

Admixtures And Special Concretes

Prof. Manu Santhanam

Indian Institute of Technology Madras

Department of Civil Engineering

Lecture -43

Mineral Admixtures : LC3 - Part 1 : Introduction

Finely ground limestone as additive:

Recap:

(Refer to slide time: 00:20)

The slide features the NPTEL logo on the left and the IIT Madras logo on the right. The title is "Finely ground limestone as additive". The main text reads: "Use of limestone – one of the 'global' solutions; makes good sense for cement industry". Below this, it states: "Up to 5% - in OPC itself as performance improver (or cost / CO₂ reducer)". The next line says: "6 – 20% - in Portland Limestone Cement blends, and in ternary systems". The final line reads: "Higher limestone additions – significant reduction in performance, but may be suitable for lower grade concretes". Handwritten red notes include: "Portland Ls - Cement EN/ASTM" next to the 5% and 6-20% lines, and "IS Composite Concr. : OPC + FA + Slag" and "EN - Composite Cement" near the bottom. A video inset of Prof. Manu Santhanam is in the bottom right corner. The footer text is "Admixtures and Special Concretes".

Right, so in the last class, yeah so we will be talking about the use of finely ground limestone as an additive to Portland cement. As we all know up to 5% of Portland cement manufacture you are permitting what we call as performance improvers and these performance improvers also include limestone. Sometimes people use slag, sometimes they use fly ash. So, but what we are primarily interested in is what will happen when we start introducing more limestone in the system because that leads to a major advantage with

respect to cutting down the overall CO₂ potential of the cement. So, 6 to 20% is what is permissible in Portland limestone blends that are available in EN and ASTM. But even beyond that if we have an opportunity to go for more limestone in lower grade concrete, we should look at that option because there is definitely some impact that can really have on the concrete choices for low grades, let us say M20, M25 where we now do not have to rely on too much cement being used.

Ternary blended system with limestone and SCM:

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The slide features a diagram of a ternary blended system with Clinker, SCM-1, and SCM-2. A red handwritten note '→ gypsum' points to the Clinker box. Below the diagram are references: Balonis and Glasser (2009), Matschei et al. (2006). To the right is a table of phases and their densities. A red circle highlights the density of Ettringite (1.77), and another red circle highlights the density of Mc (2.17). A red handwritten note 'AFw' is next to the Mc and Hc rows. The slide also includes logos for NPTEL and IIT Bombay, and the text 'Admixtures and Special Concretes'.

Phases	Phase Density (g/cc)
Clinker Phases	3.00 – 3.20
CaCO ₃	2.71
C-S-H(I), C-S-H (II)	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	1.98

Now moving on we really want to look at this system where limestone can interact with a second supplementary cementing material. So here what we want to do is try out a new chemistry about which we have discussed primarily earlier based on the availability of calcite to react with the aluminate to form carbo aluminates. So, the idea is to have a ternary blended system where you have cement clinker and of course you also have gypsum and you have 2 supplementary cementing materials, one is of course your fly ash or slag or calcined clay and second supplementary material is your limestone. So what you end up doing is let us say these are the phases that you form when cement hydrates.

When cement containing some limestone in itself hydrates these are the phases that are actually present and the densities of those phases are also given here. We know the density of cement is about 3.15, so most cement phases are in the same range of density, unhydrated cement will have that level of density. But when you hydrate the CSH that you produce gets a density of about 2.2 or 2.3, calcium hydroxide is almost the same 2.2 but interestingly if you look at the ettringite phase, density is lower. What does this mean? If I form more

ettringite what does that mean? You fill up more space, forming more ettringite means you are filling up more space. So, if I choose a system where I can actually increase the ettringite formation I can fill up more space. But what really happens in Portland cement the ettringite gets converted to monosulphate and the density is going up.

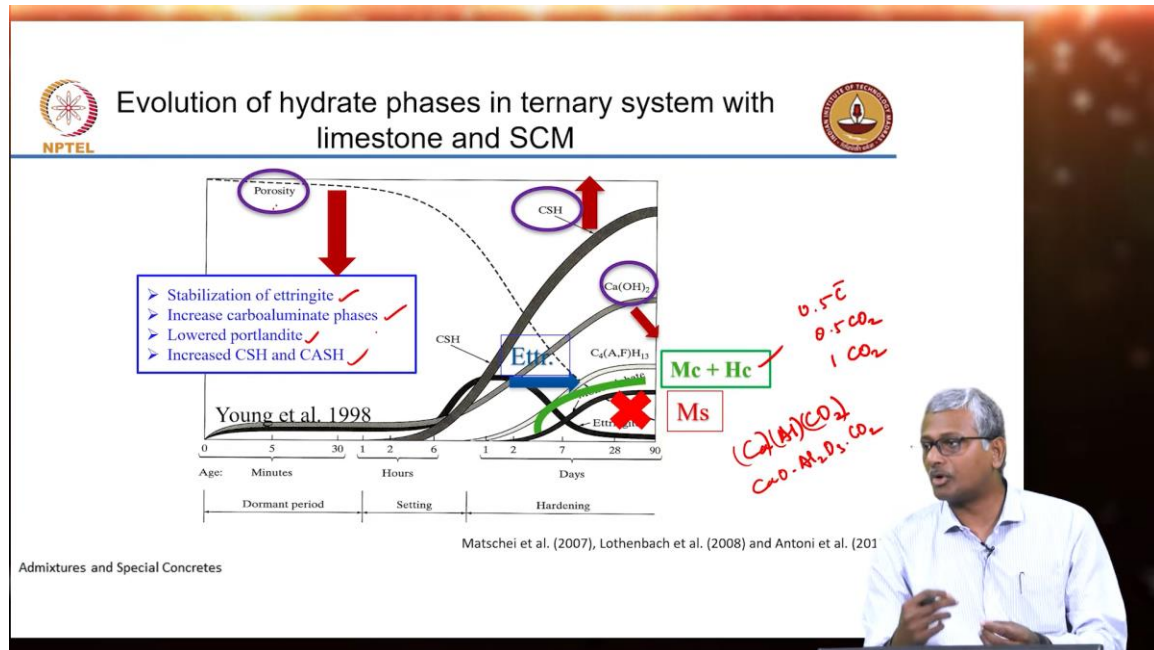
So now my system is not as efficiently packed. But what will happen if I put limestone and another supplementary cementing material in conjunction with my cement phases is I will end up with a different blend of hydration products. Of course, I will have CSH calcium hydroxide, ettringite and monosulphate still but I end up forming additional CSH or CASH by consuming calcium hydroxide. We talked about the fact that calcium hydroxide is a well-defined crystalline structure because of which its volume-filling ability is not that good. Although as a material it is solid, it is hard and so on but it is not able to fill up volume efficiently.

Secondly, you also have the formation of additional hydrate phases, monocarbonate and hemiacarbonate. So, you have of course you are removing unhydrated phases or reacting unhydrated phases to actually form these hydrated phases. But interestingly what also ends up happening in the system is that the ettringite that is forming early stabilizes. Why should that stabilize? How is ettringite formed? Because of aluminate and sulphate reacting. So, aluminate and sulphate react to form ettringite but in normal Portland cement systems there is lot of aluminate available so that aluminate interacts with ettringite to produce monosulphate.

But now I have introduced a system where I have carbonate also present and this alumina wants to combine with the carbonate and start producing monocarbonate or hemiacarbonate leaving the ettringite free. So what will happen to the ettringite? It will remain stable in the system and if you remember we discussed the fact that sulphate-resistant cement systems are designed from the perspective of low C3A so that ettringite that forms at early stages remains stable. So when you have such a system the stability of ettringite is ensured and this ettringite will remain stable for a long period of time and not really decomposed to AF_m . AF_m formation is going to reduce because you are forming other AF_m phases in terms of carbonates. You are not forming monosulphate anymore you are forming monocarbonate but you are still taking care of the alumina so the ettringite that is already formed remains as such.

Evolution of hydrate phases in ternary system with limestone and SCM:

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So I will just talk about this with respect to how products evolve in a cementitious system. This is a typical Portland cement we know that beyond a certain period of hydration CSH starts forming rapidly in the long term CSH occupies the most volume inside cement paste. We have next calcium hydroxide then we have calcium aluminate hydrate and ettringite that starts forming in the early stages decomposes to give rise to monosulphate. Ettringite that starts forming at the early stages starts giving rise to monosulphate and in the long term the stable products are CSH calcium hydroxide calcium aluminate hydrate and monosulphate in the long term for a plain Portland cement.

So what happens in the presence of limestone calcined clay or limestone and slag or limestone and fly ash is that you do not have this conversion of ettringite to monosulphate so ettringite remains stable. Monosulphate itself formation of it is reduced or almost avoided you start forming monocarbonate and hemicarbonate. So hemicarbonate is 0.5 carbon or 0.5 CO₂, molecules of CO₂ in the structure of the carbo aluminate.

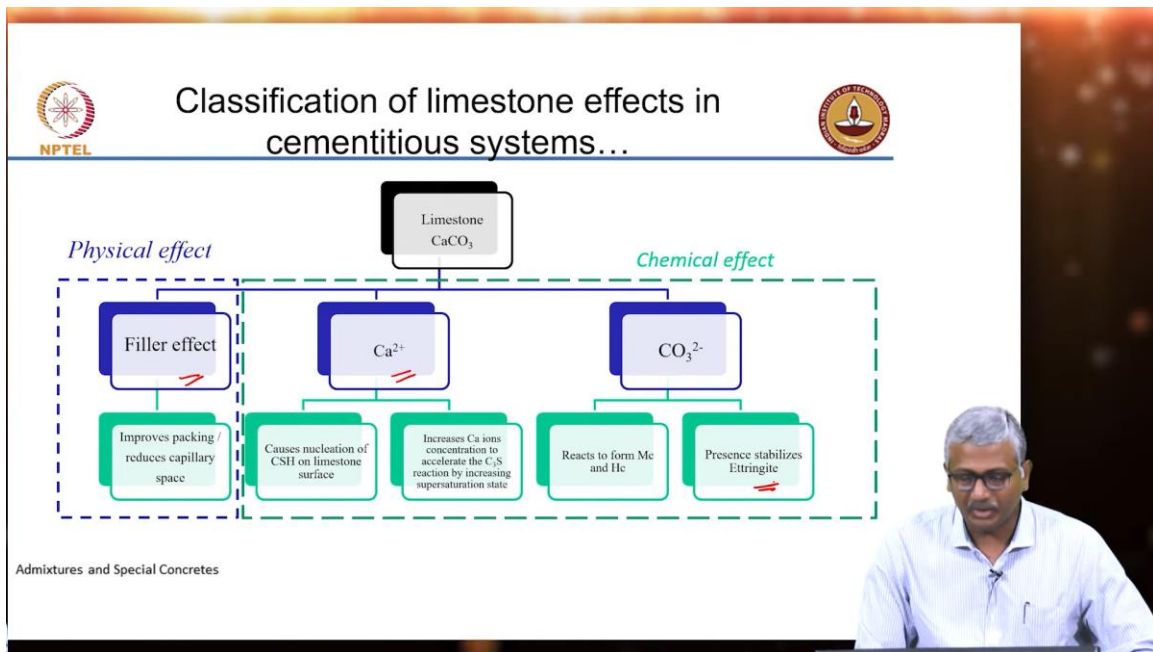
Monocarbonate is 1CO₂. So, basically it is calcium aluminium carbonate or if you have to write it correctly in terms of cement chemistry it will be a mixture of calcium oxide aluminium oxide and carbon dioxide. So, this is a monocarbonate system of course I am not writing the stoichiometry correctly in terms of how much calcium how much alumina and so on but when you have a aluminate source present like fly ash or slag or calcined clay it will combine with the carbonate to start forming these carbo aluminate phases. So you start forming carbo aluminate phases which are then filling up more of the space that

is available you start consuming calcium hydroxide and increasing the CSH formation. So in other words you are causing the system to get lowered with respect to its porosity and in general lowering porosity will also lead to lowering the permeability of the system.

Lower permeability implies better durability. So porosity reduction generally the experimental results suggest that porosity reduction is not so much as to cause a major enhancement in strength but the permeability reduction is significant and that leads to a major enhancement in durability. So these are the main aspects that you see stabilization of ettringite, increased carbo aluminate phases, lowered portlandite content and increased calcium alumina silicate hydrate. So overall your volume filling ability of the hydration products gets better and you have less interconnected porosity available in your system.

Classification of limestone effects in cementitious systems:

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So just to put this in perspective if you have limestone effects and cementitious systems, limestone is a fine filler so it will obviously have a filler effect it will improve packing and reduce capillary space just by the fact that it is a fine material because limestone gives calcium the surfaces we discussed this earlier that fine particles offer a chance of nucleation of CSH on the surfaces and that is what is happening with limestone.

The carbonate reacts to form monocarbonate and hemicarbonate so additional hydration products form and your ettringite gets stabilized. So, limestone has a real beneficial effect in cementitious system. So, what is the problem everybody knows this why have they not been using it. In Portland cement also we have alumina available, why do not we simply

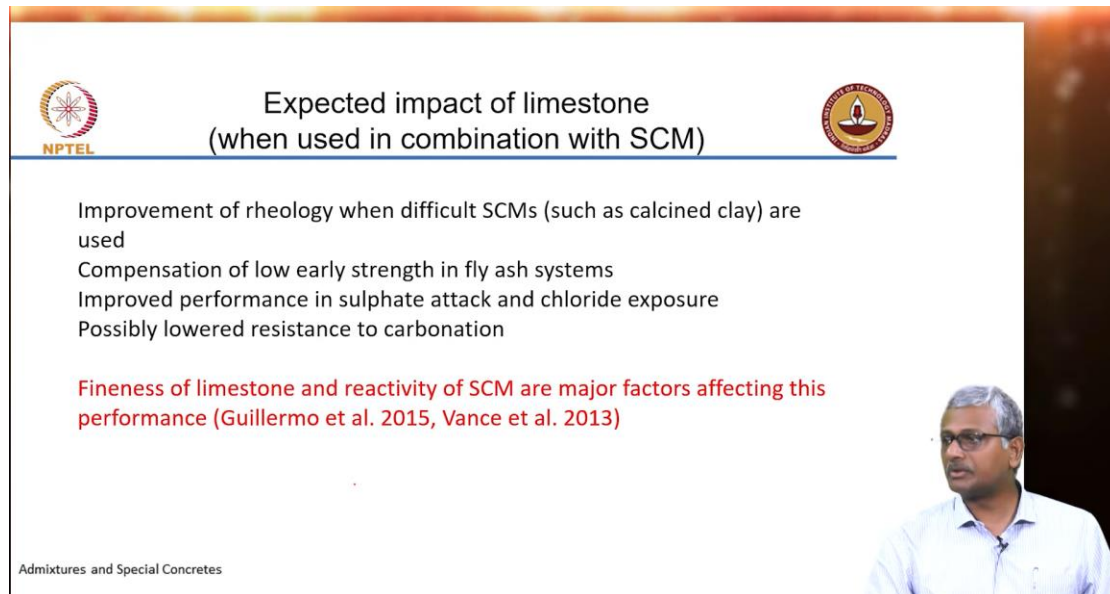
use limestone cement why cannot we do that? Alumina is there in Portland cement also C_3A you can increase if you want and you can use calcite or calcium carbonate as a replacement as a performance improver higher quantity also Portland limestone cement is basically based on that. What is happening? Maybe you will start compromising on the strength a little bit if only limestone is present because you are not forming any additional CSH if just limestone is present. What else? The main thing is the reactivity of the limestone itself only a fraction of the calcite and only if it is very fine sized will dissolve and be available for reaction.

So, you are not going to be able to have a large quantity available. So, in a use of limestone as a performance approver 5% is used so there is not enough of limestone available to give enough reactive carbonate in your system. If you put 10 or 15% you are increasing the chance that there is more reactive carbonate available in your system and by providing an alumina silicate like fly ash or slag or calcined clay you give additional alumina which is reactive to combine with the carbonate in the system. So, there are obvious benefits which you cannot get by plain Portland cement or even Portland limestone cement. So that is where you can actually harness that benefit in the case of your ternary blended systems.

Anyway, that is getting too specific we do not have to go to that extent to understand the system.

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

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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)

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So, what happens when limestone is used in combination with supplementary materials? In general, when calcined clays are used, we know that intercalation of PCEs and other superplasticizers can take place in the sheets of the calcined clay but in the presence of

limestone you are able to actually offset that effect to some extent. It gives better flowability to your system. In fact, even for your plastering to improve the applicability of plaster, limestone is an excellent material to replace Portland cement because it gives that softness to apply that plaster. In fly ash systems when early strength is compromised because of the slow reaction of fly ash the fact that your limestone can provide this increased C3S hydration by causing nucleation of CSH will improve the early age strength also.

So with fly ash, you can offset some of the early strength problems that you have with fly ash. And generally, we can expect that there is going to be an improved performance in sulphate attack because ettringite is stable and in chloride exposure why? Alumina is there it will bind the chloride so in chloride exposure also your improvement will happen with durability but problem will be the resistance to carbonation because you are cutting down your calcium hydroxide significantly. This calcium hydroxide was earlier getting used only for the pozzolanic reaction. Now it is also getting used to form monocarbonate and hemiacarbonate. The reaction of limestone with alumina has to happen in the presence of calcium hydroxide to produce this carbo phases which I will show you in just a minute.

LC3- Limestone calcined clay cement:

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NPTEL **LC3 – Limestone calcined clay cement** **UNIVERSITY OF TECHNOLOGY**

Metakaolin "MK" plus limestone
 $(Al_2O_3) : 2 \cdot (SiO_2) + CaCO_3$
 Formation of monocarbo aluminate "Mc" (AFm)
 $Al_2O_3 + CaCO_3 + Ca^{2+} + OH^- \rightarrow C_4A\bar{C}H_{11}$

Handwritten notes:
 0 embankment & Impure clay + 60% kaolinite
 30% CC + 10% LS

Country	Kaolinite content (%)
Burgess	95
India 1	80
Thai	50
India 3	20

Emission reduction (%)

Concrete Type	Silica fume (%)	Cenfuoges (%)
P-35 BY PP-25	14.3	14.4
PP-25 BY 50% B-45	20.1	22.2
P-35 BY 50% B-45	31.5	33.4

Compressive strength (MPa)

Age	OPC	B45 Burgess	B45 India 1	B45 Thai	B45 India 3
1 day	~25	~15	~15	~15	~15
3 days	~35	~35	~35	~35	~35
7 days	~45	~55	~55	~55	~55

Emission reduction by LCC components

Component	OPC (%)	MK30 (%)	B45 (%)
Clinker	~100	~70	~55
Calcined clay	0	~30	~45
Limestone	0	0	~10

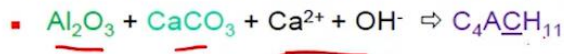
Research results from EPFL Switzerland and UCLV Cuba
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So this is the reaction.

Metakaolin "MK" plus limestone



Formation of monocarbo aluminat "Mc" (AFm)



This is your metakaolin let us say when we are considering limestone calcined clay cement where cement is replaced partially by limestone and calcined clay combination. So you have the alumina silicate given by the metakaolin or calcined clay and the limestone or calcite given by the limestone. What is the difference between calcite and limestone? What is calcite and what is limestone? Basic geology, science, limestone is the rock, calcite is a mineral. What is the difference between rock and a mineral? Come on your brother and sister at home will be asking you the same question. What is the difference between rock and mineral? Ore is different, ore is any rock that you mine for a profit.

But what is a mineral? Can I call water as a mineral? Can I call fly ash as a mineral? The official definition of a mineral involves the fact that the material should have some well-defined structure. So usually a mineral is a crystalline material. A mineral basically is a crystalline material which has a definite structure which repeats. So calcite is the mineral here but limestone is the rock which is composed of many such minerals in combination. It may also contain other impurity minerals like quartz for instance.

Quartz is another mineral and it may be present in some limestone also. Clay may be present in them. What are some clay minerals that you know of? We talked about one here kaolinite, kaolinite is a mineral, illite is a mineral, montmorillonite all these are minerals. But clay is the generic name given to the species. It is more of a geotechnical name based on the classification that we do for soils.

But the actual mineral is something else. Anyway coming back to the fact that monocarbonate formation involves alumina and calcite along with lime generated by cement hydration to form this monocarbonate structure. So calcium, aluminum, carbonate, hydrate. Now of course between calcium and carbon you can see that cement chemists do some cheating and put a line under the carbon to say that it is not calcium but it is carbon. If you take this equation to a real chemist they will throw you out of the room saying what are you talking about.

Anyway, so these were some early works done by researchers on limestone calcined clay cement where they clearly showed that the one-day strengths as compared to plain Portland cement probably were not the same but when you do 3 or 7 day strengths the calcium clay usage along with limestone even at a 45% replacement level. So here it was 30% calcined clay and 15% limestone. So by 3 days the clays that were rich in kaolinite, for instance, the

Burgess clay and the India 1 clay you can clearly see by 3 days they have a strength that is almost equal to that of Portland cement mortar. By 7 days even the cement that is 50% of kaolinite has overtaken the plain OPC in terms of the strength. So that is the advantage here, we are replacing 45% of the cement and putting in this calcined clay, limestone combination but we are able to get a strength performance at 7 days even with an impure calcined clay, we do not have to rely on metakaolin anymore, we can go for an impure calcined clay.

If you go to any of these china clay quarries where they are looking for the white china clay there is tons and tons of overburden material which is not getting used. So, lot of this material overburden plus all your impure clays may contain between 40 to 60% kaolinite and it has been shown that such clays could be good enough in a system like this. So that is why you see this 50% clay itself is able to produce a strength which is better at 7 days than Portland cement. Interestingly even a 20% kaolinite clay is able to reach 75% of the cement strength and that is really a very good achievement. That means this material which has mostly impurities not kaolinite is still able to do this excellently.

So that is what the purpose of using large replacements of cement is and we try to come to ternary combinations where we are harnessing the synergy between the calcite and the calcined clay.