it is not as much as that with flyash. So larger replacements of flyash will produce greater risk of carbonation. Whereas larger replacements of slag will produce marginally less risk of carbonation as opposed to flyash.

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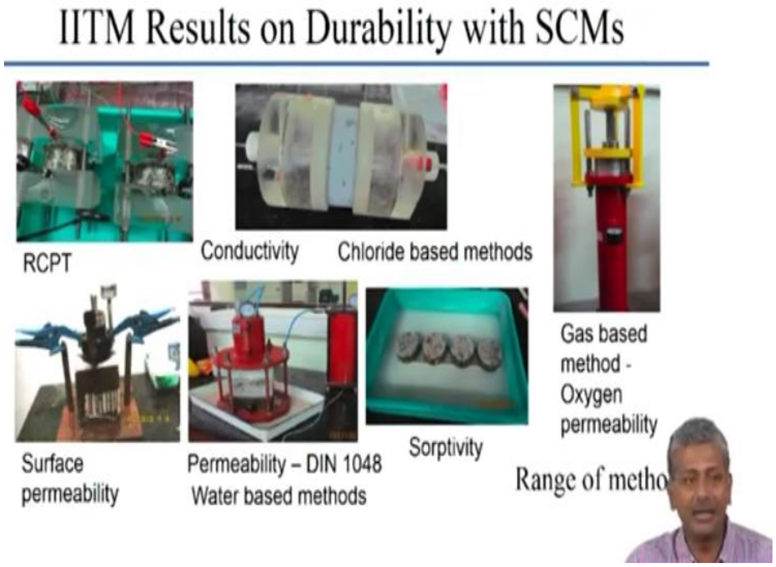

IITM Results on Durability with SCMs

RCPT

Conductivity

Chloride based methods

Gas based method - Oxygen permeability

Surface permeability

Permeability – DIN 1048 Water based methods

Sorptivity

Range of metho

So we have done an extensive durability study at IIT Madras with a number of different types of durability parameters, some of these tests we will discuss when we actually get to the chapter on durability. But for now I just wanted to put some results and perspectives so that you can get an idea about how these concretes perform when you replace cement with slag or flyash. There were several different test methods that were conducted for range of different concrete mixes.

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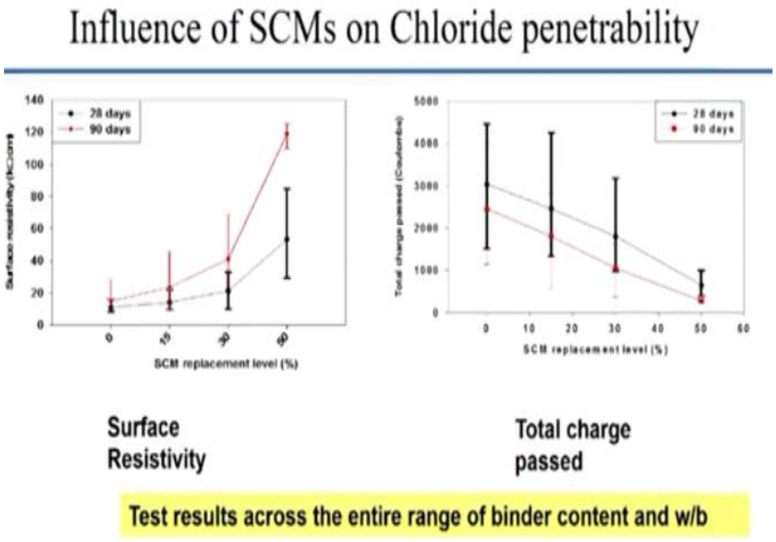

Influence of SCMs on Chloride penetrability

Surface
Resistivity

Total charge
passed

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

We have totally about 41 different concrete mixes that we used. Here, if you look at the surface resistivity, which is done by a simple technique called the 4-probe resistivity test, as you increase the extent of replacement of cement with either flyash or slag, the resistivity enhances significantly. This is actually a result that is encompassing all different concrete mixture designs and all different types of mineral additives.

So here we see that there is a major enhancement in surface resistivity when cement is replaced by mineral admixture. The black line is 28 days and the red line is 90 days. So from 28-90 days, as the level of replacement of cement increases, as in 30 to 50% replacement, there is a greater enhancement of the durability.

That shows that, extended curing with mineral admixtures can be very helpful. All this goes to show the longer you cure, the more the benefits you can actually get from the concretes with mineral admixtures. Similarly, if you look at chloride penetrability in terms of charge passed, there is a decline in the charge passed as you increase the levels of replacement. So what is interesting here is that this very low charge passed, between 1000 and 2000 coulombs is being obtained by the concrete. If you just have plain ordinary Portland cement, it is being obtained by the concrete at 400 kg of cement and 0.4 water binder ratio. or M40, M45, and another mix with 310kg of cement and 0.5 water binder ratio, if you are replacing cement with 50% of mineral admixture, you are getting an increasingly even better durability performance as compared to the plain Portland cement mix. But all this is happening at a lower binder content and a higher water binder ratio. So for a M30 concrete with mineral admixtures at 50% replacement of the cement, you can actually get a durability performance that is equivalent to an M40 or M45 concrete with just plain Portland cement.

So as reported earlier about the construction company that employed flyash as a replacement of an aggregate, because they were not allowed to be using it as a replacement for cement. All they wanted to do is get a lower charged passed in this test, which was not possible with just plain Portland cement for that grade of concrete. They simply followed the above mentioned. So mineral admixtures can help you make lower grade concrete, also quite durable. That is the main impact of mineral admixtures..

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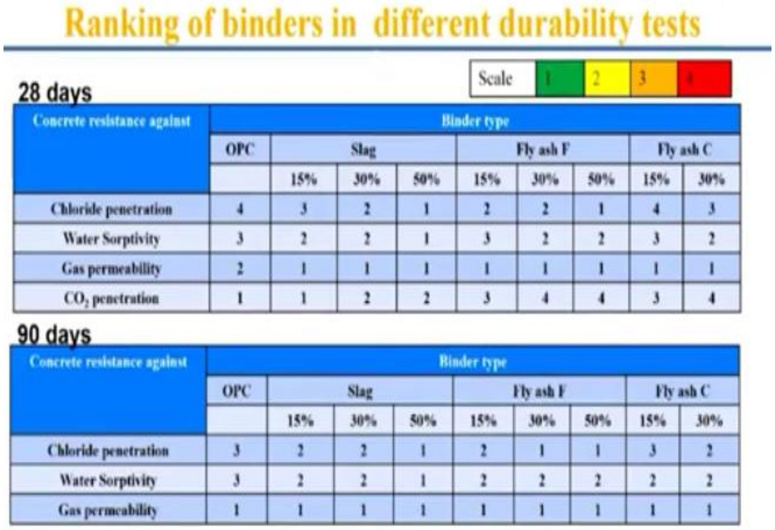

Ranking of binders in different durability tests

Scale	🟩 1	🟨 2	🟧 3	🟥 4

28 days

Concrete resistance against	Binder type								
	OPC	Slag			Fly ash F			Fly ash C	
		15%	30%	50%	15%	30%	50%	15%	30%
Chloride penetration	4	3	2	1	2	2	1	4	3
Water Sorptivity	3	2	2	1	3	2	2	3	2
Gas permeability	2	1	1	1	1	1	1	1	1
CO_2 penetration	1	1	2	2	3	4	4	3	4

90 days

Concrete resistance against	Binder type								
	OPC	Slag			Fly ash F			Fly ash C	
		15%	30%	50%	15%	30%	50%	15%	30%
Chloride penetration	3	2	2	1	2	1	1	3	2
Water Sorptivity	3	2	2	1	2	2	2	2	2
Gas permeability	1	1	1	1	1	1	1	1	1

There are positive results on water sorptivity and other chloride bearing parameters. So what we ended up doing is we looked at the entire set of data and did a qualitative ranking, which helps us understand, for example, if you are looking at a particular durability problem, like chloride penetration what is the relative ranking of these different types of mixes that we have tested compared to plain ordinary Portland cement, which is at rank 4 that means the lowest rank. The best performer is slag at 50% replacement or flyash at 50% replacement for chloride penetration characteristics.

For carbonation, obviously OPC is the best. Slag at 15% replacement does not seem to be much different as compared to OPC, but at 30% and 50%, the rate of carbonation of slag based concrete is significantly higher than that of OPC. Flyash even at 15% is actually showing a greater rate of carbonation as opposed to plain Portland cement and the performance is even worse at 30 and 50%.

So what can the concrete engineer do, is to look at this data and decide on what could be the right blend of ingredients for the particular service environment that the concrete is being designed for. So for a marine environment, I will be looking at chloride penetration and water sorptivity and again based on that you come to the conclusion that 50% slag would be the best mix, probably followed by 50% flyash. But if you have a consideration of strength at 28 days as one of the parameters, then the flyash mix may not really make it and you may have to rely on the slag mix.

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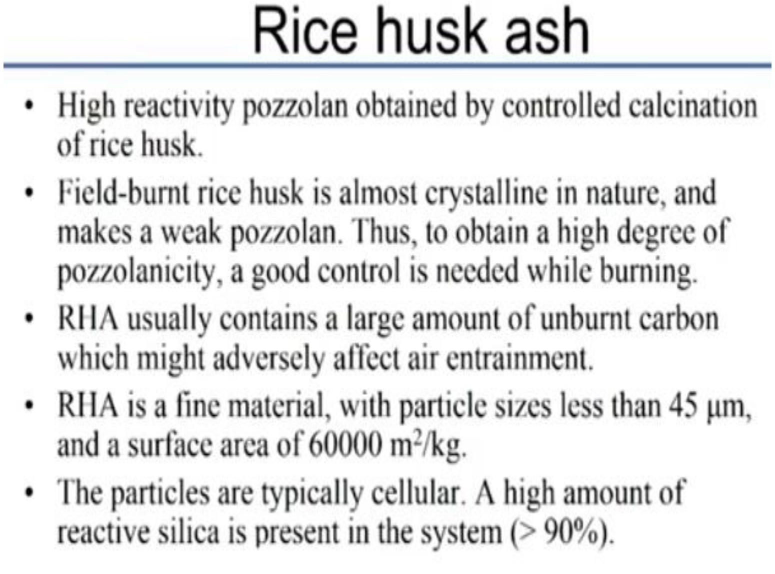

Rice husk ash

- High reactivity pozzolan obtained by controlled calcination of rice husk.
- Field-burnt rice husk is almost crystalline in nature, and makes a weak pozzolan. Thus, to obtain a high degree of pozzolanicity, a good control is needed while burning.
- RHA usually contains a large amount of unburnt carbon which might adversely affect air entrainment.
- RHA is a fine material, with particle sizes less than 45 μm, and a surface area of 60000 m^2/kg.
- The particles are typically cellular. A high amount of reactive silica is present in the system (> 90%).

Now let us look at the smaller or less used mineral admixtures. Rice husk ash is one such mineral admixture, which is used to a lesser extent primarily because there are not too many facilities that can produce the right kind of quality that is needed for enhanced pozzolanicity. So rice husk ash is the high reactivity pozzolan obtained by controlled calcinations of rice husk, where we can actually control the temperature of burning and the time of burning. So the temperature has to be controlled in such a way that the silica that you get from this rice husk becomes amorphous. If you burn it at very high temperatures, there is recrystalization that happens and then silica gets transformed to other crystalline components where it is not really usable in your system.

So field -burnt rice husk ash, you see commonly on rice fields, people who separate the husk from the paddy, take the husk and use it as a fuel source. They are able to burn it directly, but that burning in the field is not very good, because it is not controlled. They simply burn it, they do not really pay any attention to the temperatures and so on and the time for burning also can vary significantly between sites. So when you do that, you do not really get the kind of temperature control that you require to produce a material that is having good quality of amorphous silica.

Because its agro based, that means, it is derived from an agricultural product, there are obviously possibilities of finding lot of unburnt carbon in the system. So at certain temperatures, you need to burn it to get the best reactive silica. But at those temperatures, the carbon may not completely burn off as carbon dioxide. So you need to be careful about unburnt carbon content in your rice husk ash. Generally, if you look at the individual fine silicious particles of rice husk ash, the average size of the particles are quite similar to that of cement. There is not much difference. Comparing this to the silica fume where the average size was much, much smaller than cement, but with rice husk ash, the average size is nearly similar, but the particles have a very high surface area, 60,000m^2/kg., this must be because the particles have a certain texture. It got to have a lot of cavities and vesicles, because of which the surface area is extremely high. The particles are cellular with cavities and vesicles, and generally the purity of the system is very high. You have more than 90% silica present in the system.

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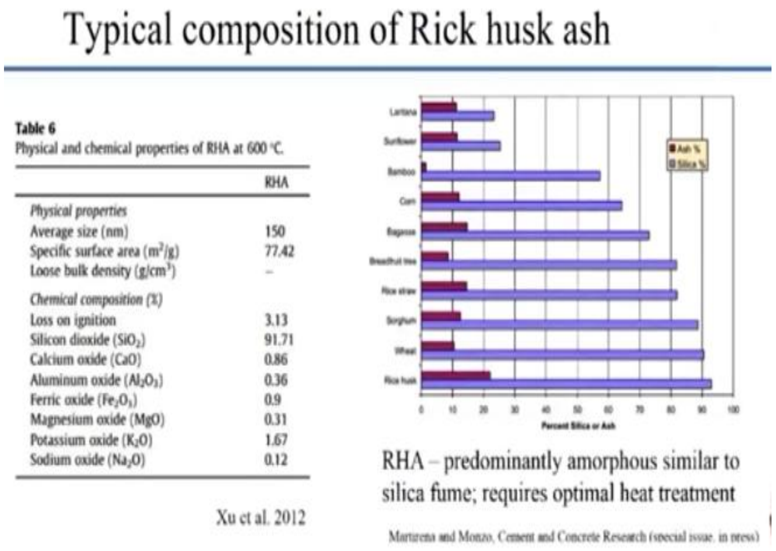

Typical composition of Rick husk ash

Table 6
Physical and chemical properties of RHA at 600 °C.

	RHA
Physical properties	
Average size (nm)	150
Specific surface area (m^2/g)	77.42
Loose bulk density (g/cm^3)	–
Chemical composition (%)	
Loss on ignition	3.13
Silicon dioxide (SiO_2)	91.71
Calcium oxide (CaO)	0.86
Aluminum oxide (Al_2O_3)	0.36
Ferric oxide (Fe_2O_3)	0.9
Magnesium oxide (MgO)	0.31
Potassium oxide (K_2O)	1.67
Sodium oxide (Na_2O)	0.12

Xu et al. 2012

RHA – predominantly amorphous similar to silica fume; requires optimal heat treatment

Martirena and Monzo, Cement and Concrete Research (special issue, in press)

So rice husk ash is predominantly amorphous silica, which is similar to silica fume and as shown in the picture above, there are different types of agro derivatives, which can be used. You can see that the silica content in the bagasse ash is up to a level of about 70-80% whereas the silica content in rice husk is generally more than 90%.

The silica , in your agro products, are coming from the soil. Because there is nutrients, which go in from the soil and a lot of silica is also derived from the soil, that goes up and rises into the structure of the plants. There is some strengthening of the plants also happens, because of the silica uptake by the plants. After you consume the good part, that is the carbohydrate, the remainder basically consists of the silica, or the husk or the external covering basically consists of the silica.

So even in corn, you can get significant quantity of silica, but then you have to determine whether the silica is usable or not. On the left side, you are given a physical and chemical characteristics of rice husk ash, which is burnt at 600 degree Celsius. So again, here you see average size in terms of nanometer is 150 nanometers; average size is given in terms of the surface area converted to a size. So it is not really the actual size of the particles. Particle sizes are much larger than that, which is quite similar to cement. Specific surface area is 77m^2/g, that means 77, 000m^2/kg. Imagine, this is a very fine material that is being used or very highly reactive surface, as long as you have the right kind of amorphous silica in the structure. Loss of ignition here is 3.13% and this corresponds to the unburnt carbon that is there in the system. Silica content is more than 90% and you may have some other impurities. Many of these agro impurities you can find significant amounts of alkalis, sodium and potassium oxide. So the alkali loading of the concrete needs to be checked carefully whenever you are replacing cement with agro waste. In bagasse ash the alkali content can be as high as 5-8%. When you use that as cementitious replacement, the overall alkali content has to be considered carefully.

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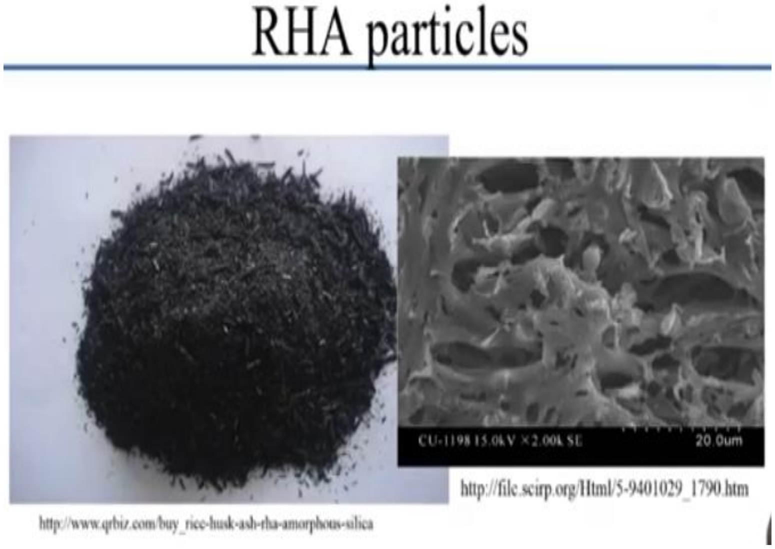

RHA particles

http://file.scirp.org/Html/5-9401029_1790.htm

http://www.qrbiz.com/buy_rice-husk-ash-rha-amorphous-silica

So these are the rice husk ash particles. You can see from the left that these particles are looking quite coarse, there seems to be some needle like particles also. Those are basically the unburnt carbon. Whereas the smaller dark-coloured particles are the silica particles. So if you look at these dark-coloured particles or silica particles, they show you a very irregular texture, lot of cavities and vesicles are inside that is responsible for the extremely high surface area of the rice husk ash.

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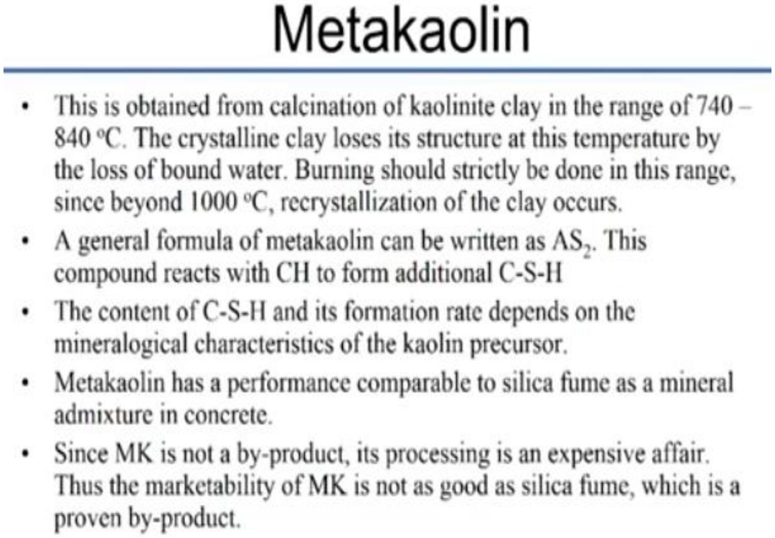

Metakaolin

- This is obtained from calcination of kaolinite clay in the range of 740 – 840 °C. The crystalline clay loses its structure at this temperature by the loss of bound water. Burning should strictly be done in this range, since beyond 1000 °C, recrystallization of the clay occurs.
- A general formula of metakaolin can be written as AS_2. This compound reacts with CH to form additional C-S-H
- The content of C-S-H and its formation rate depends on the mineralogical characteristics of the kaolin precursor.
- Metakaolin has a performance comparable to silica fume as a mineral admixture in concrete.
- Since MK is not a by-product, its processing is an expensive affair. Thus the marketability of MK is not as good as silica fume, which is a proven by-product.

The other common mineral additive that is increasingly being used these days is metakaolin or burnt clay or calcined clay basically. Calcination or controlled burning of kaolinite between 740°C and 840°C can lead to the transformation of kaolinite into metakaolin. When cement is produced also the clay that is introduced into the kiln undergoes an activation, which allows it to combine with the lime and make the different cementitious compound.

In the case of metakaolin, this activation of clay is what is making it reactive and since clay is aluminosilicate, you again get mainly a pozzolanic reaction from the system. So here you are collecting the clay, and then burning it. So there is a major processing cost involved. So processing involves burning of this clay and that sometimes takes up a lot of energy and because of that energy, the cost of that material can be significantly large.

So metakaolin is available in the market probably at about 30% lesser cost than the silica fume cost. So we still pay about 20-25 Rs/kg of metakaolin. So it could be quite expensive, but that is basically pertaining to the high purity kaolin. Brick industry doesn’t use kaolinite, as it uses the top soil or illite clay. It is not kaolinitic clay. Kaolinite is found in layers much below the earth’s surface. So you need to actually mine it to get it. This kaolinite can be mined and obtained and then burnt to form fired kaolin or calcined kaolin. Typical firing temperatures when you want to produce this calcined kaolinite is more than 1000°C. That leads to the formation of very white crystalline powder and this white crystalline powder can be used as a very good additive for stabilization of paint and for the ceramic industry. Basically this is what you call China clay. But this clay is not reactive as far as pozzolanic reactivity is concerned. For the clay to be reactive, we need to calcine it in this temperature range of 740-840°C. When you do that, the aluminosilicate gets activated, becomes amorphous and is capable of reacting with the lime that is generated from cement hydration.

Fired kaolin, which is produced at greater temperatures is used as an additive in paint industry and ceramic industry. Now for that process, they need a kaolin that is extremely white in colour. They need kaolinite content of more than 90% and generally metakaolin, also produced from a clay, has kaolinite contents in excess of 90%.

In these clay mines, you do not always get this kaolinite or pure kaolinite separately. Many times, it will be mixed with other impurities like quartz or iron oxide and things like that. Lot of the impure clay, which cannot be processed for these industries is simply dumped as a waste and later when we talk about limestone calcined clay cement, the main advantage there would be that we can utilize clay, which is of a lower grade, which does not need to be very high purity kaolinite, which can be nearly 40-60% and that can be used for the preparation of LC^3.

So chemical formula metakaolin can be written as AS2, 1 molecule of alumina to every 2 molecules of silica. That is mostly all clays, especially kaolinitic clays, are of that formulation and this compound reacts with calcium hydroxide to give you calcium silicate hydrate and calcium aluminosilicate hydrate. So lot of people have published data with metakaolin. Mostly the data seems to indicate that at levels of about 15-20%, metakaolin seems to perform quite similar to silica fume, which is used as a cement replacement. Typical blaine air permeability for metakaolin will be of the order of 900-1100m^2/kg. So it is much more reactive as opposed to slag or flyash, because of the very high purity aluminosilicate that you get from metakaolin.

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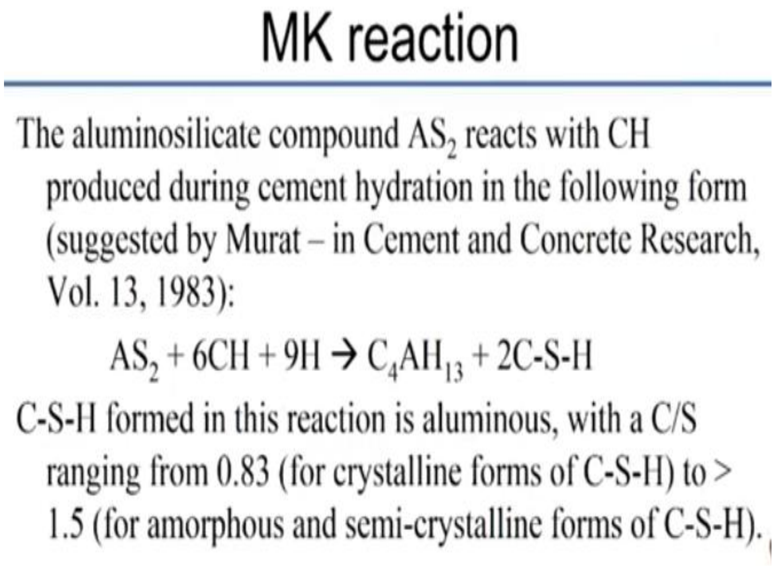

MK reaction

The aluminosilicate compound AS_2 reacts with CH produced during cement hydration in the following form (suggested by Murat – in Cement and Concrete Research, Vol. 13, 1983):

$$AS_2 + 6CH + 9H \rightarrow C_4AH_{13} + 2C\text{-}S\text{-}H$$

C-S-H formed in this reaction is aluminous, with a C/S ranging from 0.83 (for crystalline forms of C-S-H) to > 1.5 (for amorphous and semi-crystalline forms of C-S-H).

So this is the reaction, which has been studied by many people. So here aluminosilicate, calcium hydroxide, water leads to the formation of calcium aluminate hydrate and CSH, very often this calcium aluminate hydrate is mingled in the structural CSH itself.

$$AS_2 + 6CH + 9H \rightarrow C_4AH_{13} + 2CSH$$

So you often get CASH formation with the reaction of metakaolinite. You may also get other phases like stratlingite. So mostly what will happen is that the pozzolanic CSH that is produced because of the reaction of lime with your pozzolanic material will have a calcium to silica ratio, which is much smaller than that of Portland cement. Usual PC based CSH has about 1.7 to 1.8 whereas your pozzolanic replacement will produce CSH of the rate of 0.8-1. That is what you will actually get.

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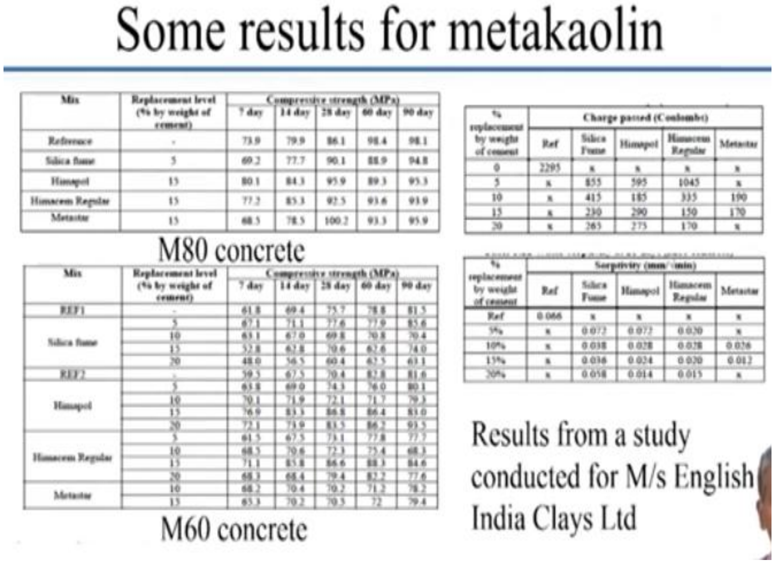

Some results for metakaolin

Mix	Replacement level (% by weight of cement)	Compressive strength (MPa)				
		7 day	14 day	28 day	60 day	90 day
Reference	-	73.9	79.9	86.1	98.4	98.1
Silica fume	5	69.2	77.7	90.1	88.9	94.8
Himapol	15	80.1	84.3	95.9	89.3	95.3
Himacem Regular	15	77.2	85.3	92.5	93.6	93.9
Metastar	15	68.5	78.5	100.2	93.3	95.9

M80 concrete

Mix	Replacement level (% by weight of cement)	Compressive strength (MPa)				
		7 day	14 day	28 day	60 day	90 day
REF1	-	61.8	69.4	75.7	78.8	81.5
Silica fume	5	67.1	71.1	77.6	77.9	85.6
	10	63.1	67.0	69.8	70.8	70.4
	15	52.8	62.8	70.6	62.6	74.0
	20	48.0	56.5	60.4	62.5	63.1
REF2	-	59.5	67.5	70.4	82.8	81.6
Himapol	5	63.8	69.0	74.3	76.0	80.1
	10	70.1	71.9	72.1	71.7	79.3
	15	76.9	83.3	86.8	86.4	83.0
	20	72.1	73.9	83.5	86.2	93.5
Himacem Regular	5	61.5	67.5	73.1	77.8	77.7
	10	68.5	70.6	72.3	75.4	68.3
	15	71.1	85.8	86.6	88.3	84.6
	20	68.3	68.4	79.4	82.2	77.6
Metastar	10	68.2	70.4	70.2	71.2	78.2
	15	65.3	70.2	70.5	72	79.4

M60 concrete

% replacement by weight of cement	Charge passed (Coulombs)				
	Ref	Silica Fume	Himapol	Himacem Regular	Metastar
0	2295	x	x	x	x
5	x	855	595	1045	x
10	x	415	185	335	190
15	x	230	290	150	170
20	x	265	275	170	x

% replacement by weight of cement	Sorptivity (mm/√min)				
	Ref	Silica Fume	Himapol	Himacem Regular	Metastar
Ref	0.066	x	x	x	x
5%	x	0.072	0.072	0.030	x
10%	x	0.038	0.028	0.028	0.026
15%	x	0.036	0.024	0.020	0.012
20%	x	0.058	0.014	0.015	x

Results from a study conducted for M/s English India Clays Ltd

Some results have been presented here for metakaolin. So here this was based on some projects that we have done for a company that produces different grades of metakaolin and we were trying to help them evaluate the best product for commercial use in the market. So here we made concrete M60 grade and M80 grade concrete at different levels of replacement of cement with silica fume and different brands of metakaolin.

You can see that mostly the performance of metakaolin and silica fume is more or less similar, marginally better than the reference concrete, which does not have any silica fume or metakaolin. With M60 concrete also, you get very similar results. There are some results, which are probably quite high as opposed to the others, but for the most part, we are getting similar result with most of the concrete mixes.

But the impact of mineral admixture seemed better with respect to durability than with respect to strength. For example, here the charge passed in terms of coulombs, if you look at replacement with silica fume at 5, 10, 15 and 20%, you can see a massive reduction as opposed to a plain Portland cement, which is over 2000 Coulombs. Again, with metakaolin, you get numbers that are quite low, quite similar to what you have with silica fumes.

So there is not much difference with respect to performance as far as comparison with silica fume is concerned. These days if you go to the Mumbai area, there is a lot of use of high performance concrete and high strength concrete, mainly for their skyscrapers. For the lower grounds storeys, it is always useful to actually go for a strength concrete. They go for strengths as high as M90, M100. When they go for such high strengths, they obviously need very finely divided mineral additives in the system, like silica fume, metakaolin, and today they also have one more option called ultrafine slag. Ultrafine slag can also have them enhance their strength potential quite well. For example, concretes of grades M90 and M100 can be produced with ultrafine slag.

Interestingly, it has been seen that the reduction in workability that you typically see with silica fume and metakaolin will not be the same with ultrafine slag. There is a slightly better performance when ultrafine slag is used. However, at the same levels of replacement, let us say 5-20% replacement, ultrafine slag can never get you these kinds of numbers that are showing extremely low rapid chloride permeability.

But in terms of other durability characteristics, for example the sorptivity or water absorption potential, you may get similar performance characteristics. But with RCPT, ultrafine slag does not give you the same result as silica fume or metakaolin. Again, this is mainly because silica fume and metakaolin, the finely divided grains can actually capture the alkalis quite effectively and lower the conductivity of your system tremendously. Slag can do that to some extent, but not as much as silica fume or metakaolin.

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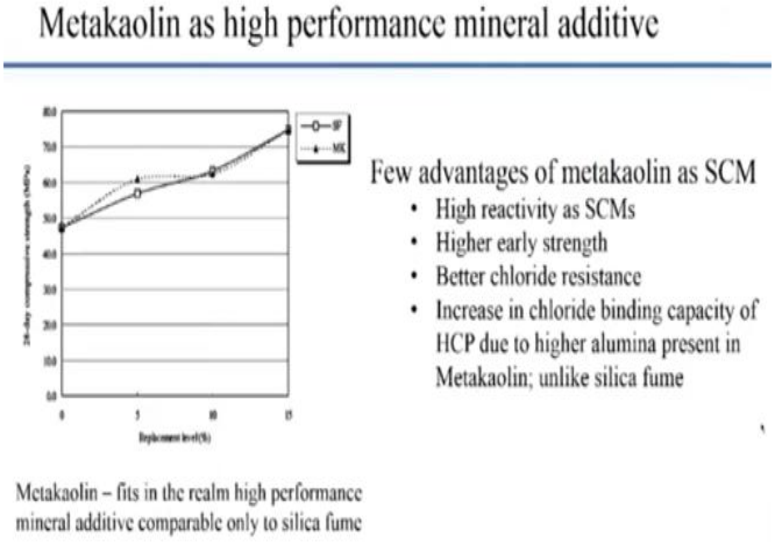

Metakaolin as high performance mineral additive

Few advantages of metakaolin as SCM
- High reactivity as SCMs
- Higher early strength
- Better chloride resistance
- Increase in chloride binding capacity of HCP due to higher alumina present in Metakaolin; unlike silica fume

Metakaolin – fits in the realm high performance mineral additive comparable only to silica fume

So as a high performance mineral additive at different replacement levels, the strength increases significantly when silica fume and metakaolin are used as cement replacement. Generally, with metakaolin, you get extremely good resistance to chlorides, because metakaolin provides reactive alumina, that is able to bind the chlorides in the concrete and prevents the chloride from reaching the surface of the reinforcing steel. With carbonation, resistance will generally tend to reduce when metakaolin is used because you are consuming lime rapidly. However, the increase in impermeability of the concrete may offset that to some extent.

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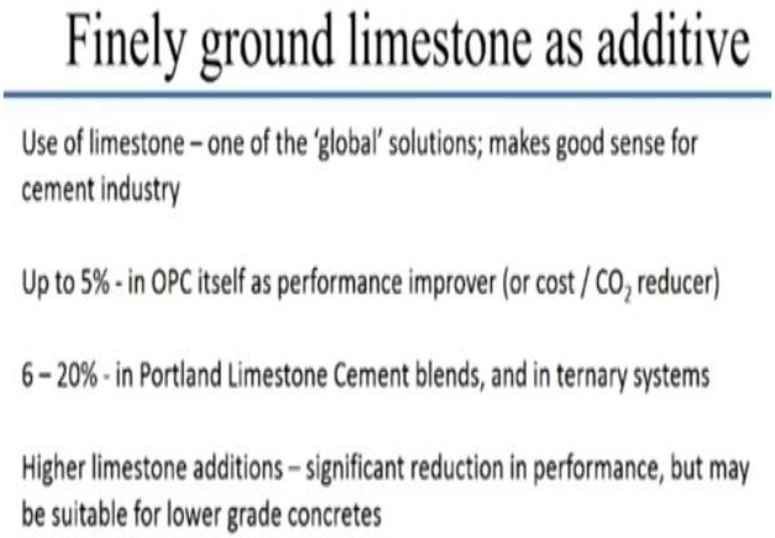

Finely ground limestone as additive

Use of limestone – one of the 'global' solutions; makes good sense for cement industry

Up to 5% - in OPC itself as performance improver (or cost / CO_2 reducer)

6 – 20% - in Portland Limestone Cement blends, and in ternary systems

Higher limestone additions – significant reduction in performance, but may be suitable for lower grade concretes

Today increasingly lot many countries are adopting limestone itself as an additive to cement and concrete. It makes economic sense to do that because first of all this limestone is already available in the cement production unit. You do not need to burn this limestone, burning requires energy, and pollutes by putting out carbon dioxide. So instead of burning and spending more energy, you take the material that is already available at the plant and use it as a partial replacement for cement.

Now already you know very well that even in ordinary Portland cement, up to 5% of performance improvers permitted; that is the most often used level of limestone at least in India. If you go to the western countries, they permit a much higher level of limestone replacement and they call the cements as Portland limestone cement. In India also a draft standard is being prepared and this may become a reality in the near future.

Up to 15% replacement of cement with limestone is happening in most countries. However, if you look at EN standards, it permits 6-20% replacement of cement with limestone. So 6-20% means, you can have a significant reduction in the amount of CO_2 that is getting emitted from your cements and lower the overall CO_2 potential from the concrete.

The problem is if you go higher and higher with limestone additions, you are simply replacing cement with a mostly unreactive material. So what will happen is the filler effect can only help to a certain extent, but beyond that since you do not have a reactive material, you may not really get the kind of performance that you want with plain Portland cement mixes.

At very high replacement levels of limestone, there is a significant reduction in performance. However, that does not mean, we cannot use it. Even for low grade concretes, like for residential construction, we may actually end up finding satisfactory performance from limestone based concrete mixes, with limestone concretes even as high as 30-40%. If you take that in terms of lifecycle cost, your overall system may be much more effective than a plain Portland cement based system.

There will be a strength reduction because limestone is not going to be reactive. The reactive component of the strength will not be getting obtained, because cement is being replaced by limestone. When we see the next chapter on high performance concrete mixture design, you will see that the filler effect is able to some extent overcome the lack of reactivity that you see from most of these filler materials. If the material is both reactive and finely graded, then it provides you much better benefits, obviously like silica fume or flyash or slag, but with just fillers, you may get an enhancement only up to a certain level.

Let us look at the use of limestone in ternary systems. So ternery implies three components. That means , one component has to be cement, one is limestone and the other is supplementary cementing materials like flyash or slag or metakaolin, or silica fume. Now this system of combination of cement with limestone and supplementary material has been looked at very closely over the last 5-10 years. There has been growing interest in looking at these ternery implement systems as a possible solution to lowering the amount of cement that needs to be used in concrete. Primarily this has come about from the perspective of reducing the CO_2 emissions and lowering the carbon dioxide footprint of concrete. Here this combination of ternery blended limestone and supplementary material can actually give a very unique sort of performance.

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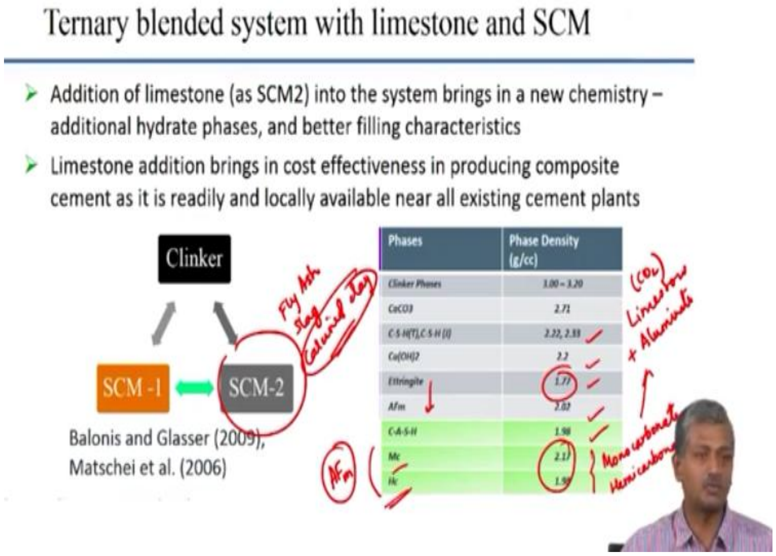

Ternary blended system with limestone and SCM

- Addition of limestone (as SCM2) into the system brings in a new chemistry – additional hydrate phases, and better filling characteristics
- Limestone addition brings in cost effectiveness in producing composite cement as it is readily and locally available near all existing cement plants

Phases	Phase Density (g/cc)
Clinker Phases	3.00 – 3.20
CaCO3	2.71
C-S-H(T),C-S-H (J)	2.22, 2.33
Ca(OH)2	2.2
Ettringite	1.77
Afm	2.02
C-A-S-H	1.98
Mc	2.17
Hc	1.9[illegible]

Balonis and Glasser (2009), Matschei et al. (2006)

So again limestone addition brings in a slightly new chemistry. There are additional hydrate phases that can actually form the system and better filling characteristics. But, earlier I was telling you limestone is simply sitting there as a filler and I am now saying that it is reactive. So what does it react with, is something that we need to look at. So again since limestone is available in the cement plant itself, they will be cost effectiveness associated with this process.

When regular cement hydrates. mostly clinker phases, which have a density of 3-3.2, 3, produce different phases like CSH, calcium hydroxide, ettringite and AFm. So I want you to pay attention to the densities of these materials. If you look at ettringite, it has got the least density 1.77. What does that mean? If you form ettringite, it will fill up more pore spaces. Whereas CSH is the highest density phase. Of course, we cannot live without CSH because it is a primary binding phase of your cement paste. What happens when I substitute these with a ternery blended system? System will form CSH, $Ca(OH)_2$, ettringite and AFm phases. But additionally you also form calcium aluminosilicate hydrate because of this supplementary cementing material. You form two more phases which are called monocarbonate and hemicarbonate and these are forming because the reaction of limestone plus aluminate. Limestone implying the CO_2 from the limestone plus the aluminate is forming the monocarbonate and hemicarbonate.

So if you look at it, these are also AFm phases. They are quite similar to AFm type phases. So to form AFm, aluminate reacts with sulfate. Here aluminate reacts with carbonate to form AFm phases where you have carbonate and not sulfate, same sort of phases. Now the interesting part is whatever aluminates were there in the system, in the early phase, start getting used up to make monocarbonate and hemicarbonate.

If you do not have an excess aluminate in the system, the ettringite to monosulfate conversion will reduce. Ettringite convert to monosulfate, because there is excess aluminate present on top of the sulfate. Now what we have done is shown the aluminates a different path. They go and react with the carbonates to form monocarboaluminate and hemicarboaluminate. So what we are doing is stabilizing this ettringite component in the system.

That means we have more pores that are filled because of ettringite being stable and then we have additional hydration products that are still going to fill up more pore spaces, monocarbonate and hemicarbonate are filling up additional pore space and this effective filling of the pore spaces obviously is going to enhance the strength and durability characteristics. You can expect that your strength and durability with ternery blended system involving limestone and supplementary cementing material that provides reactive silica and alumina can be expected to be really good.

So you can use aluminosilicate based inorganic additives that like flyash, slag, calcine clay.. But it is the calcined clay, which gives you the most reactive and significant proportion of alumina. So, the most benefits are obtained when you use limestone in combination with calcined clay.

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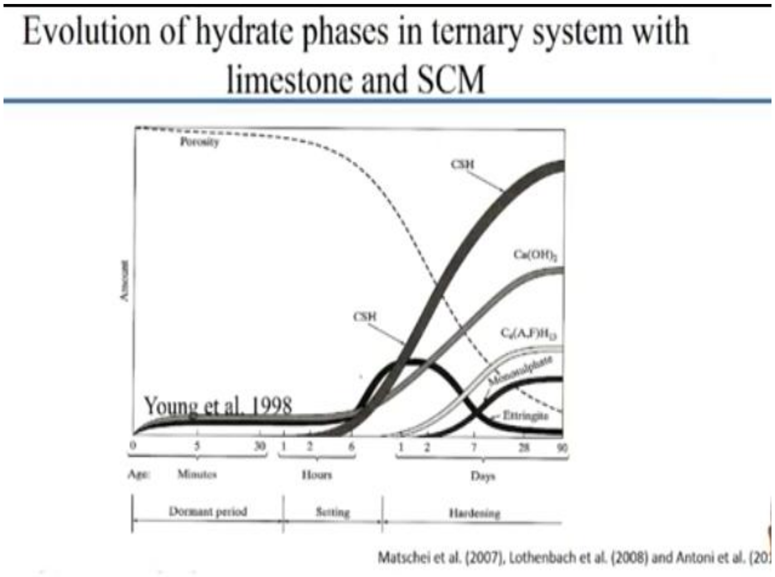

Evolution of hydrate phases in ternary system with limestone and SCM

Matschei et al. (2007), Lothenbach et al. (2008) and Antoni et al. (20

Here, just to put this in perspective with this picture that we saw earlier that when regular cement hydrates, you mainly form CSH, calcium hydroxide, calcium aluminatehydrates, monosulfate and usually ettringite goes down as monosulfate has formed more and more. So when you add this ternery blend, you still have the same reactions. But the ettringite no longer starts depleting. It continues to remain at the constant level. Monosulfate formation does not really happen because the aluminates have gone into reaction with carbonate to form monocarbonates. So you have monocarbonate formation, which takes up the space, which was meant for the monosulfate. The lime content also goes down, because your pozzolanic reaction is going to happen and your CSH content will go up. Essentially in the end, you will be ending on a CSH, calcium hydroxide much lowered as compared to plain Portland cement, you will have ettringite, you will have monocarbonate plus hemicarbonate or you may have one of the systems. (Monocarbonate means 1 carbon and Hemicarobonate means 0.5 carbon). Usually one or both of them are stable in the system, mostly monocarbonate will be ending up being stable in the system. Apart from this, you will again have the calcium aluminatehydrates, or calcium aluminoferrite hydrates, if that is permitted. That will be the end component of your system that has the ternery blend of cement with limestone and supplementary cementing material.

These components generally are going to be driving the porosity even further down. You are going to expect that, the system will actually produce much lower porosity as opposed to ordinary Portland cement system and when you have lower porosity, obviously it translates into better durability and strength.

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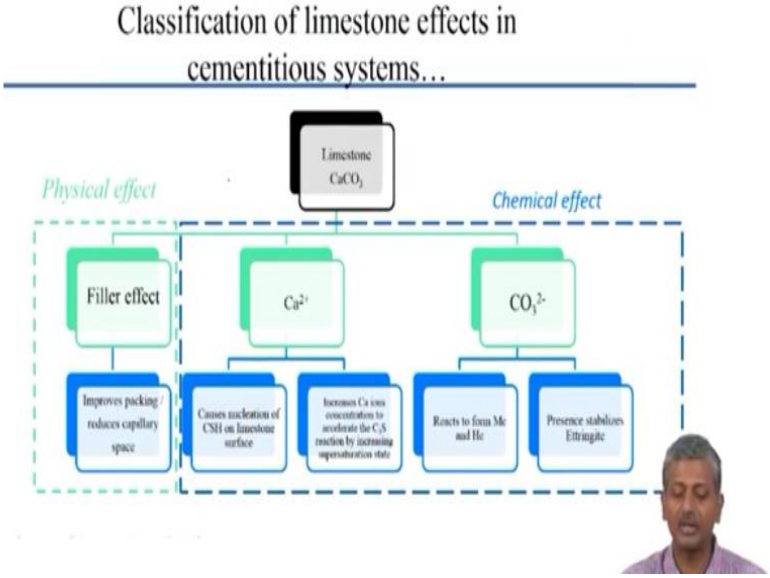

Classification of limestone effects in cementitious systems…

Limestone $CaCO_3$

Physical effect

Chemical effect

Filler effect

Ca^{2+}

CO_3^{2-}

Improves packing / reduces capillary space

Causes nucleation of CSH on limestone surface

Increases Ca ions concentration to accelerate the C_3S reaction by increasing supersaturation state

Reacts to form Mc and Hc

Presence stabilizes Ettringite

The picture above is just capturing the effect of limestone usage. You have the filler effect obviously where the limestone particles provide efficient particle packing and reduce the capillary void space. Considering the chemical effect, the calcium obviously, increased amount of calcium leads to the nucleation of calcium silicate hydrate on the small particles of the limestone itself, whereas carbonate leads to the formation of monocarbonate and hemicarbonate.

So you have overall a very positive role for limestone to play in the cementitious systems and more than that limestone causes reduction in CO_2 emission since you are no longer burning or processing the product.

In case of Portland cement with 5% addition of limestone, the aluminates are mainly from C_3A. The C_3A in cement can give aluminate, which is reactive again C_3A can react to some extent with limestone and lead to the formation of monocarbonate or hemicarbonate phases also. Because of that, you also get some benefits of that performance, but the 5% level is not high enough to give sufficient amount of calcium carbonate for reaction. That is why we want to go for limestone contents in the range of 10-15% to optimize the extent of calcium carbonate that is given for reaction in system.

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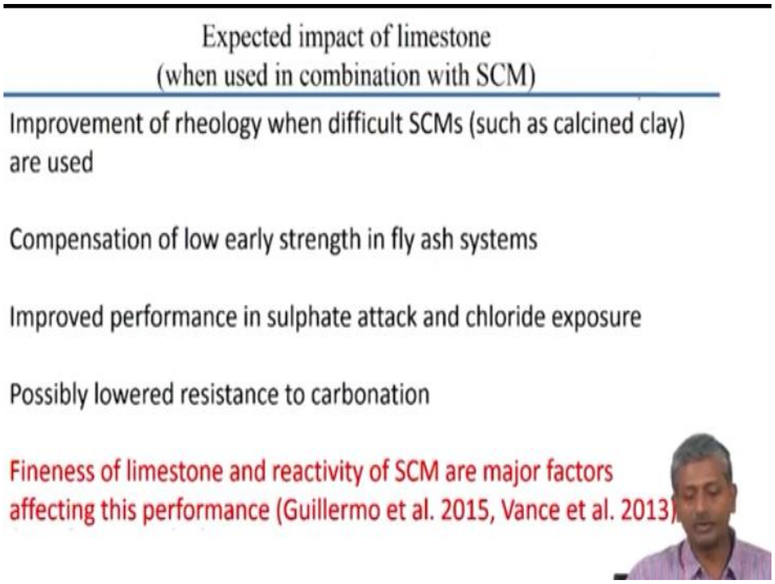

Expected impact of limestone
(when used in combination with SCM)

Improvement of rheology when difficult SCMs (such as calcined clay) are used

Compensation of low early strength in fly ash systems

Improved performance in sulphate attack and chloride exposure

Possibly lowered resistance to carbonation

Fineness of limestone and reactivity of SCM are major factors affecting this performance (Guillermo et al. 2015, Vance et al. 2013)

To discuss about the expected impact of limestone when used in combination with other SCMs, first of all, it can improve the flow properties or rheology, when difficult supplementary cementing materials such as calcine clay are used. So calcined clays are extremely small particles and having a layered particle system. So those layers basically capture the water and super plasticizer and prevent good workability of these systems. When limestone is used, that brings the workability to a much more acceptable level.

Low early strength in flyash systems can be compensated to some extent by increasing the reactivity with limestone, utilizing the blend with the limestone to reduce the extent of damage caused by increased levels of replacement of flyash. You can definitely expect improved performance in sulfate attack, because monosulfate phase is not forming. So you do not have possibilities of ettringite forming in the long term. Obviously chloride exposure, because you have brought the aluminate in the system, this aluminate is going to be reacting with the chloride to form chloroaluminate phases binding the chloride preventing it from reaching the surface of reinforcing steel. There is going to be a possibly lowered resistance to carbonation, because your calcium hydroxide is getting consumed tremendously. So your CSH phases will start getting attacked by the carbon dioxide.

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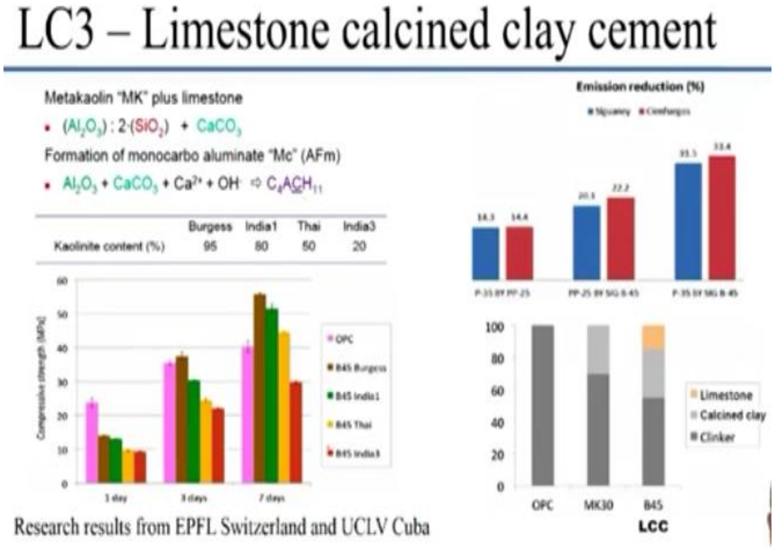

LC3 – Limestone calcined clay cement

Metakaolin "MK" plus limestone

- $(Al_2O_3):2\cdot(SiO_2)$ + $CaCO_3$

Formation of monocarbo aluminate "Mc" (AFm)

- $Al_2O_3 + CaCO_3 + Ca^{2+} + OH^- \Rightarrow C_4A\underline{C}H_{11}$

	Burgess	India1	Thai	India3
Kaolinite content (%)	95	80	50	20

Research results from EPFL Switzerland and UCLV Cuba

The basic understanding of the science of the ternery blends led to the development of what we call as LC3 or limestone calcined clay cement. This development obviously looks at the utilization of the pozzolanic properties of metakaolin and in addition, the reaction of the metakaolin with limestone, that is calcium carbonate. So here you have the alumina and the calcium carbonate in the presence of lime. Please remember here, even this alumina and calcium carbonate reaction requires the presence of lime for the formation of this system, which is monocarbonate. So this is presenting some preliminary research results from this project, which we have done about 5-10 years ago. This was originally started off as a collaborative project between Switzerland and Cuba.

They were trying to look at different types of clays. They also got some samples from India and Thailand in this case. So here they have very pure kaolinite content that means 95%, so obviously the kind of grade kaolin you will get is metakaolin grade. From India, the kind of clay that they had was 80% kaolinite content and there was one with 20% kaolinite content and from

Thailand they had 50% kaolinite content. Let us look at what happened at one day. This is plain Portland cement without any additive at all. So here B45 implies there is 30% of calcine clay and 15% of limestone, in the system. When you do it with the high purity metakaolin, by 3 days, you are able to get a strength, which is better than Portland cement system and by 7 days it is significantly better than the Portland cement system. With the 80% kaolinite content, slightly lesser than cement at 3 days, but by 7 days, there is a major enhancement in the strength. Even with the poor quality clay with 50% kaolinite content, you are still getting performance, which is little bit lower at 3 days, but at 7 days, it is marginally higher than that of the Portland cement system. If you want to match the performance of the Portland cement system with 45% total replacement, this is possibly giving you the best solution. With 50% slag, you may get some of these characteristics, but with other alternatives like calcine clay, because if you remember, we discussed earlier the availability of different types of materials, the availability of slag is much, much less as opposed to the availability of potentially calcine clay. We have to look at clay and then convert that to calcine clay. Now interestingly even with the 20% kaolinite system, there was only a difference of about 20% or 25% as opposed to plain Portland cement.. Even with low grade kaolin, you can still produce a cementitious combination that is capable of giving you a significantly good strength. So you can still work with the cement, for instance.

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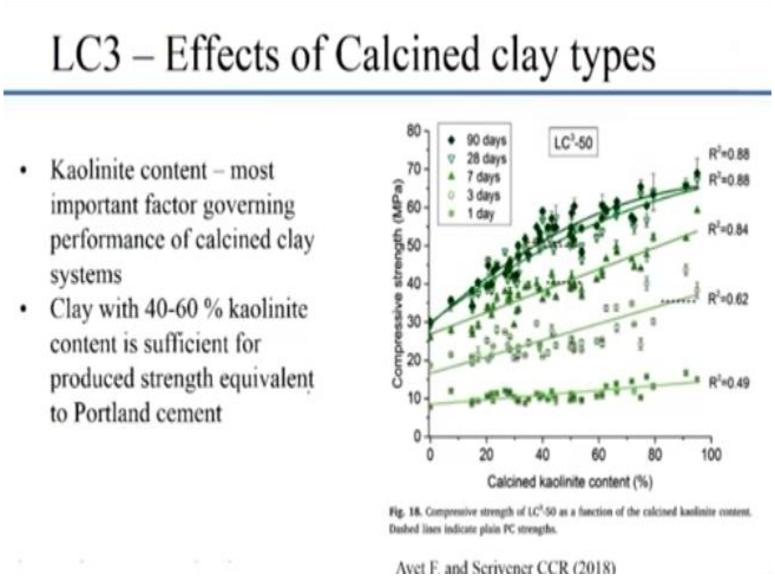

LC3 – Effects of Calcined clay types

- Kaolinite content – most important factor governing performance of calcined clay systems
- Clay with 40-60 % kaolinite content is sufficient for produced strength equivalent to Portland cement

Fig. 18. Compressive strength of LC³-50 as a function of the calcined kaolinite content. Dashed lines indicate plain PC strengths.

Avet F. and Scrivener CCR (2018)

Here in EPFL in Switzerland where the primary research on this material was done, they also tried to understand the effect of the calcined kaolin content on the performance of mortars in terms of compressive strength. So they have these figures for 1-90 days of strength. If you look at the 1-day strength, there is definitely a benefit of increasing the levels of calcine kaolinite content, obviously more the kaolin, the better the reaction and you get a much better performance with respect to higher levels of kaolin.

But what we wanted to see was where we should really cut off, because we cannot obviously go for the high grade clay, then that will totally turn this in the same direction as that of metakaolin. It is not going to be cost effective anymore and the use of high purity clay, which could be used in other industries does not make sense. We want to make use of the material that is not capable of being used for the ceramic and paint grade industries and utilize the impure clays for their performance in this ternery blended system. What we found was clay with 40-60% kaolinite was sufficiently good. For example, at 1 day, you do not see a major difference. At 90 days, your performance is only marginally lower than if you had 90% kaolinite your system. At 40-60%, you can actually maximize the potential of this material without really having to bother with producing higher grades of clay.