Admixtures And Special Concretes

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Lecture 3

Overview of Cement Chemistry: Composition of Cement and Classification of Cement

Typical Composition:

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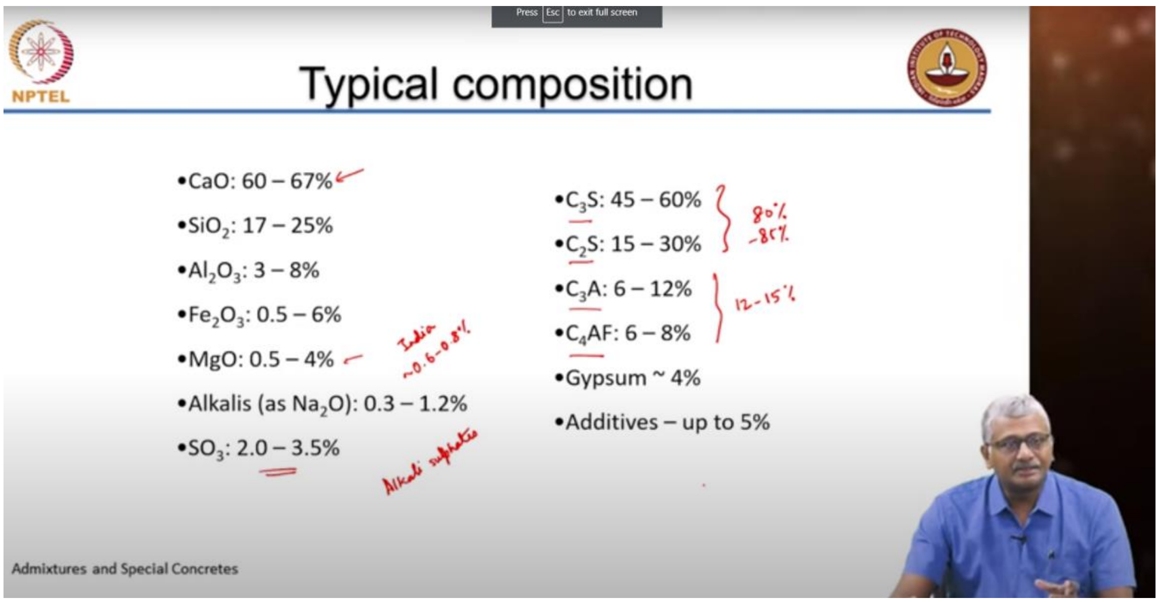

Yeah, so in terms of composition cement is composed of a few major oxides like calcium oxide, silicon dioxide, aluminum oxide and iron oxide. As you can see the primary composition of cement is in terms of lime or calcium oxide. We have nearly two thirds of cement composed of calcium oxide. Apart from these four major oxides, you can also have significant quantities of magnesium oxide depending upon the source of your limestone. There are alkalis present of about 0.3 to 1%. More typically what we see in India cements is that the alkali contents are around 0.6 to 0.8% in India. But several cements could have higher than 1% also. There are some problems with very high alkali cements which of course we will discuss in the course of this series of lectures. Cements abroad typically tend to have a higher alkali content. Now alkali content in cement helps to actually enhance the early age strength development of the cement.

Now where are these alkalis coming from? Mostly these alkalis are present in the raw material in the form of alkali sulphates. Alkali sulphates are usually present as impurities in the raw materials and these basically come into the mixture, compound mixture that we actually have. The sulphates that are indicated here are not just from the gypsum that we add in the final stages but also could be from the alkali sulphate sources that are available as impurities in the raw materials. Now in the kiln there is going to be a combination of these oxides to form the primary phases: tricalcium silicate, dicalcium silicate, tricalcium aluminate and tetra calcium alumino ferrite. And if you look at the overall composition, if you add up your C_3S and C_2S together typically around 80% would be C_3S plus C_2S irrespective of the type of cement. Then C_3A and C_4AF together will be about 12 to 15% and gypsum is around 3 to 4% that is the amount of gypsum that is available in the mix. In OPC up to 5% of additives or performance improvers are permitted. Performance improvers typically are limestone or sometimes fly ash. So these are lowering the overall CO_2 impact of the cement. At this 5% level they are also able to provide additional benefits.

C_3S

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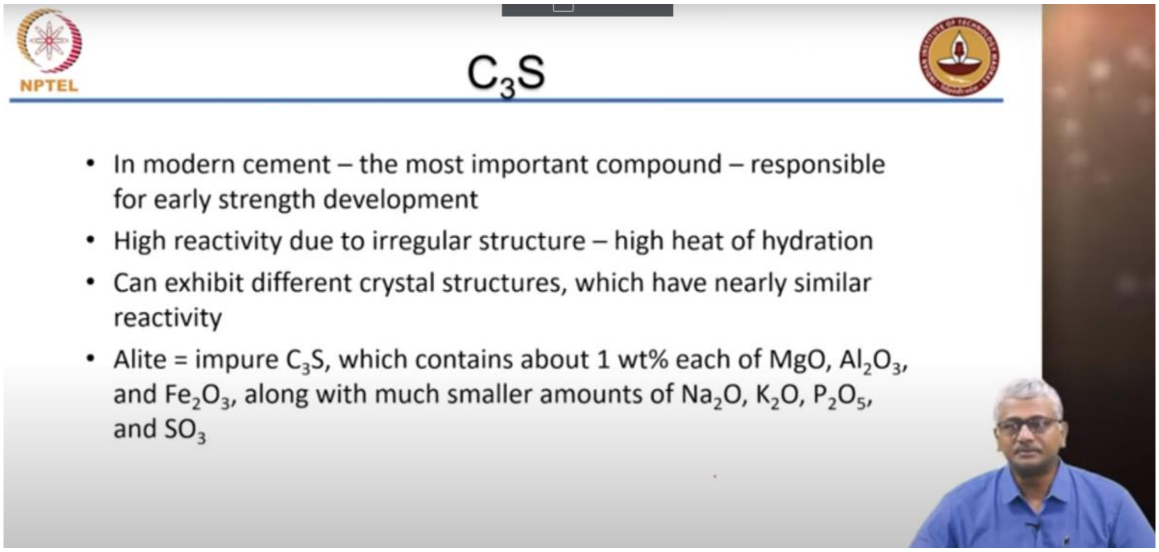

C_3S is the major component in cement, more than 50% is C3S and it is also responsible for early strength development. Nowadays you have monuments and structures that are produced or constructed in very little time and because of this the importance of C_3S as a component of cement is only increasing because C_3S is the one which leads to early strength development. This early strength development comes from the fact that C_3S has a high reactivity because of its irregular structure. We saw a picture of cement clinker earlier in which C3S had an irregular structure, polygonal structure which leads to a high reactivity. And high reactivity also means it has got a high heat of hydration. It is the heat liberated when cement reacts with water. So cement is composed of different compounds so the heat that is liberated when cement reacts depends on heat liberation of individual compounds. The compounds that react faster liberate a lot more heat. You might have seen this with lime, slaking of lime. We typically add water to calcium oxide. There is a massive heat evolution that happens from that process. Same thing even here in cement also there is an exothermic process which releases heat. Several crystal structures are possible with C_3S. Alite is nothing but impure C3S which has other impurities.

C_3S

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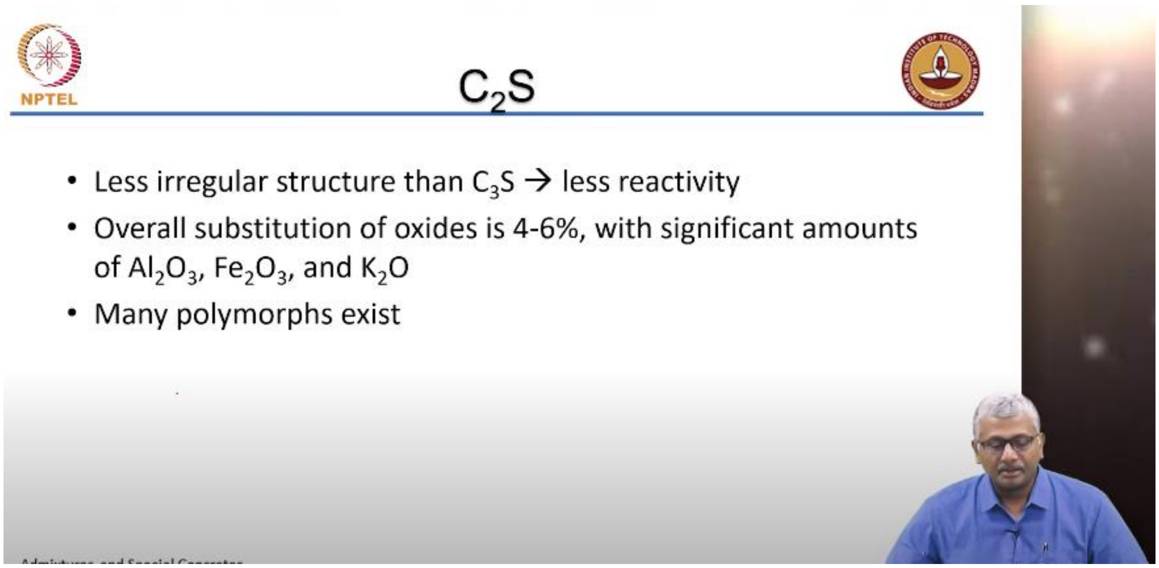

C_2S is a less irregular structure that is more rounded as we saw from the pictures of the cement clinker that I showed earlier and because of this more regular structure it has got less reactivity. Over all substitutions of oxides can be up to 4 to 6%. So in belite C_2S can have impurities in the form of these oxides and again because of the formation and the presence of different types of impurities the polymorphs exist.

C_3S

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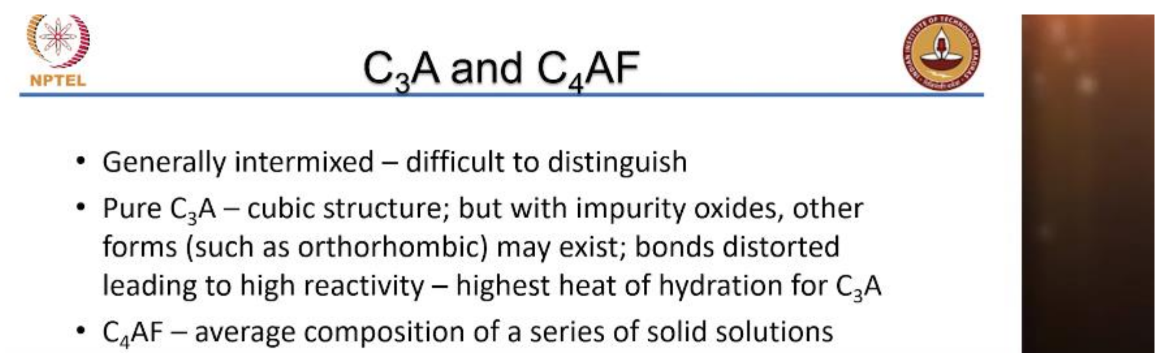

C_3A and C_4AF as you saw in the pictures earlier with the clinker are not that easy to distinguish as compared to your C_2S and C_3S which are much larger crystalline particles. C_3A and C_4AF are also crystalline but they are small enough that they are present almost in an intermixed kind of a fashion. Again in terms of crystalline composition pure C_3A will have a cubic structure but with impurities it can also get other crystal forms such as orthorhombic. The issue with C_3A is it has got the highest heat of hydration.

So if you were to produce a low heat cement what would you do? Reduce the C_3A and preferably also reduce C_3S because C_3S also liberates a lot of heat it reacts fast so if you have to produce a low heat cement.

What applications would you need low heat cement for? For mass concrete, dams, in such cases you need low heat cement. Such cements are produced typically with lower C_3A and C_3S contents.

C4AF is not really a component that matters too much in the long run except that of course to keep this balance of C_3A and C_4AF, like I said when you want low heat you reduce C_3A but when you reduce C_3A the C_4AF content will get pushed up slightly. So it does that balancing of the aluminate fractions in the cement but otherwise it does not really have a major significance with respect to the hydration reactions. Even if you take a cement which is or concrete structure which is like 50-60 years old if you take a small microscopic image from inside you will find that much of the C_4AF is present as it is in the original cement. It does not react at all. That is because iron is present and this iron makes it highly insoluble.
So cement particles have to first start solubilizing and then they react. So C_4AF is a phase that does not solubilize easily. As a result you will not find iron particles having or C_4AF phases having reacted much even in concrete that is very old.

Classification of cements:

So there are several ways of classifying cements. I am just giving you some principle classifications based on

- ASTM
- Indian standards
- European standards

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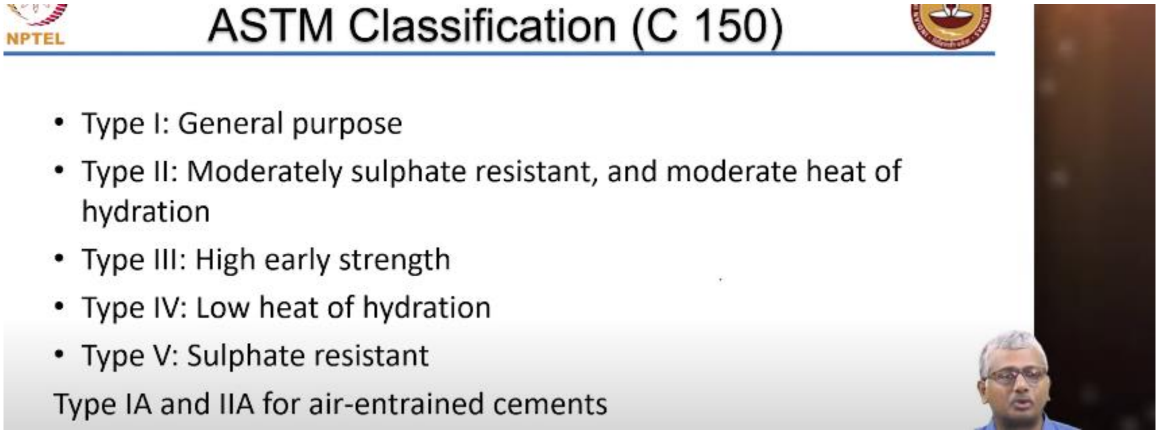

ASTM classifies regular cement which is as per the ASTM specification C150 into 5 types. One is general purpose which in India we call as ordinary Portland cement and then type 2 is moderately sulphate resistant and moderate heat of hydration. Essentially this means lower C_3A and C_3S.

Then you have type 3 which is high early strength. How will you increase the strength of cement? You increase more C_3S. Any other way in which you can increase strength, gain, rate of cement? You can grind the cement finer. Increase C_3S finer cement. So more C_3S and finer. And then you have type 4 which is low heat of hydration or low heat cement. So obviously here lower C_3A and C_3S and type 5 is sulphate resistant. If you discuss mechanisms you will see that sulphate resistance especially is brought about by the fact that you use a cement with lowest C_3A content. The aluminate content is reduced to the lowest level in the case of sulphate resistant cement. So these are the general ways of characterizing ordinary cement. In ASTM they also include some air entertaining additives in the type 1 and type 2 cements and simply call it type 1A and type 2A. Just to give you this same thing in a snapshot of the compound composition you can clearly see here that compared to type 1, type 2 has lower C_3S and C_3A. Type 4 also has lower C_3S and C_3A but the C_3S lowering in type 4 is much more than in type 2. So obviously when you lower C_3S you increase C_2S. The silicates typically will add up to nearly 80 to 85%. So if you are lowering C_3S you are increasing the C_2S. And then type 5 lower C_3A and sometimes also lower C_3S as compared to type 1 cement.

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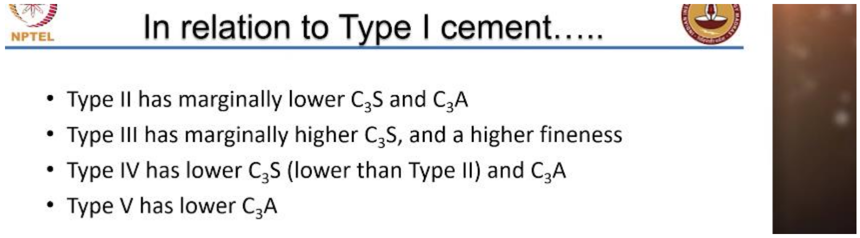

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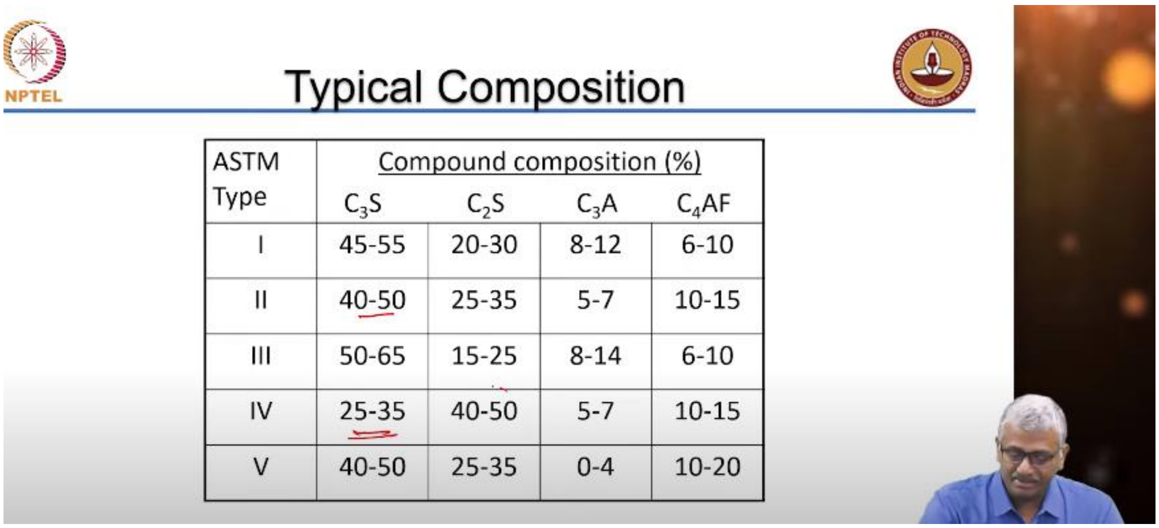

ASTM Type	Compound composition (%)			
	C_3S	C_2S	C_3A	C_4AF
I	45-55	20-30	8-12	6-10
II	40-50	25-35	5-7	10-15
III	50-65	15-25	8-14	6-10
IV	25-35	40-50	5-7	10-15
V	40-50	25-35	0-4	10-20

So this is the overall chemical composition which is quite similar if you look at the other standards like BIS, It also has a sulphate resistant cement, BIS also has low heat cement, high early strength cement, most of the characteristics are quite similar across different standards.

Blended Cements:

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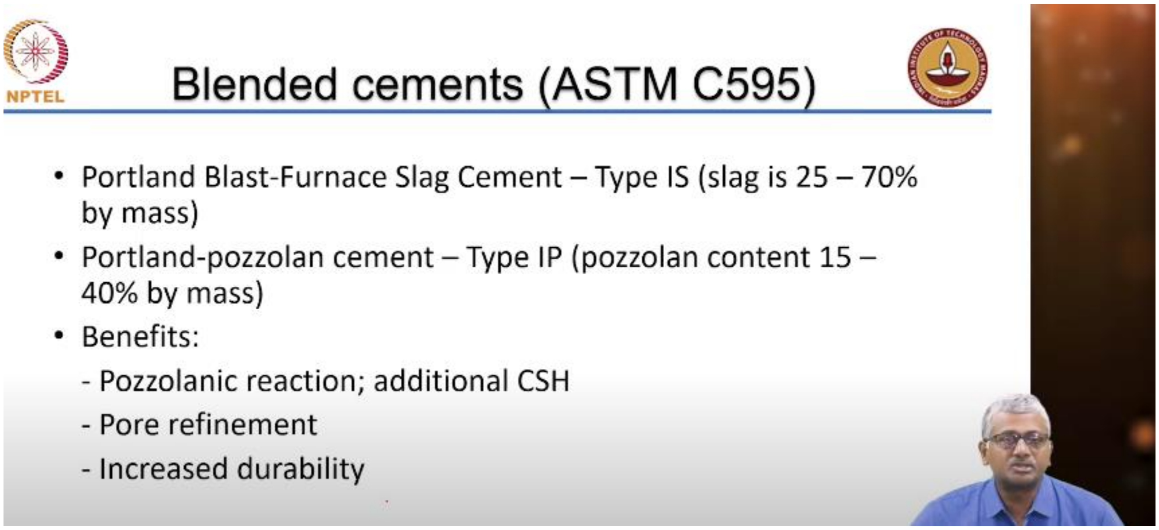

Then of course there is also blended cements about which this course will have a lot of discussion about how materials from other industries like fly ash and slag can be blended along with cement to produce very interesting cementitious properties. So Portland blast furnace slag cement, in India we call it Portland slag cement PSC. So in the US they call it type 1S and slag content typically is 25 to 70%.There is a reason for this and the reason is that slag on its own has a significantly large potential to react. Only problem is it is too slow to react on its own, it needs the presence of cement to exhibit its hydraulic reactions. So as a result slag content permitted in slag cement is quite high. Typically around 50 to 60% is used. That means the cement component or clinker component is quite low 40 to 50%.

So what does this mean? Again slag cements will have a net lower CO_2 emission potential. So it is always of benefit to use slag cement from that perspective and later when we talk about slag in more detail you will also learn that it is beneficial to use slag cement from also the perspective of higher durability in coastal conditions. Portland pozzolan cement is type 1P and pozzolan content is 15 to 40% and that is because pozzolans cannot react on their own. They need the lime that is generated from cement hydration. So lime is calcium hydroxide. That is what it is written as in cement chemistry calcium hydroxide is written as CH or written as $CaO.H_2O$ that is why we call it CH. So pozzolans are basically reactive silica. So they combine with CH to give CSH. CSH is calcium silicate hydrate which is a principle binding component of cement hydration products. So you get additional CSH and that leads to refinement of your porosity. The pores that are in concrete become finer and finer which makes concrete more durable in the long run. So it is always durability. Strength is only a secondary factor primarily you want to use blended cements for durability.

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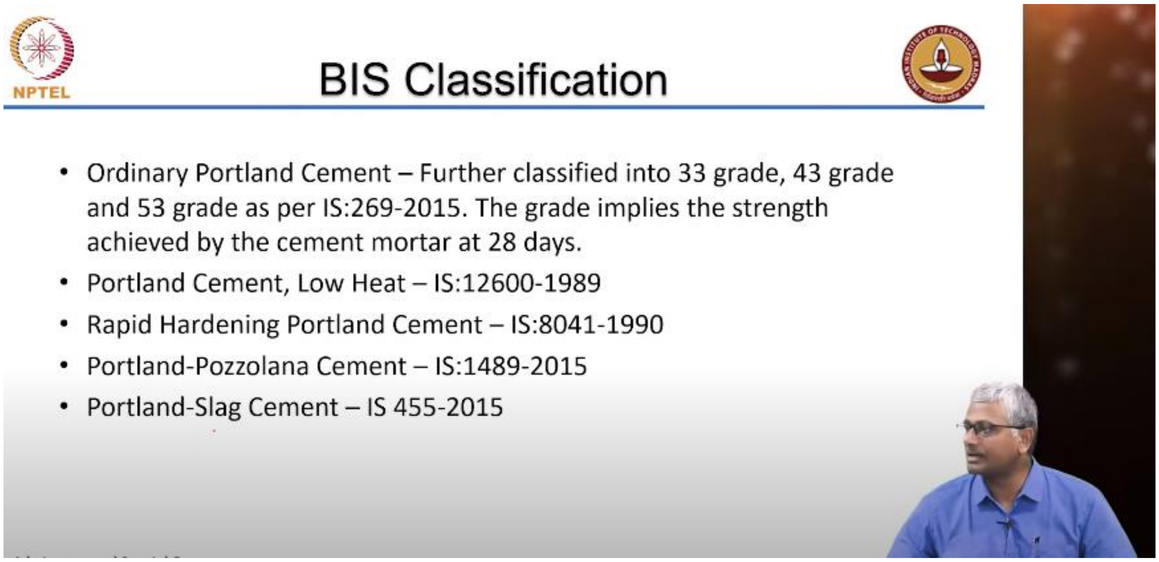

BIS has a similar classification. We have general purpose cement or ordinary Portland cement. The only difference is our ordinary Portland cement we further divide into strength classes 33, 43 and 53 grade cement. And here this grade simply implies the strength achieved by the cement mortar.

What type of cement mortar? It has to have a certain specified water content that is determined from the consistency of the cement. There is specific consistency of the cement that means the water demand and based on that you decide the water content to be used in this mix and you fix the cement to sand ratio as 1:3. Prepare a mortar and prepare 70 mm cubes and test them for 28 days. Accordingly you will get grade 33, 43 or 53. These days 33 is almost not available at all. You only get 43 and 53 produced by the cement companies. Then just like the ASTM case we have low heat cement, we have rapid hardening cement, Portland pozzolana cement, Portland slag cement.

The only problem is many of these special cements are not always available because cement manufacture is a complicated process. For them to continuously change their batch to produce other types of cement becomes a low value proposition for many of the cement companies. They would like to produce the same cement day in and day out because then they do not want to readjust their process too much. For a company to suddenly start producing low heat cement would require a dedicated kiln, because the processes could be quite different, raw material combinations are different and so on. It is not easy or profitable for a company to continuously change the type of cement that they are producing.

So here because these special types of cement are not easily available, the role of the mineral admixtures or mineral additives or supplementary cementing materials becomes all that more paramount. That is where they all come in. For instance low heat cement, if low heat cement is not available how do you start making concrete for dams where you really have to control the heat evolution. There you go for substitution of cement by what?

We use fly ash to reduce the heat of hydration because fly ash is extremely slow to react and if you substitute cement in large quantities with fly ash you will substantially reduce the amount of heat generated. So like that we need to make do with mineral additives whenever we need special properties like high early strength for instance. If rapid hardening cement is not available or is not very practical to be used because it may also start setting very quickly. So it will reduce the time that you have for concreting. Like in Mumbai you know we have high rise buildings where people are using even M90-M100 grades of concrete. In such cases imagine using a rapid hardening cement you will never be able to maintain workability. In such cases what comes to the benefit of the concrete producer is the use of fine additives like silica fume or metakaolin about which we will learn in more detail later. But all of these compounds are very important from the perspective of producing special concrete which cannot be achieved because special cements are not easily available.

So all these have these are not just technical reasons, economic reasons also are why these are not easily available because it affects the profitability of the cement manufacture.

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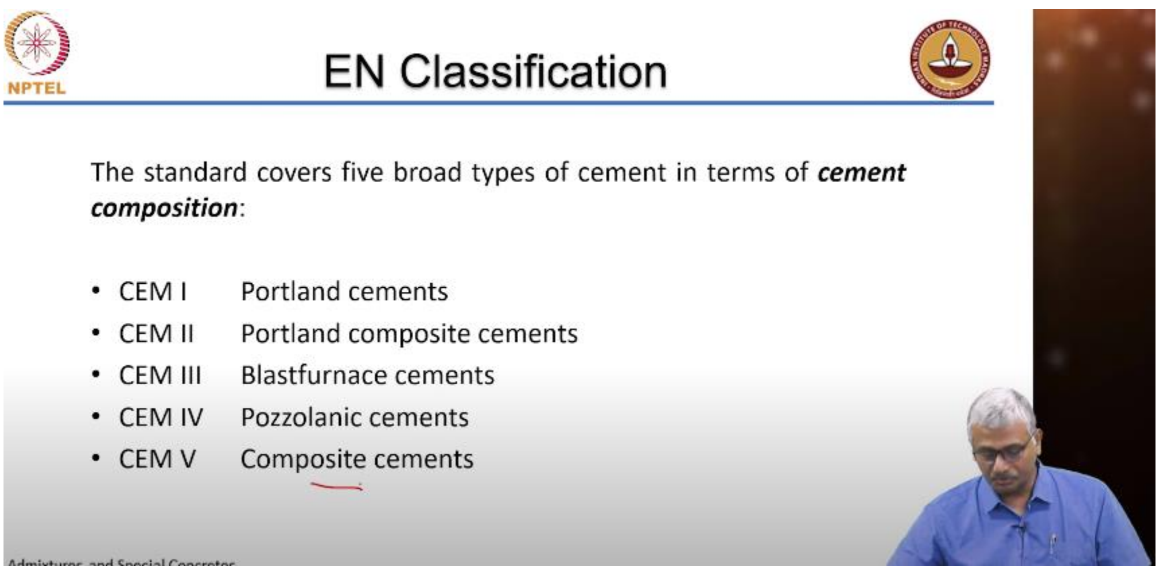

Again similar but EN has a much more diverse classification of cements. So they talk about CEM 1, 2, 3, 4 and 5 where they talk about Portland cements, composite cements, blast furnace cements, pozzolanic cements and they have composite cements which have much larger levels of substitution.

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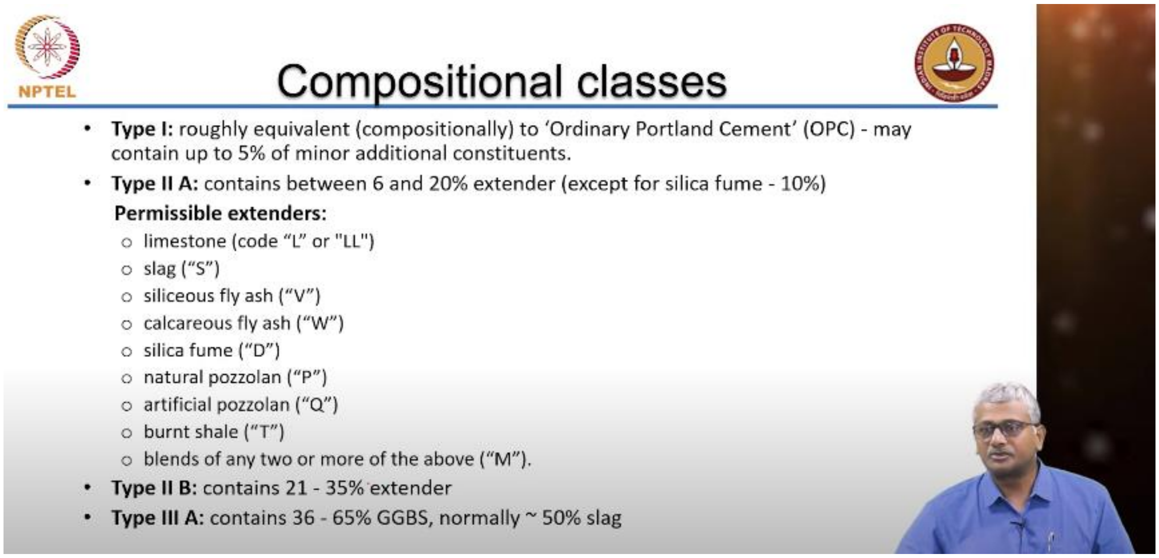

So if you look at the description it can be quite difficult for a person who is not well trained in understanding cement. So the EN standards are meant for engineers who have a high level of understanding of this entire scheme and because of which they can actually now make concrete that are niche concretes which very specific blends of cement have used in their formulations.

Not the same in India, in India the understanding of the cement is not as good with the civil engineers that are available on site. We are familiar with ordinary Portland cement but beyond that even mineral admixtures sometimes are out of reach of many people. So we need to be careful when we classify cement in too many categories, the problem is then that we have difficulty deciding which to use when.

But in Europe the degree of understanding with these special cements is very good and they have very well trained people, concrete technologists who can actually understand what each of these cements consists of. So what I wanted to say is that those of you who are working in industry convince your bosses to hire more concrete technologists because ultimately such decisions about choice of materials about design of concrete for particular combinations for particular applications is in the hands of a concrete technologist. You need to understand cement and concrete in order to be able to get maximum benefit out of all of these materials.